

Structure Property Correlation of Novel Photocurable Polymers for Light-Based 3D Printing Applications

by

Shibam Pal
10CC18A26013

A thesis submitted to the
Academy of Scientific & Innovative Research
for the award of the degree of
DOCTOR OF PHILOSOPHY
in
SCIENCE

Under the supervision of

Dr. Asha S. K.



CSIR- National Chemical Laboratory, Pune



Academy of Scientific and Innovative Research
AcSIR Headquarters, CSIR-HRDC campus
Sector 19, Kamla Nehru Nagar,
Ghaziabad, U.P. – 201 002, India

March-2024

Certificate

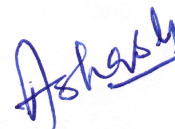
This is to certify that the work incorporated in this Ph.D. thesis entitled, "Structure Property Correlation of Novel Photocurable Polymers for Light-Based 3D Printing Applications", submitted by Mr. Shibam Pal to the Academy of Scientific and Innovative Research (AcSIR), in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Science, embodies original research work carried-out by the student. We, further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material(s) obtained from other source(s) and used in this research work has/have been duly acknowledged in the thesis. Image(s), illustration(s), figure(s), table(s) *etc.*, used in the thesis from other source(s), have also been duly cited and acknowledged.



Mr. Shibam Pal

Research Student

Date: 19-03-2024



Dr. Asha S. K.

Research Supervisor

Date: 19-03-2024

STATEMENTS OF ACADEMIC INTEGRITY

I **Mr. Shibam Pal**, a Ph.D. student of the Academy of Scientific and Innovative Research (AcSIR) with Registration No. 10CC18A26013 hereby undertake that, the thesis entitled "**Structure Property Correlation of Novel Photocurable Polymers for Light-Based 3D Printing Applications**" has been prepared by me and that the document reports original work carried out by me and is free of any plagiarism in compliance with the UGC Regulations on "*Promotion of Academic Integrity and Prevention of Plagiarism in Higher Educational Institutions (2018)*" and the CSIR Guidelines for "*Ethics in Research and in Governance (2020)*".

S. Pal

Signature of the Student

Date: *19-03-2024*

Place: Pune

It is hereby certified that the work done by the student, under my/our supervision, is plagiarism-free in accordance with the UGC Regulations on "*Promotion of Academic Integrity and Prevention of Plagiarism in Higher Educational Institutions (2018)*" and the CSIR Guidelines for "*Ethics in Research and in Governance (2020)*".

Ashash

Signature of the Supervisor

Name: Dr. Asha S. K.

Date: *19-03-2024*

Place: Pune

Declaration

*I hereby declare that the matter embodied in this thesis entitled "**Structure Property Correlation of Novel Photocurable Polymers for Light-Based 3D Printing Applications**" is the result of an investigation carried out by me at Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune, India under the supervision of Dr. Asha S.K.*

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made to the work described on the finding of other investigations.



Shibam Pal

(Student Signature)

Date - 19-03-2024

Dedicated to
My Beloved Parents and
Respected Teachers

***For support and encouragement during
my educational career...***

Acknowledgment

***“Every work has to pass through hundreds of difficulties before succeeding.
Those that persevere will see the light, sooner or later.”***

-Swami Vivekananda

I am deeply thankful to the almighty for granting me the strength and determination necessary to overcome the hurdles encountered along the path of my dream journey. Completing this pivotal step in my research journey would not have been achievable without the assistance and encouragement of numerous individuals. I extend my heartfelt gratitude to those who have unwaveringly believed in my work. Your faithful support fills me with enduring gratitude and positivity, propelling me forward with confidence.

*Firstly, with profound appreciation, I would like to extend my sincere thanks and gratitude to my supervisor **Dr. Asha. S.K.** This research association began nearly five years ago with a welcoming email from her that simply stated, "Welcome to our group" and throughout this journey, her consistent and unwavering support has been an essential aspect for completing my Ph.D. thesis. Madam, your assistance and immense support have been instrumental in helping me overcome numerous obstacles and challenges during my research. I am incredibly grateful for your invaluable contribution to my academic accomplishments.*

I am immensely grateful to you for believing in me, even knowing that mistakes were inevitable. And indeed, I did make mistakes. However, your gentle critique and patient guidance instilled confidence in me and provided invaluable lessons each time.

I am genuinely thankful to my supervisor for everything that I learned during my Ph.D. Her confident and courageous demeanour gave me the freedom to think innovatively and express my ideas without hesitation. I feel free to approach her, whenever I need to discuss on any topic and solved numerous problems. This journey was wonderful, filled with invaluable experiences and growth opportunities. I will carry these lessons throughout my entire life.

*I extend my sincere gratitude to **Professor Manickam Jayakannan** (IISER Pune) for imparting fundamental knowledge of polymer chemistry during the semester coursework. Additionally, I am grateful for the invaluable guidance provided in understanding basic calculations and setting up reactions, which enabled me to commence my research work in your laboratory. Your multi-vision perspective greatly influenced the direction of our collaborative research, offering invaluable suggestions whenever I hit an obstacle. Your strong and influential personality served as a model for improving my own professional*

Acknowledgment

demeanour, teaching me numerous ways to enhance my approach. I am incredibly grateful to you for your guidance and for teaching me how to improve not only in research but also in my personal life. I will never forget those wonderful moments that I spent in your home during the Onam and Pongal festival, and specially your secret cooking spices.

I sincerely thank Dr. Ashish Lele, Director of CSIR-NCL, and Dr. Ashwini Kumar Nangia, former Director of CSIR-NCL, for keeping an excellent research environment and providing exceptional infrastructure. Along with, access to adequate instrumentation facilities, has greatly contributed to the advancement of my research endeavours.

I thank the Council of Scientific and Industrial Research (CSIR), New Delhi, for the esteemed CSIR-JRF and CSIR-SRF fellowship and financial assistance. I am grateful for the diligent and timely cooperation provided by the Student Academic Office (SAO) staff throughout the duration of my tenure.

I would like to express deepest gratitude to my DAC members Dr. Dhanasekaran Shanmugam, Dr. Samir H. Chikkali, and Dr. Ashootosh V. Ambade for their discussion and valuable suggestions during my DAC meeting. The discussion went beyond the meeting time and they allowed me to continue our discussions even days later. Their assistance as DAC members not only enhanced my research in the right direction but also provided me with a comprehensive understanding of polymer synthesis and properties during my semester coursework.

I would also like to thank Dr. Kadiravan Shanmuganathan for his substantial contribution to enhancing my understanding of polymer rheology concepts. Your detailed discussions on polymer properties behaviour were pivotal in my research publication. Thank you for your unwavering support and encouragement.

I want to extend my heartfelt gratitude to Dr. Prakash P. Wadgaonkar for his invaluable discussions prior to embarking on a research project. His extensive knowledge of polymer chemistry has the ability to make any project feasible and effective. I am happy that I had the opportunity to share my thoughts with him and gained valuable insights from our discussions.

I am grateful to Dr. Shrikant B. Nikam, and Dr. Navnath R. Kakde, for their guidance and teaching in the lab. They helped me to learn the basic ethics and start my research journey in the lab. They patiently answered my bucket of questions and offered suggestions based on my preferences.

Acknowledgment

I also want to extend my heartfelt thanks to Dr. Moumita Roy, who means a lot to me. During my early days in the lab, I worked with her and gained experience in lab instruments, apparatus, experiment, writing, and much more. I deeply value her cooperation, time, and unwavering support at every stage.

I want to thank to my all seniors and labmates from the CSIR-NCL Mr. Nitin, Dr. Suraj, Aryan, Ganesh, Pooja, Ashok, Yogesh, Ashwani, Abhijith, Aakshai, Medha, Mitali, Chetan, Meesha, Sarath and labmates from IISER(Pune) Dr. Mehak, Dr. Kuddus, Dr. Rahul, Dr. Ruma, Utreshwar, Parshuram, Shahid, Bhushan, Sunidhi, Vinay for their help. I am thankful to Mr. Nitin Basutkar for his insightful research discussions, and the fun-filled environment that enhanced my productive outcomes.

I would like to extend a special acknowledgement to Dr. Tamanna Thakur for her invaluable friendship, support, and guidance in crucial time of my life.

I consider myself incredibly fortunate to have a multitude of friends at NCL, and I am grateful to them for crafting unforgettable memories. Additionally, I extend thanks to my hostel companions and cricket buddies for ensuring that each day is filled with memorable experiences. I am thankful to the Bengali association group members (Rahul, Dr. Subhrashis, Dr. Naru, Arindam, Biplab, Anurag) for giving me the opportunity to showcase my creativity within the organizing cultural events and programs.

I always feel privileged to acknowledge the hard work of my family for shaping me into the person I am today. I am grateful to my parents; Mr. Sudeb Pal and Mrs. Prajapati Pal, for their unconditional love and support. I consider myself incredibly fortunate to have Mr. Samir Pal as my elder brother and sister Akhi Pal. They are consistently supportive and always there for me, regardless of the circumstances.

I am thankful to the anonymous reviewers of my thesis for dedicating their time and providing valuable suggestions during the review process.

-Shibam Pal

ABBREVIATIONS AND SYMBOLS

Mn	Number average molecular weight
Mw	Weight average molecular weight
PDI	Polydispersity Index
Đ	Polydispersity index
NMR	Nuclear Magnetic Resonance
RT	Room Temperature
h	Hours
mg	Milligrams
g	Grams
mL	Millilitre
mmol	Millimole
ppm	Parts per million
SEC	Size exclusion chromatography
FE-SEM	Field emission scanning electron microscopy
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry
μm	Micrometre
mm	Millimetre
DMF	Dimethyl formamide
NaCl	Sodium chloride
KCl	Potassium Chloride
KOH	Potassium hydroxide
LiOH	Lithium hydroxide
K ₂ CO ₃	Potassium carbonate
MeOH	Methanol
THF	Tetrahydrofuran
DCM	Dichloromethane
T _m	Melting temperature
T _g	Glass transition temperature
T _d	Degradation temperature
3DP	3-dimensional printing

DLP	Digital light processing
SLA	Stereolithography
FDM	Fused deposition modeling
ACN	Acetonitrile
DMAc	Dimethyl acetamide
DMSO	Dimethyl sulfoxide
MHz	megahertz
ΔH_m	Melting enthalpy
PLLA	Poly(l-lactic) acid
PLA	Poly lactic acid
HEMA	2-Hydroxyethyl Methacrylate
HEA	2-Hydroxyethyl acrylate
PI	Photoinitiator
TPO	Phenylbis(2,4,6-trimethyl benzoyl) phosphine oxide
PEEK	Poly ether ether ketone
PAEL	Polyacryl ethyl lactate
PTSA	Paratoluene sulfonic acid
TTT	Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione
PETMP	Pentaerythritol tetrakis(3-mercaptopropionate)
TCCDA	Tricyclo[5.2.1.0 ^{2,6}]decanedimethanol diacrylate
BPAEDMA	Bisphenol A ethoxylate dimethacrylate
BBOT	2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene
AIBN	Azobisisobutyronitrile
NMP	N-methyl-2- pyrrolidone
Na ₂ SO ₄	Sodium sulphate
SOCl ₂	Thionyl chloride
TMS	Trimethylsilane
CAD	Computer-aided design
KH ₂ PO ₄	Potassium dihydrogen phosphate
Na ₂ HPO ₄	Disodium phosphate
PBS	Phosphate buffer solution
Sn(Oct) ₂	Tin(II) 2-ethylhexanoate

SYNOPSIS

1 Introduction

In recent years, there has been a growing demand for biodegradable materials to create complex 3-dimensional patient-specific biomedical implants using additive manufacturing (AM) or 3D printing (3DP) technology. Various technologies, including Selective Laser Sintering (SLS), Fused Deposition Modeling (FDM), light-based methods like Stereolithography (SLA) and Digital Light Processing (DLP), extrusion-based 3D printing, and inkjet printing, have been explored to meet these custom design and fabrication requirements.¹⁻⁴ Choosing the right biomaterial for such applications is a challenging task due to the limited availability of materials that can fulfill both the mechanical and processing demands of device fabrication while meeting stringent medical application standards. The rapid advancements in AM machinery technology over the past decade have also fueled the search for suitable materials that can match the needs of these applications. As the focus on bio 3D printing research continues to grow, there is an increasing need for the development of new materials that can meet the functional requirements of customized 3D printing technologies. Some of the commonly used biopolymers include polylactide (PLA), polycaprolactone (PCL), and polyglycolide (PGL), which are derived from natural resources such as starch, sugar cane, corn, wheat straw, and wood chips.⁵⁻⁷ These polymers are characterized by ester linkages that can undergo hydrolytic cleavage to form small molecules. PLA and its composites, as well as petroleum-based polymers with biodegradable fillers, are available in the form of solid filaments that can be directly used in additive manufacturing (AM). For high mechanical properties, poly ether ether ketone (PEEK) can be a suitable choice of material. PEEK has good mechanical properties, such as high tensile strength and stiffness, which makes it suitable for producing functional and structural parts. However, 3D printing with PEEK can be challenging due to its high melting point and the need for a heated build chamber to prevent warping and maintain part integrity. Thus there is an unmet need to develop PEEK-based materials that are processible at room temperature for 3D printing, at the same time, retaining the good mechanical properties that are intrinsically associated with PEEK. Photo-induced thiol-ene reactions combine the attributes of both photopolymerization and click reactions, including precise control, selectivity, resistance to oxygen and water, and high yields without the formation of by-products. Unlike chain-growth acrylate polymerizations, thiol-ene reactions proceed via a step-growth mechanism, offering benefits such as delayed gelation, improved monomer conversion, and reduced shrinkage stress.

Photocuring-based 3D printing technologies, such as Digital Light Processing (DLP), are well-suited for bio 3D printing due to several advantages, including high resolution and gentle processing conditions when compared to extrusion-based AM methods. Additionally, the print speed can be controlled by adjusting the light intensity or exposure time. In contrast to filament extrusion-based 3D printing, photocuring-based 3D printing offers the added benefit of improved bonding between layers, as polymerization can continue even in the absence of light, resulting in better connectivity between polymer chains across different layers.⁸⁻⁹

2 Statement of the problem

Additive manufacturing (AM), also known as 3D printing, has become a versatile technology platform for computer-assisted design (CAD) and rapid manufacturing. This innovative technology enables the creation of personalized components using metals, ceramics, and polymers, all while eliminating the necessity for molds or the machining processes commonly associated with traditional formative and subtractive fabrication methods. Additive manufacturing has moved from being a specialized manufacturing method to becoming widely recognized as user-friendly systems with quicker build rates and lower costs are now available. Despite significant progress in recent years, there are still several challenges that must be addressed for AM to become a viable large-scale manufacturing tool. The rapid progress in the technological development of machinery for AM achieved in the recent decade has also spurred the search for suitable materials that could meet the requirements of these applications. Photocuring-based 3D printing technologies like the DLP is very amenable as they offer many advantages like high resolution and gentle processing conditions compared to extrusion-based AM technologies. Moreover, the print speed can be controlled by adjusting the intensity of light or the exposure time. Compared to filament extrusion-based 3D printing technologies, photocuring-based 3D printing has the added advantage of enhanced bonding across the layers as the polymerization can continue even in the absence of light thereby connecting polymer chains across the different layers.

So, in DLP 3D printing technology there are commercial acrylate-based materials available that have limitations in terms of degradability or mechanical properties. To overcome this problem biobased materials are required which can provide degradability to reduce waste generation and the use of high-performance PEEK polymer can provide 3D printed parts with

high mechanical strength. Adopting thiol-ene-based chemistry can enhance the printing parameter in terms of printing speed for fast curing and degradability also.

3 Objective and Outline of Thesis

The primary objective of the thesis is to provide different types of photocurable crosslinkers to be utilized in the development of resin formulations. After that, the prepared resins will be used in light-based DLP 3D printing technology. The thesis also focused on the properties of the 3D printed materials like- degradability, mechanical properties, and printing resolution. These 3D printed materials are useful in different fields of applications. The detailed outline of the thesis is given below,

Chapter 1. Introduction

The introduction starts with the background study of additive manufacturing technologies which gives an overall idea about the mechanism of the technology and an understanding of the importance of the technology in terms of creating different materials without using conventional mold methods. In this chapter, the classification of AM technology is discussed followed by the types of materials that are required. The materials that are used for light-based 3D printing need to have a photo-curable group to form a crosslinked network structure. The challenges of synthesis and characterization of different crosslinker polymeric materials are discussed in the introduction chapter.

Chapter 2. Biodegradable, Solvent-Free Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing.

Chapter 3. Biocompatible PVAc-g-PLLA Resin Formulations with Tunable Mechanical Properties for DLP/SLA 3D Printing.

Chapter 4. Thiol-ene-based Degradable 3D Printed Network from bio resource derived Monomers Ethyl-lactate and Isosorbide.

Chapter 5. Room Temperature Photocurable PEEK Polymer Formulations for High-Performance 3D Printing Applications.

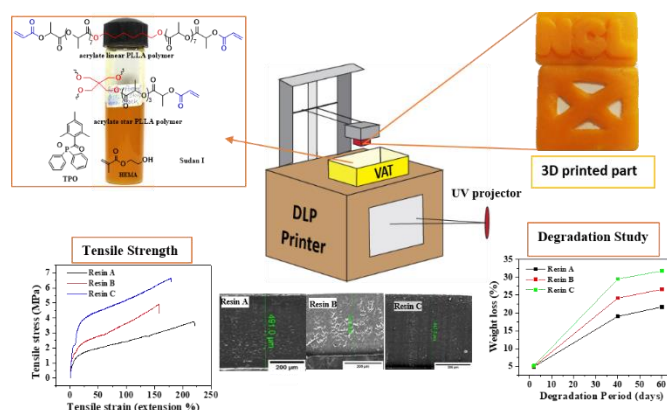
Chapter 6. Conclusion

4 Results and their interpretation

Chapter 2. Biodegradable, Solvent-Free Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing.

Synopsis

In this study, we synthesized two different low molecular weight Linear and star poly(l-lactide) (PLLA) polymers by ring-opening polymerization of lactide using 1,6-hexane diol and pentaerythritol as initiator and $\text{Sn}(\text{Oct})_2$ as a catalyst. The reaction was done in bulk condition at 130°C for 5 h reaction time. The terminal hydroxyl groups of the polymers were reacted with acryloyl chloride to introduce the photo-curable group. After the characterization of the acrylate PLLA polymer structures, the polymers were used for the resin formulation with different weight percentages of reactive diluent (2-hydroxy methacrylate) (HEMA). The diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) photoinitiator weight percentage was calculated using a photoDSC experiment and 1 wt. % of PI was confirmed. The prepared resin formulation showed very good resolution DLP 3D printability after using Sudan I dye and the 3D printed parts showed good mechanical and degradable properties.



Scheme 1 Schematic representation summarizing the conversion of 3D printable photocurable resin formulation based on PLLA into solid objects using a DLP printer.

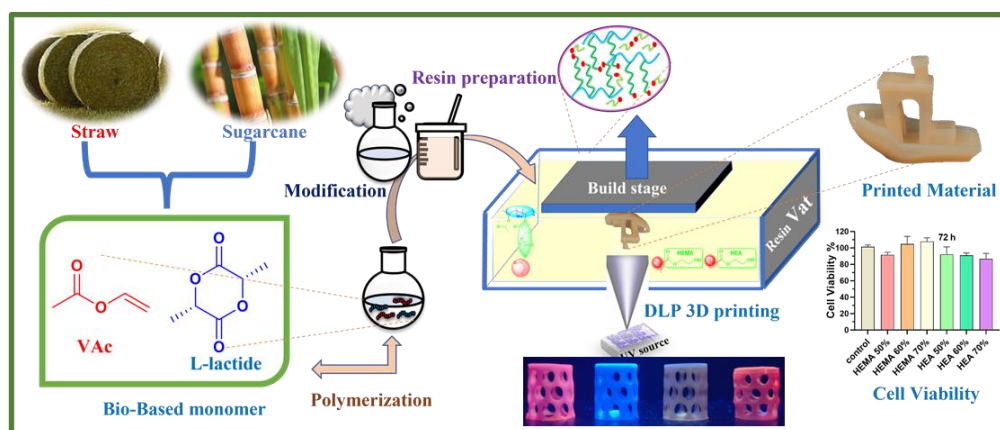
The outcome of the synthesis of Linear and star PLLA polymer and their resin formulations for the DLP 3D printing applications are summarized below,

- Low molecular weight linear and star PLLA polymers are synthesized by ring-opening polymerization and modified in the end functional acrylic group.
- Three resins were formulated using different weight % of linear and star PLLA polymer with HEMA as diluent and TPO as PI.
- Resin formulations and characterized and successfully demonstrated the DLP 3D printing.
- A degradation study was performed in PBS solution over 90 days and almost 30 % degradation was observed.

- The 3D printed materials can be used in different fields of application like Tissue engineering, Tissue culturing matrix, and Soft materials.

Chapter 3: Biocompatible PVAc-g-PLLA Resin Formulations with Tunable Mechanical Properties for DLP/SLA 3D Printing.

In this chapter, A novel biobased acrylate polymer, PVAc-g-PLLA, was designed and synthesized to create resin formulations, eliminating the need for toxic organic solvents, by incorporating reactive diluents such as HEMA and HEA. The successful synthesis of various polymers, including PVAc, partially hydrolyzed PVAc, PVA-g-PLLA, and acrylate PVA-g-PLLA (Fig. 1) was verified through NMR and FT-IR spectroscopy. The molecular weights of these polymers were determined using GPC in a chloroform solvent. The kinetics of the formulated resins were further examined by measuring viscosity and conducting photoDSC studies. The curing study revealed that the resins prepared with HEMA required 1.5 weight percentage of TPO photoinitiator, while those prepared with HEA required 1 weight percentage of photoinitiator. Furthermore, these resins were successfully used for 3D printing with a DLP printer at room temperature. They demonstrated high-resolution printing when used to create complex objects like the Elegoo Mars Test Rook and Benchy. Moreover, the resin formulations could easily incorporate a fluorescent dye, which emitted a glow under UV light. Notably, when comparing HEMA and HEA as reactive diluents, HEMA-based 3D printed parts exhibited superior mechanical and thermal properties, while HEA-based parts displayed a softer texture and higher elongation properties. This versatility holds great promise for a wide range of applications, including tissue engineering, soft robotics, tissue culture, biomedical implants, and scaffolds. Degradability and dye uptake studies were performed with 3D printed parts and showed HEA containing 3D printed parts absorbed dye at a higher rate than HEMA containing 3D printed parts.



Scheme 2: Overall schematic representation for 3D printing of acrylate PVAc-g-PLLA polymeric crosslinker.

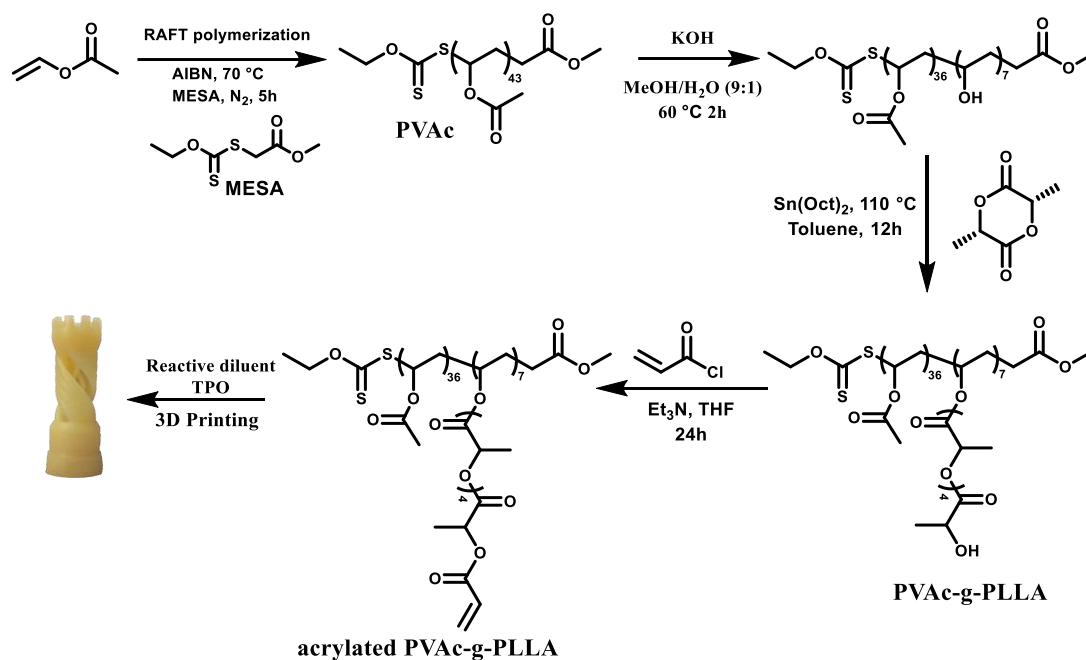


Figure 1 Overall synthetic scheme for acrylated PVAc-g-PLLA polymeric crosslinker

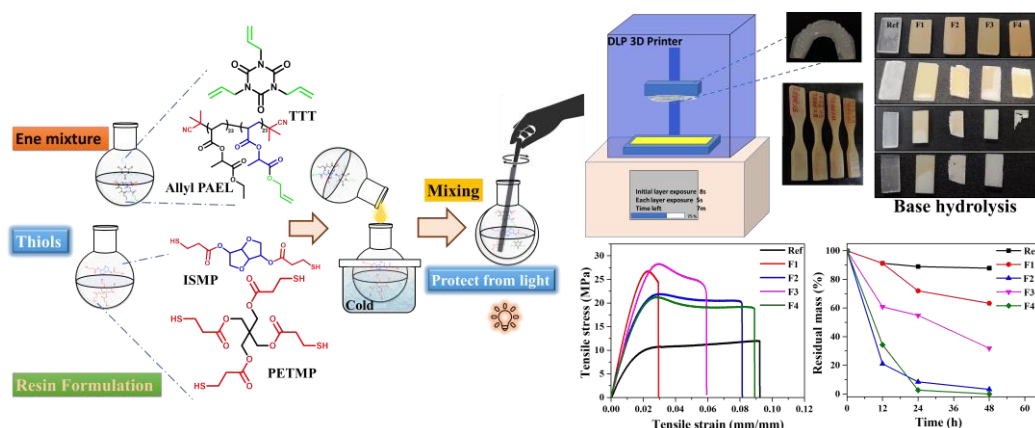
The outcome of the Acrylate PVAc-g-PLLA polymer, its resin formulation and DLP 3D printing are summarized below,

- Acrylate PVA-g-PLLA crosslinker was successfully synthesized and characterized by NMR, GPC, and DSC analysis.
- Different resins were formulated using acrylate PVA-g-PLLA crosslinker with HEMA and HEA diluents.
- Room temperature DLP 3D printing was performed using prepared resin formulations and different standard Stl. files were printed with high resolution.
- Mechanical properties of printed parts were tuned depending on the used reactive diluent HEMA and HEA. HEMA used 3D printed parts showed higher mechanical properties than the HEA used 3D printed parts
- Degradability and dye uptake studies were performed with 3D printed parts and showed HEA containing 3D printed parts absorbed dye at a higher rate than HEMA containing 3D printed parts.

Chapter 4. Thiol-ene-based Degradable 3D Printed Network from bio resource derived Monomers Ethyl-lactate and Isosorbide.

Synopsis

This study has successfully demonstrated a scalable and sustainable approach to the development of 3D printing materials using thiol-ene photochemistry. This method utilizes a polymeric ene derived from ethyl lactate and a thiol derived from isosorbide. The ethyl lactate-based polymeric ene component was synthesized through free radical polymerization of acrylate ethyl lactate monomer, followed by partial hydrolysis and subsequent reaction with allyl bromide. The study also involved an analysis of thiol-ene photo kinetics through photo DSC experiments, shedding light on the chemical reactions occurring during the curing process. Mechanical and thermal property analyses were conducted, providing valuable insights into the potential applications and performance of these innovative biobased thiol-ene materials. The practical application of these materials was demonstrated through 3D printing using a commercial DLP 3D printer, showcasing their suitability for manufacturing and prototyping purposes. Notably, the research highlighted the hydrolytic degradability of 3D printed parts in a 1 M NaOH solution, emphasizing the eco-friendly nature of these materials and their potential to address the issue of non-degradable acrylate-based 3D printed waste. This research sets the stage for the development of environmentally responsible materials that could revolutionize the 3D printing industry. The rapid degradability of polymeric thiol-ene 3D print materials derived from Poly(acrylate ethyl Lactate) (PAEL) opens new possibilities for rapid prototyping in mass production applications, offering a promising solution to sustainability challenges associated with traditional acrylate-based materials. By combining the advantages of biobased sourcing, scalability, and degradability, these materials represent a significant step toward a more sustainable and environmentally conscious future in the field of 3D printing.



Scheme 3: Schematic representation of thiol ene resin formulation with allyl PAEL, Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT), Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), and Isosorbide thiol (ISMP) and DLP 3D printing.

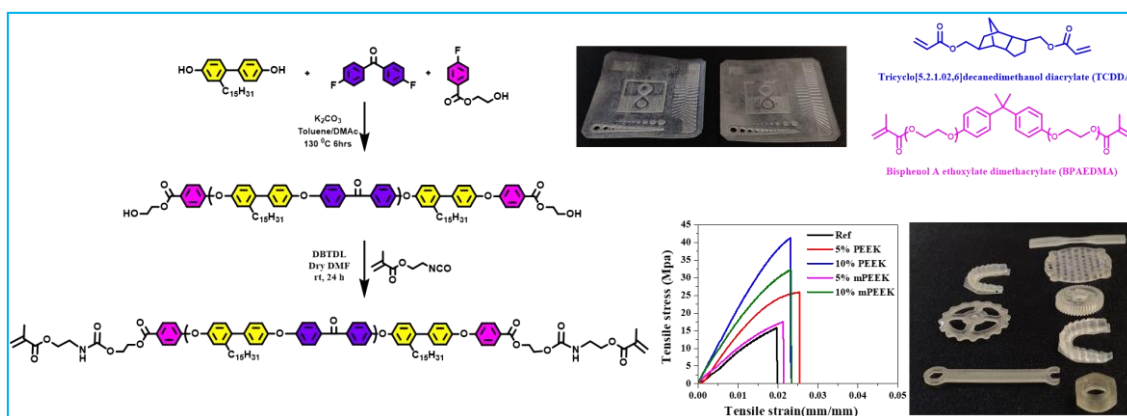
Synopsis

The outcome of the all PAEL polymer, its resin formulation and DLP 3D printing are summarized below,

- Poly(acrylate ethyl lactate), hydrolysis of PAEL, and allyl PAEL polymer were Synthesised successfully and characterized by NMR, GPC, and DSC analysis.
- Allyl PAEL resin formulations were prepared and DLP 3D printing was performed with less exposure time (5s).
- 3D printed thiol-ene network showed good mechanical properties.
- 3D printed thiol-ene network showed very good acid resistance whereas totally degraded in an alkaline medium.

Chapter 5: Room Temperature Photocurable PEEK Polymer Formulations for High-Performance 3D Printing Applications.

In this chapter, we synthesized two different modified acrylate PEEK polymers that were used in DLP 3D printing. The first modified PEEK was synthesized using Bisphenol A, difluoro benzophenone, and 4-fluoro benzoate ester as the end-capping group. Whereas, the second modified PEEK polymer was synthesized using an alkyl chain containing diol which was synthesized according to the literature report.¹⁰ Further, these PEEK polymers were reacted with isocyanate methacrylate to introduce a photocurable group in the terminal position of the polymer. Then Tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate (TCDDA) and Bisphenol A ethoxylate dimethacrylate (BPAEDMA) were used as a reactive diluent for the preparation of resin formulation for DLP 3D printing. The DLP 3D-printed parts showed very high mechanical properties with Young's modulus of almost 55 % of commercial PEEK polymer. The PEEK polymer containing a long alkyl chain in the repeat unit showed good warpage-free properties after 3D printing. And finally, 3D printed materials showed very high thermal stability almost 400 °C for 10 % weight loss.



Scheme 4: Schematic representation of modified PEEK polymer and its DLP 3D printed with high mechanical tensile strength and warpage-free properties.

The outcome of the modified PEEK polymers, its resin formulation, and DLP 3D printing are summarized below,

- A new monomer was synthesized and used for the synthesis of low molecular weight mPEEK polymer.
- Urethane acrylate PEEK resin formulations were prepared for DLP 3D printing.
- High mechanical properties achieved using a low weight percentage of urethane acrylate PEEK polymers.

Chapter 6. Conclusion

The thesis describes the synthesis of different polymeric crosslinkers that were utilized in light-based 3D printing applications. The thesis also explored the systematic synthesis of crosslinkers to achieve a particular outcome after 3D printing either improvement of resolution of the 3D printed parts with expected mechanical properties or degradation properties. After a discussion of the background history of 3D printing and the availability of the materials for liquid-based 3D printing in the first chapter, from next working chapter, synthesis of PLLA-based linear and star PLLA crosslinker was described. In this chapter, the formulation of organic solvent-free resins was prepared with a different weight percentage of acrylate linear and star PLLA polymer and reactive diluent (HEMA). The prepared resin showed good printability and the resolution of the 3D printed parts can be improved using sudan I dye. The 3D printed parts exhibited promising mechanical properties for use in tissue culture application and degradability in PBS solution at ambient conditions. In spite of having good printing and mechanical properties, these resin formulations were not able to print very complex 3D print structures with high resolution. To tackle this problem, in our third project, we introduced the grafting polymerization technique to increase the number of curing groups in the synthesized PVAc-g-PLLA crosslinker. This crosslinker was used to formulate resin with two different reactive diluents with different weight percentages. The prepared resin showed good printability with higher resolution even with complex 3D print structures. The mechanical properties can be also tuned depending on the choice of reactive diluent. Additionally, the 3D-printed materials showed good dye absorption properties from the solution depending on their swelling behavior in the dye solution. Finally, these 3D printed parts showed degradability in PBS solution by 15 % over 90 days of time period. With these

Synopsis

printing experiences, we moved to the fourth chapter where we showed thiol-ene chemistry in DLP 3D printing. Thiol-ene chemistry is usually used for faster reactions and high crosslinking density resulting in higher mechanical properties. We synthesized ethyl lactate-based poly(acrylate ethyl lactate) (PAEL) which was modified to allyl PAEL polymer and used as poly ene crosslinker. This crosslinker is used for resin formulation with thiol molecule and the prepared resin formulation is used for DLP 3D printing. The printing parameter of the thiol-ene resin formulation was very fast and it was curing one layer within only 5 sec. The thiol-ene 3D printed parts showed very high mechanical properties due to high curing density. An isosorbide thiol crosslinker was synthesized by reacting isosorbide with 3-mercapto propionic acid. Incorporation of this thiol crosslinker in thiol-ene resin formulation improves the degradation 100 % weight reduction within 2 days of 3D printed parts in 1M NaOH basic solution without much change in mechanical properties. Whereas, the 3D-printed parts showed very good acid resistance in 1M HCl solution over 7-day time period without changing any weight loss. In the fifth chapter, we synthesized two different modified PEEK polymers and used them in resin formulations. The PEEK polymer containing 3D-printed parts showed very high mechanical properties. Young's modulus of the 3D printed part of PEEK polymer achieved almost 55 % of the values of commercial PEEK polymer. Incorporating a long alkyl chain into the repeat unit of PEEK polymer helped alleviate the warpage issue observed in PEEK 3D-printed parts.

Overall, the thesis described the synthesis of different photo-sensitive polymeric crosslinkers and their relation with different fields of application by creating DLP 3D printed parts. The tuning of the physical properties of 3D printed materials and also giving future aspects of making more suitable crosslinkers depends on the demands needed.

References

1. S. Pal, SK. Asha, *Macromol. Chem. Phys.* **2022**, 223, 2200139
2. C. Yu, J. Schimelman, P. Wang, K. L. Miller, X. Ma, S. You, J. Guan, B. Sun, W. Zhu, S. Chen, *Chem. Rev.* **2020**, 120, 10695.
3. S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, *Chem. Rev.* **2017**, 117, 10212.
4. R. Ajdary, N. Kretzschmar, H. Baniasadi, J. Trifol, J. V. Seppälä, J. Partanen, O. J. Rojas, *ACS Sustainable Chem. Eng.* **2021**, 9, 2727.
5. K. L. Sampson, B. Deore, A. Go, M. A. Nayak, A. Orth, M. Gallerneault, P. R. L. Malenfant, C. Paquet, *ACS Appl. Polym. Mater.* **2021**, 3, 4304.

Synopsis

6. A. Harynska, H. Janik, M. Sienkiewicz, B. Mikolaszek, J. Kucinska- ´Lipka, ACS Sustainable Chem. Eng. **2021**, 9, 6923.
7. J. R. Rocca-Smith, O. Whyte, C.-H. Brachais, D. Champion, F. Piasente, E. Marcuzzo, A. Sensidoni, F. Debeaufort, T. Karbowiak, ACS Sustainable Chem. Eng. **2017**, 5, 2751.
8. B. Gross, S. Y. Lockwood, D. M. Spence, Anal. Chem. **2017**, 89, 57.
9. G. Tafuro, A. Costantini, G. Baratto, S. Francescato, A. Semenzato, ACS Omega **2020**, 5, 15280.
10. B.V. Tawade, S. V. Shaligram, N. G Valsange, U. K. Kharul, P.P. Wadgaonkar, Polym Int **2016**, 65, 567–576

Publications

1. **Shibam Pal**, and Asha SK. Biodegradable, Solvent-Free Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing. *Macromolecular Chemistry and Physics*. **2022**, 223 (22), 2200139.
2. **Shibam Pal**, and Asha SK. Thiol-ene-based degradable 3D printed network from bio resource derived monomers ethyl-lactate and isosorbide. *European Polymer Journal*. **2024**, 205, 112761.
3. **Shibam Pal**, Yogesh Gaikwad, and Asha SK. Room Temperature Photocurable PEEK Polymer Formulations for High-Performance 3D Printing Applications. *ACS Applied Engineering Materials*. **2024**, 2, 6, 1450-1459.

Patent

1. **Shibam Pal**, and Asha SK. Acrylated Polyvinyl-grafted-poly(l-lactide) (PVAc-g-PLLA) Based Compound and Compositions Thereof for 3D Printing (*Provisional patent Application number 202311061154*).
2. **Shibam Pal**, and Asha SK. Modified Photocurable Peek Photopolymer for 3D Printing and Preparations Thereof. (*Provisional patent Application number 202411004776*)

Table of Contents

Content

	Page No.
Acknowledgement	i
Abbreviation and symbol	iv
Synopsis	vi

CHAPTER 1

General Introduction and Literature

1.1	Definition of Additive Manufacturing	1
1.2	Historical Evolution of Additive Manufacturing	1
1.3	Impact of additive Manufacturing Process	2
1.4	Production Process of 3D Printing	4
1.5	Challenges of the AM Technology	5
1.6	Applications of AM Technology	6
1.7	Classifications of Additive Manufacturing	7
	1.7.1 Vat Photopolymerization	7
	1.7.2 Material Extrusion	8
	1.7.3 Powder Bed Fusion	8
	1.7.4 Directed Energy Deposition	8
	1.7.5 Material Jetting	8
	1.7.6 Binder jetting	9
	1.7.7 Sheet Lamination	9
1.8	Different Types of Vat Photopolymerization	9
	1.8.1. Stereolithography (SLA)	9
	1.8.2. Digital Light Processing (DLP)	10
	1.8.3 Continuous Liquid Interface Production (CLIP)	10
	1.8.4 Computed Axial Lithography (CAL)	11
1.9	Materials for the DLP 3D Printing	11

	Page No.
1.9.1 Commercial (meth)acrylate Molecules	11
1.9.2 Photo initiator	13
1.9.3 Reactive diluents	14
1.10 Development of Bio-Based Photopolymer for DLP 3D Printing	15
1.10.1 Polylactide	16
1.10.2 Synthesis of the PLA polymer	17
1.10.3 Introducing Acrylate Bond in the PLA Polymer	18
1.10.4 Thiol -Ene Chemistry in DLP 3D Printing	21
1.10.5 Biobased Thiol-Ene Polymers for DLP 3D Printing	23
1.11 High Performance Polymer in 3D Printing	24
1.11.1 Polyether Ether Ketone (PEEK) polymer	25
1.11.2 3D Printing of the PEEK Polymer	25
1.12 Aim of the Thesis	27
1.13 REFERENCES	28
CHAPTER 2	
Biodegradable, Solvent-Free Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing	
2.1 Introduction	34
2.2 Experimental Section	
2.2.1 Materials	36
2.2.2 Measurements	36
2.2.3 Methods	
A) Resin Formulation with Acrylate Linear and Star PLLA Polymer	37
B) Spot Curing of the Prepared Resin Formulations	37
C) Photo-Differential Scanning Calorimetry	37
D) Viscosity Measurement	39
E) Cure Depth Measurement of each Resin Formulations	39
F) Calculation of Critical Energy and Penetration Depth Measurement	39

	Page No
G) 3D Printing of Prepared Resin Formulations	40
H) Custom Built 3D Printer (Direct Ink Writing)	40
I) Mechanical Test of the 3D Printed Parts	40
J) In Vitro Degradation Study	40
K) Scanning Electron Microscopy Imaging	41
2.2.4 Synthesis and Characterizations	42
a) Synthesis of Acryloyl Chloride from Acrylic Acid	43
b) Synthesis of Linear Poly (l-lactide) Polymer (PLLA)	43
c) Synthesis of Acrylate Linear PLLA Polymer	44
d) Synthesis of Star PLLA Polymer	45
e) Synthesis of Acrylate Star PLLA Polymer	46
2.3 Result and Discussion	
2.3.1 Synthesis and Characterizations of Polymers	48
2.3.2 Photo Calorimetric Studies of Acrylate Polymers and HEMA	49
2.3.3 Viscosity Measurement	53
2.3.4 Resin Cure Characteristics	54
2.3.5 3D Printing of Formulated Resins	55
2.3.6 Mechanical and Thermal Properties of 3D Printed Parts	56
2.3.7 In Vitro Degradation Studies	58
2.4 Conclusions	59
2.5 References	59
CHAPTER 3	
Biocompatible PVAc-g-PLLA Resin Formulations with Tunable Mechanical Properties for DLP/SLA 3D Printing	
3.1 Introduction	63
3.2 Experimental Section	
3.2.1 Materials	64
3.2.2 Measurements	65
3.2.3 Methods	66
A) DLP Resin Preparation	66

	Page No.
B) Curing kinetics of Resins	66
C) DLP 3D Printing of the Resins	66
D) Mechanical Test	67
E) In vitro Degradation and Swelling Study	67
F) Cell Viability Test	67
G) Dye Absorption and Release Study	68
H) Photo calorimetric curing percentage calculation	68
3.2.4 Synthesis and Characterization	69
1) Synthesis of the small molecule	70
a) Synthesis of the Acryloyl Chloride from acrylic Acid	70
b) Synthesis of Methyl (ethoxy carbonothioyl) sulfanylacetate (MESA)	70
2) Synthesis of the PVAc, hydrolyzed PVAc, PVAc-g-PLLA, PVAc-g-PLLA acrylate Polymers	71
c) Synthesis of poly(vinyl acetate) (PVAc)	71
d) Synthesis of Partially hydrolysis of PVAc	72
e) Synthesis of graft copolymer of poly(vinyl acetate)-graft-poly(L-lactide) (PVAc-g-PLLA)	73
f) Synthesis of PVAc-g-PLLA Acrylate Polymer	74
3.3 Result and Discussion	
3.3.1 Synthesis and characterization of PVAc, hydrolysed PVAc-g-PLLA, PVA-g-PLLA acrylate	76
3.3.2 Resin Formulations, Viscosity, and Photo-calorimetric Studies	80
3.3.3 DLP 3D Printing Using Formulated Resins	82
3.3.4 Tuneable Mechanical and Thermal Properties of DLP Printed Parts	84
3.3.5 Water uptake and Dye Absorption Study	86
3.3.6 Cell Viability Test and In Vitro Degradation Study	89

	Page No.
3.4 Conclusions	90
3.5 References	91
CHAPTER 4	
Thiol-Ene-based Degradable 3D Printed Network from Bio Resource Derived Monomers Ethyl-lactate and Isosorbide	
4.1 Introduction	95
4.2 Experimental Section	
4.2.1 Materials	97
4.2.2 Measurements	97
4.2.3 Methods	
A) Thiol-Ene Resin Formulation for 3D Printing	98
B) Photo-Differential Scanning Calorimetry (Photo-DSC)	98
C) Viscosity Measurement	98
D) 3D Printing of Thiol-Ene Resin Formulations	99
E) Mechanical Test of 3D Printed Part	99
F) Hydrolytic Degradation of 3D Printed Parts	99
4.2.4 Synthesis and Characterization	100
1) Synthesis of the AEL and ISMP	101
a) Synthesis of Acrylate Ethyl Lactate (AEL) Monomer	101
b) Synthesis of isosorbide bis(3-mercapto) propionate	102
2) synthesis of the PAEL, partially hydrolyzed PAEL, allyl PAEL polymers	103
c) Polymerization of Acrylate Ethyl Lactate Monomer	103
d) Partial hydrolysis of poly (acrylate ethyl lactate	104
e) Allylation of hydrolyzed poly (acrylate ethyl Lactate)	105
4.3 Result and Discussion	
4.3.1 Synthesis of PAEL, hydrolyzed of PAEL, allyl PAEL and ISMP	107
4.3.2 Resin Formulation and Photo Calorimetric Studies	110
4.3.3 Rheology and Viscosity of Prepared Resin Formulations	113

	Page No.
4.3.4 3D Printing of Thiol-Ene Resins	114
4.3.5 Mechanical and Thermal Properties of The Thiol-Ene Polymer Network	115
4.3.6 Degradation of thiol-ene polymer network	117
4.4 Conclusions	119
4.5 References	120
CHAPTER 5	
Synthesized Tailored Photocurable PEEK Polymers for High-Performance 3D Printing Applications	
5.1 Introduction	123
5.2 Experimental Section	124
5.2.1 Materials	124
5.2.2 Measurements	125
5.2.3 Methods	
A) Resin Preparation for DLP 3D Printing of Urethane Methacrylate PEEK Polymers	125
B) Curing Kinetics of Resin Formulations (Photo-DSC)	126
C) Measurement of Resin Viscosity	126
D) DLP 3D Printing of Urethane Methacrylate PEEK Polymer Resins	126
E) Mechanical Test of 3D Printed Part	127
5.2.4 Synthesis and Characterization	127
1) Synthesis of 3-pentadecyl 4,4'-biphenol and Synthesis of 2-hydroxyethyl 4-fluorobenzoate	128
a) Synthesis of 3-pentadecyl 4,4'-biphenol	128
b) Synthesis of 2-hydroxyethyl 4-fluorobenzoate	129
2) Synthesis of PEEK, mPEEK, and urethane methacrylate of PEEK, and mPEEK	130
c) Synthesis of polyether ether ketone (PEEK) polymer	130
d) Synthesis of modified polyether ether ketone (mPEEK) polymer	132

	Page No.
e) Synthesis of urethane methacrylate polyether ether ketone (UMPEEK) polymer	133
f) Synthesis of urethane methacrylate modified polyether ether ketone (UMmPEEK) polymer	134
5.3 RESULT AND DISCUSSION	
5.3.1 Synthesis and characterization of urethane methacrylate PEEK (UMPEEK) and urethane methacrylate mPEEK (UMmPEEK) polymers	136
5.3.2 Resin formulations and photocuring experiments	138
5.3.3 Viscosity Measurement	140
5.3.4 DLP 3D printing of PEEK resin formulations	140
5.3.5 Mechanical and Thermal Properties of Printed Parts	142
5.4 Conclusion	144
5.5 References	144
CHAPTER 6	
Conclusion and Future Perspective	
6.1 Conclusions	147
6.2 Future Perspective	150
Abstract for indexing	152
List of publications and patents	153
List of poster presentation with details	154
About the Author	158
Erratum	

CHAPTER 1

General Introduction and Literature

1. INTRODUCTION

1.1 Definition of Additive Manufacturing

Additive Manufacturing (AM) has revolutionized various aspects by enabling the development of intricate 3-dimensional (3D) structures through layer-by-layer deposition of materials. AM involves converting digital files into physical objects using 3D printers. This process, also known as 3D printing, starts with a Computer Aided Design (CAD) model that guides the printer in creating the desired object layer by layer. While 3D printing is a crucial component of AM, the latter encompasses a broader innovation production process. AM involves multiple steps beyond printing, making it a sophisticated workflow that includes design, material selection, printing, post-processing, and quality assurance. This technology enables the construction of complex forms that were previously challenging or impossible to achieve using traditional manufacturing methods.¹

1.2 Historical Evolution of Additive Manufacturing

In 1970, Johannes F. Gottwald invented and patented a technology where metal was melted at its melting temperature using an electrical field and deposited onto a carrier. Upon contact with the carrier, the molten metal solidifies, allowing for the continuous deposition of molten metal to form a metal object. This concept represents one of the earliest forms of material printing by depositing one layer upon another. The patent's statement, *"It is therefore an additional object of the invention to minimize the use of materials in a process of the indicated class"* highlights the advantage of utilizing a layer deposition approach, even in its early stages.² In 1980, Hideo Kodama invented an XYZ plotter equivalent to the 3D printer and filed a patent; but the work was not recognized and the project was terminated.³ Later on, in 1984, Charles Hull made a groundbreaking contribution to the field of additive manufacturing by introducing a fundamental SLA (stereolithography) 3D printing method. Utilizing photocurable adhesive materials composed of urethane dimethacrylate, acrylic acid, and a benzophenone photo initiator with a hydroquinone inhibitor, Hull aimed to significantly enhance the efficiency, reliability, and precision of 3D printing processes. This innovation addressed critical challenges prevalent in traditional plastic part production, particularly the time-consuming and expensive nature of design iterations and prototyping phases. Hull's invention marked a pivotal moment in the evolution of additive manufacturing, providing a solution to the complexities associated with previous methods involving radiation beams and fluid mediums. By filing a patent for his pioneering work, Hull cemented his legacy as a visionary figure often hailed as the *"father of 3D printing."*⁴ In 1989, Scott Crump introduced a pivotal advancement in additive

manufacturing with the invention of fused deposition modeling (FDM), a widely adopted 3D printing technology. Driven by the vision of fabricating three-dimensional objects layer by layer, FDM utilizes a process where successive layers of selectively chosen materials in fluid form are deposited onto a base and solidified through controlled temperature differentials until the entire object is completed. Unlike SLA 3D printing, which relies on photocurable adhesive materials, FDM requires solid filament materials that undergo melting to a fluid state for deposition onto the base, subsequently solidifying to achieve the final object.⁵ Since 1990, numerous companies and institutes have developed various 3D printing technologies, expanding the range of printable materials to include metals and polymers for diverse end-use products. As printed objects grew in complexity, the use of support materials became common, aiding in their creation and easy removal post-printing. Despite advancements, the printing resolution and cost of 3D printers remained a notable consideration in adopting this technology widely. With time the technology of the 3D printer matured and are able to print more fine structures. Nowadays, the cost of 3D printer has reduced considerably and become more affordable.

1.3 Impact of additive Manufacturing Process

The impact of additive manufacturing (AM) techniques has increased enormously in the domain of scientific and industrial innovation, revolutionizing traditional manufacturing processes and enabling unprecedented levels of customization, efficiency, and complexity in product design and production. It has started from the 1980s with the innovation of the SLA liquid photo-resin based 3D printer. Since, last 40 years AM technology finds the place in every field of application from medical to aerospace area. Figure 1.1 represents the enhancement trends in terms of publication in the field of the AM and 3D printing which is generated from the Sci-finder search engine with the key words “Additive Manufacturing, 3D printing, and vat polymerization, DLP 3D printing.

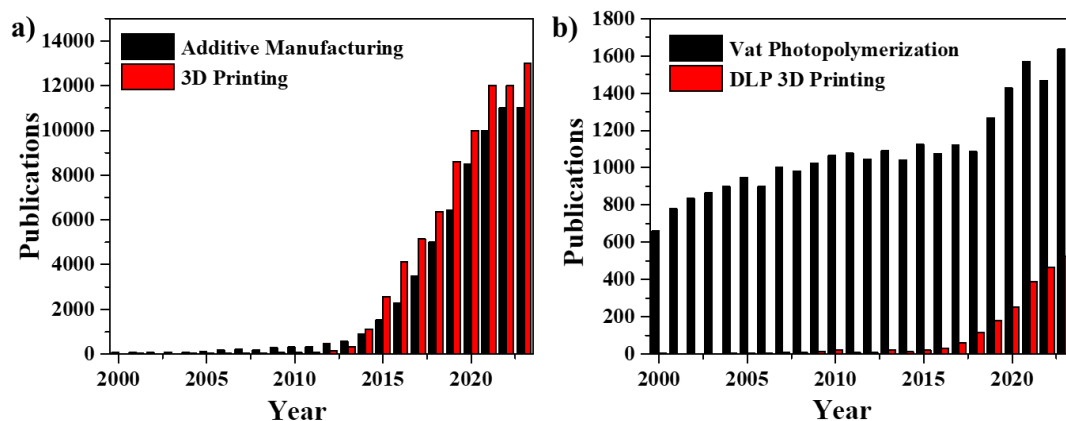


Figure 1.1 Sci-finder search indicating increase in number of publications since 2000 for keywords a) additive manufacturing, 3D printing, b) vat photopolymerization, DLP 3D printing.

From the graph it can be seen that since the last two decades there is an impressive increase in the number of the publications related to AM. From the industrial point of view, the impact of the AM method was in the rapid production of the end product with lesser time and cost in comparison with conventional subtractive method. Manufacturers started to use additive manufacturing depending on its ability to produce custom-made parts with less wastage and series of products which makes the AM more flexible than conventional moulding or casting method. The report of the Wolhers 2015, mentions the significant growth rate of the AM technique in terms of the generation of revenue from materials sales. In 2015, AM generated revenue over 900 million USD in the field of all kinds of materials either metal, polymer, or ceramics. Among these Photopolymer itself generated more than over 350 million USD in 2016.⁶ According to the Formlabs report 2022 which is based on more than 400 responses from different industries, the 3D printing has been a significant uptick in new applications within the recent adopters who has invested in the last two years. Among them 63 % inventors use end-use parts which is almost double than the.⁷ The Indian 3D printing industry is expected to develop at a compound annual growth rate (CAGR) of 20.3% between 2023 and 2030, indicating that it is set for spectacular expansion. With sales expected to reach an amazing \$705.1 million by 2030, the growth is expected to continue on its upward trend, which saw strong revenue increase to \$111.0 million in 2022.⁸

1.4 Production Process of 3D Printing

The 3D printing process relies on three key steps. Initially, a computer-aided design (CAD) model is created using specialized software. Next, the CAD file is transferred to another software called slicer where the CAD file is converted into a pack of layers with definite dimensions (Figure 1.2). Then this file is supplied to the 3D printer, where the object is built layer by layer. Finally, in the post-processing stage, the printed products are refined for use. In the preprocessing step, a 3D model is designed using CAD software and then converted into a Standard Triangulation Language (STL) format. This format, established in 1987, serves as the standard for 3D model production in additive manufacturing (AM). The resolution of the 3D printed model is determined by its triangular mesh as defined in the STL file. In the processing step, the STL file is transferred to another software where the 3D model is sliced into layers based on the desired thickness of the printing layers. Additionally, adjustments to the size of

the model can be made during this stage. For complex 3D models, support structures may be generated within the slicing software to prevent printing failures. Ensuring the proper orientation of the 3D model is crucial; typically, the model's surface should be parallel and touching the XY plane, but adjustments can be made in both the XY and Z directions. Once the 3D model is sliced, the file is transferred to the 3D printer, which then proceeds to print each layer of the model sequentially. The printing technique may involve either a top-down or bottom-up approach, depending on the specific printer and printing method used. In the postprocessing step, the 3D printed part is removed from the platform and refined to the final product. In the case of the vat polymerization 3D printing process, the 3D printed part needs to be washed with isopropyl alcohol solvent to remove the unreacted materials, and a post curing treatment is necessary. Other post-processes like removal of supports, polishing, heat treatment, coating, sterilization, etc. can be applied after the removal of the 3D print object.⁹

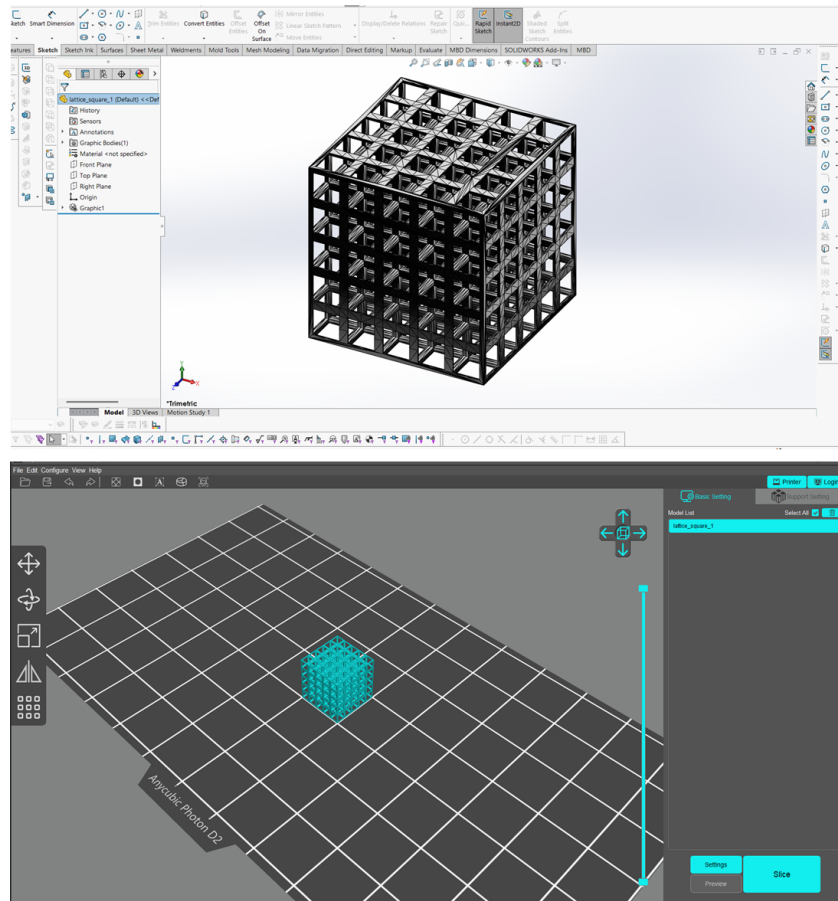


Figure 1.2 CAD file prepared from CAD file software (solid works) (top), the CAD file was sliced in the slicer software (anycubic slicer software)

1.5 Challenges of the AM Technology

Although additive manufacturing (AM) technology has many benefits, there are a few noteworthy challenges that need to be taken into consideration.

During the early stages of additive manufacturing (AM) technology, a significant challenge revolved around sourcing suitable materials for 3D printing. Various printing methods necessitated distinct material properties to ensure optimal performance. For instance, in extrusion-based 3D printing, materials had to align their melting temperatures with the printer's limits. Conversely, in liquid-based printing, resin viscosity had to remain within specific parameters for effective printability. Over time, advancements in 3D printer technology addressed these issues. Through innovations in temperature control mechanisms, printers now accommodate a broader range of materials. Furthermore, precise regulation of resin bed heat enables fine-tuning of resin viscosity, thereby enhancing the smoothness of printing processes. Achieving high resolution in 3D printed products posed a significant challenge in the development of additive manufacturing. While liquid-based 3D printing has made substantial strides in improving resolution, micro-level resolution remains a concern for extrusion-based methods. Post-processing steps are often required for extrusion-based prints to achieve a smoother resolution. However, advancements in both printing technologies continue to refine the resolution capabilities of 3D printed products over time.¹

In comparison to traditional manufacturing methods, 3D printing is generally slow. However, it offers significant advantages in terms of flexibility and cost-effectiveness. Unlike traditional processes that require changing the entire mould for material alterations, 3D printing allows for swift modifications by simply adjusting the CAD file. This capability reduces both time and expenses associated with material changes. On the other hand, post-processing of 3D printed products remains a major challenge, adding an extra step that increases both cost and time before the product can be utilized in its final form.

One significant issue with AM technology is scalability. When it comes to mass production, traditional manufacturing techniques frequently perform better than AM because of things like slower print rates and smaller build quantities. Furthermore, the initial expenses linked to additive manufacturing equipment and materials may provide a barrier to their widespread implementation. Notwithstanding these obstacles, further developments in AM technology, such as quicker printing methods and bigger build platforms, are progressively resolving scaling issues and broadening the use of AM in several sectors.¹⁰

1.6 Applications of AM Technology

There are many potential applications for AM technology in different fields, including medical, education, aerospace, automobile, electronics etc (Figure 1.3). 3D printing serves a multitude

of purposes across various industries. Primarily utilized for prototyping, it provides designers with a rapid and cost-effective means to bring their concepts into physical form. Furthermore, its ability to facilitate custom or low-volume production without the need for expensive tooling makes it invaluable in manufacturing.

In medicine, 3D printing contributes to the development of medical devices, implants, and potential organ and tissue engineering.^{11,12} A group of researchers invented a novel 3D printed class III medical device architecture of tracheobronchial splint for the patient-specific uses.¹³ In the field of tissue engineering by rapid prototyping, Albino Martins et al. showed the culture of human osteosarcoma-derived cells in a 3D print scaffold structure prepared with 30:70 (wt. %) blend of starch and polycaprolactone.¹⁴

The aerospace industry has been a prominent sector propelling the expansion of the AM market, contributing to 18.2% of its revenue. Revenue estimates for the AM industry reached \$2.7 billion in 2016, with projections exceeding \$100 billion in the next two decades, predominantly driven by aerospace applications through the supply chain and repair operations.¹⁵

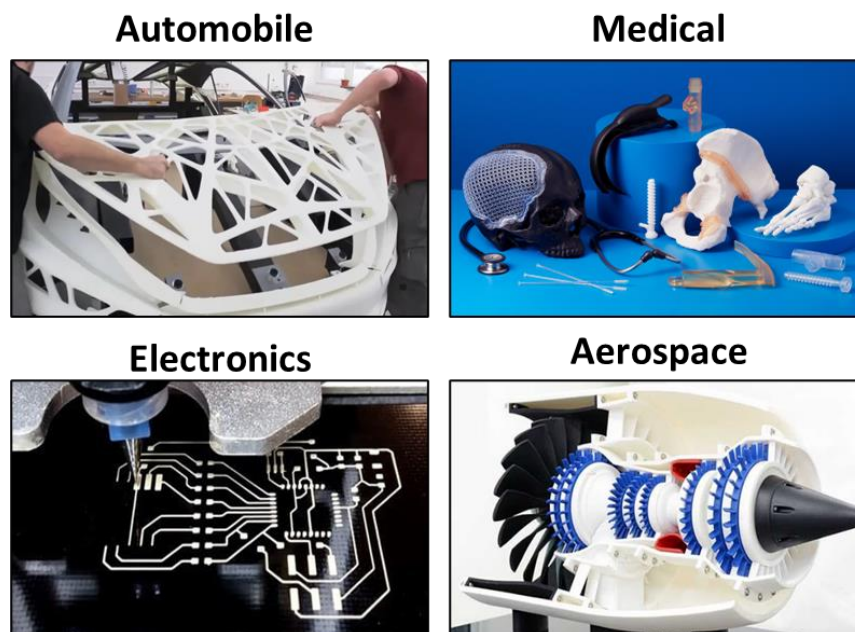


Figure 1.3 Application of additive manufacturing in different fields like Automobiles, Medical, electronics, and aerospace.

Automobile industries are acquiring the AM technology for the creation of complex geometries and intricate components with reduced material waste. AM technology is rapidly revolutionizing the electronics industry by offering innovative solutions for end-use production, customization, and prototyping. This technology enables the creation of electronic parts and assemblies in small batches and prototypes without the requirement for expensive

tooling and lengthy lead times. Patel et al. investigated the mechanical characteristics of highly stretchable and UV curable (SUV) elastomer systems, specifically designed for DLP-based 3D printing. The ink formulation comprised epoxy aliphatic acrylate (EAA), aliphatic urethane diacrylate (AUD), and a photoinitiator. Their study primarily focused on assessing the impact of varying proportions of EAA and AUD on the mechanical properties of the elastomers. Notably, the authors observed a direct correlation between the quantity of AUD and the enhancement of mechanical properties. They demonstrated that increasing the amount of AUD resulted in significant improvements, with elongation capabilities reaching up to 1100%.¹⁶ It also extends the applications of AM technology to food customization, and fashion where it enables the creation of tailored products ranging from custom-fit lightweight parts.^{17,18,19}

1.7 Classifications of Additive Manufacturing Technologies

The AM technology can be classified into seven major categories which are mentioned below. The details of each category are explained here; since the thesis work depends on the materials development for vat polymerization, the main focus is given to the Vat photopolymerization and a sub section for the different types of vat polymerization AM techniques.²⁰

1.7.1 Vat Photopolymerization

Among the different AM technology vat photopolymerization is an attractive strategy for fabricating 3D printed parts with high resolution and accuracy. In this 3D printing method, the liquid resin materials are selectively cured in the presence of UV light or laser layer-by-layer either in a top-down or bottom-up fashion. Firstly, the liquid resin is poured into the vat and build platform is dipped into the resin, light of a selective wavelength is exposed to solidify the resin according to the CAD file. Vat photopolymerization lithography-based 3D printing approach is used in Digital light processing (DLP), stereolithography (SLA), Continuous Liquid Interface Production (CLIP), Computed Axial Lithography (CAL). The details of those are given in the next section.²¹⁻²³

1.7.2 Material Extrusion

Material extrusion is a dynamic 3D printing process in which a plastic or metal filament is deposited onto a build platform layer-by-layer through a heated nozzle, constructing the complete 3D printed product. Fused Deposition Modeling (FDM) is a material extrusion AM technique, where plastic filament is heated to its molten state and extruded through the nozzle of the 3D printer. In response to varying demands and the intricacy of the 3D print material, FDM 3D printers can incorporate multiple nozzles, enabling the creation of multi-material filament prints with enhanced versatility and functionality.^{24,25}

1.7.3 Powder Bed Fusion

Powder bed fusion is an AM technique, involving the gradual fusion of powdered materials layer by layer under the influence of heat sources such as laser beams, electron beams, and infrared beams. These heat sources selectively fuse the powder materials at precise layer thicknesses, facilitating the creation of intricate three-dimensional objects. In this AM techniques different types of powder materials of plastics, ceramics, composite, glass, metals and its alloys are used. The products manufactured using this technique find applications across various fields including aerospace, the energy sector, transportation, and more.^{26,27}

1.7.4 Directed Energy Deposition

The DED process, which is classified as an AM method, fuses materials during the depositing process by using concentrated heated energy. The concepts of welding and cladding are combined in this technique. Thermal energy sources that are focussed on the layer before them include electron beams, lasers, and welding heat flux. The concentrated thermal energy zone is simultaneously supplied with feedstock materials, such as wires and powders. The feedstock around the thermal energy point melts along with the preceding layer to produce the resulting molten pool. After cooling the molten layers, the deposited bed form according with the CAD file. Only metal materials or metal alloys are used in this AM technique.^{28,29}

1.7.5 Material Jetting

In material jetting AM technology, the 3D printed product is formed through the deposition of photocurable droplets onto a build platform, which are then cured by a UV light source typically ranging from 100 to 400 nm. Photo polymers are stored in air-excluding tanks and transferred to the nozzle through heating. They are then deposited onto the build platform as droplets, forming a thin layer. After curing the thin layer, the platform is lowered, and the next layer begins to form on top of the previous one. This method offers adaptability to thin layer thicknesses, resulting in high-quality parts with minimal staircase effects and thin wall features. The technology also allows for the combination of different materials, enabling a multi-material approach and facilitating the production of composite parts.^{30,31}

1.7.6 Binder jetting

Binder jetting AM technology involves depositing a liquid binding agent onto a powder bed to selectively bind the powder polymeric or ceramics particles together without using energy beam. This AM technique has several steps starting from the printing to annealing and finishing the 3D print product completely. The binder agent is deposited on the powder bed only on the specific region (according to the CAD file) and first layer is formed. After that the first layer is

lowered and next layer of powder material is supplied. This process continues until the whole green body print is finished.^{32,33}

1.7.7 Sheet Lamination

Sheet lamination is an AM technology where the whole 3D printed part is created by bonding layers of sheet on top of another. Laminated object manufacturing (LOM) is one category of the sheet lamination where materials are supplied from a roll of sheet and cut into a desired shape with laser and the layers of sheets are bonded together using heat activated resin.^{34,35}

1.8. Different Types of Vat Photopolymerization

Vat photopolymerization technique is further classified into four types depending on the work function of 3D printer. These vat photopolymerization techniques are stereolithography (SLA) and Digital Light Processing (DLP), Continuous Liquid Interface Production (CLIP), Computed Axial Lithography (CAL). The details of each type vat photopolymerization are described in the next section.

1.8.1. Stereolithography (SLA)

Stereolithography (SLA) is a 3D printing technology that uses a laser to cure resin into a solid object. It is one of the oldest and most widely used 3D printing technologies and is commonly used to create high-precision and high-quality parts. In an SLA printer, a laser beam is directed onto a surface of liquid resin, which is contained in a vat. The laser trace is used to cure the resin into a solid form, layer by layer. The object is built up from the bottom of the vat, and the platform on which the object is built is lowered as each layer is cured. Once the object is complete, it is removed from the vat and any remaining resin is cleaned off using isopropyl alcohol. SLA is known for its high precision and ability to produce smooth surfaces with fine features. It is commonly used for prototyping and producing custom or low-volume parts, as well as for creating unique one-off items. The materials used in SLA printing include photopolymers, which are liquid resins that are cured by light, making thermosetting three-dimensional network polymers.³⁶⁻³⁸

1.8.2. Digital Light Processing (DLP)

Digital Light Processing (DLP) is a 3D printing technology that uses a digital projector to cure resin into a solid object (Figure 1.4 Schematic representation). Unlike the stereolithography, in the DLP 3D printing technique a digital projector light source is used rather than a laser to cure the resin formulations. The projector is used to cure the resin into a solid form, layer by layer, as the object is built up from the bottom of the vat. Once the object is complete, it is removed

from the vat and any remaining resin is cleaned off. DLP is known for its fast-printing speeds and high resolution, as it can cure resin at a pixel level.

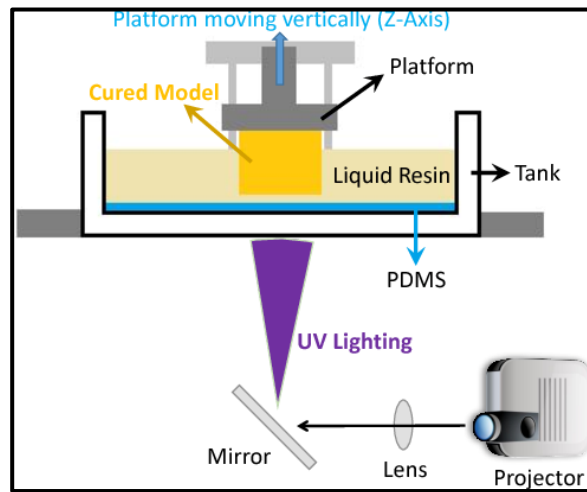


Figure 1.4 Schematic representation of a DLP 3D printing technology³⁹ Copyright © 2016, IEEE

It is commonly used for prototyping and producing custom made products, as well as for creating unique solitary objects. DLP printing is often used for prototyping, jewellery making, and other applications that require fine detail and high resolution. It is also used in the manufacturing of end-use products, such as dental crowns and bridges, hearing aids, and other medical devices. The materials used in DLP printing include photopolymers, which are resins that are cured by light. Bio-based photo-polymeric resin formulations are also used for DLP 3D printing. The resolution of the 3D printed products from DLP 3D printing also depends on the layer thickness and the curing time of the resin formulation.⁴⁰⁻⁴²

1.8.3 Continuous Liquid Interface Production (CLIP)

Continuous liquid interface production vat photopolymerization is an advanced version of the DLP 3D printing. Unlike the DLP technique in this 3D printing an oxygen permeable film is used which inhibits the polymerization making a dead zone above the thin film. The printing process of CLIP like UV exposure, resin renewal, and part elevation are continuous. Just above the dead zone the cured 3D printed part can be continuously pulled out making a suction for the renewal of reactive resin. The size of the dead zone is nearly 20-30 μm for the fast and precise CLIP 3D printing.^{43,44}

1.8.4 Computed Axial Lithography (CAL)

Computed axial lithography also called volumetric lithography is an advanced DLP 3D printing technique. In this technique the whole 3D printed part is formed by the arbitrary projection of

the 2D image in a rotational resin bed and the photosensitive resin is cured in the presence of the UV light source. After forming one layer, resin cylinder rotates for the next layer. The enhancement of material properties of this 3D printed product is still challenging but this 3D printing technique showed promise of higher printing speed with high resolution.^{45,46}

1.9 Materials for the DLP 3D Printing

The materials that can be used for DLP 3D printing are liquid curable resins. The exact formulations of commercial resin materials are often proprietary and undisclosed. Typically, these commercial resins consist of a blend of acrylates or methacrylate along with a photo initiator. DLP printers utilize a diverse list of resins tailored to specific 3D printing requirements. Some resins are optimized for swift printing with a variety of colours, while others are specialized for prototyping applications demanding high toughness and elongation properties or for bio-medical application. This section gives a detailed insight into the structures and curing chemistry of commercial acrylates and methacrylate's, photo initiator, and reactive diluents utilized in DLP 3D printing.⁴⁷⁻⁴⁹

1.9.1 Commercial (meth)acrylate Molecules

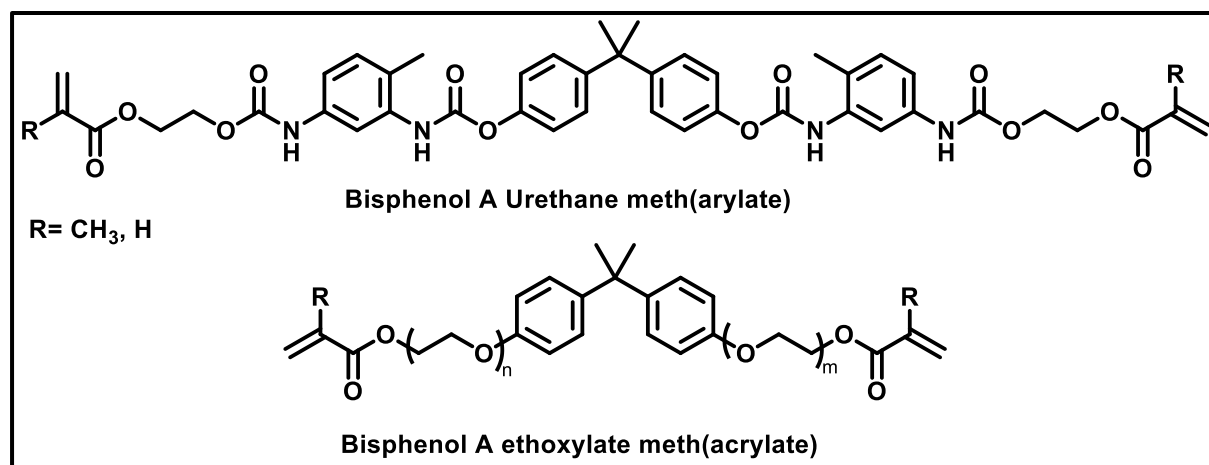


Figure 1.5 Structural representation of some (meth)acrylate oligomers

The commercial materials containing acrylates or methacrylate double bonds undergo radical polymerization during the 3D printing process, involving initiation, propagation, and termination stages (Figure 1.5). Different weight percentage of these (meth)acrylate molecules are used for the preparation of the resin formulations with organic solvent or reactive diluents to optimize the resin viscosity. The viscosity of the resins is a crucial parameter for the DLP 3D printing. The viscosity of the resin should be less than 10 Pa.s⁵⁰ to perform smooth DLP 3D printing. Higher viscosity will make it challenging for the resin to flow during 3D printing, which will lead to printing failure at room temperature. A photo initiator is mixed with the resin

formulation in minimum quantities to start the curing of the (meth)acrylate group and after that it will form a crosslinked polymer network. The presence of urethane group in the (meth)acrylate molecule has been shown to improve the mechanical toughness after 3D printing by inter molecular hydrogen bonding and also improve the elongation properties of the 3D printed parts.⁵¹ The photo initiator present in the resin triggers the radical formation upon exposure to light from the printer projector which react with the (meth)acrylate double bond and starts the polymerization propagation, resulting in the formation of layered solid polymer. This process is repeated for each layer formation to complete the whole 3D printed part. Chiappone A. et al. reported 3D printing for creating hybrid nanocomposites with superior mechanical properties using commercial silica-based acrylate molecules. A complex multi-layered architecture was 3D printed in the building area of 100 X 56.25 X 150 mm using a mixture of 3-(trimethoxy silyl) tetraethyl orthosilicate (TEOS), propyl methacrylate (MEMO), and poly(ethylenglycol)diacrylate (PEGDA, Mw 600 g mol⁻¹) in the presence of photoinitiators (Irgacure 819 and Irgacure 1173). The mechanical properties of the 3D printed structure was improved by acidic vapour treatment, which caused the formation of metal-alkoxysilane linkages in the polymeric network, resulting in the in-situ creation of inorganic nanoparticles (Figure 1.6a).⁵²

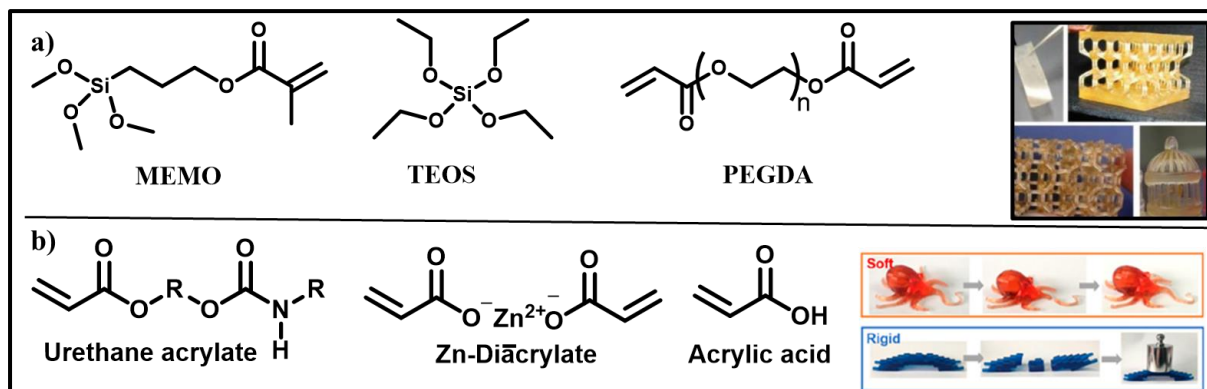


Figure 1.6 a) Commercial silica acrylate used for the fine 3D printed product formation, **Ref 52**. Copyright © 2016, American Chemical Society b) urethane acrylate used for tuneable (soft or hard) DLP 3D printed product. **Ref 53**. Copyright © 2021, American Chemical Society.

Zhu G et. al. reported a 3D printed structure with recyclable and healable properties using the commercial urethane mono-acrylate and zinc metal-based di-methacrylate as crosslinker, camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate as photo-initiator. The 3D printed parts from this resin formulation showed tuneable mechanical properties depending on the

acrylic acid monomer ratio. This is attributed to the hydrogen bonding within the 3D print network polymer. (Figure 1.6b).⁵³

The commercial resin formulations come in various formulations tailored for specific properties and applications, including strength, flexibility, transparency. Selecting the right resin is crucial for achieving desired outcomes, considering their distinct characteristics.⁹ Moreover, strict adherence to manufacturer guidelines regarding resin handling and storage is paramount due to potential toxicity and skin/eye irritation risks. Researchers are continuously working to improve the materials used in DLP 3D printing, aiming for better printing ability and application in bio-medical, aerospace, etc fields. Additionally, the development of degradable polymeric materials for DLP 3D printing, aiming to create eco-friendly solutions for sustainable manufacturing.

1.9.2 Photo initiator

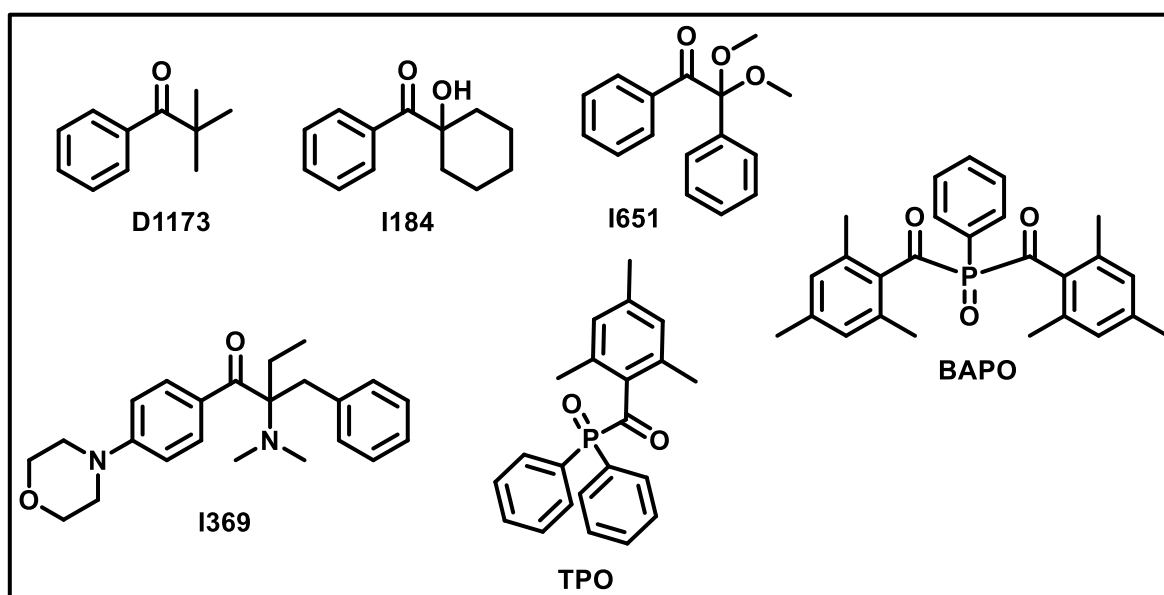


Figure 1.7 List of photo initiators generally used for 3D printing resin formulations.

The photo initiator is a crucial component of photo resin formulation, initiating the photopolymerization process of (meth)acrylate, thiol-ene, or thiol/acrylate resin formulations through radical generation. It breaks down into radicals upon absorbing light energy, thereby initiating radial polymerization. Typically, photo initiators used in resin formulations are classified into two categories known as Norrish type I and Norrish type II. In type I, photo initiators consist of single molecules that cleave into radicals when exposed to light at an appropriate wavelength. The Darocure 1173 is an example of type I photo initiator, which cleaves into radical by exciting the energy from $n \rightarrow \pi^*$ transitions when 350-360 nm

wavelength light falls on it. Similarly, Irgacure 184, Irgacure 651 and Irgacure 369 belong to the same type of photo initiator (Figure 1.7). Phosphine oxide-based photoinitiators (TPO and BAPO) also fall under the category of type I photo initiators. They are widely preferred due to their high wavelength (405 nm) absorption capability. The presence of a phosphorus atom adjacent to the carbonyl group in the photoinitiator structure lowers the energy level of π^* , facilitating the $n \rightarrow \pi^*$ energy transition.⁵⁵ Norrish type II is generally two component system for generating the radical. A co-catalyst is required for the formation of the radical in type II photo initiator which make it not so favourable for the DLP 3D printing. Lim S. K. et. al. used metal-based photo initiator, tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (Ru) with sodium persulfate for the visible light initiation of the DLP 3D printing resin.⁵⁵ Sandmeier M. et. al. used a polymeric photo initiator consisting of a cross linkable group in the terminal position of the photo initiator. Two different types of polymeric photo initiators have been reported for the ring opening polymerization of ϵ -caprolactone. Finally, different weight percentage of the low molecular weight BAPO containing photo initiator was used for the heat assisted DLP 3D printing.⁵⁶ Recently, a smartphone-powered projector portable DLP 3D printer fabricated for generating designed patterns of hydrogel of polyethylene glycol diacrylate (PEGDA) reported tris(2,2'-bipyridyl) dichloro-ruthenium (II) hexahydrate with sodium persulfate, Ru/SPS mixture as photo initiator.⁵⁷

1.9.3 Reactive diluents

Synthetic photopolymers or highly viscous commercial (meth)acrylates are difficult to 3D print with DLP 3D printer at room temperature. The desirable viscosity for printable resin formulations should not exceed 10 Pa.s.⁵⁰ Various types of diluents are employed to decrease the viscosity of resin formulations, with organic solvents being a common choice. They effectively reduce viscosity and aid in achieving a homogeneous solution of dissolved photopolymer. However, the utilization of organic solvents presents several challenges:⁵⁸⁻⁶⁰

1. While organic solvents can effectively reduce viscosity, they may lead to issues such as solvent leaching post-printing, resulting in shrinkage of the 3D printed product.
2. Uneven shrinkage caused by solvent evaporation can lead to warping or the generation of cracks in the printed part.
3. Toxicity concerns associated with organic solvents pose a significant obstacle, rendering the 3D printed part non-biocompatible.

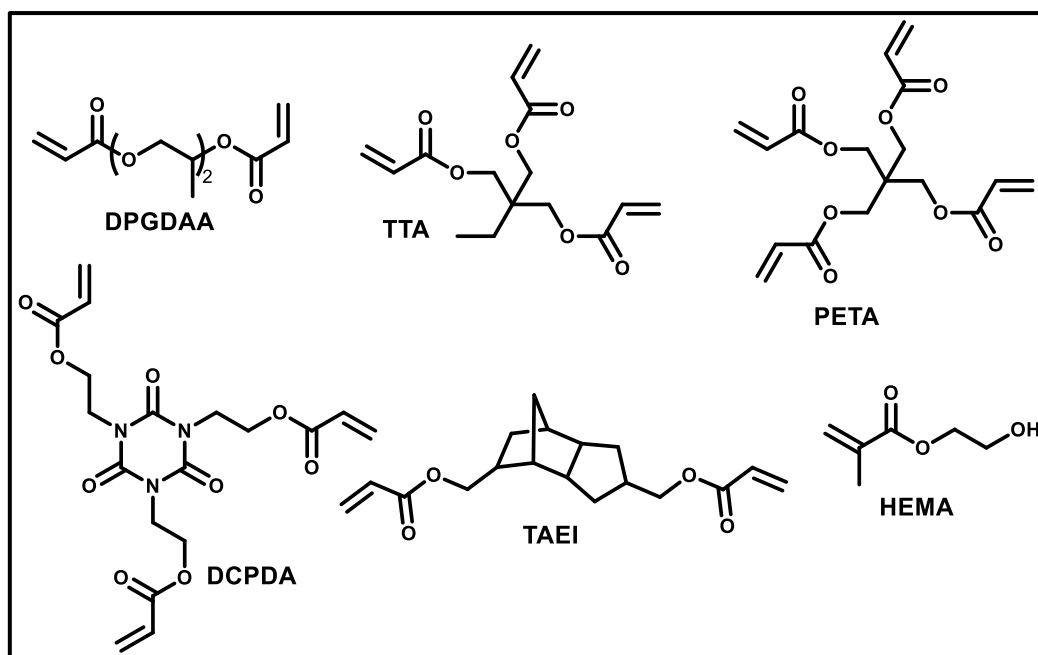


Figure 1.8 Commercially available reactive diluents used to reduce the viscosity of the resin formulation for convenient smooth DLP 3D printing.

According to the literature reports it was found that different types of organic solvents have been used for the preparation of the resin formulation. Seck T. M. et. al. prepared resin formulation adding 54 weight percentage (wt. %) of water and 11 wt. % of dimethyl sulfoxide (DMSO).⁶¹ Ferry P.W. M. et. al. and Green B. J. et. al., used 19 wt. % of ethyl lactate as non-reactive diluent and dioxane in 1:1 ratio with photopolymer for the stereolithographic resin preparation.^{62,63} Arvin B. S. et. al. used 20 wt. % of 2-ethyl-2-hydroxymethyl- Trimethacrylate (TMPTMA) as reactive diluent and 20 wt. % of n-methyl pyrrolidone as non-reactive diluent.⁶⁴ Instead, of using organic solvent, a reactive diluent can be used which possess one or more than one reactive functional group and can take part in the network polymer formation during the photopolymerization 3D printing. By using the reactive diluent there is no chance of leaching, making the 3D printed part more reliable. Luo Y. et al. used diethyl fumarate (DEF) as reactive diluent for the reduction of the viscosity as well for the enhancement of the mechanical properties of the 3D printed part.⁶⁵ Finally, it can be concluded that by selective use of the reactive diluent for a particular resin formulation both viscosity and the mechanical properties can be fine-tuned (Figure 1.8). Using biobased reactive diluents, the 3D printed parts become amenable for nontoxic biomedical applications.

1.10 Development of Bio-Based Photopolymer for DLP 3D Printing

Commercial resin formulations containing (meth)acrylate small molecules or oligomers are widely utilized in rapid prototyping across various fields. However, in biomedical applications,

commercial (meth)acrylate-based materials face limitations due to their toxicity and lack of biocompatibility. Moreover, these materials are often non-degradable, leading to significant waste generation after use. To address these challenges, there is a growing need for the synthesis of bio-based polymers tailored to meet the specific requirements of biomedical applications. These bio-based polymers are anticipated to offer solutions by providing biocompatible alternatives while also addressing concerns regarding toxicity and waste generation associated with acrylate-based materials.⁶⁶ Numerous research groups have successfully developed bio-based photopolymers designed for DLP 3D printing applications. The most commonly employed bio-based polymers are polylactide (PLA), polycaprolactone (PCL), and polyglycolide (PGL). These polymers are derived from renewable natural resources such as corn, sugar cane, starch, wheat straw, and wood chips.⁶⁷⁻⁶⁸ By introducing photocurable groups into the polymer backbone, these materials can be utilized as photo-polymers. Different weight percentage of these photopolymers are used for the resin formulation with reactive diluents enabling them to solidify under light exposure during the printing process.

1.10.1 Polylactide

Polylactide (PLA) is a renewable bio-based polymer. PLA is synthesised from the monomer lactic acid or lactide. Lactic acid is produced from bio-based sources like- corn, sugarcane, potatoes, and biomass. PLA is bio-compatible and biodegradable which make it a bio-medical polymer. PLA exhibits favourable physical (glass transition temperature 50-70 °C and melting temperature 170-190 °C) and mechanical properties (tensile strength 28-50 MPa and modulus 1.2-3 GPa) along with changeable functionality. With acid and hydroxyl groups present at the terminal positions, PLA can undergo reaction with other molecules to introduce various functional groups. This capability to modify functionality makes PLA to be a highly promising polymer for biomedical applications.⁶⁹⁻⁷¹ PLA is used to make biomedical implants, tissue engineering, suture, etc. The presence of the ester linkage in the PLA backbone makes this polymer susceptible for the degradation by ester bond cleavage. The cleavage of the ester bond of the PLA polymer can be enhanced by introducing esterification enzymes resulting in the non-toxic byproduct of lactic acid.⁷² The incorporation of PLA in the DLP 3D printing is an evolutionary step to make customizable bio-compatible products. Many research groups have reported the use of functionalized PLA in the production of DLP 3D printing products for application in tissue engineering, bio-scaffold, dental implants, biodegradable implantable screws, etc.^{64,62,73} The synthesis of PLA and introduction of the curable functional groups are described in the next section.

1.10.2 Synthesis of the PLA polymer

The synthesis of the PLA polymer can be done in three different steps: a. direct condensation polymerization of the lactic acid b. azeotropic dehydration condensation c. ring opening polymerization (ROP) of the lactide as shown in the figure 1.9.

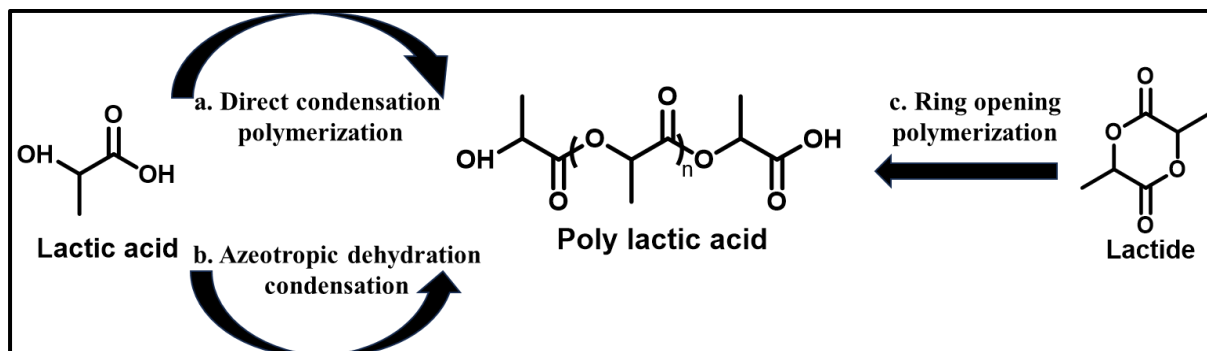


Figure 1.9 Different methods for the synthesis of the PLA polymer

The ROP of lactide is the most widely used polymerization technique in the industries for attaining well-defined molecular weights. Lactide has three different stereoisomers, L-lactide, D-lactide, and D, L-lactide. Among them L-lactide is the more commercially available and mostly used stereoisomer for the synthesis of the poly(l-lactide) polymer.⁷⁴ By employing various types of initiator molecules for the ROP of lactide, it is possible to create different architectures of PLA polymer.⁷⁵ Stannous octoate ($\text{Sn}(\text{Oct})_2$) is the predominant catalyst utilized in the ROP of lactide. Several metal-free catalysts are available for ROP of lactide. Some of these include 4-dimethylaminopyridine (DMAP), 4-pyrrolidinopyridine (PPY), 1,8-diazabicycloundec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and its N-methylated analogue (MTBD).⁷⁴ For the synthesis of the linear PLA polymer primary, or secondary alcohol or amine can be used. The coordination complex between the hydroxyl group and lactide monomer initiates the ring-opening polymerization of lactide with the catalyst. This process generates the repeat unit of the lactide and a secondary hydroxyl group, which forms a complex with the catalyst, facilitating the propagation of the ROP polymerization. For the synthesis of star or branched PLA polymers, multifunctional initiators are employed. Alternatively, grafting serves as another method to create branched polymers. Graft copolymers offer versatility and can be finely adjusted using various synthetic grafting techniques, including grafting through, grafting to, and grafting from methods.⁷⁶ The objective behind synthesizing different architectures of PLA polymers is to tailor their mechanical properties to suit diverse application requirements.

1.10.3 Introducing Acrylate Bond in the PLA Polymer

PLA polymers can be transformed into photosensitive polymers by incorporating cross-linkable groups. Linear, star, and branched PLA polymers all possess hydroxyl groups at their terminal positions, making them susceptible to modification by reacting with other molecules to introduce curable groups. Various curable groups such as acrylate, methacrylate, and fumarate can be incorporated into the polymer structure (Figure 1.10). These groups facilitate the formation of a crosslinked network polymer during DLP 3D printing when combined with a photo initiator.

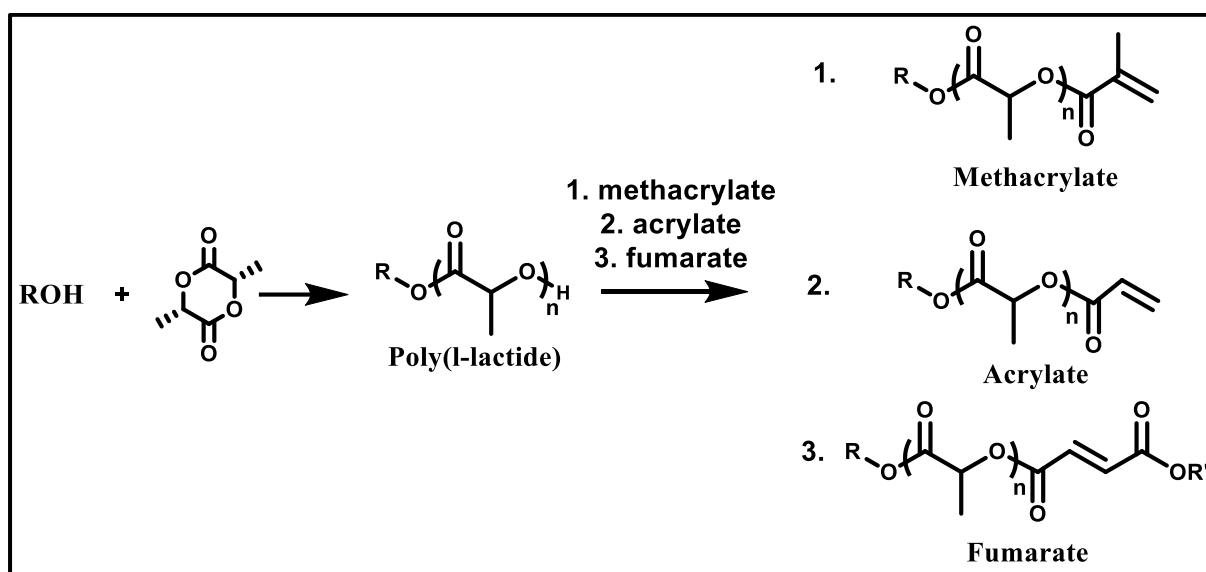


Figure 1.10 Modified PLA polymers with methacrylate, acrylate, and fumarate curable group.

Sawhney A. S. et al. synthesized a degradable copolymer consisting of Poly(ethylene glycol)-co-poly(α -hydroxy acid (Figure 1.11a). The copolymer was produced through ring-opening polymerization of lactide and glycolide under bulk conditions at 130°C using different molecular weight of polyethylene glycol as ROP initiator. Subsequently, the terminal hydroxyl group of the copolymer underwent reaction with acryloyl chloride to introduce the curable acrylate group. Finally, the photocurable copolymers were utilized for the formation of three-dimensional hydrogels with 2,2-dimethoxy-2-phenylacetophenone as the photoinitiator, under low wavelength UV light. It was observed that hydrogel formation occurred rapidly, even in the presence of oxygen.⁷⁷ Coullerez G. et. al. synthesized telechelic PLA oligomers through a transesterification reaction of PLA polymer with a commercial diacrylate in the presence of a titanium catalyst (figure 1.11b). The resulting acrylate-containing PLA oligomer was employed in the formation of a crosslinked hard network polymer. This polymer exhibited a softening

effect in open atmospheric conditions, indicating moisture-induced hydrolytic degradation.⁷⁸ Moeinzadeh S. et al. developed a novel star poly(ethylene oxide-co-lactide-glycolide acrylate) macromonomer to create a network structure (figure 1.11c). This multi-armed polymer formed a crosslinked hydrogel structure with water uptake properties and degradability in PBS solution. The mechanical properties of the hydrogel were improved by incorporating a small amount of n-vinyl pyrrolidone as a solvent.⁷⁹

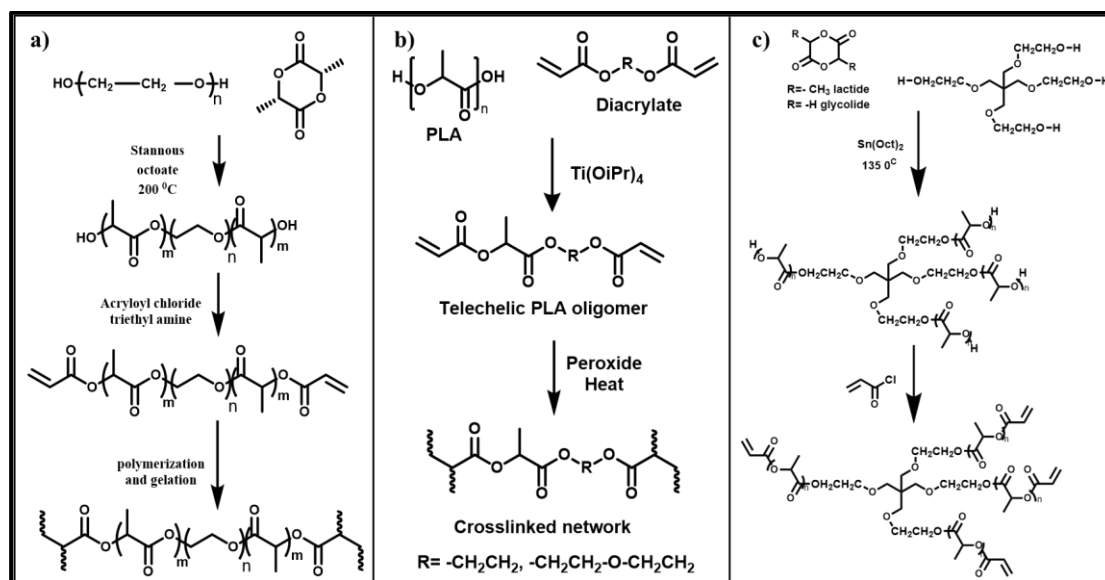


Figure 1.11 Introduction of the acrylate groups in the terminal position of the PLA polymer to form telechelic acrylate PLA polymer. **Ref 77.** Copyright © 1993, American Chemical Society, **Ref 78.** Copyright © 1969, Kluwer Academic Publishers, **Ref 79.** Copyright © 2011 Elsevier Ltd. All rights reserved.

Many researchers have developed photocurable PLA polymers for resin formulations in DLP 3D printing applications by incorporating curable groups into the bio-based PLA polymer backbone and understanding the curing kinetics based on factors such as molecular weight and multi-arm curable chain formation. Melchels et al. developed a resin formulation for stereolithography, using poly(D, L-lactide) macromers functionalized with methacrylate end-groups and ethyl lactate as a non-reactive diluent (figure 1.2a). They achieved sturdy structures and permeable scaffolds suitable for tissue engineering applications. The resin composition included dye, inhibitor, visible light photoinitiator, and 0.6 k PDLLA macromer. Successful photo-crosslinking was achieved with blue light exposure, resulting in specimens with comparable mechanical properties to those produced by compression moulding. The viscosity of the resin formulation was controlled by adjusting the molecular weight of oligomers and the weight percentage of ethyl lactate.⁶²

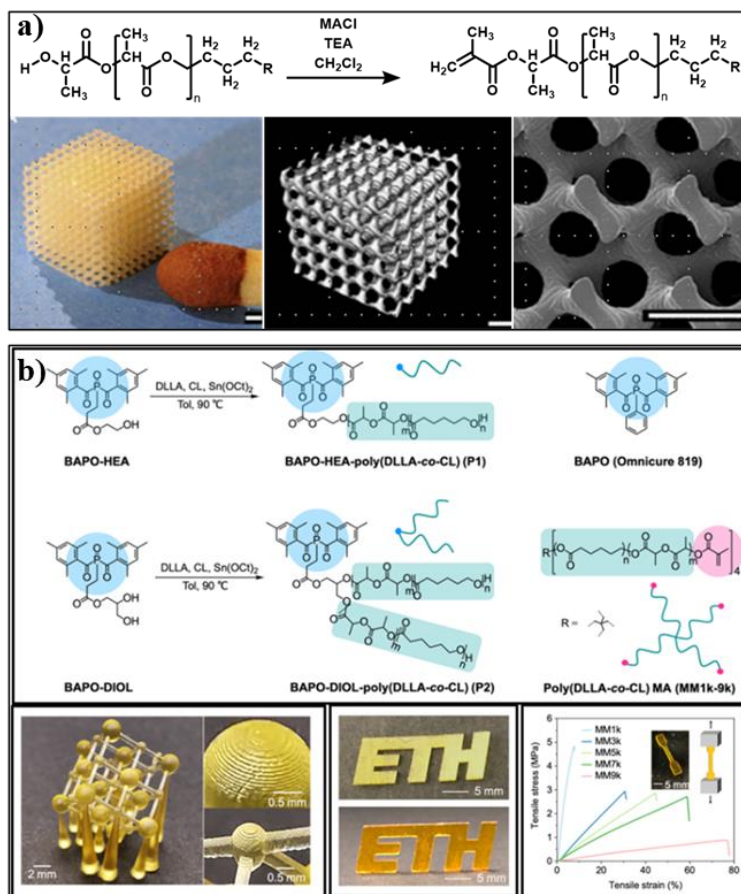


Figure 1.12 a) Synthesis of the telechelic acrylate PLA polymer and resin 3D printing with same polymer for tissue engineering. *Ref. 62* Copyright © 2009 Elsevier Ltd. All rights reserved. b) Synthesis of the photo initiator containing PCL-b-Pla polymer for the DLP 3D printing with moderate tensile strength. *Ref. 56* Copyright © 2021 Open access

Sandmeier et al. developed a versatile approach for solvent-free 3D printing of biodegradable polymeric materials by covalently bonding the photoinitiator to a polymer chain structurally similar to macromonomers (figure 1.12b). They synthesized random copolymers of caprolactone and lactide with a photoinitiator containing hexyl ethyl acrylate, creating two types of copolymers with varying molecular weights. These copolymers were used in resin formulations with PEGDA or DUDMA for printing with a heat-assisted DLP 3D printer. Tensile testing revealed significant impacts of polymer chain length on mechanical properties, with Young's modulus and tensile strength decreasing as molecular weight increased. The research offers new possibilities for solvent-free 3D printing of functional devices, particularly for scaffolds and implants made of bioresorbable materials.

1.10.4 Thiol -Ene Chemistry in DLP 3D Printing

Thiol-ene chemistry involves the organic reaction between a thiol and an alkene group, resulting in the formation of a thioether bond. Much like the radical photopolymerization of acrylic monomers, thiol-ene polymerization is also a rapid process and acquire lots of advantages. It proceeds via a step-growth mechanism. The reaction begins with the initiation of a photo initiator, which forms a thiyl radical from the thiol group. Subsequently, this thiyl radical reacts with the alkene molecule, leading to the formation of a thioether bond linkage (figure 1.13a). In thiol-ene polymerization, no solvent is necessary, and no byproducts are generated during the reaction. The propagation of the thiol-ene reaction is not hindered by the presence of oxygen. By utilizing multifunctional thiol and ene molecules, crosslinked thiol-ene polymers can be formed, exhibiting exceptionally high mechanical properties.^{80,81} Stewart, S. A. et al. demonstrated the formation of a polymer hydrogel using thiol-ene chemistry. They synthesized a series of cysteamine vinyl sulfone-functionalized poly(methyl vinyl ether-alt-maleic acid) polymers and subsequently reacted them with a poly ethylene glycol dithiol crosslinker to produce the hydrogel. Through cytotoxicity testing, they established the biocompatibility of the resulting hydrogel structure.⁸² Similarly, the multifunctional commercial thiol and ene molecules can be used for the resin formulation and DLP 3D printing. A list of several commercial thiol and ene containing molecules and their structures are shown in the figure 1.13b. The minimal shrinkage properties exhibited by thiol-ene crosslinked networks enhance their suitability for 3D printing applications, offering improved precision and dimensional stability during the printing process.⁸³ Oesterreicher A. et al. developed alkyne carbonate molecules, which were combined with multifunctional thiol-containing molecules to create resin formulations for room temperature DLP 3D printing. They synthesized di- and tri-functional alkyne molecules with varied chemical structures to improve mechanical properties. The resulting resin formulations were utilized in DLP 3D printing, where different combinations of alkyne and thiol molecules were tested to adjust mechanical and biocompatibility properties.⁸⁴ Chen L. et al. presented resin formulations comprising commercial primary, secondary thiol, and tri-functional ene molecules for DLP 3D printing. They assessed the stability of the resin formulation containing secondary thiol, finding it to last approximately 7 days, while observing similar mechanical properties across all functional thiols.⁸⁵ Concerns arose regarding the degradability of commercial thiol or ene molecules after forming the thermoset crosslinked network polymer in DLP 3D printing which generates non-degradable plastic pollution. Hence, there is increasing interest in the development of bio-based and degradable thiol-ene resin formulations.

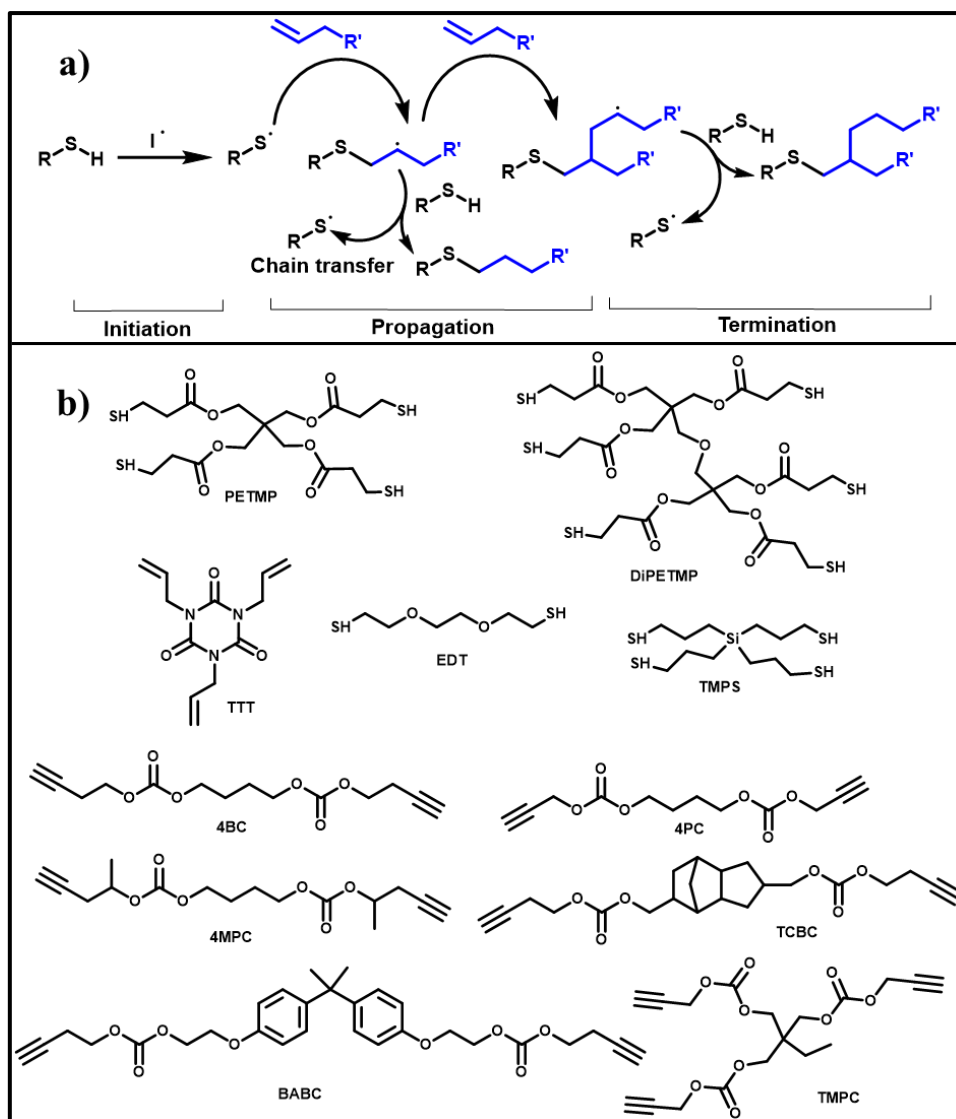


Figure 1.13 a) Reaction of the thiol-ene polymerization via three steps initiation, propagation, and termination, b) Commercial thiol and ene containing small molecule.

1.10.5 Biobased Thiol-Ene Polymers for DLP 3D Printing

Biobased polymer production is now growing as a sustainable alternative to mitigate the environmental impact of non-degradable rapid prototyping materials generating from commercial (meth)acrylate polymers. Thiol-ene chemistry, with its numerous advantages, is gaining increasing interest as a viable approach in this transition towards more eco-friendly materials.

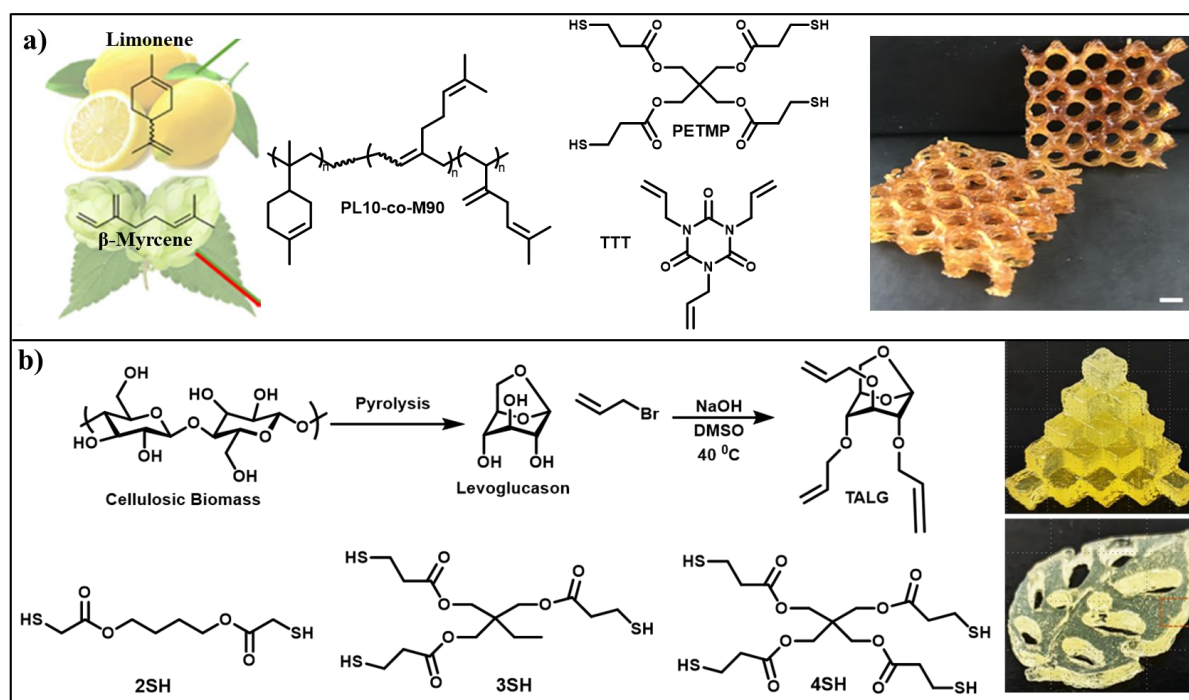


Figure 1.14 a) Synthesis of the bio-based poly(limonene-co-myrcene) and resin formulation with thiol molecules for thiol ene DLP 3D printing, **Ref. 86** Copyright © 2022, American Chemical Society, b) The DLP 3D printing of the allylic levoglucoson with different thiol molecule and the 3D printed part showed degradability in basic medium. **Ref. 87** Copyright 2023, The Royal Society of Chemistry

Weems et al. synthesized Poly(limonene-co-myrcene) with various ratios of Limonene and β -myrcene. Among these, the PL10-co-M90 variant was utilized in a photopolymer resin formulation (figure 1.14a). This formulation included 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) and pentaerythritol tetrakis(3-mercaptopropionic acid) (PETMP) added sequentially as reactive diluents, along with Irgacure 819 as the photoinitiator. DLP 3D printing was conducted, with each layer printed within 3-5 seconds. The resulting 3D printed products exhibited a tensile strength of 55 MPa and a modulus of 1 GPa, along with positive cytocompatibility test results.⁸⁶ Similarly, Porwal et al. extracted Levoglucosan, a bio-based compound, from cellulose biomass through a pyrolysis process (figure 1.14b). Levoglucosan was then utilized in the synthesis of an ene-containing molecule, which formed the basis for a thiol-ene network polymer designed for use in 3D printing technology. The resulting 3D-printed objects demonstrated promising degradability characteristics in THF/NaOH solution, thus presenting a viable solution for rapid prototyping applications and reducing waste generation associated with acrylate-based printing. The 3D printed product prepared with bio-based polymer offers a combination of bio-compatibility and sustainability,

making it ideal for applications requiring environmentally friendly materials. Additionally, use of these products reduces the dependency on traditional petroleum-based raw materials.⁸⁷

1.11 High Performance Polymer in 3D Printing

In high-performance applications, bio-based polymers face challenges with mechanical properties that restrict their application. Achieving high mechanical properties in DLP 3D printing requires the use of high-performance polymers (HPP). Within the category of HPPs, several options exist, including polyether ether ketone (PEEK), polyimide, and polysulfone (figure 1.15).⁸⁸ These polymers possess a strong aromatic polymer backbone and pi-pi interactions within their chains, resulting in exceptional mechanical strength (tensile strength 90-100 MPa and Young's modulus 3.5-4 GPa).⁸⁹⁻⁹¹

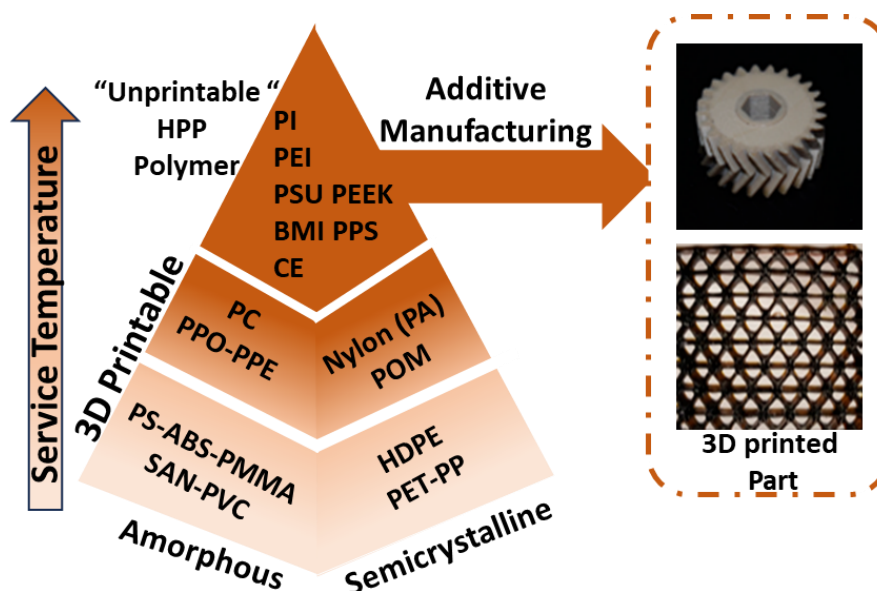


Figure 1.15 Schematic representation of high-performance polymers with printability and processing temperature. *Ref. 88 Copyright* © 2020, American Chemical Society

Processing these polymers typically necessitates high-energy instrument setups, whether for extrusion moulding or compression moulding. This requirement reflects the complex nature of these materials and the need for precise conditions to achieve the desired mechanical properties in the final product. Additive manufacturing brings advantages in the processing of High-Performance Polymers (HPPs) by enabling the creation of new technologies and facilitating changes in the chemical structure of these polymers, thereby making it possible to process them in a more efficient and customizable manner.

1.11.1 Polyether Ether Ketone (PEEK) polymer

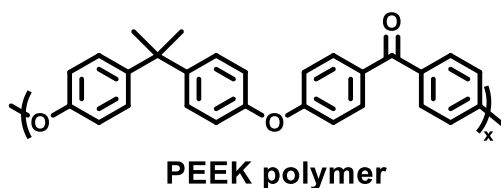


Figure 1.16 General chemical structure of PEEK polymer.

Polyether ether ketone (PEEK) (figure 1.16) belongs to the class of high-performance aromatic polymers and stands as a promising contender for modern industrial applications. With its commendable mechanical properties and resistance to chemicals and solvents, PEEK finds utility across diverse sectors including aviation, aerospace, and electronics. Consequently, the refinement of PEEK polymer through modified chemical structures emerges as a promising research approach. The synthesis of PEEK polymer can be achieved via either electrophilic or nucleophilic substitution reactions. However, the nucleophilic substitution pathway presents a more convenient route for PEEK polymer synthesis compared to electrophilic methods, owing to certain mechanistic advantages. The solubility of PEEK polymer poses a challenge due to its aromatic backbone structure and the strong packing tendency of the ketone and phenyl ether linkage. To address this challenge, various strategies have been pursued, including the incorporation of non-planar structures into the PEEK polymer backbone. Introducing pendent groups, meta or para substitutions, or aromatic repeat units, as well as incorporating cardo groups, represent attractive approaches aimed at enhancing solubility and reducing the glass transition temperature for improved processability.⁹²⁻⁹⁴ Additive manufacturing of the PEEK polymer is promising for the production of complex structures with high mechanical strength. The filament of the PEEK polymer can be prepared by the extrusion process and the filaments can be used for the FDM 3D printing by melt deposition. The high melting temperature of the PEEK polymer and handling of the high temperature FDM 3D printer makes 3D printing quite challenging and energy consuming. Modifying the chemical structure and molecular weight of the PEEK polymer makes it possible to process PEEK at lower temperatures. 3D printing of PEEK polymer with improved processability are reported with modified chemical structure.⁹⁵⁻⁹⁸

1.11.2 3D Printing of the PEEK Polymer

In a study conducted by Inan T. Y. et al., they detailed the synthesis of a curable modified PEEK urethane polymer aimed at producing UV-curable lenses. Initially, PEEK polymer was

synthesized with tertiary butyl moieties as pendent groups in each repeat unit. Subsequently, the PEEK polymer underwent end-capping with an isocyanide-containing capping group, which further reacted with 2-hydroxyethyl methacrylate to introduce curability into the polymer (figure 1.17a). Various weight percentages of this modified polymer were then blended with acrylate diluents to prepare a curable resin. This resin was employed in the fabrication of lenses, exhibiting desirable properties such as short UV-light blocking capabilities.⁹⁹

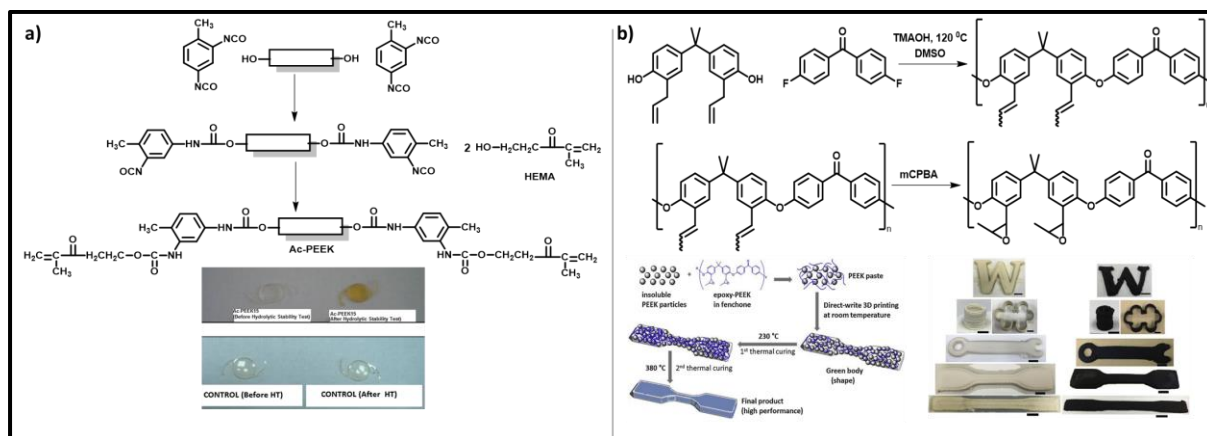


Figure 1.17 a) Synthetic strategy for the preparation of urethane acrylate PEEK polymer for the preparation of the lens, *Ref. 99* Copyright © 2014, Springer Science Business Media New York, b) Introduction of the curable epoxy group in the PEEK polymer for room temperature processing. *Ref 100.* © 2019 Elsevier B.V. All rights reserved.

Recently, the research group of Lee C. U. et. al. reported the preparation of thermally curable PEEK polymer paste based on epoxy-containing PEEK polymer and formulated a thermally curable paste (figure 1.17b). This paste was created by blending 10 wt. % of the curable PEEK polymer into fenchone solvent at 100 °C for 3 hours, followed by mixing high molecular weight PEEK powder in a 1:2 ratio to form the paste material. Subsequently, this material was utilized for Direct Ink Writing 3D printing to produce green bodies. Post-printing, the green bodies underwent heating within a temperature range of 100-380 °C for varying durations. The resulting 3D printed parts exhibited significantly improved mechanical properties, with a 62% increase in modulus compared to commercial PEEK polymer. Additionally, the 3D printed parts displayed favourable chemical resistivity.¹⁰⁰ However, it is to be noted that DLP 3D printing of PEEK polymer has not been reported yet. In our research work we have demonstrated for the first time the synthesis of curable PEEK polymer and their DLP 3D printing.

1.12 Aim of the Thesis

The comprehensive literature review focuses on the importance of developing bio-based polymeric materials for liquid-based DLP 3D printing technology. DLP 3D printing stands as a widely utilized additive manufacturing technology, offering rapid production, design flexibility, and high-resolution outputs. Its adoption allows for the creation of complex structures with ease. However, a significant challenge lies in the development of bio-based polymeric resin materials suitable for DLP 3D printing. Polymeric materials have garnered attention due to their favourable processability and the ability to adjust curing properties to achieve desired mechanical properties. The primary objective of the thesis is to develop different types of photocurable crosslinkers to be utilized in the development of resin formulations. After that, the prepared resins will be used in light-based DLP 3D printing technology. The thesis also focuses on the properties of the 3D printed materials like degradability, mechanical properties, and 3D printing resolution. These 3D printed materials are useful in different fields of applications. In **chapter 2**, we have developed two different architectures of the linear and star PLLA polymer by the ring opening polymerization. These polymers were further functionalized with photo curable methacrylate groups in the terminal position. The polymeric crosslinkers were then used for the preparation of resin formulation and DLP 3D printing. The resin showed good printability with moderate mechanical and degradable properties. **Chapter 3** focused to improve the printability and the mechanical properties of the DLP 3D printing materials. PLLA was grafted on to Poly(vinyl acetate) backbone after partial hydrolysis, followed by end functionalization with acrylate moieties. Different weight percentage of the grafted acrylate PVAc-g-PLLA was mixed with HEMA and HEA as reactive diluents for the formulation of the resins. The prepared resin showed promising DLP 3D printing with tuneable mechanical properties. Very interestingly, the 3D printed parts exhibited swelling and dye absorption from solution of various dyes. **Chapter 4** describes the incorporation of the thiol-ene chemistry in the bio-based polymer and the DLP 3D printing of the thiol-ene resin formulations. Poly(ethyl acrylate lactate) was synthesised by the radical polymerization of the acrylate ethyl lactate, which was partially hydrolysed to acid. The acid group was reacted with allyl bromide to introduce ‘ene’ functionality in the polymer structure. The ene polymer was used for the resin formulation with tetra thiol molecule and DLP 3D printing was performed. The 3D printed parts showed high modulus (1.8 GPa) and degradability in basic solution. **Chapter 5** described the development of high-performance polymer resin formulation for DLP 3D printing. In this work, low molecular weight PEEK and its derivatives incorporating long alkyl pendent group were synthesised by nucleophilic

substitution condensation polymerization. Further, urethane acrylate groups were introduced at the terminal to develop photo curable PEEK polymers. These PEEK polymers were used for the resin formulation with reactive diluents and applied for DLP 3D printing. The 3D printed parts showed high modulus (2.2 GPa) with high tensile strength. Chapter 6 gives a brief overview of all the chapters along with a discussion for potential improvements in the design of monomer and polymers for high resolution and mechanical properties for the DLP 3D printed parts.

1.13 REFERENCES

- (1) S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, *Chem. Rev.* **2017**, *117*, 10212.
- (2) Johannes F. Gottwald, Park Ridge, U.S. Patent 3596285, **1969**.
- (3) Hideo Kodama, Patent Magazine of Japan Patent Attorneys Association, 67, 13, 109-118, **2014**.
- (4) Hull, C.U.S. Patent 4575330, **1986**.
- (5) S. Scott Crump. U.S. Patent 5121329, **1989**.
- (6) Wohlers Report 2015:3D Printing and Additive Manufacturing State of the Industry Wohlers Associates: Fort Collins, CO, **2015**.
- (7) Formlabs report, Max Lobovsky, The 2022 3D Printing Applications Report, **2022**.
8. India 3D Printer Market Report 2022: Increasing Demand for Medical Equipment Drives Growth October 12, **2022**.
9. Pagac, M.; Hajnys, J.; Ma, Q.-P.; Jancar, L.; Jansa, J.; Stefek, P.; Mesicek, J. *Polymers*. **2021**, *13*, 598.
10. Wohlers Report 2023, Challenges and Future Trends in Additive Manufacturing **2023**.
11. Revilla-León, M., Sadeghpour, M. and Özcan, M. *Journal of Prosthodontics*. **2020**, *29*, 579-593.
12. Culmone C., Smit G., Breedveld P., *Addit Manuf*, **2019**, *27*, 461-473
13. Morrison, R.J., Kashlan, K.N., Flanagan, C.L., Wright, J.K., Green, G.E., Hollister, S.J. Weatherwax, K.J. *Clinical and Translational Science*. **2015**, *8*, 594-600.
14. Martins, A., Chung, S., Pedro, A.J., Sousa, R.A., Marques, A.P., Reis, R.L. and Neves, N.M. *J Tissue Eng Regen Med*. **2009**, *3*, 37-42.
15. Joel C. Najmon, Sajjad Raeisi, Andres Tovar, *Additive Manufacturing for the Aerospace Industry*. **2019**, 7-31,
16. D. K. Patel, A. H. Sakhaei, M. Layani, B. Zhang, Q. Ge, S. Magdassi, *Adv. Mater.* **2017**, *29*, 1606000.

17. Jeffrey I. Lipton, Meredith Cutler, Franz Nigl, Dan Cohen, Hod Lipson, *Trends in Food Science & Technology*. **2015**, 43, (1) 114-123.
18. Khajavi, S.H. *Appl. Sci.* **2021**, 11, 8994.
19. Alain Le-Bail, Bianca Chiericato Maniglia, Patricia Le-Bail, *Current Opinion in Food Science*. **2020**, 35, 54-64.
20. Ribeiro, Inês, Florinda Matos, Celeste Jacinto, Hafiz Salman, Gonçalo Cardeal, Helena Carvalho, Radu Godina, and Paulo Peças. *Sustainability*. **2020**, 12, (3), 929.
21. Peterson, G. I.; Schwartz, J. J.; Zhang, D.; Weiss, B. M.; Ganter, M. A.; Storti, D. W.; Boydston, A. J. *ACS Appl. Mater. Interfaces*. **2016**, 8, 29037–29043.
22. W. Li, L. S. Mille, J. A. Robledo, T. Uribe, V. Huerta, Y. S. Zhang, *Adv. Healthcare Mater.* **2020**, 9, 2000156.
23. K. L. Sampson, B. Deore, A. Go, M. A. Nayak, A. Orth, M. Gallerneault, P. R. L. Malenfant, C. Paquet, *ACS Appl. Polym. Mater.* **2021**, 3, 4304.
24. Das, A.; Gilmer, E. L.; Biria, S.; Bortner, M. J. *ACS Applied Polymer Materials*. **2021**, 3 (3), 1218–1249.
25. Peng Zhuo, Shuguang Li, Ian A. Ashcroft, Arthur I. Jones, *Composites Part B: Engineering*, **2021**, 224, 109143.
26. R. Singh, A. Gupta, O. Tripathi O., Sashank S., Bharat S., Ankita A., S.K. Rajput, Pankaj S., Piyush S., Kuldeep K. Saxena *Materials Today: Proceedings*. **2020**, 26, 3058-3070.
27. Awad A, Fina F, Goyanes A, Gaisford S, Basit A. W. *Advanced Drug Delivery Reviews*. **2021**, 174, 406-424.
28. Gyu Ahn D. *Int. J. Precis. Eng. Manuf. - Green Technol.* **2021**, 21, 703–742.
29. D. Svetlizky, M. Das, B. Zheng, A.L. Vyatskikh, S. Bose, A. Bandyopadhyay, J. M. Schoenung, E.J. Lavernia, N. Eliaz, *Mater. Today* **2021**, 49, 271–295.
30. Gülcan, O.; Günaydın, K.; Tamer, A. *Polymers* **2021**, 13, 2829.
31. Yap, Y.L.; Wang, C.; Sing, S.L.; Dikshit, V.; Yeong, W.Y.; Wei, J. *Precis. Eng.* **2017**, 50, 275–285.
32. Ming Li, Wenchao Du, Alaa Elwany, Zhijian Pei, Chao Ma. *J. Manuf. Sci. Eng.* **2020**, 142(9), 090801.
33. Mirzababaei S., Pasebani S., *J. Manuf. Mater. Process.* **2019**, 3, 82.
34. Gibson, I., Rosen, D., Stucker, B. (2010). Springer, Boston, MA. https://doi.org/10.1007/978-1-4419-1120-9_8.
35. Bhatt P. M, Kabir A. M., Peralta M., Bruck H. A., Gupta S. K., *Addit Manuf.* **2019**, 27, 278e89.

36. Vincent S. D. Voet, Tobias Strating, Geraldine H. M. Schnelting, Peter Dijkstra, Martin Tietema, Jin Xu, Albert J. J. Woortman, Katja Loos, Jan Jager, and Rudy Folkersma *ACS Omega*. **2018**, 3 (2), 1403-1408.
37. J. Z. Manapat, Q. Chen, P. Ye, R. C. Advincula, *Macromol. Mater. Eng.* **2017**, 302, 1600553.
38. Shuyang Zhang, Mi Li, Naijia Hao, and Arthur J. Ragauskas *ACS Omega*. **2019**, 4 (23), 20197-20204.
39. C. Wu, R. Yi, Y. -J. Liu, Y. He and C. C. L. Wang, 2016 IEEE/RSJ International Conference on Intelligent Robots and Systems (IROS), Daejeon, Korea (South), 2016, pp. 2155-2160, doi: 10.1109/IROS.2016.7759338.
40. Dowon Ahn, Lynn M. Stevens, Kevin Zhou, and Zachariah A. Page, *ACS Cent. Sci.* **2020**, 6 (9), 1555-1563.
41. Xinpan Li, Ran Yu, Yangyang He, Ying Zhang, Xin Yang, Xiaojuan Zhao, and Wei Huang *ACS Macro Lett.* **2019**, 8 (11), 1511-1516.
42. Maines, Erin M. and Porwal, Mayuri K. and Ellison, Christopher J. and Reineke, Theresa M. *Green Chem.*, **2021**, 23, 6863-6897.
43. Rolland J. P., Ermoshkin A., Samulski E. T., And Desimone J. M. *Science*. **2015**, 347, 1349-1352.
44. Lipkowitz G., Coates I, Krishna N., Shaqfeh E. S.G., DeSimone J. M., *Giant*, **2024**, 17, 100239.
45. J. T. Toombs, M. Luitz, C. C. Cook, S. Jenne, C. C. Li, B. E. Rapp, F. Kotz-Helmer, H. K. Taylor, *Science*. **2020**, 376, 308–312.
46. Kelly B. E., Bhattacharya I., Shusteff M., Taylor1 H. K., and Spaddacini C. M., Solid Freeform Fabrication 2017: Proceedings of the 28th Annual International Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference.
47. Steinmann, B.; Wolf, J.-p.; Schulthess, A.; Hunziker, M. (CibaGeigy Corp.) U.S. Patent 5658712, **1997**.
48. Steinmann, B.; Schulthess, A. (Ciba Specialty Chemicals Corp.) U.S. Patent 5972563, **1999**.
49. Ueda, M.; Takase, K.; Kurosawa, T. (DSM IP Assets BV). U.S. Patent 8980971, **2015**.
50. Kuhnt, T.; Morgan, F.L.C.; Baker, M.B.; Moroni, L. *Addit. Manuf.* **2021**, 46, 102102.
51. Chen, H.; Lee, S.-Y.; Lin, Y.-M. *Polymers*. **2020**, 12, 1500.
52. Chiappone A., Fantino E., Roppolo I., Lorusso M., Manfredi D., Fino P., Pirri C. F., and Calignano F. *ACS Appl Mater Interfaces* **2016**, 8 (8), 5627-5633.

53. Guangda Zhu, Yi Hou, Junfeng Xiang, Jian Xu, and Ning *ACS Appl Mater Interfaces*. **2021**, 13(29), 34954-34961.
54. Qin, Xiao-Hua, Ovsianikov, Aleksandr, Stampfl, Jürgen and Liska, Robert. *Bio Nano Materials*, **2014**, 15, (3-4), 49-70.
55. Khoon S. Lim, Benjamin S. Schon, Naveen V. Mekhileri, Gabriella C. J. Brown, Catherine M. Chia, Sujay Prabakar, Gary J. Hooper, and Tim B. F. Woodfield. *ACS Biomater. Sci. Eng.* **2016**, 2 (10), 1752-1762.
56. M. Sandmeier, N. Paunović, R. Conti, L. Hofmann, J. Wang, Z. Luo, K. Masania, N. Wu, N. Kleger, F. B. Coulter, A. R. Studart, H. Grützmacher, J. C. Leroux, Y. Bao, *Macromolecules*. **2021**, 54, 7830.
57. W. Li, M. Wang, L. S. Mille, J. A. RobledoLara, V. Huerta, T. Uribe Velázquez, F. Cheng, H. Li, J. Gong, T. Ching, C. A. Murphy, A. Lesha, S. Hassan, T. B. F. Woodfield, K. S. Lim, Y. S. Zhang, *Adv. Mater.* **2021**, 33, 2102153.
58. M. N. Cooke, J. P. Fisher, D. Dean, C. Rimnac, A. G. Mikos, *J. Biomed. Mater. Res., Part B* 2003, 64, 65.
59. H. Quan, T. Zhang, H. Xu, S. Luo, J. Nie, X. Zhu, *Bioact. Mater.* 2020, 5, 110.
60. J. Zhang, P. Xiao, *Polym. Chem.* 2018, 9, 1530.
61. T. M. Seck, F. P. W. Melchels, J. Feijen, D. W. Grijpma, *J. Controlled Release* **2010**, 148, 34.
62. F. P. W. Melchels, J. Feijen, D. W. Grijpma, *Biomaterials* **2009**, 30, 3801.
63. Green, B. J.; Worthington, K. S.; Thompson, J. R.; Bunn, S. J.; Rethwisch, M.; Kaalberg, E. E.; Jiao, C.; Wiley, L. A.; Mullins, R. F.; Stone, E. M.; Sohn, E. H.; Tucker, B. A.; Guymon, C. A. *Biomacromolecules*. **2018**, 19 (9), 3682– 3692.
64. Saed A. B, Behraves A. H., Sadegh Hasannia, Ardebili A. A. S., Akhoundi B., Pourghayoumi M., *J. Manuf. Process.* **2020**, 56, 550-561.
65. Luo Y., Fer G. L., Dean D., and Becker M. L. *Biomacromolecules* **2019**, 20 (4), 1699-1708.
66. M.A. Pemberton, B.S. Lohmann, *Regul. Toxicol. Pharmacol.* **2014**, 69, 467–475.
67. A. Harynska, H. Janik, M. Sienkiewicz, B. Mikolaszek, J. Kucinska Lipka, *ACS Sustainable Chem. Eng.* **2021**, 9, 6923.
68. J. R. Rocca-Smith, O. Whyte, C.-H. Brachais, D. Champion, F. Piasente, E. Marcuzzo, A. Sensidoni, F. Debeaufort, T. Karbowiak, *ACS Sustainable Chem. Eng.* **2017**, 5, 2751.
69. B. R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, **2000**, 12, 1841–1846.
70. K. A. Athanasiou, G. G. Niederauer and C. M. Agrawal, *Biomaterials*, **1996**, 17, 93–102.
71. R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, 4, 835–864.

72. Dana da Silva, Maya Kaduri, Maria Poley, Omer Adir, Nitzan Krinsky, Janna Shainsky-Roitman, Avi Schroeder, *J. Chem. Eng.* **2018**, *340*, 9-14.
73. A. Bagheri Saed, A. H. Behraves, S. Hasannia, B. Akhoundi, S. K. Hedayati, F. Gashtasbi, *Eur. Polym. J.* **2020**, *141*, 110057.
74. F. Nederberg, E. F. Connor, M. Moller, T. Glauser and J. L. Hedrick, *Angew. Chem., Int. Ed.*, **2001**, *40*, 2712–2715
75. Corneillie S. and Smet M. *Polym. Chem.*, **2015**, *6*, 850-867.
76. Y. Ohya, A. Takahashi and K. Nagahama, *Springer*, **2012**, 65–114.
77. Amarpreet S. S., Chandrashekhara P. P., and Jeffrey A. *Macromolecules*, **1993**, *26*,(4), 581-587.
78. Coullerez, G., Lowe, C., Pechy, P., H. H. Kausch & J. Hilborn. *J. Mater. Sci.: Mater. Med.* **2000**, *11*, 505–510
79. S. Moeinzadeh, S. N. Khorasani, J. Ma, X. He, E.I Jabbari, *Polymer*, **2011**, *52*, *18*, 3887-3896.
80. N. B. Cramer, T. Davies, A. K. O'Brien, and C. N. Bowman, *Macromolecules*. **2003**, *36* (12), 4631-4636.
81. N. B. Cramer, S. K. Reddy, A.K. O'Brien, and C. N. Bowman, *Macromolecules*. **2003**, *36* (21), 7964-7969.
82. S. A. Stewart, M. B. Coulson,^a C. Zhou,^a N. A. D. Burke, *Soft Matter*, **2018**, *14*, 8317-8324.
83. S. Bertlein, G. Brown, K. S. Lim, T. Jungst, T. Boeck, T. Blunk, J. Tessmar, G. J. Hooper, T. B. F. Woodfield, J. Groll, *Adv. Mater.* **2017**, *29*, 1703404.
84. A. Oesterreicher, J. Wiener, M. Roth, A. Moser, R. Gmeiner, M. Edler, G. Pinter and T. Griesser, *Polym. Chem.*, **2016**, *7*, 5169-5180.
85. L. Chen, Q. Wu, G. Wei, R. Liu, and Z. Li, *J. Mater. Chem. C*, **2018**, *6*, 11561-11568.
86. E. Constant, O. King, and A. C. Weems, *Biomacromolecules*, **2022**, *23* (6), 2342-2352.
87. M.K. Porwal, M.M. Hausladen, C.J. Ellison, T.M. Reineke, *Green Chem.* **2023**, *25*, 1488–1502.
88. A. J. Boydston, J.Cui, C. U. Lee, B. E. Lynde, and C. A. Schilling, *ACS Macro Letters* **2020**, *9* (8), 1119-1129.
89. Weyhrich, C.W. and Long, T.E. *Polym Int*, **2022**, *71*, 532-536.
90. A. Das, C.A. Chatham, J.J. Fallon, C.E. Zawaski, E.L. Gilmer, C.B. Williams, M.J. Bortner, *Addit. Manuf.* **2020**, *34*, 101218.

91. Al C. de Leon, Q. Chen, N. B. Palaganas, J. O. Palaganas, J. Manapat, R.o C. Advincula, *Reactive and Functional Polymers*, **2016**, *103*, 141-155.
92. Maher, D.M., Nagane, S.S., Jadhav, U.A., Salunkhe, P.H., Tawade, B.V. and Wadgaonkar, P.P. *J. Polym. Sci. Part A: Polym. Chem.*, **2019**, *57*, 1516-1526.
93. Tawade, B.V., Shaligram, S.V., Valsange, N.G., Kharul, U.K. and Wadgaonkar, P.P., *Polym. Int.*, **2016**, *65*, 567-576.
94. S. S. Nagane, S. Verma, B. V. Tawade, P. S. Sane, S. A. Dhanmane, P. P. Wadgaonkar, *Eur. Polym. J.* **2019**, *116*, 180–189.
95. Hanemann, T.; Klein, A.; Baumgärtner, S.; Jung, J.; Wilhelm, D.; Antusch, S. *Polymers*. **2023**, *15*, 3412.
96. Chen, W., Zhang, X., Tan, D., Xu, P., Yang, B., Shi, K., Zhu, B., Liu, Q., Lei, Y., Liu, S. and Xue, L., *Macromol. Rapid Commun.*, **2022**, *43*, 2100874.
97. Abid Haleem, Mohd Javaid, *Clinical Epidemiology and Global Health*, **2019**, *7(4)*, 571-577.
98. ankole I. Oladapo, S. Abolfazl Zahedi, Sikiru O. Ismail, Francis T. Omigbodun, *Colloids and Surfaces B: Biointerfaces*, **2021**, *203*, 111726.
99. İnan, T.Y., Yıldız, E., Karaca, B. et al. *J Mater Sci: Mater Med* **2014**, *25*, 2027–2039.
100. C. Lee, J. Vandenbrande, A. E. Goetz, M. A. Ganter, D. W. Storti, A. J. Boydston, *Addit. Manuf.* **2019**, *28*, 430-438

CHAPTER 2

Biodegradable, Solvent-Free Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing

2.1 INTRODUCTION

In recent years there is an increasing demand for biodegradable materials for fabricating complex 3D biomedical patient specific implants.¹⁻³ The additive manufacturing (AM) or 3D printing technology has been trying to meet these requirements for custom-designed device fabrication using various technologies like the selective laser sintering (SLS), fused deposition modeling (FDM), light based technologies like the stereolithography (SLA) and digital light processing (DLP), extrusion-based 3D printing, inkjet printing, etc.⁴⁻⁹ The challenge for suitable biomaterial selection is uphill with severe limitation in the availability of materials that can meet all the mechanical and processing requirements of device fabrication and at the same time meet the stringent requirements acceptable for medical application.¹⁰ The rapid progress in technological development of machinery for AM achieved in the recent decade has also spurred the search for suitable materials that could meet the requirements of these applications.¹¹ With the on-going focus on research in bio 3D printing, there is a need for the development of more new materials that meets the functional requirements of customized 3D printing technologies.^{12,13} The examples of some of the most commonly used biopolymers are polylactide (PLA), polycaprolactone (PCL), and polyglycolide (PGL), which are all derived from natural resources such as starch, sugar cane, corn, wheat straw, and wood chip.^{14,15} These polymers are characterized by the ester linkage that is amenable to hydrolytic cleavage to form small molecules.^{16,17} PLA and its composite or petroleum-based polymers with bio fillers are available in the form of solid filaments that can be used directly in additive manufacturing.^{18,19} Photocuring based 3D printing technologies like the DLP is very amenable for bio 3D printing as they offer many advantages like high resolution and gentle processing conditions compared to the extrusion-based AM technologies.²⁰⁻²² Moreover, the print speed can be controlled by adjusting the intensity of light or the exposure time.^{23,24} Compared to filament extrusion-based 3D printing technologies, the photocuring based 3D printing has the added advantage of enhanced bonding across the layers as the polymerization can continue even in the absence of light thereby connecting polymer chains across the different layers.^{25,26} Although many natural polymers satisfy the biological function requirements, they seldom possess the mechanical properties and structural integrity that are required to develop printable resin formulations.²⁷ One approach to improve the mechanical integrity is to incorporate crosslinking strategy. Among the available biopolymers, PLA is the most promising one for 3D printing due to its biocompatibility and biodegradability. Photocurable PLA can be developed by end functionalization with acrylate or by transesterification reactions to obtain oligomeric crosslinkers.²⁸⁻³¹ Recent work has also reported 3D printing using photocurable monomer

incorporating tri-thiocarbonate that could undergo photo-Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization.^{32,33} Melchels et al. reported photocurable formulations based on methacrylate end functionalized star shaped poly(d,l-lactide) diluted with ethyl lactate as a nonreactive diluent for 3D printing by SLA technique. They demonstrated porous 3D printed scaffolds that exhibited around 10% isotropic shrinkage upon removal of the nonreactive diluent. The 3D printed scaffold exhibited excellent mechanical properties and was compatible for cell attachment and proliferation.³⁴ Seck et al. reported synthesis and formulation of an aqueous photo-curable resin based on methacrylate-functionalized poly(ethylene glycol) / poly(d,l-lactide), which was demonstrated for printing porous scaffolds using SLA technique with pore size in the range of 400–500 microns that was compatible for cell seeding.³⁵ Ronca et al. prepared a composite resin formulation with methacrylate end capped poly(d, l-lactide) macromer and nano-hydroxyapatite which was dispersed with N-methyl-2- pyrrolidone (NMP) as nonreactive diluent and demonstrated for 3D printing schwarz pore network structure with the help of micro-stereolithography.³⁶ Arvin et al. reported the synthesis of methacrylic end-functionalized PLLA which was formulated into a photocurable resin by adding 20 wt. % 2-ethyl-2-hydroxymethyl-trimethacrylate as crosslinker, 20 wt. % of NMP as nonreactive diluent along with 4 wt. % phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) as photoinitiator (PI). This formulation was used to 3D print gyroid scaffold with interconnected pores using a DLP 3D printer; the 3D printed part exhibited good cell viability although it had comparatively feeble mechanical strength to be applicable for actual bone grafting.³⁷ In most of the reported PLA based literature, nonreactive solvents are used as diluent for the preparation of resin formulation in order to avoid the use of nondegradable reactive diluents like methyl methacrylate. However, the nonreactive diluents lead to shrinkage of the printed object upon its removal with solvent after 3D printing. Recently, Sandmeier et al. reported the solvent free resin formulation to 3D print biodegradable elastomer using heat-assisted DLP 3D printer.³⁸ This was achieved by covalently incorporating the photoinitiator bisacylphosphane oxide (BAPO) as part of macro-photoinitiator into random copolymers of d,l-lactide, and ϵ -caprolactone, resulting in viscous liquid polymers that were 3D printed using customized DLP printer equipped with heating facility. In this work, we demonstrate the development of solvent-free resin formulations based on star and linear PLLA polymer crosslinkers, which was utilized to generate 3D network structure using DLP 3D printer at room temperature. Two different resin formulations were developed by diluting the linear and star PLLA acrylate crosslinkers with 50 % by weight of biodegradable hydroxy ethyl methacrylate (HEMA) as a reactive diluent. A third resin formulation with a 50 wt. % of PLLA oligomer (50:50 wt. % of mixture

of linear and star PLLA acrylate crosslinkers) and 50 wt. % of HEMA, had optimum viscosity for DLP 3D printing and exhibited compatible tensile strength, Young's modulus and elongation for 3D printing tissue engineering scaffold. The photocuring kinetics of formulated resins with respect to photoinitiator concentration was studied using photo-differential scanning calorimetry (photo-DSC). The PLLA based formulation is anticipated to add to the palette of photocurable materials for DLP printing that do not exhibit shrinkage after printing and are also biodegradable.

2.2 EXPERIMENTAL SECTION

2.2.1 Materials

(3S, 6S)-3, 6-dimethyl-1, 4-dioxane-2, 5-dione, 1, 6-hexanediol, pentaerythritol, stannous 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$), Hydroxyethyl methacrylate were purchased from Sigma-Aldrich (India) and used as such without further purification. Acrylic acid was purchased from Sigma Aldrich and purified by distillation. Phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide was purchased from TCI chemical (India) Pvt. Ltd and used as such. Thionyl chloride (SOCl_2), Tetrahydrofuran (THF), Chloroform (CHCl_3), Methanol (MeOH), Dichloromethane (DCM) and Sodium sulphate (Na_2SO_4) were purchased locally. For gel permeation chromatography HPLC grade THF was purchased from Merck Chemicals (India).

2.2.2 Measurements

Proton NMR spectra were recorded using 400 MHz Bruker-AVENS NMR spectrophotometers using CDCl_3 as solvent with small amounts of Trimethylsilane (TMS) added as an internal standard. BRUKER alpha-E Fourier transform (FTIR) spectrometer was used to record the FTIR spectra. The molecular weights of polymers were determined using gel permeation chromatography (GPC) equipped with Viscotek VE 3580 RI detector. The GPC was calibrated with polystyrene standard and THF solvent as eluent at 1 mL min^{-1} flow rate. The thermal properties of all polymers were analysed using thermal gravimetric analysis (TGA), TA discover 550 second-generation TGA instrument, under nitrogen atmosphere by heating from 50 to 900°C at the heating rate of $10^\circ\text{C min}^{-1}$. The glass transition temperature (T_g) was determined using TA Discover 250 second-generation differential scanning calorimeter under nitrogen atmosphere by heating from -30 to 180°C at the heating rate of $10^\circ\text{C min}^{-1}$. The DSC was calibrated with indium standards before measurement. 2–3 mg of sample was taken in an aluminium pan, sealed, and measured at the same heating rate.

2.2.3 Methods

A) Resin Formulation with Acrylate Linear and Star PLLA Polymer

Photocurable resin formulations were prepared by mixing 50 wt. % of PLLA acrylate crosslinker (linear or star; resin A and resin B, respectively) in HEMA as a reactive diluent with 1% by weight of TPO as a photoinitiator in a 30 mL vial. The third formulation resin C was prepared by mixing a 50:50 wt. % mixture of the linear and star PLLA acrylate crosslinkers with 50 wt. % of HEMA along with 1 wt. % of TPO. The vial was sonicated for 1 h at room temperature while covered with an aluminum foil and stored in the fridge until the time of 3D printing. Just before use for DLP 3D printing, the resin was shaken in a vortex mixer for 5 min at room temperature. To print in custom-built 3D printer one more resin formulation was prepared by mixing of 80 wt. % of 50:50 mixture of linear and star acrylate PLLA, 19 wt. % of HEMA and 1 wt. % of TPO. The materials were taken in a round bottom flask and sonicated for 1 h at room temperature after covering the flask with aluminum foil to protect from light.

B) Spot Curing of the Prepared Resin Formulations

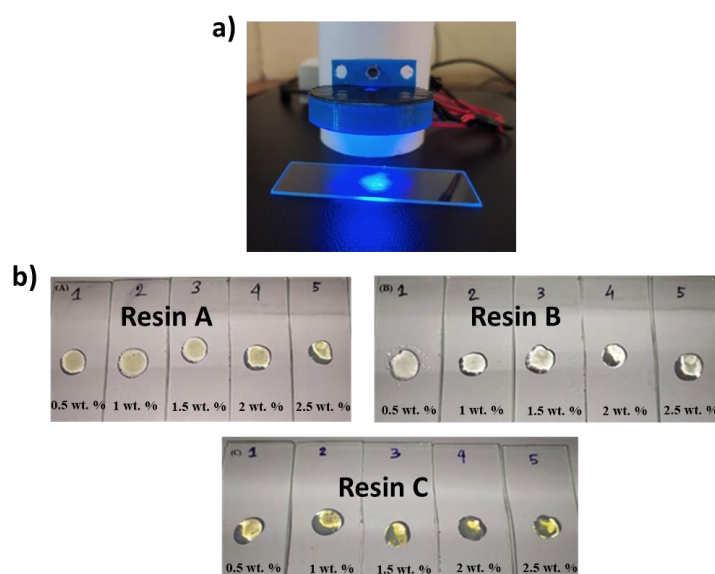


Figure 2.1 a) Photograph of the home-made spot curing setup b) spot curing experiment of the three resins formulation with different weight percentage of TPO photo initiator.

For the spot curing experiment, a homemade setup having six commercial LED lights positioned in a circular fashion was made use of. The wavelength of light was 365 nm and the intensity of the light was measured to be 35 mW cm^{-2} , with the help of UNO Gentec laser power meter (from a distance that was approximately equal to the space between the projector and the lower part of the vat in the 3D printer). Five samples each of resin A, resin B, or resin C (without the PI) were taken in 5 ml vials to which different weight percentages of TPO (from

0.5 to 2.5 wt. %) were added. The resin mixtures were sonicated for a period of 30 min for proper mixing of the resin formulation. After that one drop of resin was taken on a glass slide and kept under the homemade light setup at a specific distance and irradiated for 60 s. After 60 s the glass slide was tilted to visually inspect if the drop had solidified into a film or still exhibited liquid nature by flowing.

C) Photo-Differential Scanning Calorimetry

The photo-DSC studies were carried out in a TA Discover 250 second-generation differential scanning calorimeter equipped with a photo calorimetric unit (Omni cure series 2000). A 200 W high pressure mercury lamp which transmits the light of wavelength 320–500 nm, provides the irradiation to the sample chamber via dual-quartz light guide with neutral density.³⁹ The sample preparation was similar to that described for the spot cure studies. 5.5 mg of samples were weighed out exactly into the sample pan and measurement was carried out under constant nitrogen flow rate of 60 mL min⁻¹. For the photo DSC experiment, the sample was initially held in isothermal condition for 2 min under nitrogen atmosphere and equilibrated at 30 °C, following which the electronic UV light shutter was opened and sample was exposed to UV light for 2 min of irradiation. The shutter was closed automatically at the end of irradiation time and the baseline was recovered. The peaks were integrated to get the curing enthalpy from a plot of normalized heat flow as a function of irradiation time.

D) Viscosity Measurement

Rotational parallel plate measurements of formulations without added photoinitiator were performed on a Brookfield DV-II+ pro viscometer using Spindle CPE-42 and CPE-52 to analyse viscosity of the resins. The gap between the upper and lower plate was 1 mm; the amount of sample was 0.5 mL and 1 mL for the CPE-52 and CPE-42 spindle respectively. The temperature was constant at 30 °C throughout the experiment and the rotation was 0.3 to 12 rpm. The evaluation of viscosity as a function of shear rate was determined using the Anton Paar Physica Modular Compact Rheometer (MCR) 301. The test was performed in cup and bob with the diameter of 18.08 mm and 16.66 mm respectively. The shear rate was performed from 1 to 1000 s⁻¹.

E) Cure Depth Measurement of each Resin Formulations

In light-based 3D printing, the cure depth is a critical parameter that provides a rough estimate of the curing time required to print each layer. This parameter can be obtained using the Jacob's equation based on the Beer-Lambert law shown in Equation (1).^{40,41}

$$C_d = D_p \ln \frac{E_0}{E_c} \quad (1)$$

Here, C_d is the thickness of the printed part, D_p is the penetration depth or the depth to which the light can cure inside the liquid resin, E_c is the critical exposure energy required for starting the curing process of the resin at room temperature, E_0 is the energy of the incident light at the surface. Photocuring properties of the formulated resin like penetration depth and critical energy dose were determined using a Solus DLP 3D printer. The resin was irradiated in a square-shaped area on the vat of the 3D printer with different exposure times ranging from 20 to 60 s. The thickness of the crosslinked part was measured using a micro meter calliper. The value of the E_c and D_p was evaluated from the slope of the working curve and x-axis intercept, respectively.

F) Calculation of Critical Energy and Penetration Depth Measurement

The critical energy of each resin is where the extrapolated line touches the X-axis.

The extrapolated line touches the X-axis for: resin A- 2.75, resin B- 2.44, and resin C- 2.7

The intensity of the projector light was 31.67 mW/cm²

In case of **Resin A** the X axis value is 2.75

So, $\log(E_c) = 2.75$; $E_c = \text{antilog}(2.75) = \mathbf{631 \text{ mJ/cm}^2}$

For **Resin B** the X axis value is 2.44

So, $\log(E_c) = 2.44$; $E_c = \text{antilog}(2.44) = \mathbf{251 \text{ mJ/cm}^2}$

For **Resin C** the X axis value is 2.7

So, $\log(E_c) = 2.7$; $E_c = \text{antilog}(2.7) = \mathbf{501 \text{ mJ/cm}^2}$

These are the critical energy values of resin A, resin B and resin C.

Now the Penetration Depth (D_p) was calculated using this equation

$$C_d = D_p \ln \frac{E_0}{E_c}$$

For all resin, E_0 at 40 s i.e $31.67 \text{ mW/cm}^2 \times 40 \text{ s} = 1266.8 \text{ mJ/cm}^2$

Cure depth (C_d) at 40 s for resin A- 0.478 μm , resin B- 1.11 μm and resin C- 0.539 μm

So, the D_p for resin A = $C_d / \ln(E_0 / E_c)$

$$= 0.478 / \ln(1266.8 / 631)$$

$$= 0.478 / 0.697 = 0.686 \text{ mm} = \mathbf{686 \mu\text{m}}$$

D_p for resin B = $C_d / \ln(E_0 / E_c)$

$$= 1.11 / \ln(1266.8 / 251)$$

$$= 1.11 / 1.62 = 0.685 \text{ mm} = \mathbf{685 \mu\text{m}}$$

D_p for resin C = $C_d / \ln(E_0 / E_c)$

$$=0.539/\ln(1266.8/501)$$

$$=0.539/0.928=0.581 \text{ mm} = \mathbf{581 \text{ }\mu\text{m}}$$

G) 3D Printing of Prepared Resin Formulations

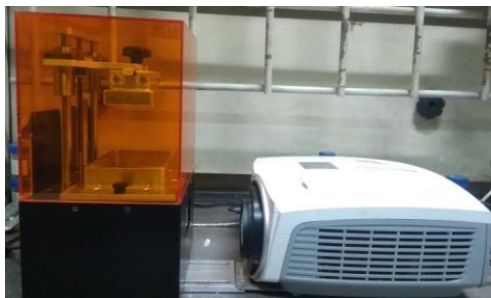


Figure 2.2 Photograph of the DLP 3D Printer with light projector.

The prepared solvent-free resin formulations were printed using the commercial Solus DLP 3D printer at room temperature. The DLP 3D printer was connected with a projector having light source of H1186HD projector. The intensity of the projector light was 31.67 mW cm^{-2} measured using UNO Gentec laser power meter. The printing was performed at room temperature, with layer thickness of $50 \text{ }\mu\text{m}$ and exposure time 40 s for initial 5 layers to enable proper adherence to the aluminum build platform followed by 25 s for the rest of the layers. After 3D printing, the printed objects were washed with isopropyl alcohol three times.

H) Custom Built 3D Printer (Direct Ink Writing)

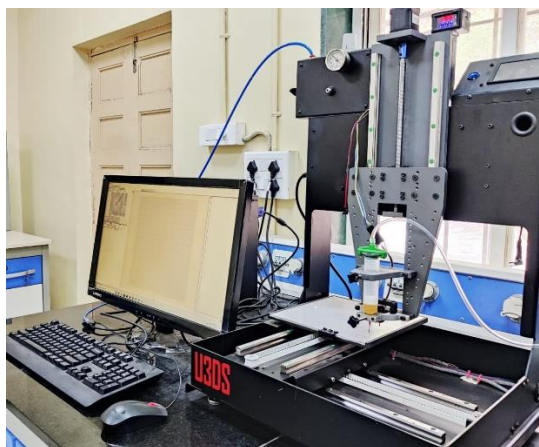


Figure 2.3 Photograph of the DIW 3D Printer

A direct ink writing 3D printer was custom built (Manufacturer: Utpal 3dsystems, U3DS, Gujarat, India) to additionally have a UV light source attached to it so as to cure the resin as it was deposited on the substrate bed (Figure 2.3). The viscous resin was taken in a 25 cm diameter syringe connected with an 18-gauge diameter needle and fitted to the 3D printer. For the extrusion of the resin from the syringe through the needle, controlled pneumatic pressure (50 psi) was applied and the printing speed was 8 mm s^{-1} . The resin formulation was taken in

the syringe and each layer thickness was set at 200 μm and filling density was 100%. The printer was connected with a 365 nm UV light source which cured the photo curable resin. The intensity of the light was 35 mW cm^{-2} . After supplying the CAD file information to the printer through the software, the printer recognized the bed levelling automatically and printed the file. To print an object from this printer, the parameters like layer thickness, printing speed, and pressure of the air could be controlled. After printing, the object was kept in a UV chamber for 1 h to ensure complete curing of the printed part.

I) Mechanical Test of the 3D Printed Parts

The tensile test measurements of the 3D printed parts were obtained using a Universal Testing Machine (Instron, Series 5943) with a 500 N capacity load cell at room temperature. Tensile tests were performed on dog bone-shaped objects which were cut from 3D printed films. The size of the testing sample was approximately $30 \times 10 \times 0.5 \text{ mm}^3$ and the gauge length was 5 mm with the stretching rate of 5 mm min^{-1} . 5 samples were tested for each resin formulation. The tensile strength, Young's modulus, and elongation at break were determined.

J) In Vitro Degradation Study

3D printed square specimens of each resin formulation were immersed in 150 ml of neutral PBS solution (pH 7) at 25 °C. The buffer solution (Sørensen solution) was prepared by mixing two different concentrations of salt solution. The first solution was prepared by dissolving 1/15 mol (9.078 g) of potassium dihydrogen phosphate (KH_2PO_4) in 1 L of de-ionized water. The second solution was prepared by dissolving 1/15 mol (11.876 g) of disodium phosphate (Na_2HPO_4) in 1 L of de-ionized water. The PBS solution was prepared by mixing 18.2 v/v % of first solution and 81.8 v/v % of the second solution.⁴² The printed samples were weighed to obtain the initial weight and then kept inside a 2k dialysis tube inside the PBS solution with constant stirring at 25 °C. The first weight loss reading was taken by removing the samples from the tube, wiping it gently with soft tissue paper and drying under a vacuum at 50 °C for overnight. The PBS solutions were replaced every week keeping the pH level same as before.

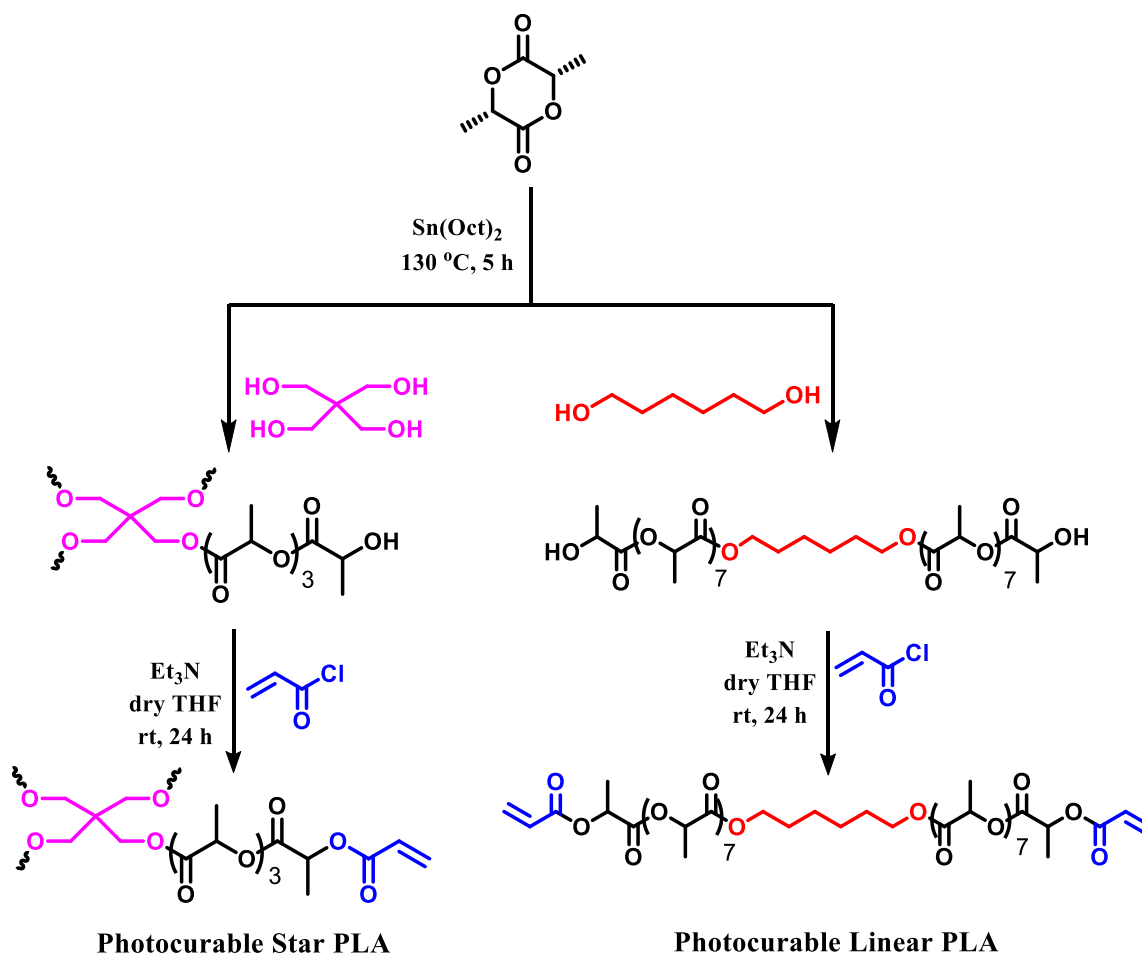
K) Scanning Electron Microscopy Imaging

A cross-section of the 3D printed part was examined using FE-SEM with an FEI Nova Nano SEM 450. The surface of the 3D printed films before and after degradation were examined with the same instrumentation. To examine the cross-section the samples were prepared by cutting the 3D printed film with a sharp blade and the cross-section part was mounted on the measurement stub vertically with the black carbon tape. To examine the surface of 3D printed

film before degradation, a small part of the fresh 3D printed film was cut and washed with deionized water and dried in vacuum oven. After 28 days of degradation, the film was removed from the dialysis tube and a small part was cut, washed and dried in vacuum oven. After that, the samples were mounted on the stub with carbon tape. All the samples were coated with gold prior to the SEM analysis.

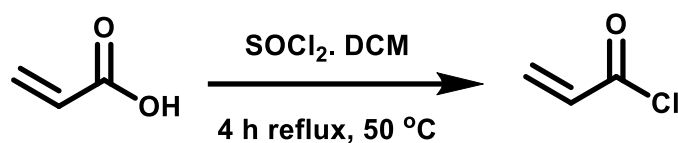
2.2.4 Synthesis and Characterizations

Low molecular weight linear and star PLLA polymers were synthesized by the ring opening polymerization of L-Lactide with stannous 2-ethylhexanoate as the catalyst and 1,6-hexane diol as initiator for the linear and pentaerythritol as the initiator for the star PLLA respectively as detailed in Scheme 2.1. The details of synthesis and structural characterization of the polymers are given below. The molecular weight (M_n and M_w) and polydispersity index ($\bar{D}$) for the linear and star PLLA was obtained from GPC and the values are shown in the Table 2.1.



Scheme 2.1 Overall synthetic scheme for acryloyl functionalized linear and star PLLA crosslinkers.

a) Synthesis of Acryloyl Chloride from Acrylic Acid



Acrylic acid (10.5 g, 145 mmol) was taken in a two-neck round-bottomed (RB) flask, to which 30 ml of dry DCM was added under a nitrogen atmosphere. Then 10.58 ml of SOCl_2 (17.25 g, 145 mmol) was added drop-wise under cold conditions. The reaction was refluxed for 4 h at 50°C . For workup, DCM was removed by distillation at 50°C followed by acryloyl chloride by increasing the temperature to 75°C . Yield: 85 %. ^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 6.65 (dd, 1H), 6.32-6.38 (dd, 1H), 6.20 (dd, 1H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 166.06, 136.29, 132.72.

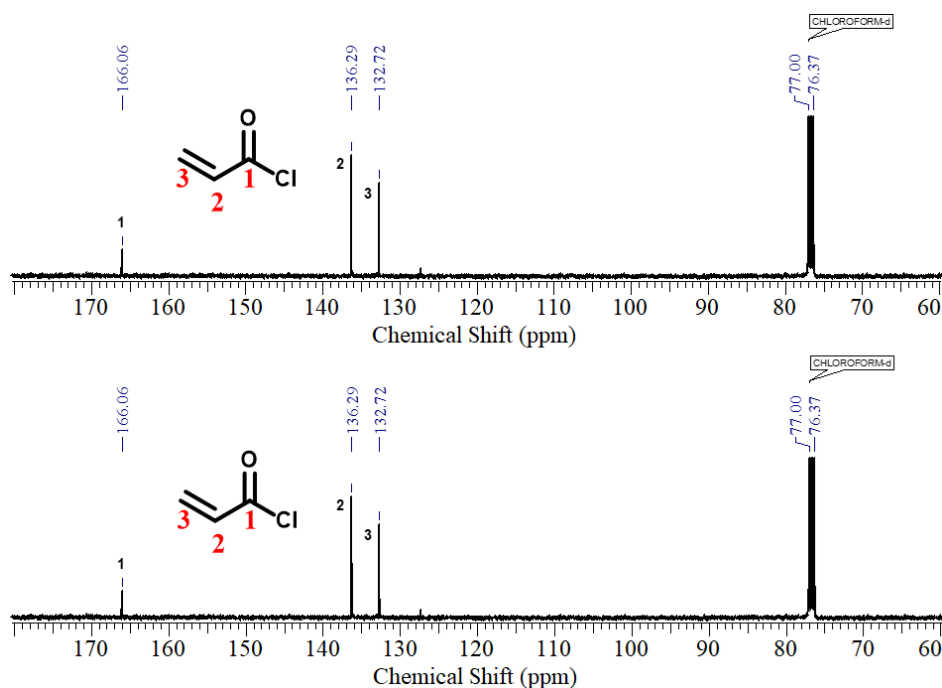
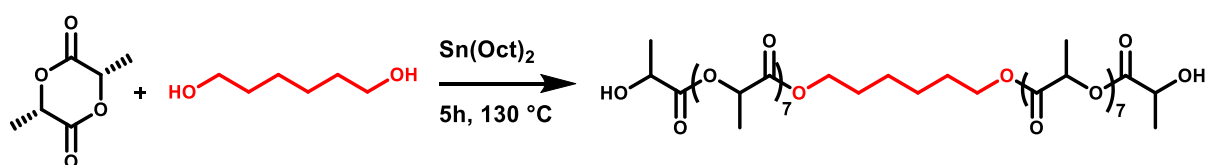


Figure 2.4 a) ^1H and b) ^{13}C NMR spectrum of acryloyl chloride (CDCl_3)

b) Synthesis of Linear Poly (l-lactide) Polymer (PLLA)



L-lactide (15 g, 104.07 mmol), 1, 6-hexanediol as initiator (1.54 g, 13.009 mmol) and Sn(Oct)_2 catalyst (0.1 mol % of 1,6-hexanediol) were taken in 50 mL RB along with stir bar. The vacuum was applied for 1 h with stirring to remove any trace of moisture from the mixture. Then the RB was immersed into a pre-heated oil bath at 130°C for 5 h with constant stirring. After the

completion of polymerization, the RB was cooled to room temperature. Then the polymer was dissolved in a minimum volume of chloroform and precipitated in ice-cold petroleum ether and the procedure was repeated three times. The polymer was dried in a vacuum oven at 50 °C for overnight. Yield: 98%. ^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 4.13 (t, 4H), 4.35 (q, 2H), 5.15 (m, 16H), 1.57 (m, 64H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 169.60, 69.00, 66.69, 28.32, 25.32, 20.52, 16.63.

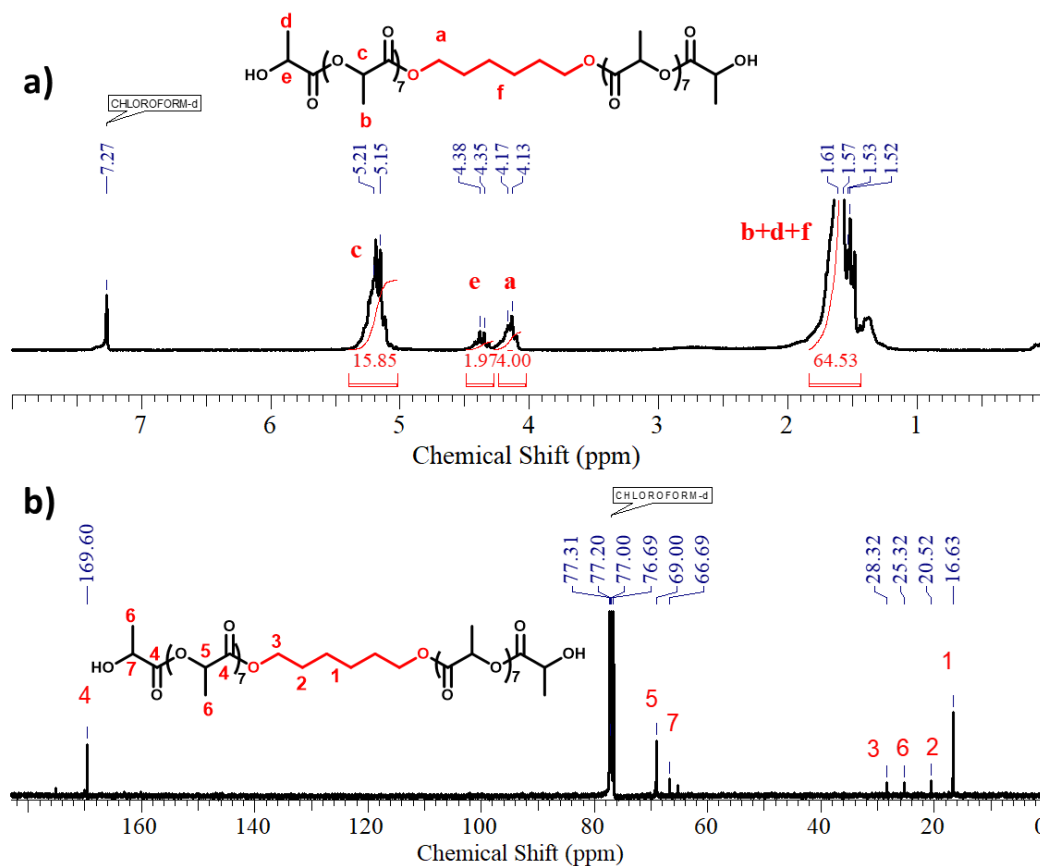
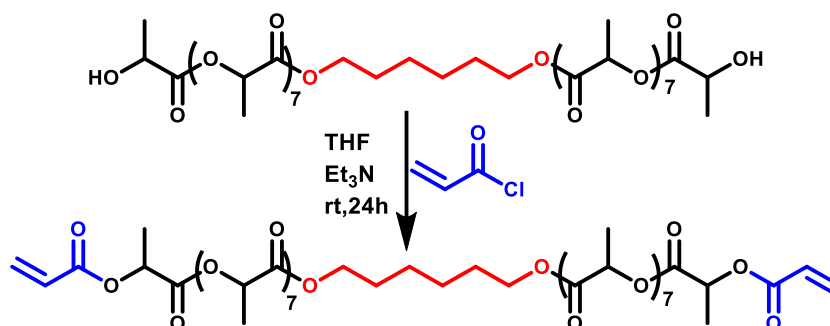


Figure 2.5 a) ^1H and b) ^{13}C NMR spectrum of linear PLLA (CDCl_3)

c) Synthesis of Acrylate Linear PLLA Polymer



Linear poly (l-lactide) (5 g, 3.93 mmol) was taken in a 50 mL two-necked RB along with a magnetic stir bar. 30 mL of dry THF was transferred into the RB by syringe under nitrogen

atmosphere. Triethyl amine (0.99 g, 9.83 mmol) was added slowly maintaining 0 °C followed by slow addition of acryloyl chloride (3.56 g, 39.3 mmol). The reaction was allowed to stir for 24 h under nitrogen atmosphere at room temperature. After that, the reaction mixture was filtered using Whatman filter paper. The filtrate was evaporated with the help of a rotary evaporator and the polymer was dissolved in chloroform and washed with brine solution three times. The organic layer was dried using anhydrous sodium sulfate. Finally, the chloroform was evaporated and the polymer was dried in a vacuum oven at 40 °C for overnight. Yield: 80%. ^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 4.13 (t, 4H), 5.18 (broad, 15H), 5.91 (dd, 1H), 6.19 (dd, 2H), 6.55 (dd, 2H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 169.27, 165.08, 131.65, 127.21, 68.67, 68.08, 27.99, 24.99, 20.17, 16.30.

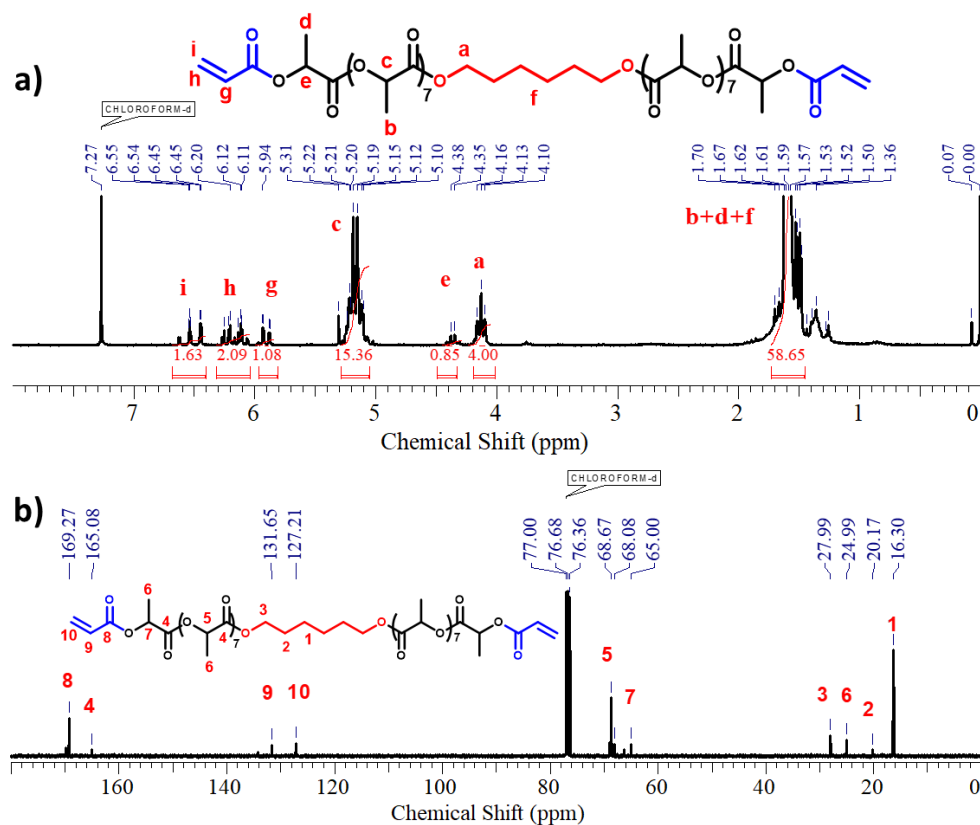
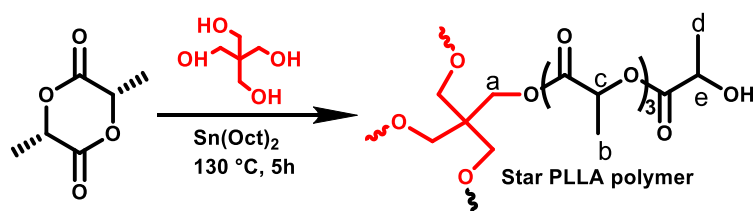


Figure 2.6 a) ^1H and b) ^{13}C NMR spectrum of acrylate linear PLLA (CDCl_3)

d) Synthesis of Star PLLA Polymer



L-lactide (15 g, 104.07 mmol), pentaerythritol (PET) as an initiator (1.77 g, 13.009 mmol), and $\text{Sn}(\text{Oct})_2$ catalyst (0.1 mol % of PET) were taken in 50 mL RB along with magnetic stir bar. The vacuum was applied for 1 h to remove any trace of moisture from the mixture. Then the RB was immersed into a pre-heated oil bath at 130 °C for 5 h with constant stirring. After the completion of polymerization, the RB was cooled to room temperature. Then the polymer was dissolved in a minimum volume of chloroform and precipitated in ice-cold petroleum ether and the procedure was repeated three times. The polymer was dried in a vacuum oven at 50 °C for overnight. Yield: 97%. ^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 4.35 (broad, 12H), 5.19 (broad, 16H), 1.59 (broad, 63H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 174.85, 169.33, 68.73, 66.44, 62.00, 53.15, 20.06, 16.44.

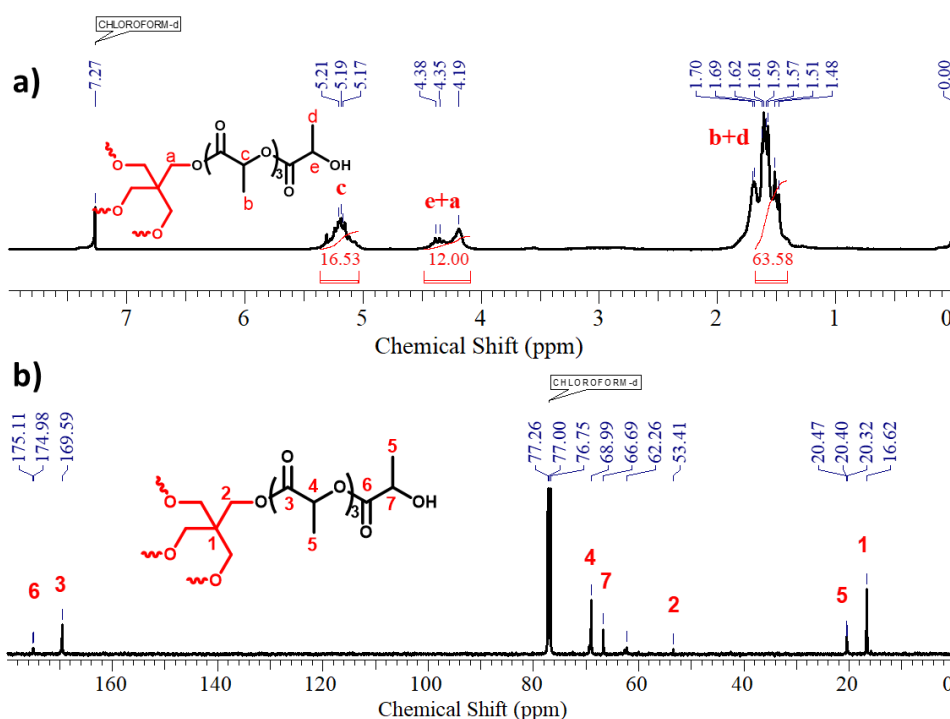
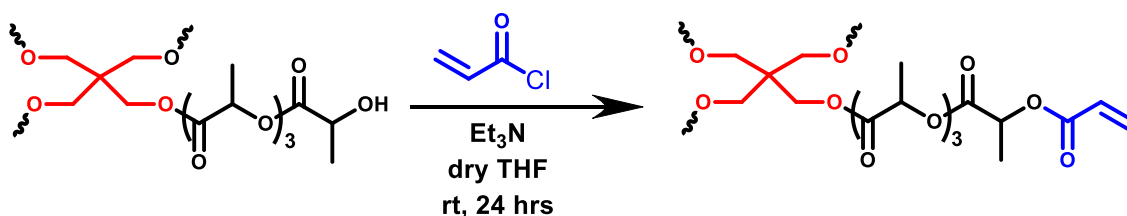


Figure 2.7 a) ^1H and b) ^{13}C NMR spectrum of star PLLA (CDCl_3)

e) Synthesis of Acrylate Star PLLA Polymer



Star poly (l-lactide) (5 g, 3.88 mmol) was taken in a 50 mL two-necked RB along with a magnetic stir bar. 30 mL of dry THF was transferred into the RB by syringe under nitrogen atmosphere. Triethyl amine (1.77 g, 17.46 mmol) was added slowly maintaining 0 °C

temperature followed by slow addition of acryloyl chloride (7.02 g, 77.63 mmol). The reaction was allowed to stir for 24 h under a nitrogen atmosphere at room temperature. After that, the reaction mixture was filtered using Whatman filter paper. The filtrate was evaporated with the help of a rotary evaporator and the polymer was dissolved in chloroform and washed with brine solution three times. The organic layer was dried using anhydrous sodium sulfate. Finally, the chloroform was evaporated and the polymer was dried in a vacuum oven at 40 °C for overnight. Yield: 80%. ¹H NMR spectrum (400 MHz, CDCl₃) δ in ppm: 4.18 (s, 8H), 5.17 (m, 16H), 6.10 (dd, 2H), 6.13 (dd, 4H), 6.50 (dd, 3H), 1.59 (broad m, 53H). ¹³C NMR spectrum (100 MHz, CDCl₃) δ in ppm: 175.18, 169.82, 134.90, 132.67, 128.21, 127.68, 69.22, 66.92, 20.70, 16.85.

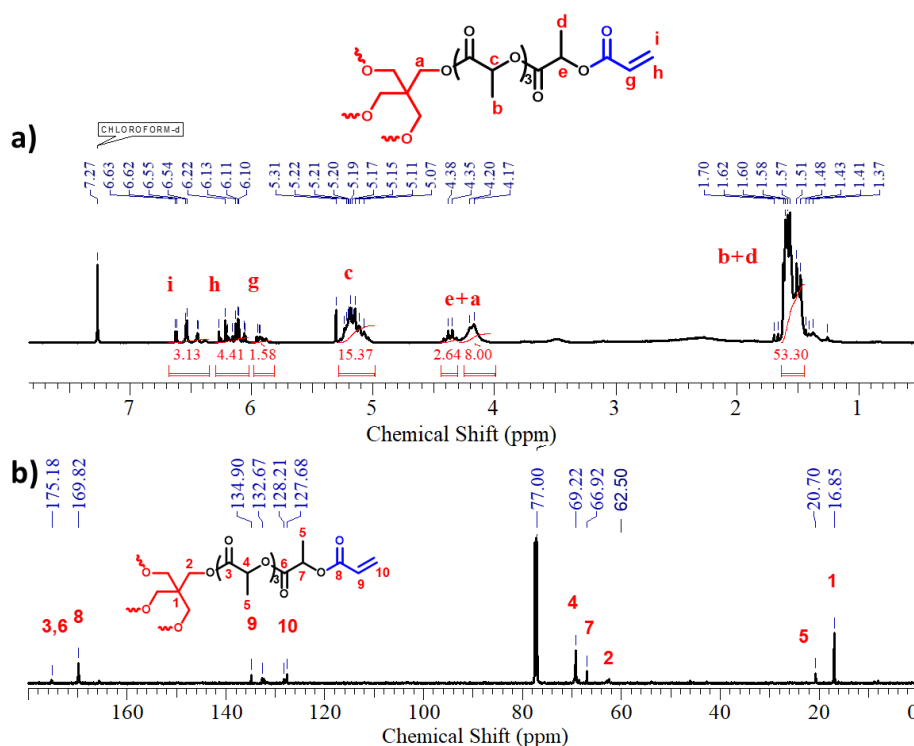


Figure 2.8 ¹H and ¹³C NMR spectrum of star PLLA acrylate (CDCl₃)

Sr. no.	Polymers	Molecular weight			
		Mn (NMR) (gmol ⁻¹)	Mn ^a (gmol ⁻¹)	Mw ^a (gmol ⁻¹)	Đ ^a
1	Linear PLLA	1200	2600	3500	1.34
2	Star PLLA	1.5	2300	2700	1.17
3	Linear PLLA Acrylate	1.3	2700	3700	1.37
4	Star PLLA Acrylate	1.6	2600	3400	1.31

Table 2.1. The molecular weight of all four synthesized PLLA polymers

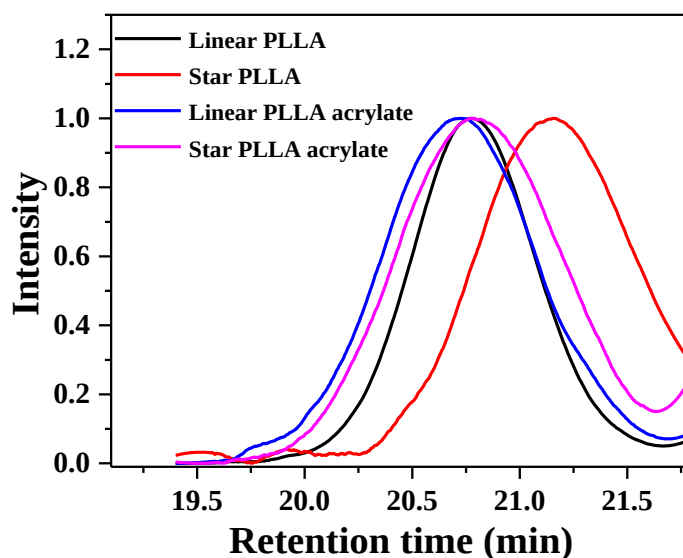


Figure 2.9 GPC spectra of all four synthesized PLLA polymers

2.3 RESULT AND DISCUSSION

2.3.1 Synthesis and Characterizations of Polymers

In Figure 2.10a, the two terminal methine protons of linear PLLA labeled “e” appeared at 4.38 ppm, while the methine protons in the repeat unit labelled “c” (on either side of the central hexamethylene chain), appeared at 5.15 ppm. From the ratio of these two peak areas, the number of repeat units on either side of the central hexamethylene spacer could be assigned as 8 for the linear PLLA in accordance with the theoretical calculation. In the case of the star PLLA, shown in Figure 2.10b, the central methylene (CH_2) protons of the initiator (labelled “a”) was integrated for 8 protons for the four arms. The methine proton of the terminal (total 4 for four arms, labelled “e”) was also partially merged with the “a” protons. So, the total integration of the peaks in the range 4.19 to 4.38 ppm was taken as 12. The integration for the methine protons of the repeat units at 5.19 ppm was obtained as 16. Taking the ratio of this peak area with respect to the e+a protons, the average number of repeat units per arm was obtained as 4 which match with the theoretical monomer to initiator ratio. The linear and star PLLA was reacted with acryloyl chloride in presence of triethyl amine as base to convert the terminal hydroxyl units into acryloyl functionality. This reaction was optimized in THF as solvent to obtain reasonable yields in the range of 80 to 85%.^{43,44} The introduction of the acryloyl functionality was confirmed by the appearance of the new peak corresponding to the acryloyl double bond in the range of 5.8–6.63 in the proton NMR spectra. The formation of the acryloyl double bond could be further confirmed with ^{13}C NMR and FT-IR spectroscopy as well. Comparing the ^{13}C NMR spectra data of linear and star PLLA polymers with their

respective PLLA acrylate polymer, it was observed that two new peaks appeared at 131 ppm and 127 ppm in linear PLLA acrylate, 135 and 127 ppm in star PLLA acrylate due to the presence of carbon–carbon double bond.

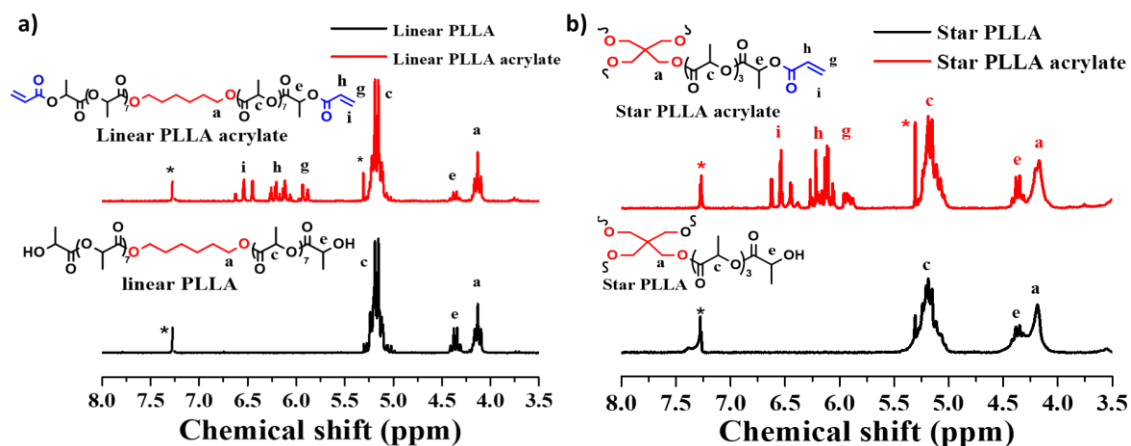


Figure 2.10 Comparison of the expanded region (3.5 to 8.0 ppm) in the ^1H NMR spectra in CDCl_3 of a) linear PLLA and linear PLLA acrylate; b) star PLLA and star PLLA acrylate.

Similarly, the stack plot of the FT-IR spectra of linear and star PLLA before and after acrylation (Figure 2.11) clearly indicated the appearance of new peaks at 1629 cm^{-1} in case of linear and 1627 cm^{-1} for star PLLA corresponding to $\text{C}=\text{C}$ stretching frequency respectively. The molecular weights of the polymers were determined using GPC recorded in THF using polystyrene standards. The GPC plot is provided Figure 2.9 and the molecular weight is tabulated in Table 2.1. The GPC data revealed almost similar molecular weight for the linear and star PLLA, and their acrylate derivatives. The polydispersity index for all four polymers was in the range of 1.17–1.37. The number average molecular weight of linear and star PLLA were 2600 and 2700 g mol^{-1} respectively while that after their modification with acrylate moieties were 2300 and 2600 g mol^{-1} respectively.

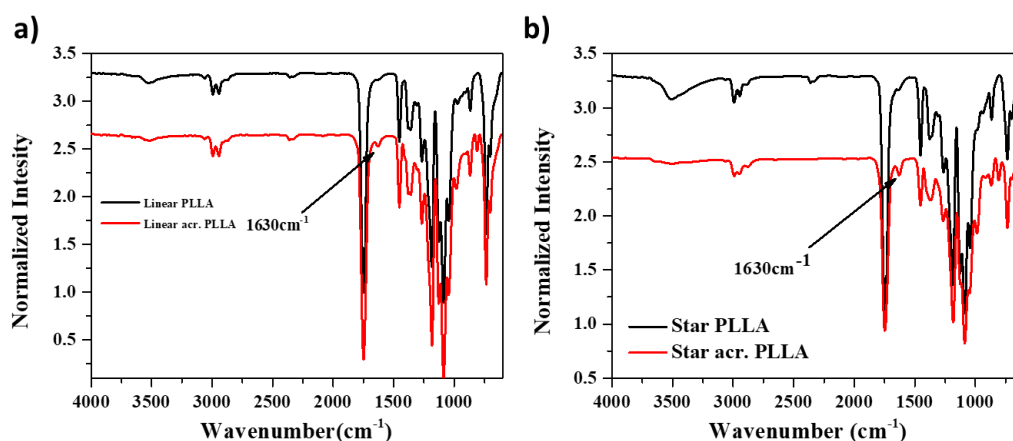


Figure 2.11 Comparison of FT-IR spectra of (a) linear PLLA and linear PLLA acrylate; (b) star PLLA and star PLLA acrylate.

2.3.2 Photo Calorimetric Studies of Acrylate Polymers and HEMA

Isothermal (at 30 °C) photo-DSC studies under nitrogen atmosphere were undertaken to extract information regarding the enthalpy of double bond conversion. Figure 2.12 compares the specific heat flow obtained for HEMA, Linear PLLA acrylate and Star PLLA acrylate with 1 wt. % of PI. The theoretical heat of polymerization (ΔH_p) of HEMA was estimated as 421.16 J g⁻¹ based on literature value for heat of polymerization of 13.1 Kcal mol⁻¹ per methacrylate double bond.⁴⁵ Similarly theoretical heat of polymerization was calculated for the linear and star PLLA oligomers based on literature values of 20.6 Kcal mol⁻¹ per acrylate double bond. The calculated ΔH_p values were 125.09 J g⁻¹ for the linear PLLA acrylate and 229.24 J g⁻¹ for the star PLLA acrylate. Here due consideration was taken to account for two acrylic double bonds for the linear PLLA acrylate and 4 double bonds for the star PLLA acrylate. The details of the calculation are provided in section 2.2.3.F. From the theoretical heat of polymerization for 100% double bond conversion the extent of cure achieved for HEMA was estimated to be 92.9% while the percentage cure for the linear and star acrylate oligomers were 62.1% and 49.5% respectively at 1 wt. % of PI concentration.⁴⁶ Table 2.2 lists the curing parameters determined for HEMA, Linear PLLA acrylate and star PLLA acrylate. A shoulder peak was observed in the reaction rate curve for HEMA, which has been attributed to fast reaction leading to microgel formation in the bulk material as reported in the literature.⁴⁷ However, it did not impact the final conversion rate achieved for HEMA. The lower cure rate observed for the acrylate compared to the methacrylate double bond (HEMA) is due to the higher viscosity of the oligomeric acrylates—linear as well as star PLLA.

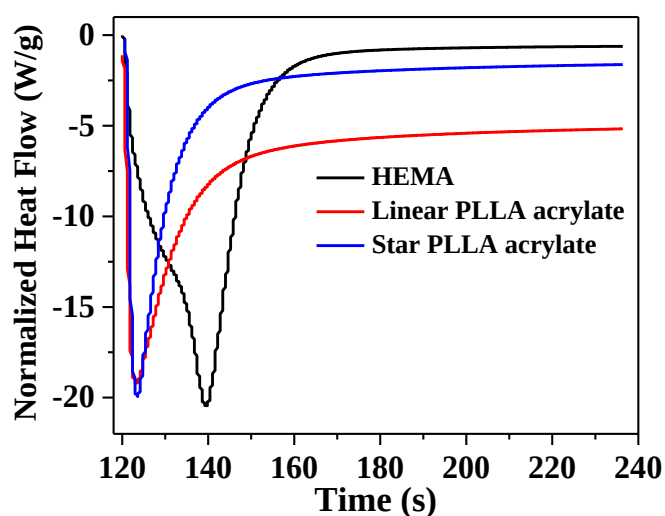


Figure 2.12 Specific Heat flow obtained from Photo DSC measurements at 30 °C for HEMA, Linear PLLA acrylate and Star PLLA acrylate with 1 wt. % of PI.

Materials	Curing enthalpy (J/g)	Theoretical heat of polymerization (ΔH_p) (J/g)	Curing (%)
HEMA	391.47	421.16	92.9
Acrylate Linear PLLA	77.71	125.09	62.1
Acrylate Star PLLA	113.37	229.24	49.5

Table 2.2 Photocuring Enthalpy (J/g) of 1 wt. Percentage of TPO as Photo-initiator

Sl. no.	Linear PLLA wt. %	Star PLLA wt. %	HEMA wt. %	TPO wt. %	Viscosity Pa.s
Resin A	49.5	-	49.5	1	0.072
Resin B	-	49.5	49.5	1	0.051
Resin C	24.75	24.75	49.5	1	0.060

Table 2.3 Composition of the resin formulations used.

Table 2.3 lists the composition of the three resin formulations that were prepared by mixing 50 wt. % HEMA with equal weight percentage of linear PLLA acrylate (Resin A), star PLLA acrylate (Resin B), and the third formulation Resin C with 50 wt. % HEMA and 50 wt. % each of linear and star PLLA acrylate. Prior to 3D printing, screening experiment was designed by varying the amounts of the PI TPO used for the three resin formulations A, B and C. A drop each of these formulations was placed on a clear glass slide and irradiated for 60 s using a set of 6 commercial LEDs of wavelength 365 nm fitted into a circular holder in a homemade setup. The detail of the homemade setup is provided under 2.2.3.b (Spot Curing of the prepared resin formulations) and the photo of the setup is provided in the figure 2.1b. At the end of the specified time of irradiation, the glass slide was tilted to observe if the formulation had solidified or exhibited liquid-like flow behaviour. Figure 2.1b shows the image of glass slides for three formulations. The weight % of the PI TPO was varied from 0.5 to 2.5 wt. % for each of the 3 resin formulations. From these screening experiments, it could be observed that formulations with PI concentration >1 wt. % exhibited incomplete curing with the sample flowing at the end of the 60 s irradiation, while those with 0.5 and 1 wt. % PI formed solid films. At higher PI concentration, the rate of recombination also increased resulting in reduced conversion.⁴⁸

Isothermal photo-DSC analysis was carried out for the 3 resin formulations, i.e., Resin A with 50–50 wt. % of HEMA and linear PLLA acrylate, Resin B having 50–50 wt. % of HEMA and star PLLA acrylate and Resin C having 50 wt. % HEMA and 25–25 wt. % linear and star PLLA acrylate each. Figure 2.13 shows the Photo-DSC plots for the 3 resins at various PI concentrations ranging from 0.5 to 2.5 wt. % and the corresponding enthalpy values are listed in Table 2.3. From the values of enthalpies listed in the table, it could be observed that for all 3 resin formulations the heat of photopolymerization increased initially from 0.5 to 1 wt. %, after which it continuously decreased with an increase in the concentration of PI. This indicated that the highest cure conversion was obtained at the optimum PI concentration of 1 wt. %. This was in corroboration with the screening studies carried out on the glass slides. Insufficient amounts of PI can lead to incomplete curing, while larger amounts of PI can lead to higher absorption of the incident light. This would result in insufficient light for the bulk of the sample leading to incomplete curing. Therefore, an optimum concentration of PI is necessary for photocurable formulations.⁴⁹ Thus, the resin formulations were optimized with 1 wt. % of TPO as PI for the 3D printing (the formulation used for 3D printing is given in Table 2.2).

Resin formulations	Curing enthalpy (J/g) at different PI wt. %				
	0.5	1.0	1.5	2.0	2.5
Resin A	-237	-283	-279	-272	-256
Resin B	-244	-284	-256	-250	-242
Resin C	-251	-309	-277	-275	-273

Table 2.3 Photocuring enthalpy (J/g) of Resin A, Resin B, and Resin C with different weight % of PI (TPO).

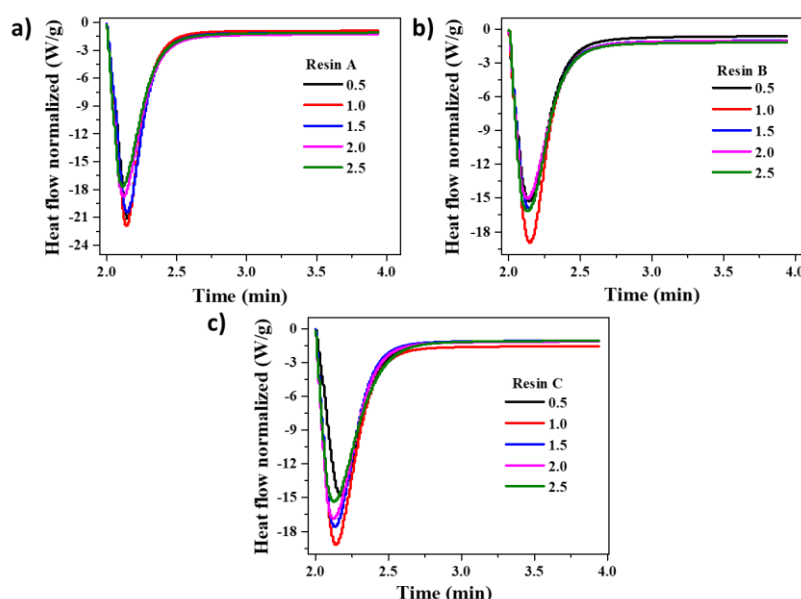


Figure 2.13 Isothermal curing of a) resin A, b) resin B and c) resin C with different weight percentage of photo initiator.

2.3.3 Viscosity Measurement

For DLP 3D printing, the viscosity of the photocurable resin is a critical parameter to ensure easy flow as well as smooth, warpage-free printed material at room temperature. Ideally, the viscosity of photo resin used in room temperature DLP 3D printing should not exceed 5 Pa s.^{50,51} Figure 2.14a compares the increase in viscosity of resin formulation with increasing wt. % addition of linear or star acrylate PLLA in HEMA which were determined using an isothermal parallel plate rotational rheometer. From the figure, it could be seen that the linear polymer exhibited slightly higher viscosity compared to the star polymer for all the studied compositions in HEMA. Figure 2.14b shows the plot of viscosity of resin formulations versus shear rate for the three resin formulations (without added PI) from which the viscosity was calculated. From Figure 2.14b it could be observed that the formulated resins exhibited viscosity in the range of 0.051 to 0.072 Pascal-second (Pa s) with resin A having the highest viscosity at 0.072 Pa s, Resin B lowest at 0.051 Pa s, and Resin C exhibiting viscosity value in between that of Resin A and Resin B at 0.060 Pa s (Table 2.3). The viscosity at 30 °C remained constant with increasing shear rate, indicating the Newtonian fluid-like behaviour of the materials. Although the viscosity values of the 3 resin formulations were lower than those reported in the open literature, it was adequate for 3D printing using a commercial DLP 3D printer at room temperature.

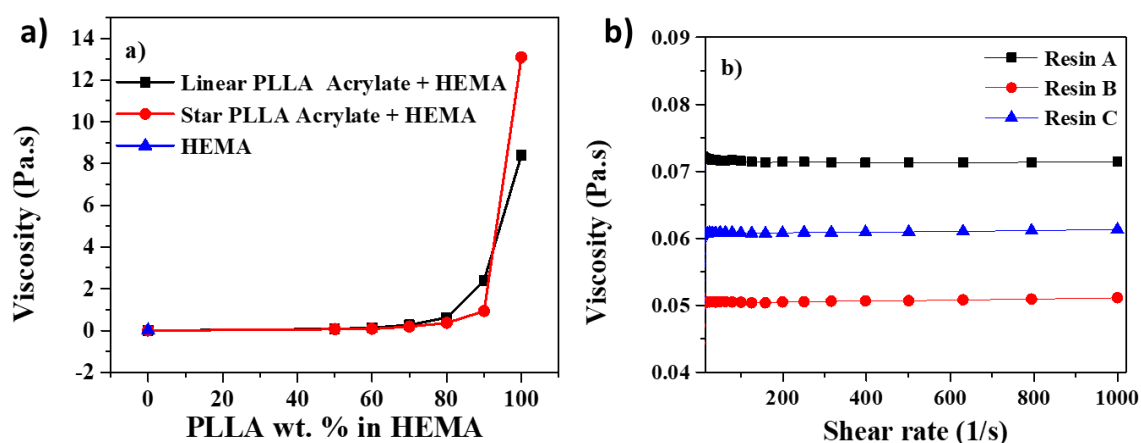


Figure 2.14 a) Viscosity as a function of increased weight percentage of the oligomer (linear or star PLLA acrylate) in HEMA; b) plot of complex viscosity of resin formulations (without photoinitiator) versus shear rate (1/s).

2.3.4 Resin Cure Characteristics

Figure 2.15a compares the cure depths of the resins as a function of increasing energy density. From the plot, it could be observed that the cure depth gradually increased with increasing exposure time from 20 to 60 sec for all three resin formulations (the photograph of the cured square objects with different exposure times is shown in Figure 2.15b). Extrapolation of the trend line on the x-axis provided the critical exposure energy and the slope of the trend line provided the depth of penetration of light into the resin formulation. Table 5 summarizes the critical energy and penetration depth of the 3 resin formulations determined from the working curve and Equation (1). Higher penetration depth indicated that the resin allowed more photons to enter deeper inside, which could result in crosslinking of regions outside the required area leading to poor resolution. From Table 5, it could be seen that the penetration depth of both resin A and resin B were similar but the critical energy of resin B was lower compared to resin A. This could be attributed to the higher concentration of crosslinkable groups in resin B—the star PLLA acrylate with four terminal acrylate groups, which facilitated the formation of a larger polymer network structure and easy solidification under low exposure of light energy compared to Resin A (only two terminal acrylate curable groups of linear PLLA acrylate).

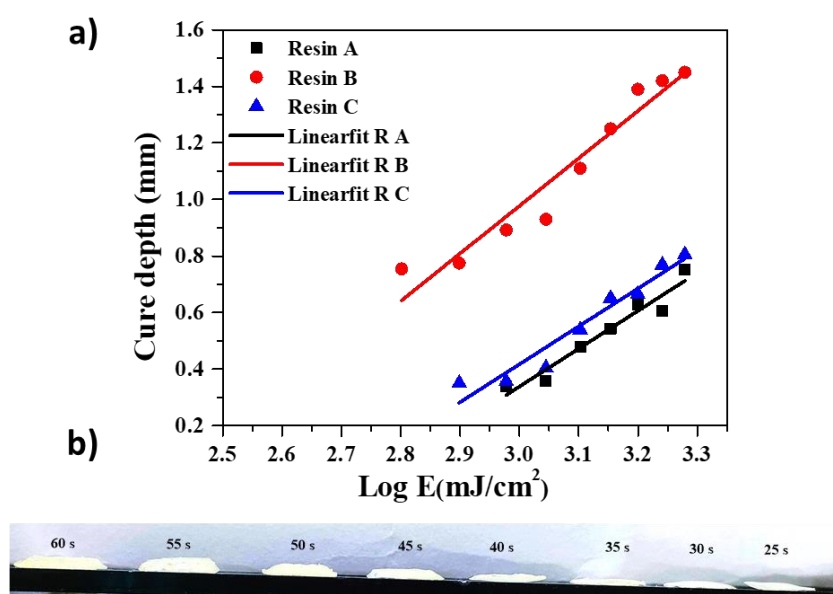


Figure 2.15 a) Working curve of the three new resin formulations irradiated using the projector of the DLP printer for different exposure time. b) Photograph of cure depth analysis of resin C.

On the other hand, Resin C which is a mixture of 50:50 wt. % of resin A and resin B, showed curing behavior which was in between that of resin A and resin B. Based on this evaluation of

the curing characteristics, the printing parameter like the layer thickness of the 3D printed object was fixed at 50 μm . The exposure time required for each layer was calculated from the cure-depth experiment. For instance, the exposure time required for each layer for the DLP 3D printing using resin C was estimated by dividing the critical energy of resin C–501 mJ cm^{-2} by the DLP projector light intensity of 31.67 mJ cm^{-2} to get the critical exposure time of 16 s. The critical exposure time indicates the time required to start the curing of the resin using the DLP printer. Therefore, the exposure time was set higher than the critical exposure time to ensure complete curing. The printing was performed at room temperature, with layer thickness of 50 μm and exposure time 40 s for initial 5 layers to enable proper adherence to the aluminum build platform followed by 25 s for the rest of the layers.

2.3.5 3D Printing of Formulated Resins

The printing ability of the three formulated resins was evaluated using a DLP 3D printer at room temperature. The designed structures could be successfully printed without any organic solvent. All three resins could successfully print films of 500 micrometres thickness which were further used for the mechanical test measurements. Resin C was taken up for further optimization for complex structure 3D printing. Resin C was further mixed with Sudan I dye to improve the resolution of the printed object. Absorbers like Sudan dyes have good spectral overlap with the light source (LED lamp of 405 nm normally used in DLP 3D printers), which helps to limit the penetration depth of the light from the LED and thus control the cure depth of the resin.^{52,53} In the absence of the dye, the light from the source LED will penetrate deeper causing unwanted polymerization inside voids, around edges etc. resulting in loss of resolution of the 3D printed object. Figure 2.16a compares the absorption spectra of Sudan dye I and TPO photoinitiator recorded in chloroform. Sudan dye has good absorption in the 405 nm thereby ensuring its usefulness for improving resolution in DLP-based 3D printing.⁵⁴

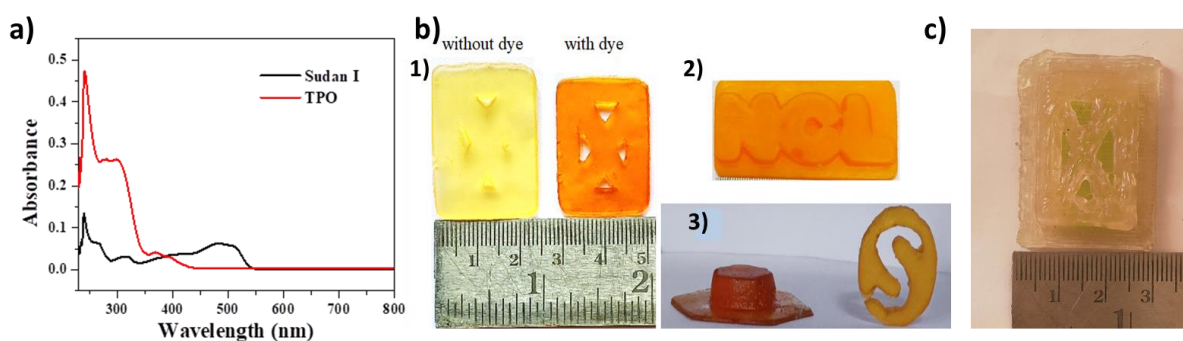


Figure 2.16 a) Absorption spectra of Sudan I and TPO photoinitiator, b) Image of 3D printed

objects made using Resin C incorporating Sudan I dye, c) 3D printing materials printed from DIW 3D printer.

Figure 2.14b1 shows the 3D printed structures, where without dye incorporation the areas with triangular holes are also filled and the object has a larger dimension because areas beyond the edges also got polymerized. Figure 2.16b also shows 3D print of the institute name tag (2) NCL: National Chemical Laboratory and (3) some 3D printed objects demonstrating 3D printing ability of vertical designs with intricate holes and patterns using the resin. Visual evaluation of the print quality like sharp edges and the designed holes demonstrated very good build geometry and resolution of the printed object using the newly developed PLLA resin formulation. The resin could also be customized to print using a Direct Ink Writing custom-designed 3D printer fitted with a UV light source. The consistency of the resin required for the extrusion-based 3D printer is much more viscous compared to the DLP-based printing technique. The viscosity could be adjusted by reducing the wt. % of HEMA as the diluent. Thus, 80 wt. % of a 50:50 mixture of the linear and star PLLA was mixed with only 20 wt. % of HEMA and used as the resin for the custom-built Direct Ink 3D printer. The details of the printing parameters are provided under the method section. The image of the printed object is given in Figure 2.16c. The resolution of the printed object was not as good as that obtained from the DLP printer; nevertheless, the process demonstrated the versatility of the photocurable resin formulation.

2.3.6 Mechanical and Thermal Properties of 3D Printed Parts

The mechanical properties of thin dog bone-shaped samples which were prepared from the 3D printed film of three different resin formulations were measured at room temperature. The results obtained for uniaxial tensile testing using the three resin formulations is plotted in Figure 2.17a. Table 2.4 lists the tensile strength, Young's modulus, and elongation at break for the samples. 3D printed film using Resin A exhibited the lowest tensile strength (3.7 MPa) and highest elongation (220%) compared to the other two formulations. Resin B printed part exhibited tensile strength at 4.8 MPa and elongation up to 156 %. 3D printed film using Resin C exhibited the highest tensile strength (6.6 MPa) as well as highest Young's modulus (60 Mpa) along with good elongation (178%). Compared to resin A printed part, the printed part of resin B reflected higher tensile strength and Young's modulus due to the formation of higher polymer network structure as the latter possessed higher density of crosslinking group. The reason for the highest tensile strength and Young's modulus for 3D printed parts from resin C could be a synergistic effect of physical interlocking along with chemical crosslinking upon mixing resin

A and resin B.^{55,56} Generally, PLA is a brittle material with less than 10 % elongation at break;⁵⁷ the design of PLLA as star and linear acrylate crosslinkers endowed the 3D printed object with stretchable characteristics. Thermogravimetric analysis was carried out to study the thermal stability of the 3D printed parts (Figure 2.18a). The 3D printed parts exhibited good thermal stability with 10 % weight loss observed above 250 °C for all samples. Glass Transition Temperature (T_g) of the 3D printed parts were observed in the range of 20–26 °C which indicated the soft nature of the polymers (Figure 2.18b). The values of 10 % weight loss and T_g of the 3D printed parts are tabulated in Table 2.4.

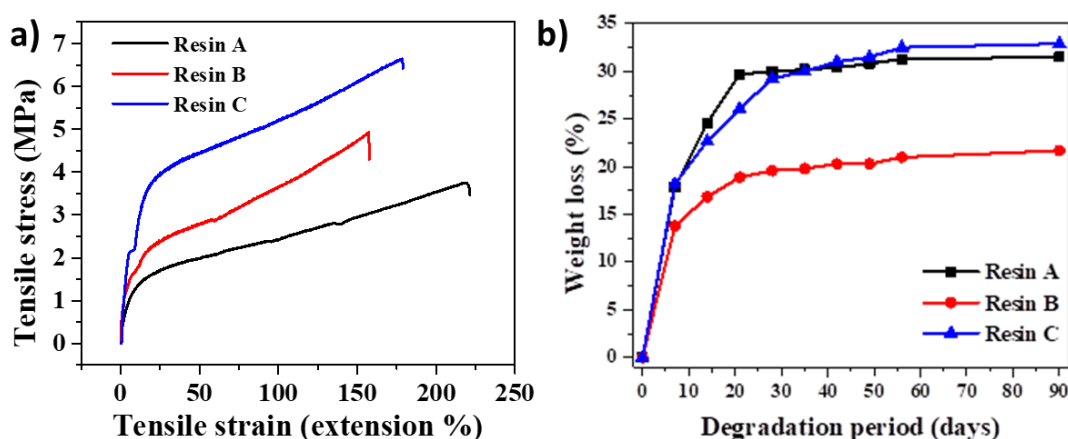


Figure 2.17 a) Tensile-strain curves of 3D printed part of resin A, resin B and Resin C formulations, b) Weight loss of the three different 3D printed parts over a period of 90 days in PBS solution.

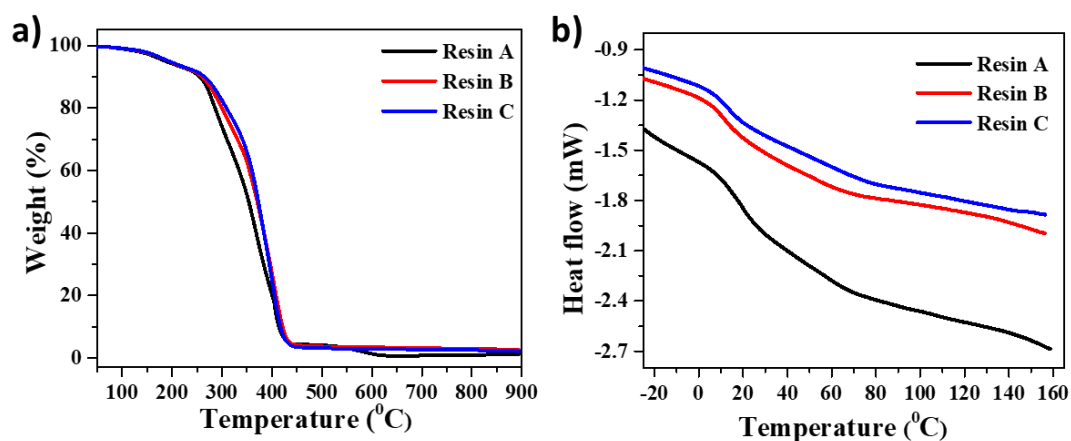


Figure 2.18 a) Thermogravimetric analysis and b) DSC second heating curves of 3D printed films using resin A, B, and C.

Printed film	Tensile Strength [Mpa]	Young's Modulus [Mpa]	Elongation (%)	T _g [°C]	T _{d10} % [°C]	Weight Loss % (from in vitro degradation studies)
Resin A	3.7±0.92	13.10±2.10	220 ±9.87	24	256	32
Resin B	4.8±0.23	23.63±2.06	156±6.28	26	260	22
Resin C	6.6±0.42	60.29±9.74	178±7.32	20	264	33

Table 2.4 Tensile strength, Young's modulus, Elongation, Glass transition and 10 weight % degradation temperature of 3D printed parts along with their weight loss over a period of 90 days in PBS buffer.

2.3.7 In Vitro Degradation Studies

The degradation profile of 3D printed parts was evaluated by carrying out degradation studies of 3D printed films cut into square specimens and immersed in PBS solution (comparable to biological conditions) maintained at a pH of 7 at 25°C and monitored over a period of 90 days. An initial fast weight loss was followed by the slowdown of the degradation with an almost steady state beyond 30 days. The 3D printed film from Resin B exhibited a slightly lower extent of weight loss at around 22% compared to around 30% weight loss exhibited by 3D printed films from resin A and resin C. This could be attributed to the higher extent of crosslinking present in the star polymer-based formulation (4 acrylic units) (B), which slows down the degradation. Attempts to extract the products of degradation from the buffer solution for characterization using FT-IR or proton NMR studies were not very fruitful as the concentration of degraded products was below the detection limit for these techniques. However, there is ample evidence in the literature suggesting the formation of L-lactic acid as the product of degradation of PLLA, which was measured by an enzymatic method using an L-lactic acid assay kit.⁵⁸ As degradation sets in, the pH of the solution changes from neutral to acidic due to the presence of degraded by-products of PLLA. The PBS solutions were replaced periodically to maintain the pH throughout the course of the study. The weight loss percentage observed for the 3D printed objects in the PBS solution is shown in Figure 2.17b and the values are listed in Table 2.4. Scanning electron microscopy (SEM) images were recorded for the 3D printed samples before degradation and after 28 days of degradation, which is shown in Figure 2.19. The images on the top (Figure 2.19a–c) were for the fresh 3D printed samples of resin A, resin B, and resin C before they were subjected to degradation in the PBS solution. The images on the bottom panel (Figure 2.19d–f) which were recorded after 28 days of degradation, demonstrate the presence of microcracks and surface roughness due to the onset of degradation.

The ester linkage present on the backbone of the PLLA resin formulation undergoes hydrolytic degradation leading to the formation of the microcracks that are observed in the SEM images.^{59,60} SEM was performed to reveal the qualitative information of connectivity across adjacent layers of the 3D printed parts.

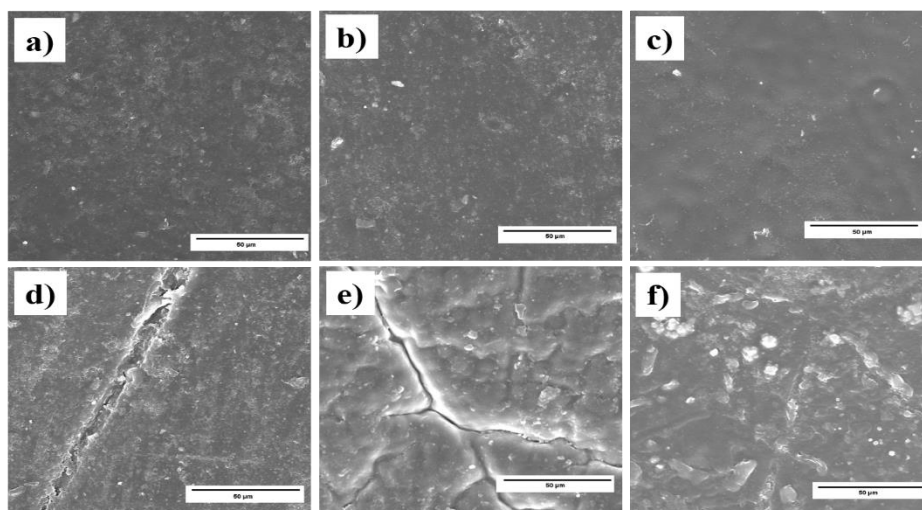


Figure 2.19 SEM images of the surface of 3D printed film a–c) before degradation of resins A, B, and C, respectively, and after 28 d degradation of resins A, B, and C respectively

2.4 CONCLUSIONS

In summary, we report the synthesis and formulation of a solvent-free photo cross-linkable PLLA-based resin and its application in room temperature 3D printing using a commercial DLP 3D printer as well as direct ink writing 3D printer. Oligomeric linear and star PLLA acrylate crosslinkers were synthesized and characterized and photocurable resin formulations were prepared by mixing with HEMA as the diluent and 1 wt. % TPO as the photoinitiator. The 3D printed parts exhibited promising mechanical properties with biodegradability in phosphate buffer solution highlighting the potential of the new PLLA-based biodegradable photocurable formulation for 3D printing prototypes as well as for medical application, bone tissue engineering, etc.

2.5 REFERENCES

- (1) R. Du, Y. X. Su, Y. Yan, W. S. Choi, W. F. Yang, C. Zhang, X. Chen, J. P. Curtin, J. Ouyang, B. A. Zhang, *Engineering* **2020**, *6*, 1291.
- (2) H. Saniei, S. Mousavi, *Polymer* **2020**, *196*, 122467.
- (3) H. Zhao, F. Yang, J. Fu, Q. Gao, A. Liu, M. Sun, Y. He, *ACS Biomater. Sci. Eng.* **2017**, *3*, 3083.

- (4) C. Yu, J. Schimelman, P. Wang, K. L. Miller, X. Ma, S. You, J. Guan, B. Sun, W. Zhu, S. Chen, *Chem. Rev.* **2020**, *120*, 10695.
- (5) S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, *Chem. Rev.* **2017**, *117*, 10212.
- (6) R. Ajdary, N. Kretzschmar, H. Baniasadi, J. Trifol, J. V. Seppälä, J. Partanen, O. J. Rojas, *ACS Sustainable Chem. Eng.* 2021, *9*, 2727.
- (7) K. L. Sampson, B. Deore, A. Go, M. A. Nayak, A. Orth, M. Gallerneault, P. R. L. Malenfant, C. Paquet, *ACS Appl. Polym. Mater.* 2021, *3*, 4304.
- (8) V. Shanmugam, M. V. Pavan, K. Babu, B. Karnan, *Polym. Compos.* 2021, *42*, 5656.
- (9) A. Schwab, R. Levato, M. D'este, S. Piluso, D. Eglin, J. Malda, *Chem. Rev.* 2020, *120*, 11028.
- (10) J. Zhang, P. Xiao, *Polym. Chem.* 2018, *9*, 1530.
- (11) M. Guvendiren, J. Molde, R. M. D. Soares, J. Kohn, *ACS Biomater. Sci. Eng.* 2016, *2*, 1679.
- (12) A. Atala, *Chem. Rev.* 2020, *120*, 10545.
- (13) M. Shahbazi, H. Jäger, *ACS Appl. Bio Mater.* 2021, *4*, 325.
- (14) A. Harynska, H. Janik, M. Sienkiewicz, B. Mikolaszek, J. Kucińska-Lipka, *ACS Sustainable Chem. Eng.* 2021, *9*, 6923.
- (15) J. R. Rocca-Smith, O. Whyte, C.-H. Brachais, D. Champion, F. Piasente, E. Marcuzzo, Sensidoni, F. Debeaufort, T. Karbowiak, *ACS Sustainable Chem. Eng.* 2017, *5*, 2751.
- (16) W. K. Lee, J. A. Gardella, *Langmuir* 2000, *16*, 3401.
- (17) H. J. Kim, M. A. Hillmyer, C. J. Ellison, *J. Am. Chem. Soc.* 2021, *143*, 15784.
- (18) S. Wasti, S. Adhikari, *Front. Chem.* 2020, *8*, 315.
- (19) N. Tripathi, M. Misra, A. K. Mohanty, *ACS Eng. Au* 2021, *1*, 7.
- (20) Z. Fang, Y. Shi, Y. Zhang, Q. Zhao, J. Wu, *ACS Appl. Mater. Interfaces* 2021, *13*, 15584.
- (21) X. Li, R. Yu, Y. He, Y. Zhang, X. Yang, X. Zhao, W. Huang, *ACS Macro Lett.* 2019, *8*, 1511.
- (22) V. S. D. Voet, T. Strating, G. H. M. Schnelting, P. Dijkstra, M. Tietema, J. Xu, A. J. J. Woortman, K. Loos, J. Jager, R. Folkersma, *ACS Omega* 2018, *3*, 1403.
- (23) S. Barone, P. Neri, A. Paoli, A. V. Razionale, F. Tamburrino, *Procedia Manuf.* 2019, *38*, 1017.
- (24) J. Zhang, Q. Hu, S. Wang, J. Tao, M. Gou, *Int. J. Bioprint.* 2020, *6*, 12.
- (25) S. T. Jaber, M. Y. Hajeer, T. Z. Khattab, L. Mahaini, *Clin. Exp. Dent. Res.* 2021, *7*, 591.
- (26) B. Gross, S. Y. Lockwood, D. M. Spence, *Anal. Chem.* 2017, *89*, 57.

- (27) G. Tafuro, A. Costantini, G. Baratto, S. Francescato, A. Semenzato, ACS Omega 2020, 5, 15280.
- (28) F. Chen, G. Hochleitner, T. Woodfield, J. Groll, P. D. Dalton, B. G. Amsden, Biomacromolecules 2016, 17, 208.
- (29) F. P. W. Melchels, A. M. C. Barradas, C. A. Van Blitterswijk, J. De Boer, J. Feijen, D. W. Grijpma, Acta Biomater. 2010, 6, 4208.
- (30) S. Moeinzadeh, S. N. Khorasani, J. Ma, X. He, E. Jabbari, Polymer 2011, 52, 3887.
- (31) G. R. Coullerez, C. Lowe, P. Pechy, H. H. Kausch, J. N. Hilborn, J. Mater. Sci. Mater. Med. 2000, 11, 505.
- (32) A. Bagheri, K. E. Engel, C. W. A. Bainbridge, J. Xu, C. Boyer, J. Jin, Polym. Chem. 2020, 11, 641.
- (33) A. Bagheri, H. Ling, C. W. A. Bainbridge, J. Jin, ACS Appl. Polym. Mater. 2021, 3, 2921.
- (34) F. P. W. Melchels, J. Feijen, D. W. Grijpma, Biomaterials 2009, 30, 3801.
- (35) T. M. Seck, F. P. W. Melchels, J. Feijen, D. W. Grijpma, J. Controlled Release 2010, 148, 34.
- (36) A. Ronca, L. Ambrosio, D. W. Grijpma, Acta Biomater. 2013, 9, 5989.
- (37) A. Bagheri Saed, A. H. Behraves, S. Hasannia, B. Akhoundi, S. K. Hedayati, F. Gashtasbi, Eur. Polym. J. 2020, 141, 110057.
- (38) M. Sandmeier, N. Paunovi'c, R. Conti, L. Hofmann, J. Wang, Z. Luo, K. Masania, N. Wu, N. Kleger, F. B. Coulter, A. R. Studart, H. Grützmacher, J. C. Leroux, Y. Bao, Macromolecules 2021, 54, 7830.
- (39) Y. Huang, J. Xu, J. Shao, G. Sun, D. Li, Q. Fan, Langmuir 2020, 36, 11676.
- (40) J.-T. Miao, S. Peng, M. Ge, Y. Li, J. Zhong, Z. Weng, L. Wu, L. Zheng, ACS Sustainable Chem. Eng. 2020, 8, 9415.
- (41) S. Peng, Y. Li, L. Wu, J. Zhong, Z. Weng, L. Zheng, Z. Yang, J.-T. Miao, ACS Appl. Mater. Interfaces 2020, 12, 6479.
- (42) A. Bagheri Saed, A. H. Behraves, S. Hasannia, S. A. Alavinasab Ardebili, B. Akhoundi, M. Pourghayoumi, J. Manuf. Process. 2020, 56, 550
- (43) M. Danko, J. Libiszowski, T. Biela, M. Wolszczak, A. Duda, J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 4586.
- (44) A. Kulkarni, A. Lele, S. Sivaram, P. R. Rajamohanan, S. Velankar, A. Chatterji, Macromolecules 2015, 48, 6580.
- (41) R. V. Ghorpade, S. M. Bhosle, S. Ponrathnam, C. R. Rajan, N. N. Chavan, R. Harikrishna, J. Polym. Res. 2012, 19, 9811.

- (45) J. Wei, R. Lu, F. Liu, J. Polym. Res. 2011, 18, 1001.
- (46) L. Ling, L. J. Lee, Kobunja Kwahak Kwa Kisul 2005, 46, 11540.
- (47) P. Castell, M. Wouters, H. Fischer, G. De With, J. Coat. Technol. Res. 2007, 4, 411.
- (48) B. Steyrer, P. Neubauer, R. Liska, J. Stampfl, Materials 2017, 10, 1445.
- (49) G. A. Appuhamillage, N. Chartrain, V. Meenakshisundaram, K. D. Feller, C. B. Williams, T. E. Long, Ind. Eng. Chem. Res. 2019, 58, 15109.
- (50) K. Pooput, S. Channasanon, P. Tesavibul, P. Pittayavinai, W. Taweelue, J. Polym. Res. 2020, 27, 322.
- (51) H. Quan, T. Zhang, H. Xu, S. Luo, J. Nie, X. Zhu, Bioact Mater 2020, 5, 110.
- (52) C. Kolb, N. Lindemann, H. Wolter, G. Sextl, J. Appl. Polym. Sci. 2021, 138, 49691.
- (53) M. P. Lee, G. J. T. Cooper, T. Hinkley, G. M. Gibson, M. J. Padgett, L. Cronin, Sci. Rep. 2015, 5, 9875.
- (54) S. Nouri, C. Dubois, P. G. Lafleur, J. Rheol. 2015, 59, 1045.
- (55) P. E. Theodorakis, A. Avgeropoulos, J. J. Freire, M. Kosmas, C. Vlahos, J. Chem. Phys. 2007, 126, 174904.
- (56) N. Kiuna, C. J. Lawrence, Q. P. V. Fontana, P. D. Lee, T. Selerland, P. D. M. Spelt, Composites, Part A 2002, 33, 1497.
- (57) A. Göpferich, Biomater. Silver Jubilee Compend. 1996, 17, 117.
- (59) N. F. Zaaba, M. Jaafar, Polym. Eng. Sci. 2020, 60, 2061.
- (60) I. Grizzi, H. Garreau, S. Li, M. Vert, Biomaterials 1995, 16, 305.

CHAPTER 3

Biocompatible PVAc-g-PLLA Resin Formulations with Tunable Mechanical Properties for DLP/SLA 3D Printing

3.1 INTRODUCTION

Additive manufacturing (AM), also known as 3D printing technology, has grown in strength in recent years., opening up new possibilities for the on-demand production of complex 3D structures in fields as diverse as tissue engineering,¹⁻⁴ drug delivery,⁵⁻⁶ medical device fabrication,^{7,8} optical engineering,⁹ soft robotics,^{10,11} dentistry,¹² and many others. Among the various 3D printing techniques like fused deposition modelling (FDM), direct ink writing (DIW), digital light processing (DLP), etc the light-based DLP 3D printing shows greater advantage in terms of precision, resolution, and layer unification compared to the other 3D printing techniques.¹³⁻¹⁵ Despite the rapid growth of AM technology, research for the development of suitable materials is still insufficient to expand the range of materials available for 3D printing.¹⁶⁻¹⁸ Most of the photocurable resins commonly employed are either traditional epoxy resins or small-molecule acrylate-based resins readily accessible in the market. Their usage in creating biological implants is constrained since they are often neither biocompatible nor biodegradable.¹⁹⁻²¹ In order to create biodegradable and biocompatible materials, AM technology makes considerable use of biobased polymers such as polylactic acid (PLA),²²⁻²⁴ polycaprolactone (PCL),^{25, 26} polyglycolide (PGL),²⁷ and Poly(propylene fumarate) (PPF).^{28, 29} For synthesizing biobased and degradable materials, PLA is the first choice due to its biodegradability and low environmental impact.^{4,30, 31}

The previous chapter discussed PLA based polymeric crosslinkers in the form of acrylate terminated linear and star PLA for DLP 3D printing.²⁴ Another synthetic approach to synthesize polymeric crosslinkers is by graft polymerization. To enhance the morphological, chemical, and physical characteristics of the entire polymer structure, polymer grafts are introduced as branches of one polymer component covalently attached to the main polymer backbone. The chemical composition and structure of graft copolymers can be fine-tuned based on various synthetic grafting techniques (grafting through, grafting to, and grafting from).³² The grafting of the PLLA polymer has been reported by several research groups.^{33,34} The most commonly used backbones are polysaccharides,³⁵⁻³⁷ poly(vinyl alcohol),³⁸ and poly(acrylates).^{39,40} Nan D. et al. and Jing D. et. al. conducted a systematic investigation of PLLA grafting with partially hydrolyzed PVAc, examining the structure-property correlations among the crystallization rates, graft density, and length of PLLA graft copolymers.^{41,42} Similarly, Nadia G. et al. synthesized poly(ϵ -caprolactone)-graft-poly(vinyl alcohol) (PCL-g-PVA) and poly(L-lactide)-graft-poly(vinyl alcohol) (PLLA-g-PVA) using the non-toxic catalyst magnesium hydride (PVA/MgH₂ macroinitiator), under melt conditions, which could be used for biomedical

applications due to the environment-friendly approach.⁴³ Polyvinyl acetate (PVAc) is a non-toxic biocompatible polymer while PLLA is a biodegradable polymer derived from lactic acid, which is a naturally occurring material. There are several reports for the use of the grafted copolymer in different fields of applications.^{44,45} Grafted copolymers find application in both dye absorption and as carriers for drug molecules.⁴⁶ Dolatkhan et al. reported the Polymeric graft and their iron oxide composites for the methylene blue dye adsorption and pH-responsive desorption.⁴⁷ Similarly, Ghorai et al. prepared polyacrylamide grafted xanthan gum incorporated nano silica for the removal of cationic dye effectively from aqueous solution.⁴⁸ However, their use in additive manufacturing has not been much explored. Introducing photocurable moieties to grafted polymer chains makes them suitable for photocurable resin formulation for light-based 3D printing technologies like DLP and SLA.

The current work reports the design and synthesis of new low molecular weight photo-cross linkable graft polymer of partially hydrolysed PVAc and poly(lactide). PVAc polymer of predefined repeat units was synthesized, which were partially hydrolysed to polyvinyl alcohol, followed by grafting with l-lactide by the ring-opening polymerization process. Further, the terminal hydroxyl group of the grafted PLA chains were functionalized with acryloyl chloride to obtain Poly(vinyl alcohol)-graft-poly(l-lactide) crosslinker. The graft copolymer crosslinker was used to formulate resins with different weight ratios of hydroxy ethyl methacrylate (HEMA) or hydroxy ethyl acrylate (HEA) as reactive diluents, avoiding the use of non-reactive organic solvents that can potentially leach out of the 3D printed object. The resins showed optimum viscosity and printability at room-temperature in DLP 3D printer with very high resolution. The printed structure showed variation in mechanical properties depending on the use of reactive diluent HEMA/HEA. The 3D printed parts exhibited selective dye absorption and pH or enzyme responsive release behaviour. As far as we are aware, this is the first report of the application of acrylate modified poly(vinyl alcohol)-graft-poly(l-lactide) for the formulation of photocurable resins. Cell attachment studies using wild type mouse embryonic (WT-MEF) cell line on 3D printed structures demonstrated excellent viability.

3.2 EXPERIMENTAL SECTION

3.2.1 Materials

Vinyl acetate, (3S, 6S)-3, 6-dimethyl-1, 4-dioxane-2, 5-dione, 2-hydroxy ethyl acrylate (HEA), stannous 2-ethyl hexanoate ($\text{Sn}(\text{Oct})_2$), 2-Hydroxy ethyl methacrylate (HEMA), were bought from Sigma Aldrich and utilized without additional purification. Acrylic acid and triethyl amine were purchased from Sigma Aldrich and purified by distillation. Phenylbis(2,4,6-trimethyl

benzoyl) phosphine oxide (TPO) was purchased from TCI chemical Pvt. Ltd and used as such. Carbon disulfide (CS₂), Ethanol, Potassium hydroxide (KOH), Methyl bromoacetate, Azobisisobutyronitrile (AIBN), Toluene, Thionyl chloride (SOCl₂), Tetrahydrofuran (THF), Chloroform (CHCl₃), Methanol (MeOH), isopropyl alcohol (IPA), Dichloromethane (DCM), Hexane and Sodium sulfate (Na₂SO₄) were purchased locally. For gel permeation chromatography HPLC grade chloroform was purchased from Sigma Chemicals. Five distinct dyes, including 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS), Rhodamine B (RhB), Doxorubicin (DOX), Sulphonate Rhodamine (SRhB), and methylene blue (MB), were selected to formulate dye solutions.

3.2.2 Measurements

¹H and ¹³C NMR spectra were recorded using Bruker-AVENS 400 and 200 MHz spectrometers and chemical shifts were reported in ppm at 25 °C using CDCl₃ as a solvent with small amounts of Trimethylsilane (TMS) added as an internal standard. The Fourier transform (FTIR) spectra were acquired using a BRUKER alpha-E spectrometer. The molecular weights of polymers were determined using gel permeation chromatography (GPC) equipped with Viscotek VE 3580 RI detector. The GPC was calibrated with polystyrene standard and chloroform (HPLC grade) solvent was used as eluent at a 1 ml/min flow rate. The viscosity of the formulated resins as a function of shear rate was determined using the Anton Paar Physica Modular Compact Rheometer (MCR) 301. The test was performed in the cup and bob with the diameters 18.08 mm and 16.66 mm respectively. The shear rate was applied from 1 to 1000 per second at 30 °C. The thermal properties of all 3D printed parts were analysed using Thermal Gravimetric Analysis (TGA), TA discover 550-second generation TGA instrument, at a temperature range of 50 °C to 900 °C under the nitrogen atmosphere (60 mL/min), and the heating rate was 10 °C/min. The glass transition temperature (T_g) was determined using TA Discover 250 second generation differential scanning calorimeter under nitrogen atmosphere (50 ml/min) by heating from -30 °C to 180 °C at the heating rate of 10 °C/min. The DSC was calibrated with indium standards before measurement. A photo-DSC experiment was performed using the same DSC instrument equipped with an optical UV light source Omni Cure series 2000. Scanning electron microscopy imaging was recorded using FE-SEM with an FEI Nova SEM 450. The surface and the cross-section images of the 3D printed sample was recorded after coating with gold and mounted on the SEM stub with carbon tape.

3.2.3 Methods

A) DLP Resin Preparation

The PVAc-g-PLLA acrylate crosslinker was combined with varying weight percentages of reactive diluents (HEMA or HEA) to prepare photocurable resins. The precise weight percentage of photoinitiator TPO was determined based on photo DSC experiments. Resins R1, R2, and R3 were prepared using 30, 40, and 50 weight percent of PVAc-g-PLLA acrylate crosslinker with 70, 60, and 50 weight percentages of HEMA. Similarly, resins R4, R5, and R6 were prepared with similar weight percentage of HEA. In a 50 ml vial, the resins were made by combining the photoinitiator, reactive diluent, and crosslinker. Following mixing, the vial was sonicated at room temperature for one hour. To prevent the vial from prematurely curing during the sonication, aluminum foil was placed over it. The vial was kept in the fridge for storage. The vial was left outside to come to room temperature and mixed for five minutes in a vortex mixer before printing. A reference resin was prepared with 30 wt. % of HEA, 70 wt. % of TMPTA, and 1 wt. % total weight TPO was used as photo initiator.

B) Curing kinetics of Resins

A TA Discover 250 second-generation differential scanning calorimeter fitted with a photo calorimetric unit (Onmi cure series 2000) was used for the Photo-Differential Scanning Calorimetry (Photo-DSC) investigations. The sample chamber was irradiated by a 200 W high-pressure mercury lamp that emits light with a wavelength of 320–500 nm through a dual-quartz light guide with neutral density.⁴⁹ The sample preparation followed the same guidelines as specified in the resin formulation. The sample pan was filled with 5 mg of materials, and the pan was stored in a DSC cell. The nitrogen flow rate used for the measurement was 50 ml/min. The sample was initially allowed to equilibrate at 30 °C in an isothermal environment for two minutes in a nitrogen environment. Subsequently, the electronic UV light shutter was opened, subjecting the sample pan to a five-minute UV light exposure. The curing enthalpy was calculated by integrating the peaks in the graph of normalized heat flow as a function of duration of irradiation.

C) DLP 3D Printing of the Resins

The 3D printing was carried out in a DLP 3D printer supplied by Utpal3DSysstem, Gujarat, India. The 3D printer had a 405 nm LED as light source and a resin bed measuring 120 X 68 X 200 mm³ dimensions. The 3D printing was carried out at ambient temperature using solvent-free resin compositions. A UNO Genetic laser power meter was used to measure the LED light source's intensity, which was 10 mW cm⁻². The resin was initially filled inside the resin bed to

a predefined level before the printing setting was fixed. Each layer had a thickness of 100 microns, and the bottom layer was exposed for 50 seconds for the first ten layers while the remaining layers were exposed for 45 seconds. The quality of the resin formulation was tested using a printed version of the Mars Rook and Benchy Standard STL file. The printed part was cleaned with isopropyl alcohol in a resin washer for three minutes before being placed in a UV chamber for an hour for post-cure.

D) Mechanical Test

The Universal Testing Machine (Instron, series 33R4204) was utilized to evaluate the tensile strength of the 3D printed objects using a 1 kN capacity load cell at room temperature. For the tensile test, an average of five specimen samples from the ASTM D638 type V sample were utilized. The experiment was conducted with a 5 mm min⁻¹ stretching rate at room temperature and a gauge length of 10 mm for each sample. Tensile strength, Young's modulus, elongation, and toughness were measured during the break.

E) In vitro Degradation and Swelling Study

Three rectangular 3D printed specimen parts per formulation were immersed in 200 ml Phosphate Buffer Solution (PBS) maintaining the pH 7 at 37 °C temperature. The buffer solution was prepared by mixing NaCl, KCl, Na₂HPO₄, and KH₂PO₄ in ratios of 137 mM, 2.7 mM, 10 mM, and 1.8 mM respectively in 1000 ml deionized water. The rectangular specimens were kept inside a sealed dialysis tube and immersed into the PBS solution with constant stirring over period of 2 months at 37 °C. At regular intervals (every week), samples were removed, dried in a vacuum oven at 50 °C, and cleaned with tissue paper to determine the water absorption and degradation and returned back to the dialysis tube. The water uptake was calculated using equation 1

$$\text{water uptake} = \frac{wt_{\text{wet}} - wt_{\text{dry}}}{wt_{\text{dry}}} \times 100 \quad \text{eq. 1}$$

where the wt_{wet} is the weight of the specimens in wet state after wiping with the tissue paper and the wt_{dry} is the weight after drying in vacuum oven. The PBS solution was replaced every week maintaining a constant pH of the PBS solution.⁵⁰

F) Cell Viability Test

The biocompatibility and cytotoxicity of the polymers were evaluated using a 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay in 96 well plates. Initially, complete media were prepared by combining 1% penicillin-streptomycin, 10% fetal bovine serum, and Dulbecco's Modified Eagle Medium (DMEM) media. Subsequently, 1000

wild-type mouse embryonic (WT-MEF) cells were seeded into each well and incubated for 16 hours in a 5% CO₂ environment at physiological temperature. After the incubation period, the media were removed, and 2 mg of 3D printed film was added to each well in 300 µL of fresh media. The cells were then further incubated for different time periods, namely 24 hours, 48 hours, and 72 hours, under physiological conditions. Each experiment was conducted in triplicate. For the control row, only media was added without any polymer sample. Following the incubation, the media were aspirated, and any remaining films were removed from the wells. Next, MTT molecules were dissolved in complete media, and 100 µL of a 0.5 mg/mL concentration was added to each well. The cells were then incubated for an additional 4 hours at physiological temperature. During this incubation, the MTT molecule is reduced by the mitochondrial reductase NADPH cellular oxidoreductase enzyme, leading to the formation of purple formazan crystals. These crystals are insoluble in the media. After the 4-hour incubation, 100 µL of HPLC-grade DMSO was added to each well and placed on a shaker for 15 minutes to completely dissolve the MTT crystals in the DMSO. The absorbance of the 96 well plates was then measured at 570 nm using a Vario scan reader. The obtained data were plotted to show the percentage cell viability against the concentrations of the tested polymers.⁵¹

G) Dye Absorption and Release Study

For the dye absorption study, 5 different solutions of dye (HPTS, RhB, DOX, SRhB, and MB) were prepared by dissolving them in milli-Q water and adjusting the absorbance at 2 OD by UV absorption spectroscopy. A rectangular 3D printed part was immersed into the solution for a period of 12 h. The absorption of the solution was measured at 30 min intervals to quantify the dye absorption. In the release study, pH and enzyme were used as stimuli. After dye absorption, the 3D printed part was dipped into different pH buffer solutions to release the dye. Two different enzymes were used to enhance the dye release study.

H) Photo calorimetric curing percentage calculation

The theoretical values of heat of polymerization of acrylate and methacrylate are 20.6 kcal mol⁻¹ and 13.1 kcal mol⁻¹ respectively. The molecular weights of HEMA, HEA, and PVAc-g-PLLA acrylate crosslinker are 130.14, 116.1, and 5800 g mol⁻¹ respectively. The experimental heat of polymerization values which were collected from the photo DSC experiment for HEMA, HEA, and PVAc-g-PLLA acrylate crosslinker were 403.61 J/g, 590.23 J/g, and 91.24 J/g respectively. From these values, the percentage conversion of HEMA, HEA, and PVA-g-PLLA acrylate was calculated as-

$$\frac{20.6 \times 4.184 \times 10^3}{130.14}$$

Theoretical heat of polymerization of HEMA

$$J/g = 421.16 \text{ J/g.}$$

(1 calorie = 4.184 Joule)

$$\text{The percentage conversion of HEMA} = \frac{403.61}{421.16} \times 100 \% = 95.83 \%$$

$$\text{Theoretical heat of polymerization of HEA} = \frac{20.6 \times 4.184 \times 10^3}{116.1} = 742.38 \text{ J/g}$$

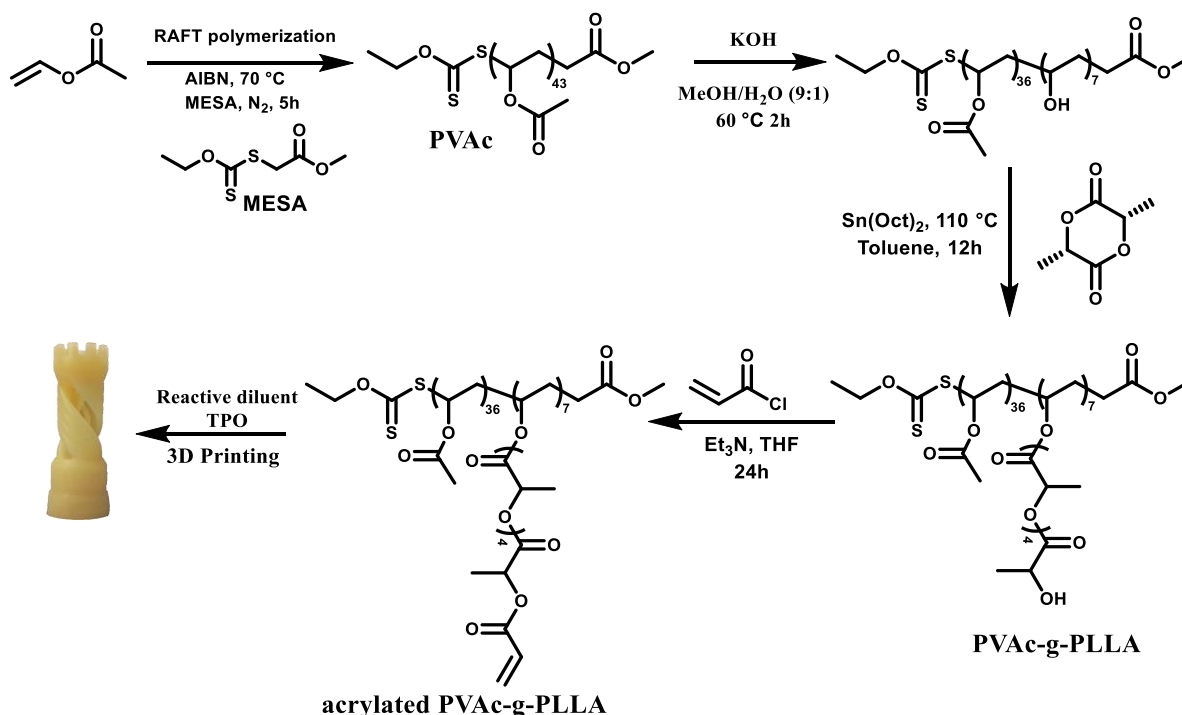
$$\text{The percentage conversion of HEA} = \frac{590.23}{742.38} \times 100 = 79.50 \%$$

$$\text{Theoretical heat of polymerization of PVAc-g-PLLA acrylate} = \frac{20.6 \times 4.184 \times 10^3}{5800} = 104.02 \text{ J/g}$$

$$\text{The percentage conversion of PVAc-g-PLLA acrylate} = \frac{91.24}{104.02} \times 100 = 87.71 \%$$

3.2.4 Synthesis and Characterization

Poly(vinyl acetate) (PVAc) of pre-defined molecular weight was synthesized starting from vinyl acetate using Reversible Addition Fragmentation chain Transfer (RAFT) polymerization in the bulk where 2,2'-azobisisobutyronitrile (AIBN) was used as the initiator and Methyl (ethoxy carbonothioyl) sulfanyl acetate (MESA) was used as the chain transfer agent (Scheme 3.1).



Scheme 3.1 Overall synthetic scheme for PVAc-g-PLLA acrylate polymeric crosslinker

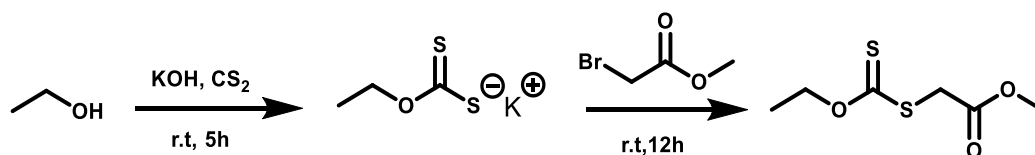
MESA was synthesized according to the literature procedure.⁵² Further the PVAc polymer was partially hydrolysed in methanol with KOH as base. Then the hydrolysed PVAc polymer was used as macro initiator for the ring opening polymerization (ROP) of l-lactide to form PVAc-g-PLLA polymer. Finally, the PVAc-g-PLLA was reacted with acryloyl chloride to synthesize PVAc-g-PLLA acrylate. The monomer and the polymers were structurally characterized using NMR and FTIR spectroscopy. The molecular weights and the glass transition temperature (T_g) of the polymers were measured by GPC and DSC analysis. The photo curing kinetics of the PVAc-g-PLLA acrylate polymer and reactive diluents were checked by photo-DSC experiments. The plots of GPC, DSC, and photo-DSC are given in the figure 3.6. The values of the molecular weights are tabulated in the table T 3.1.

1) Synthesis of the small molecule

a) Synthesis of the Acryloyl Chloride from acrylic Acid

The details of the synthesis of the acrylic acid and the characterization are described in the chapter 1 section 2.2.4.

b) Synthesis of Methyl (ethoxy carbonothioyl) sulfanylacetate (MESA)



Methyl (ethoxy carbonothioyl)sulfanyl acetate (MESA) was prepared by adding potassium hydroxide (0.05 mol) in 20 ml of ethanol and stirring until the formation of a clear solution in a 100 ml round bottom flask. Carbon disulfide (10 ml, 0.1655 mol) was added into the reaction mixture dropwise with constant stirring and the reaction was left to stir for 5 hrs. Methyl 2-bromoacetate (7.65 g, 0.05 mol) was added slowly and the reaction was further run for 12 hrs. The formed precipitate was filtered out using Whatman filter paper and the filtrate was evaporated in a rotary evaporator. Diethyl ether was added to the product and it was run through basic alumina on a glass funnel with filter paper. Finally, diethyl ether was evaporated and a light-yellow coloured product was obtained. Yield: 96%. ^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 4.13 (t, 4H), 4.35 (q, 2H), 5.15 (m, 16H), 1.57 (m, 64H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 169.60, 69.00, 66.69, 28.32, 25.32, 20.52, 16.63.

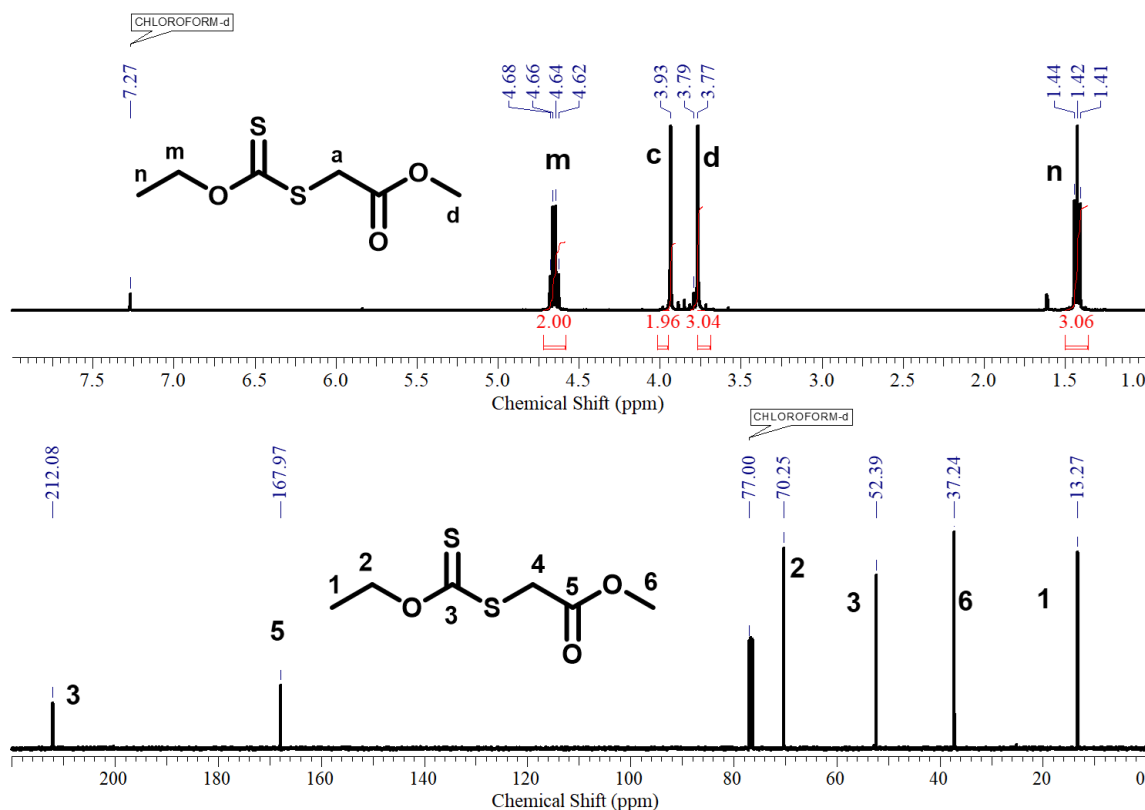
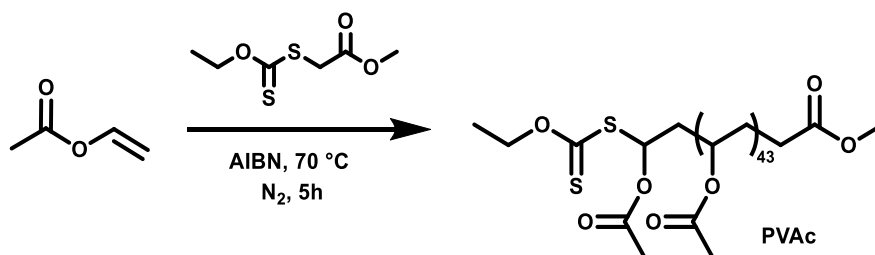


Figure 3.1 ¹H and ¹³C NMR spectra of methyl (ethoxycarbonothioyl)sulfanyl acetate in CDCl₃

2) Synthesis of the PVAc, hydrolyzed PVAc, PVAc-g-PLLA, PVAc-g-PLLA acrylate Polymers

c) Synthesis of poly(vinyl acetate) (PVAc)



Poly(vinyl acetate) was synthesized from vinyl acetate monomer using the bulk Reversible Addition Fragmentation chain Transfer (RAFT) polymerization method. 16 ml (174 mmol) of vinyl acetate was taken in a 50 ml RB flask, 2,2'-azobisisobutyronitrile (AIBN) (15 mg, 0.091 mmol) was used as initiator and Methyl (ethoxy carbonothioyl)sulfanyl acetate (MESA) (676 mg, 3.84 mmol) was used as the chain transfer agent. The reaction mixture was thoroughly deoxygenated by three consecutive freeze–pump–thaw cycles. The RB flask was immersed into a preheated oil bath at 70 °C for 5 hrs. After that, the RB was taken out from the oil bath and cooled to room temperature. Yield: 80 %. ¹H NMR spectrum (400 MHz, CDCl₃) δ in ppm:

4.86 (t, 44H), 4.62 (q, 2H), 3.66 (s, 3H), 2.32 (t, 3H), 2.02 (m, 139H), 1.77 (m, 88H), 1.42 (t, 3H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 170.63, 62.20, 66.63, 51.91, 39.43, 21.28, 13.09.

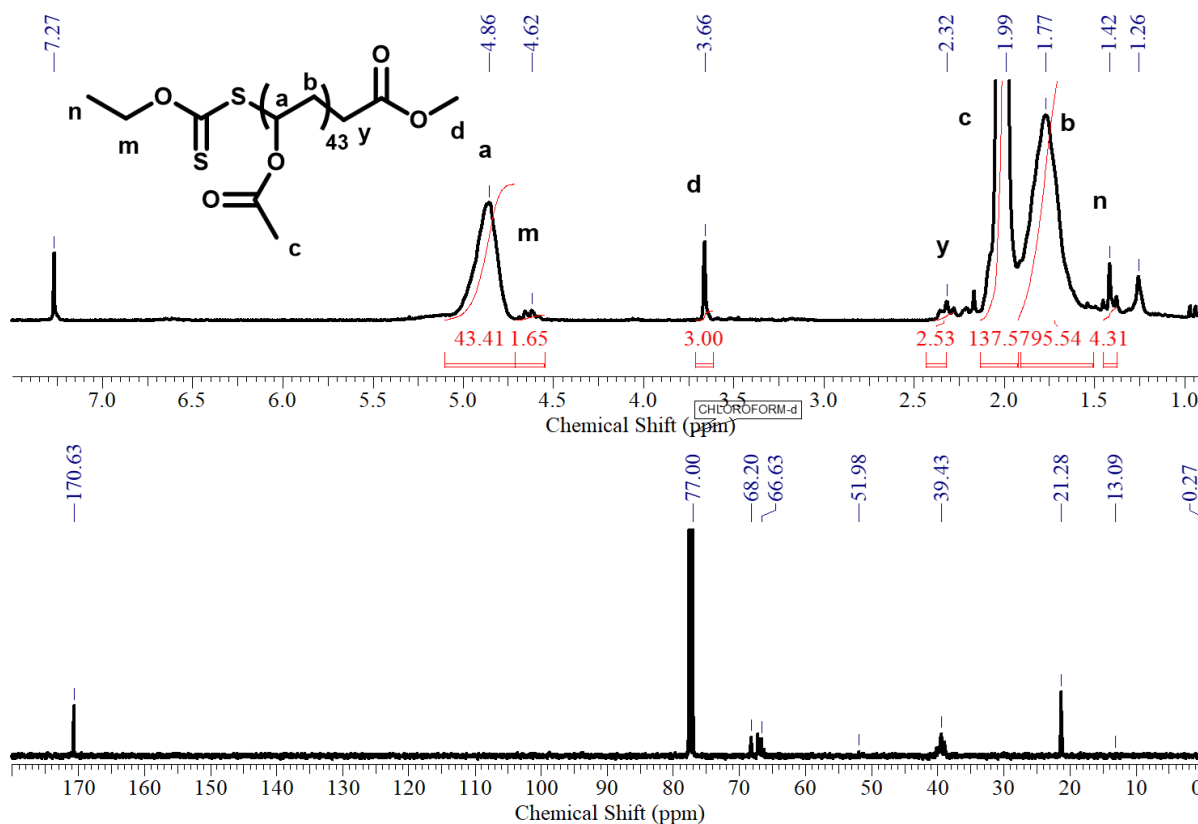
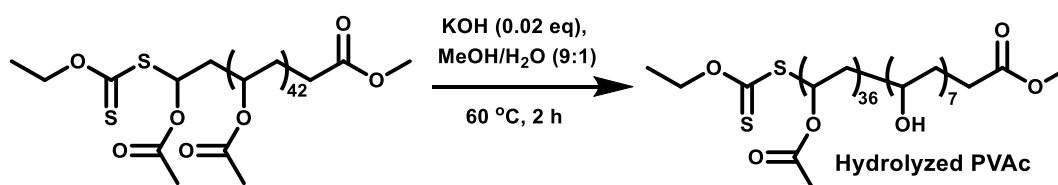


Figure 3.2 ^1H and ^{13}C spectra of poly(vinyl acetate) in CDCl_3

d). Synthesis of Partially hydrolyse PVAc



Poly(vinyl acetate) was partially hydrolysed with KOH. Poly(vinyl acetate) (10 g, 116.2 mmol) was taken in a 250 ml RB flask and dissolved in methanol-water mixture in 9:1 ratio. Potassium hydroxide (140 mg, 2.5 mmol) was dissolved in methanol and added to the reaction. The RB was immersed in preheated oil bath at 60 °C for 2 hrs. The solvent was evaporated and the product was dissolved in a minimum quantity of methanol. The hydrolysed polymer was precipitated in deionized water two or three times to remove the trace amounts of potassium hydroxide. The polymer was dried in an oven under vacuum at 80 °C. Yield: 94%. ^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 4.88 (m, 37), 4.65 (q, 2H), 3.66 (s, 3H), 2.35 (s, 11H),

2.04 (m, 113H), 1.78 (m, 80H), 1.41 (t, 3H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 170.36, 67.85, 66.52, 66.25, 51.71, 38.65, 21.00, 13.73.

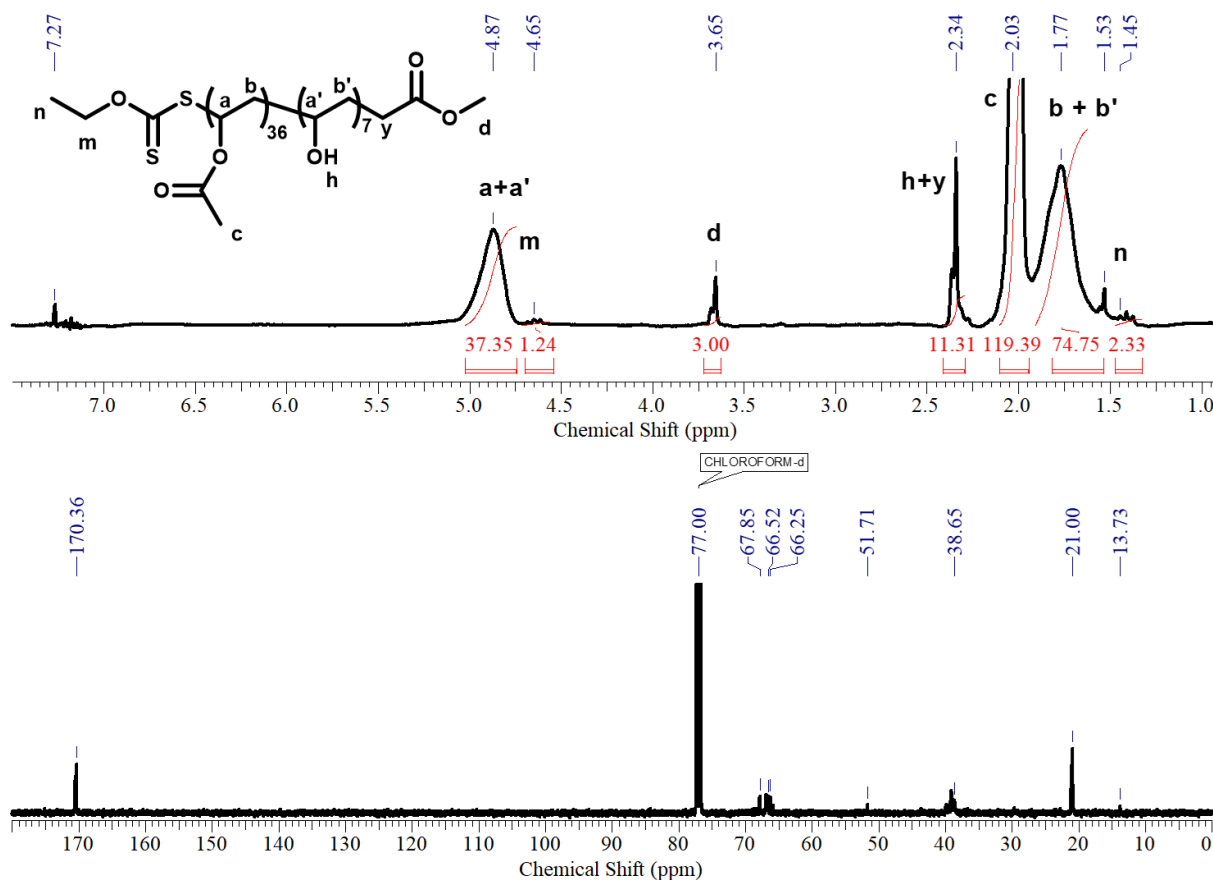
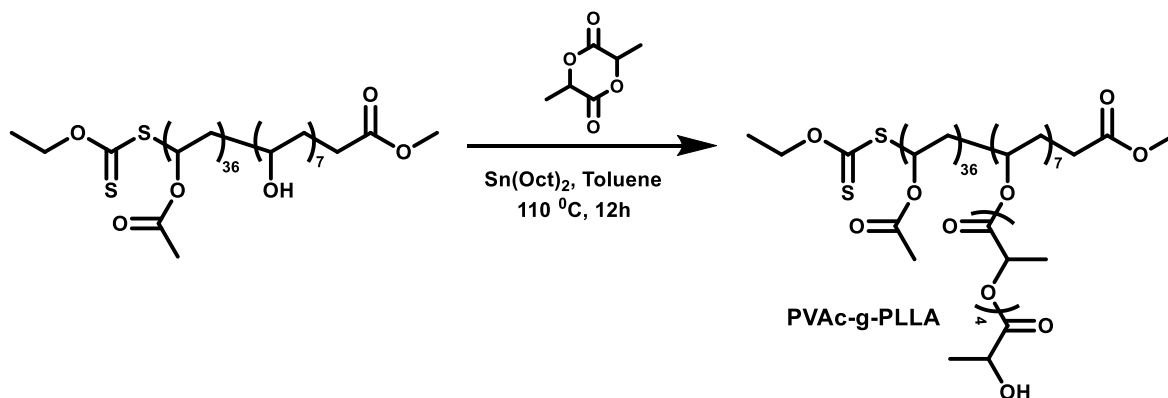


Figure 3.3 ^1H and ^{13}C spectra of partially hydrolyzed PVAc in CDCl_3 .

e). Synthesis of graft copolymer of poly(vinyl acetate)-graft- poly(L-lactide) (PVAc-g-PLLA)



The partially hydrolysed polymer PVA-co-VA was used as a macroinitiator for the ring-opening polymerization of L-lactide. 10 g (0.002 mol) of partially hydrolysed PVA, (10 g, 0.069 mol) of L-lactide, and (0.1 g, 0.25 mmol) of $\text{Sn}(\text{Oct})_2$ (1 wt. % with respect to the amount of L-lactide)

monomer) were taken in a 250 ml RB flask. High vacuum was applied for 1 h to the reaction mixture to remove any trace quantity of moisture. 40 ml of dry toluene was added to the reaction flask and it was immersed into a preheated oil bath at 110 °C and reaction allowed to proceed for 12 hr. For workup, the reaction was cooled to room temperature and the polymer was precipitated in pet ether 3-4 times to remove unreacted monomers. The graft polymer was dried under a vacuum oven overnight at 70 °C. Yield: 94%. ^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 5.18 (m, 6H), 5.05 (m, 147H), 4.87 (m, 40H), 4.64 (q, 2H), 4.35 (q, 1H), 3.67 (s, 3H), 1.99-2.02 (m, 123H), 1.77-1.85 (m, 75H), 1.69 (m, 156H), 1.50-1.57 (m, 16H), 1.43 (m, 6H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 170.02, 166.99, 72.12, 67.62, 60.02, 38.76, 20.67, 15.47.

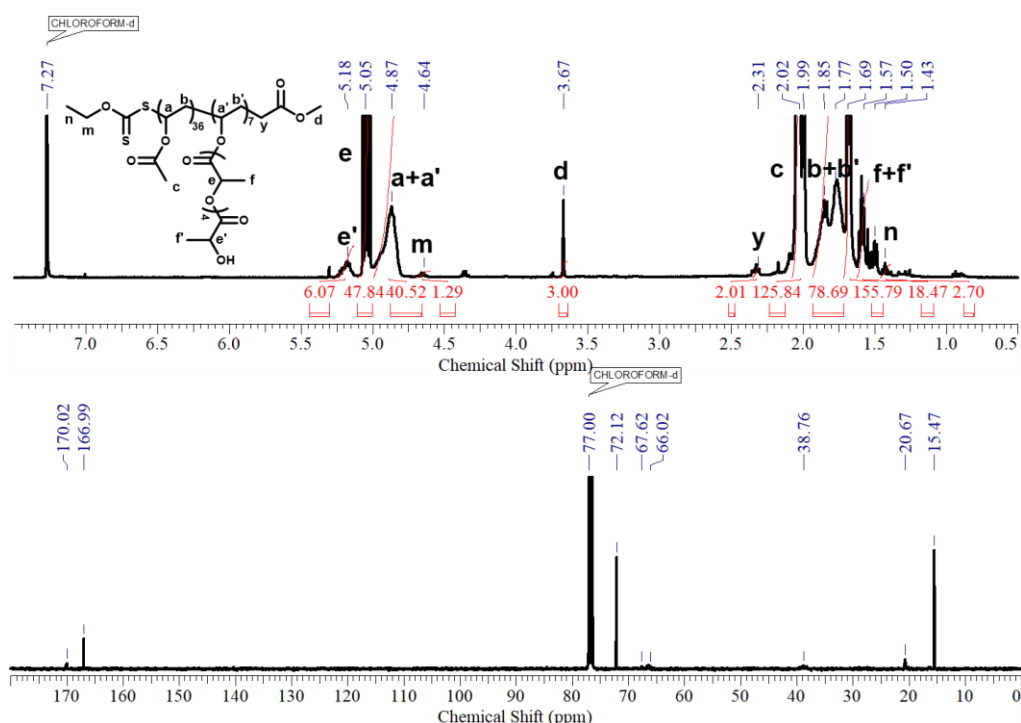
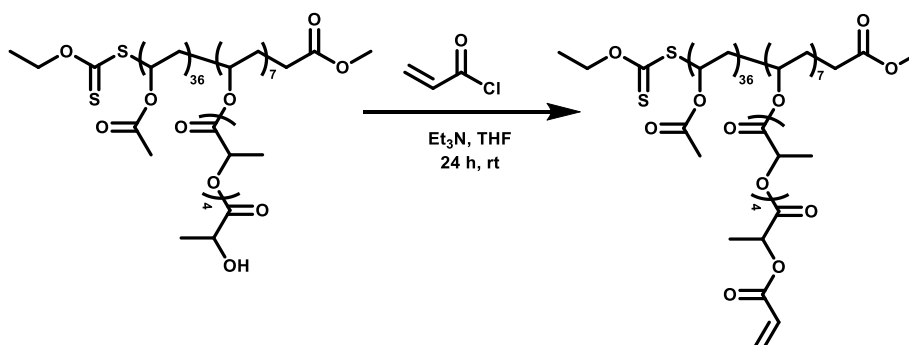


Figure 3.4 ^1H & ^{13}C NMR spectrum of PVAc-g-PLLA in CDCl_3 .

f) Synthesis of PVAc-g-PLLA Acrylate Polymer



Acrylation of terminal hydroxyl group of the grafted polylactide in PVAc-g-PLLA polymer was done using acryloyl chloride. (5 g, 0.0008 mol) PVAc-g-PLLA polymer was taken in a two-necked 100 ml round bottom flask, followed by the addition of 50 ml of dry THF by syringe under nitrogen atmosphere. The flask was covered with ice to maintain the temperature at 0 °C and Triethyl amine (1.5 ml, 0.011 mol) was added and stirred for 30 min. Acryloyl chloride (2 ml, 0.025 mol) was added slowly for a period of 15 min at 0 °C. The reaction was allowed to stir for 24 h at room temperature. After the completion of the reaction, THF was evaporated and chloroform was added to dissolve the polymer. The polymer was washed with brine three times and dried over anhydrous sodium sulfate. Finally, chloroform was evaporated and acrylate graft polymer was dried in a vacuum oven overnight at 40 °C. Yield: 94 %. ^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 6.55-6.59 (m, 9H), 6.16-6.23 (m, 16H), 6.10 (m, 2H), 5.19 (m, 5H), 5.03 (m, 27H), 4.87 (m, 35H), 4.66 (q, 1H), 4.36 (q, 2H), 3.67 (s, 3H), 2.00-2.03 (m, 112H), 1.76-1.84 (m, 74H), 1.57-1.69 (m, 102H), 1.43 (m, 6H). ^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 169.28, 167.05, 134.41, 127.09, 72.12, 68.66, 25.24, 20.67, 16.29, 15.45.

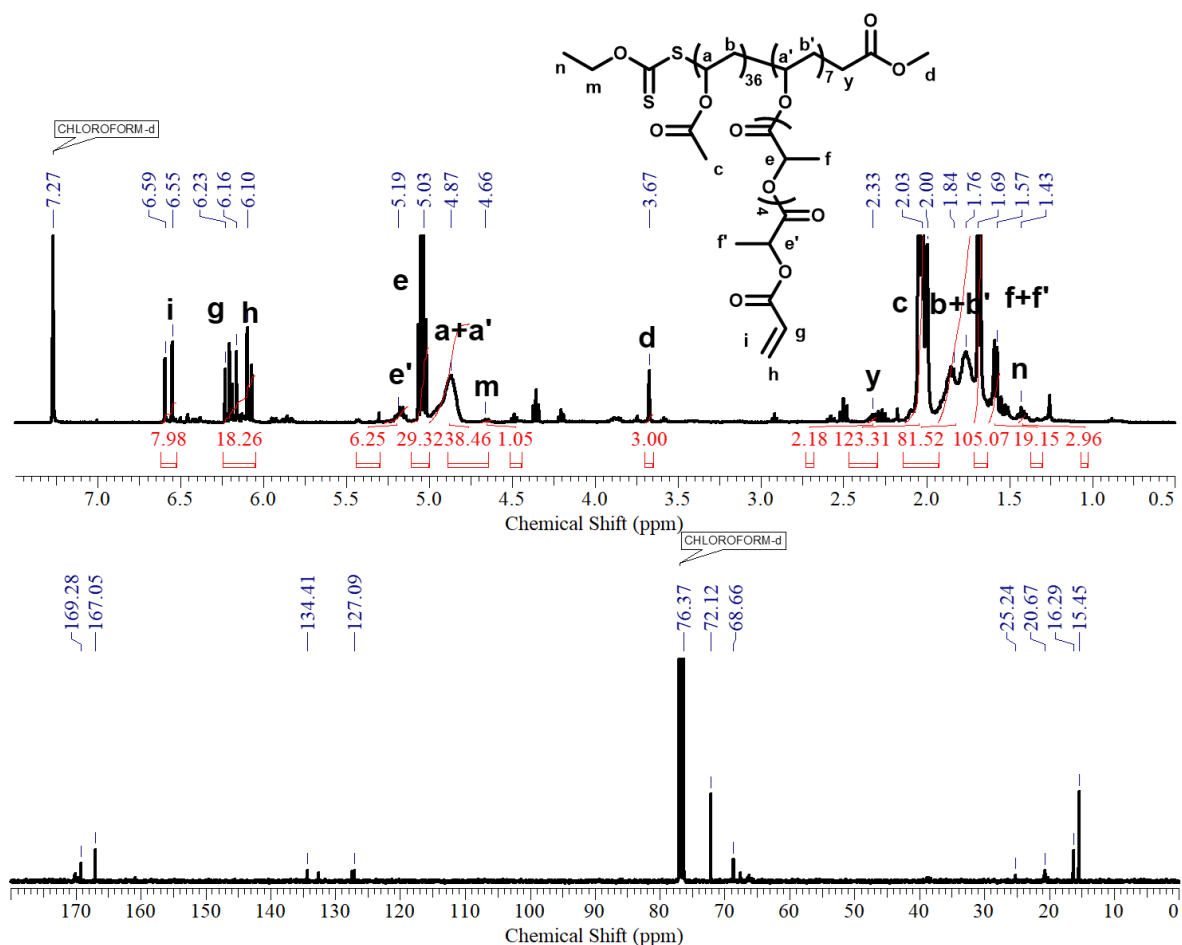


Figure 3.5 ^1H & ^{13}C NMR spectrum of PVAc-g-PLLA acrylate in CDCl_3 .

3.3 RESULT AND DISCUSSION

3.3.1 Synthesis and characterization of PVAc, hydrolysed PVAc-g-PLLA, PVA-g-PLLA acrylate

Figures 3.3 to 3.5 gives the ^1H and ^{13}C NMR spectra of the polymers. A stack plot of the ^1H NMR spectra are given in figure 3.6 for ease of comparison. Figure 3.6 shows the proton NMR spectrum of PVAc (bottom most plot). PVAc was obtained in 95 % yield and the integration of proton signals of the terminal $-\text{CO}(\text{O})\text{CH}_3$ unit (labelled 'd' in Figure 3.6) versus the proton labelled 'a' on the backbone or $-\text{OC}(\text{O})\text{CH}_3$ of the repeat unit (labelled 'c') revealed a number average molecular weight (M_n) of 43 which was close to the targeted M_n of 50 units. The PVAc polymer was partially hydrolysed at 60 °C in KOH/MeOH basic medium resulting in 85 % yield. In the figure 3.3 shows the proton NMR spectra of the partially hydrolysed PVAc.

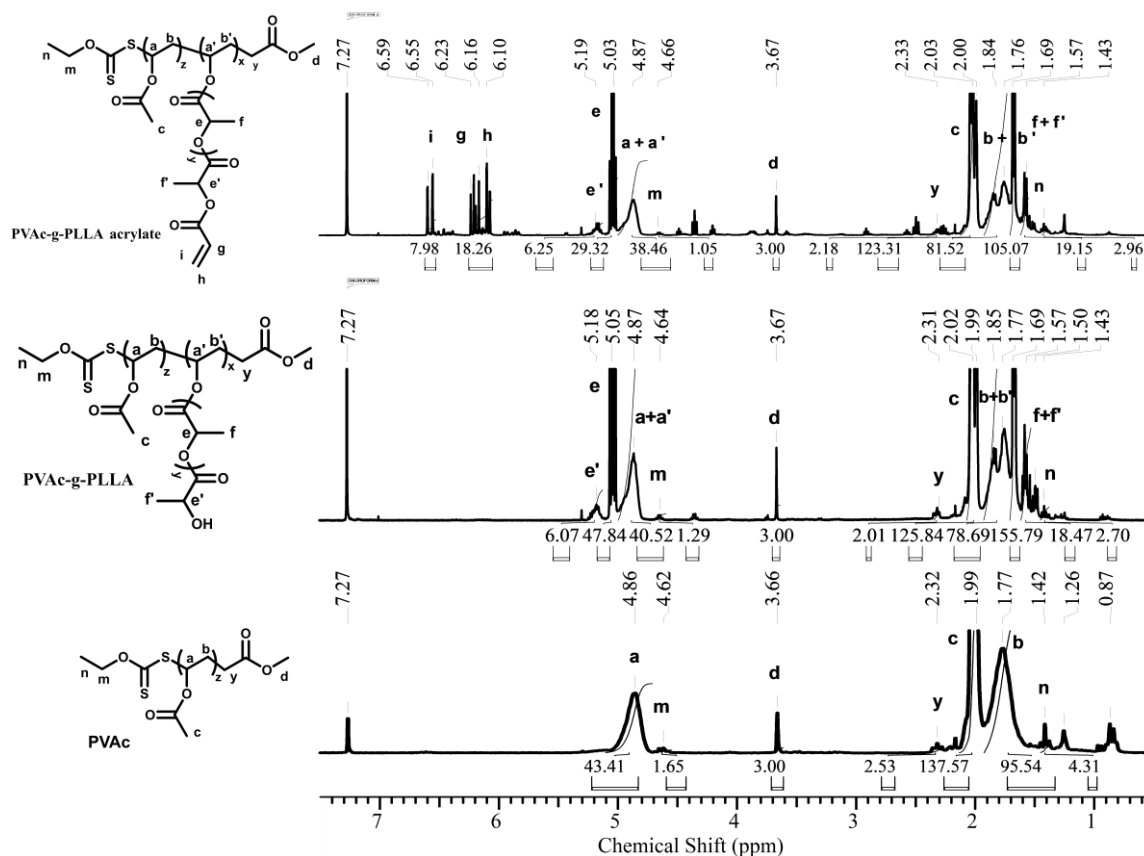


Figure 3.6 Comparison of the ^1H -NMR spectra of PVAc, PVAc-g-PLLA, and PVAc-g-PLLA acrylate polymers.

The appearance of a sharp peak at 2.34 ppm corresponding to the hydroxyl group (which overlaid with terminal $-\text{CH}_2$ protons) and slight changes in the properties like reduced solubility in chloroform compared to the starting PVAc polymer indicated partial hydrolysis. However, it was difficult to extract the information regarding the extent of hydrolysis from the proton NMR spectra as the peaks corresponding to protons of $-\text{OC}(\text{O})\text{CH}_3$ of the repeat unit

(labelled 'c') were merged with the protons of the backbone, making it challenging to extract information about the degree of hydrolysis from the proton NMR spectra.

The partially hydrolysed PVAc was used as a macroinitiator for the ring opening polymerization (ROP) of L-lactide using $\text{Sn}(\text{Oct})_2$ as a catalyst following the literature report.⁴¹ The formation of PLLA graft on the PVAc backbone was confirmed by the appearance of new peaks corresponding to the PLLA backbone (protons labelled 'e') around 5.05 ppm and also at 1.50-1.69 ppm corresponding to the methyl group on the graft backbone (labelled 'f and f') as seen in Figure 3.6 (middle spectrum). A peak at 5.18 ppm corresponding to the terminal -C(O)CH(CH₃)OH (protons labelled 'e') accounted for an average of about 7 protons. Since the terminal group of the PLLA graft on the PVAc backbone gives a direct indication of the number of graft chains (in turn the number of hydrolysed units), it could be hypothesized that on an average 7 hydrolysed units were present per repeat chain (average degree of hydrolysis nearly 15 %).

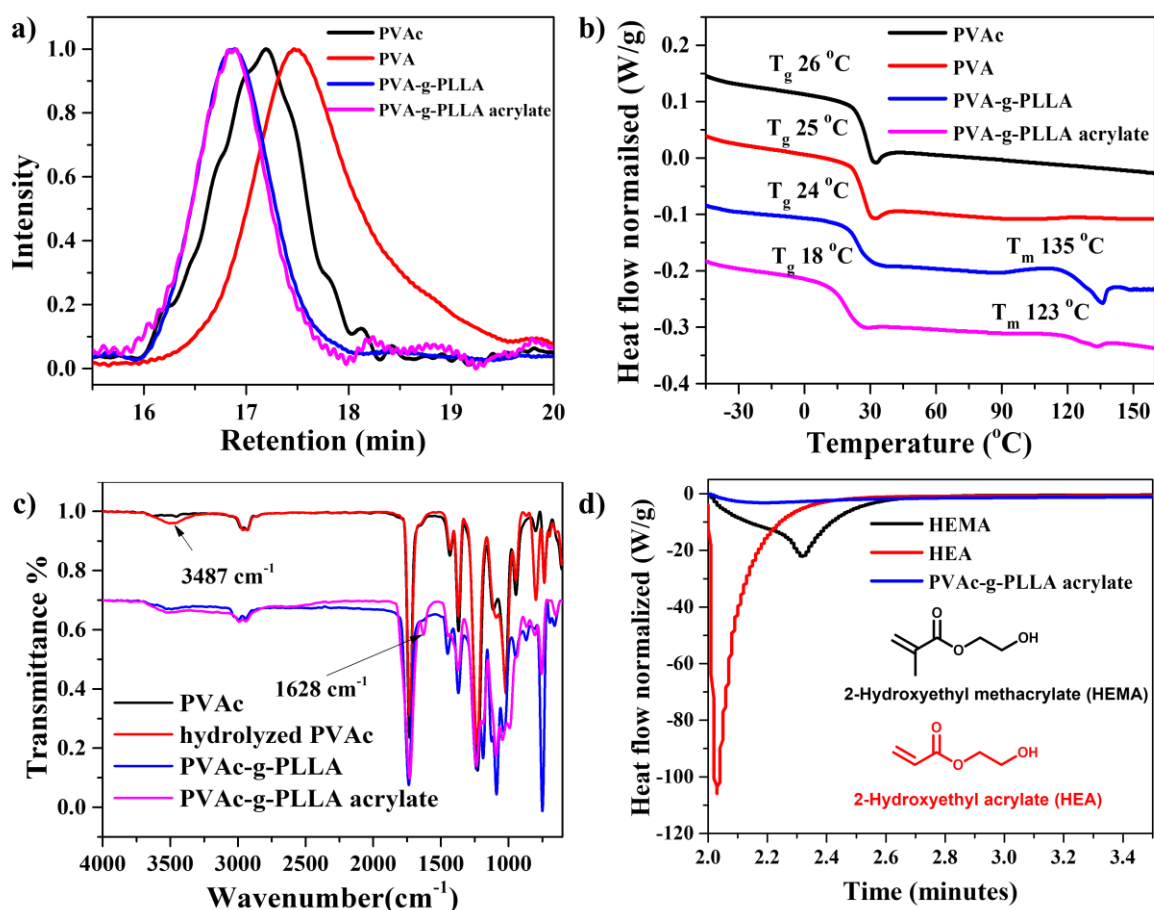


Figure 3.7 a) GPC spectra of PVAc, hydrolysed PVAc, PVAc-g-PLLA, and PVAc-g-PLLA acrylate polymers. b) Specific heat flow comparison of HEMA, HEA, and PVAc-g-PLLA acrylate measured from photo-DSC at 30 °C with 1 wt. % of TPO as photoinitiator. Inset shows the structures of HEMA and HEA. c) Comparison of FT-IR spectra of PVAc,

hydrolysed PVAc, PVAc-g-PLLA, and PVAc-g-PLLA acrylate d) The DSC curves for the PVAc, partially hydrolysed PVAc, PVAc-g-PLLA, and PVAc-g-PLLA acrylate polymers. The terminal hydroxyl group of PVAc-g-PLLA was converted to acryloyl groups by reaction of the graft polymer with acryloyl chloride. The final product PVAc-g-PLLA acrylate crosslinker was obtained as a viscous liquid in 94 % yield after the workup followed by drying. Figure 3.6 (top) compares the proton NMR spectra of the starting PVAc polymer and the graft polymer with the final PVAc-g-PLLA acrylate crosslinker. The characteristic peaks of acrylate double bonds could be observed in the region 6.10 to 6.59 ppm. The integration indicated about 8 acrylate units, which was in agreement with the previous assignment of an average of about 7 graft chains per PVAc backbone chain. The SEC analysis of the polymers is shown in the figure 3.7a and the molecular weight of the polymers are tabulated in the Table 3.1

Sl. no.	Polymer	Mn (NMR) (g/mol)	Mn ^a (g/mol)	Mw ^a (g/mol)	Đ ^a	T _g ^b (°C)	T _m ^b (°C)
1	PVAc	3600	5400	6500	1.20	26	-
2	Hydrolysed PVAc	3400	4300	6000	1.37	25	-
3	PVAc-g-PLLA	5400	5700	6600	1.14	24	135
4	PVAc-g-PLLA Acrylate	5800	6500	8600	1.25	18	123

a) molecular weight from NMR, b) Molecular weight from GPC (chloroform as solvent)

Table 3.1 The molecular weights, polydispersity index, glass transition and the melting temperatures of the polymers PVAc, hydrolysed PVAc, PVAc-g-PLLA, and PVAc-g-PLLA acrylate.

along with a comparison of Mn extracted from the proton NMR spectra. The number average molecular weights of the PVAc, partially hydrolysed PVAc, PVAc-g-PLLA and PVAc-g-PLLA acrylate polymers calculated from the respective proton NMR spectra were 3600, 3400, 5400, and 5800 g/mol respectively. The GPC analysis also revealed the number average molecular weight (Mn) of polymers as 5400, 4300, 5700, and 6500 g/mol respectively with very narrow polydispersity values (Đ) in the range of 1.14 to 1.37. The number average molecular weights obtained from GPC analysis for all four polymers are slightly higher than the values derived for Mn from due to variations in the hydrodynamic behaviour of the polymer in solution. The thermal characteristics of the polymers were investigated using differential scanning calorimetric analysis (figure 3.7b). Table 1 lists the glass transition temperatures (T_g) of the polymers. The T_g of the starting PVAc polymer was observed around 26 °C; which was not

much affected by the partial hydrolysis. Grafting of PLA chains reduced the T_g slightly to 24°C, which reduced to 18 °C upon end functionalization with acryloyl groups. According to the literature reports, the glass transition temperature of PVAc, PLLA polymers are 40 °C, and 60 °C respectively and the glass transition temperature of grafted PVAc-g-PLLA polymer varies from 40 °C to 50 °C depending on the grafting density and the number of the repeat units of PLLA polymer in the branching chains.⁴¹ The low molecular weight PVAc reported in our work exhibited low T_g values which after grafting with PLLA polymer showed melting transition at 136 °C indicating the successful grafting of the PLLA with the PVAc backbone. Compared to the melting temperature of commercial PLLA polymer (around 160 °C), PVAc-g-PLLA polymer showed a lower melting temperature indicating the retardation of crystallization by branching of PLLA polymer. The introduction of terminal acrylate groups within the PVA-g-PLLA polymer structure resulted in further reduction of both the T_g and melting temperature, likely due to the interference with hydrogen bonding interactions. By replacing the hydroxyl groups with various alternative functional groups, it becomes possible to finely adjust the thermal stability of the PLLA polymer, presenting a versatile approach for tailoring its thermal properties.^{41,53} The structural analysis of the hydrolysed PVAc and PVA-g-PLLA acrylate polymer was extended through FT-IR spectra (figure 3.6c). The emergence of peaks at 3487 cm^{-1} in the hydrolysed PVAc polymer confirms the presence of hydroxyl groups resulting from hydrolysis. Likewise, the appearance of the peak at 1628 cm^{-1} corresponds to the carbon-carbon double bond, validating the formation of the acrylate functionality in the PVAc-g-PLLA acrylate polymer.

After the structural characterization of the PVAc-g-PLLA acrylate crosslinker, the polymer was used for the formulation of a photocurable resin with HEMA or HEA as reactive diluents. Photo-DSC experiments were undertaken to determine the optimum weight percentage of photoinitiator (TPO) to be used based on their curing enthalpies. According to the literature, the theoretical heat of polymerization per methacrylate double bond is 13 kcal mol^{-1} while the heat of polymerization per acrylate double bond is 20.6 kcal mol^{-1} .⁵⁴ The theoretical heat of polymerization and curing percentage of HEMA, HEA, and PVAc-g-PLLA acrylate crosslinker were calculated using the above reported values (details of calculations are given in method H section). Figure 3.6d compares the heat flow plot for the three samples. The experimental heat of polymerization of HEMA, HEA, and PVAc-g-PLLA acrylate crosslinker were obtained from the photo-DSC studies as 403.6 Jg^{-1} , 590.2 Jg^{-1} , and 91.24 Jg^{-1} respectively with 1 wt. % of TPO as photo-Initiator (PI). This corresponded to 95.8 % conversion of methacrylate double

bonds in HEMA, 79.5 % acrylate double bond conversion in HEA and 87.7 % conversion of acrylate double bond in PVAc-g-PLLA acrylate crosslinker.

3.3.2 Resin Formulations, Viscosity, and Photo-calorimetric Studies

Six photocurable resin formulations that were developed by adjusting the component weight percentages are listed in Table 3.2. The PVAc-g-PLLA acrylate was mixed in 50, 40, and 30 weight percent with HEMA in the first three formulations (R1, R2, and R3), while the remaining three resins (R4, R5 and R6) were prepared by mixing same weight percentage of PVAc-g-PLLA acrylate with HEA. The solubility and miscibility of the PVAc-g-PLLA acrylate in HEMA as well as HEA enabled formulating the resin without the use of any organic solvents to solubilize the synthesized polymeric crosslinker.

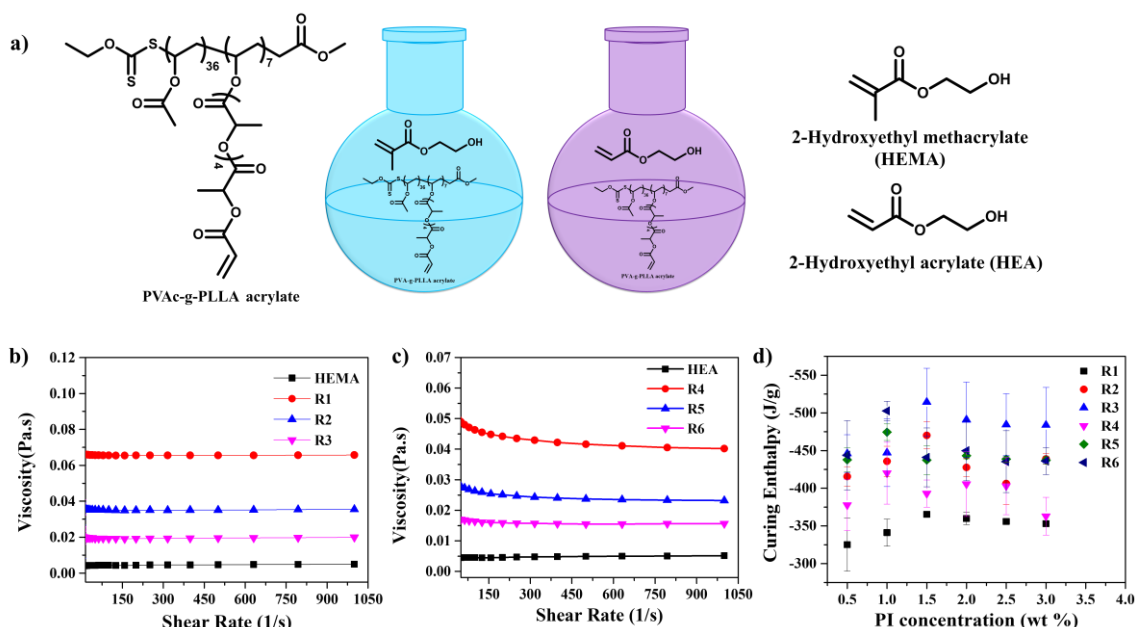


Figure 3.8 Schematic representation of the preparation of six resins formulated with HEMA and HEA b) & c) The resin viscosity as a function of increasing shear rate (d) Optimized curing enthalpy curve from photo-DSC analysis for the six resin formulations.

Resins	wt. % of PVAc-g-PLLA Acrylate	HEA wt. %	HEMA wt. %	TPO PI wt. %	Viscosity (Pa.s) ^a
R1	50	-	48.5	1.5	0.065
R2	40	-	58.5	1.5	0.035
R3	30	-	68.5	1.5	0.019
R4	50	49	-	1	0.042
R5	40	59	-	1	0.023
R6	30	69	-	1	0.016

a. Viscosity of HEMA: 0.006 Pa.s; HEA: 0.005 Pa.s

Table 3.2 Composition and Viscosity of the resin formulations.

For room temperature DLP 3D printing, viscosity is an important parameter to optimize for printability with high-resolution, smooth, and damage-free printed products. To obtain a good 3D printed part the viscosity should be less than 10 Pa.s.⁵⁵

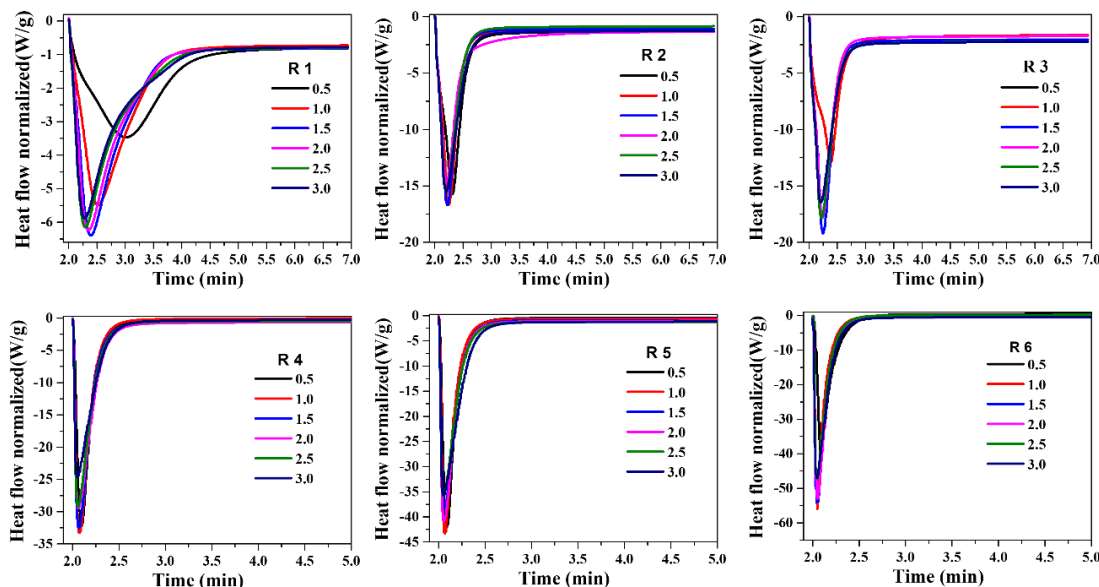


Figure 3.9 Photo-DSC plots of all resin formulations with different weight percentage of PI.

The viscosity of DLP resin depends on various factors, including the resin formulation, diluents, the printing temperature, and the adhesiveness of the formulated resin materials. The viscosities of the resin formulation were measured at 30 °C without adding a photoinitiator. Figure 3.8b and 38c compares the viscosity as a function of shear rate and the values are listed in Table 3.2 in Pa.s. The viscosity of each resin was constant with increasing shear rate up to 1000 s⁻¹, confirming the Newtonian fluid-like properties of the formulations. In both set of resin formulations, the viscosity increased with increase in concentration of PVAc-g-PLLA acrylate. Resins prepared with HEMA showed a viscosity ranging from 0.019 Pa.s to 0.065 Pa.s whereas resins prepared with HEA showed little lower viscosity ranging from 0.016 Pa.s to 0.042 Pa.s. All the prepared resin formulations were appropriate for the DLP 3D printing at room temperature for smooth and warpage-free 3D printed materials.

Figure 3.8d compares the curing enthalpy of all six-resin formulations with increasing PI concentration. From the curve, it can be seen that for the HEMA series of resin formulations (R1, R2, R3) the optimum curing enthalpy was observed at 1.5 wt. % of photoinitiator, while for the HEA series of resins (R4, R5, R6) the optimum was observed at 1 wt. % of PI. The optimum weight percentage of TPO required for these formulations were arrived at by

following photo DSC experiments where the TPO weight percentage was varied from 0.5 to 3 wt. % (Figure 3.9 and Table 3.3).

Resins	TPO wt. %					
	0.5	1.0	1.5	2.0	2.5	3.0
R1	-377.80±34	-341.2±18	-365.45±3	-359.72±8	-355.89±2	-353.05±2
R2	-415.63±13	-435.75±20	-470.18±18	-427.71±12	-406.25±28	-438.96±7
R3	-445.96±25	-447.25±45	-514.38±45	-490.89±50	-484.50±41	-483.82±50
R4	-377.80±34	-420.08±41	392.96±18	-405.47±43	-355.89±38	-353.05±25
R5	-437.73±16	-474.43±11	-437.38±19	-443.18±40	-438.69±4	-437.20±5
R6	-443.89±46	-502.65±13	-441.01±39	-449.87±40	-435.36±41	-436.05±18

Table 3.3 Curing enthalpy of six resin formulations

3.3.3 DLP 3D Printing Using Formulated Resins

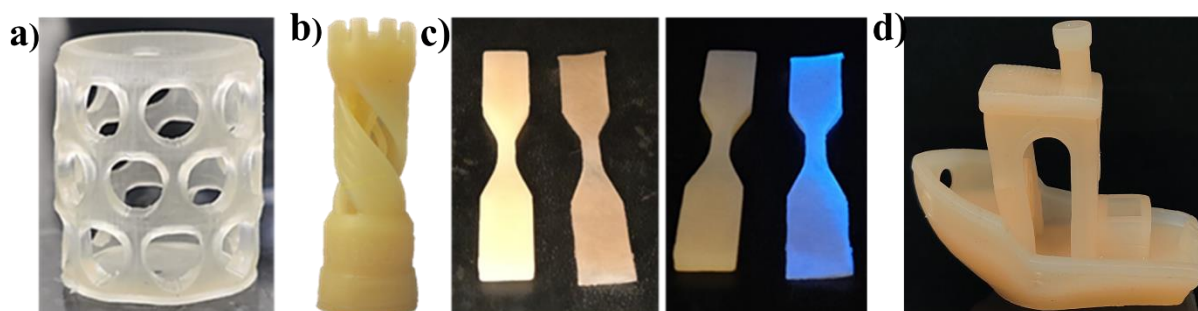


Figure 3.10 a) 3D printed objects made using R6 resin, b) Elegoo Mars Test Rook 3D printed using resin R2 c) 3D printing of tensile bars using R3 resin with and without dye under visible light and UV light d) 3D Benchy printed using resin formulation R5.

A commercial U3DS ultra DLP 3D printer was used to print at room temperature (the printer's settings are described in the experimental section). The 3D printed objects had extremely sharp edges and high visual resolution. Figure 3.10 shows the images of a few 3D printed objects. The first printed part (Figure 3.10a) was printed using formulation R6 where 70 wt. % HEA was used as a diluent. It was observed that the holes in the printed part were sharp and reproducible and no warpage or bending was observed after printing. Figure 3.10b shows an Elegoo Mars Test Rook printed using formulation R2 which had 60 wt. % of HEMA. The high resolution of the printed part justifies the suitability of the formulated resin for 3D printing application.

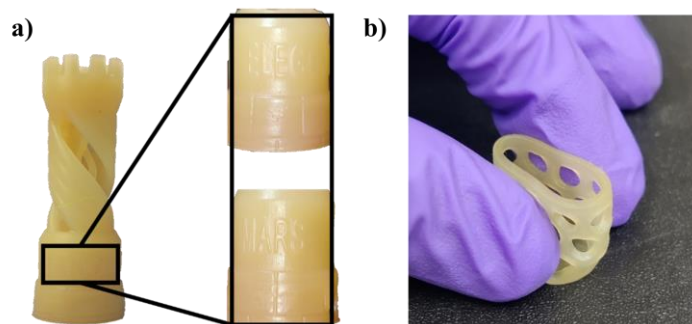


Figure 3.11 a) Enlarged mars rook 3D printed part with visible resolution demonstration. b) Flexibility of HEA mixed 3D printed part using R6 formulation.

The enlarged Mars rook shown in Figure 3.11a illustrates the print resolution by rendering the small 3D-printed text on it easily legible. The 3D printed objects using the HEA formulation were soft and elastomeric in nature (shown in the Figure 3.11b), whereas those printed using the HEMA formulation were strong and sturdy. A fluorescent dye (2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene) (BBOT) was added to the formulation and dumbbell shapes were printed. The uniform emission emanating throughout the dumbbell under UV light (Figure 3.10c) demonstrated excellent miscibility of the dye with the formulation resin 3 and similarly, the dye could be used for other resin formulations also.⁵⁶ Figure 3.10d shows a 3D printed benchy, which is usually considered a demonstration of the 3D printing ability of a formulation or for the calibration/benchmarking of the 3D printer. The benchy was prepared using R5 and it showed good flexibility. Our resin formulations have successfully demonstrated 3D printability by printing the standard 3D benchy and mars rook with exact size and resolution. Figure 3.12 shows images of more 3D-printed objects using all the resin formulations. The resin prepared with HEMA imparted higher mechanical strength to the 3D-printed objects whereas the resin prepared with HEA imparted higher elongation properties.

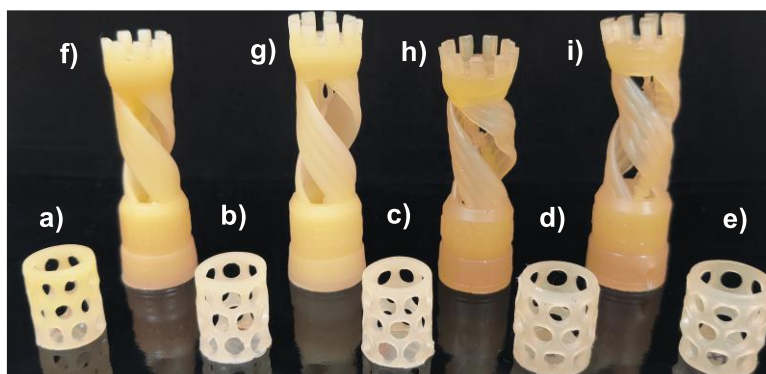


Figure 3.12 3D printed part of all resin formulations

Figure 3.12a-3.12c shows 3D printed porous cylindrical parts using R1, R2, and R3 respectively. Figure 3.12f and 3.12g are the mars rook printed part (10 cm) using R2 and R3

respectively which are high in resolution. Figure 3.12d, 3.12e, are the flexible porous cylinders printed using resin 4, resin 5, while figures 3.12h and 3.12i are mars rook printed parts using R6. The printed parts using R5 and R6 shown in figure 3.12h and 3.12i are somewhat distorted because the printed materials were flexible and soft though the resolution of the printed parts was intact. R4 prepared by mixing 50 wt. % polymeric crosslinker exhibited a high adhesive nature making it difficult for 3D printing large parts using the DLP printer.

3.3.4 Tuneable Mechanical and Thermal Properties of DLP Printed Parts

A set of five 3D printed ASTM D638 type V dumbbell-shaped samples were used to assess the mechanical characteristics of each resin formulation. Table 3.4 displays the tensile strength, Young's modulus, and percentage elongation of the 3D printed components. Figure 3.13 shows the tuneable mechanical characteristics of the 3D printed parts depending on HEMA or HEA used as reactive diluents. From Table 3.4 it can be seen that the mechanical properties were dependent on the reactive diluent used for the resin formulations. Figure 3.13a illustrates the tensile strength of R1, R2, and R3 resin printed parts, while Figure 3.13b depicts the relationship between tensile strength and Young's modulus in 3D printed parts produced with HEMA, highlighting an increase in both parameters with the rising weight percentage of HEMA. Similarly, Figure 3.13c displays the tensile strength of the R4, R5, and R6 resin printed parts, and Figure 3.13d indicates a minimal increment in both tensile strength and Young's modulus.

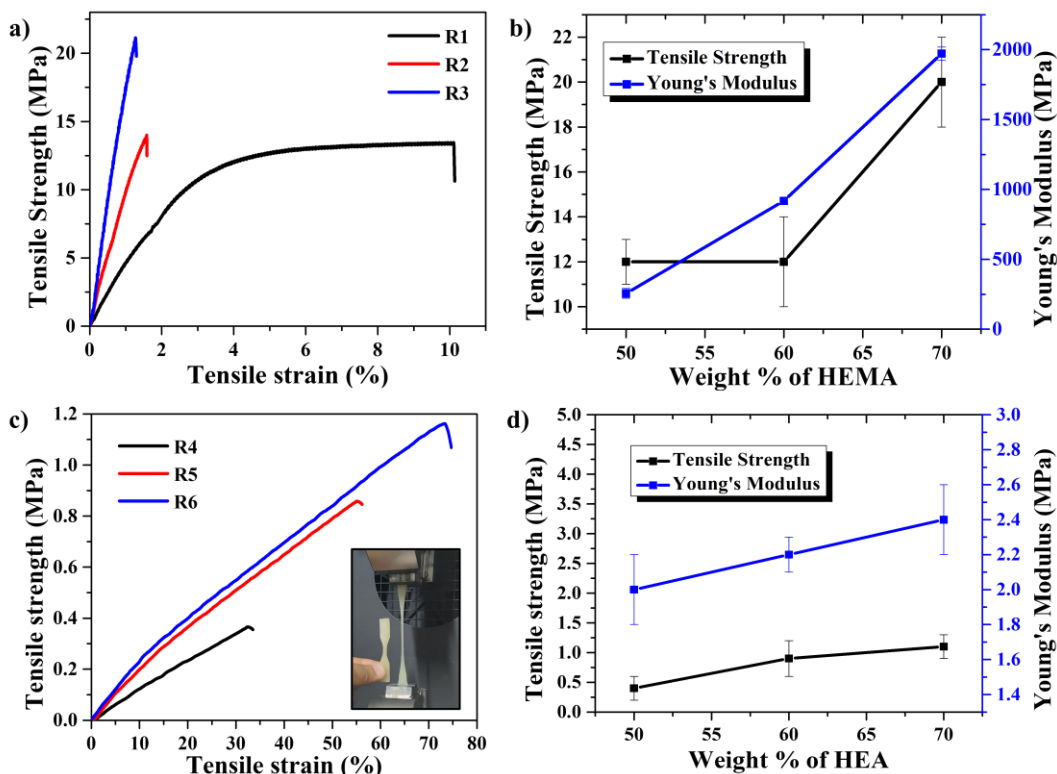


Figure 3.13. Representative stress-strain curves of the 3D printed specimen a) prepared with HEMA, b) Tensile strength and Young's modulus as a function of increasing weight percentage of HEMA c) stress-strain curves of the 3D printed specimen prepared with HEA, inset image is the real photograph of elongation of the R6 resin printed part compared with normal specimen, d) Tensile strength and Young's modulus as a function of increasing weight percentage of HEA.

Resin	Tensile strength [Mpa]	Young's Modulus [Mpa]	Elongation (%)	T _g [°C]	T _{d10%} [°C]
R1	12.3 ±1.1	256.5±35	11.1±3.7	50	264
R2	13.3±1.9	918.2±21	4.9±0.5	76	287
R3	20.6±2.4	1972.1±36	2.1±0.2	82	297
R4	0.4±0.2	1.8±0.6	32.3±1.4	20	276
R5	0.9±0.1	2.1±0.1	55.7±3.7	14	298
R6	1.1±0.2	2.2±0.4	73.3±8.2	13	304

Table 3.4 Mechanical properties of the 3D printed part with glass transition, and 10 weight % degradation temperature.

Resins containing HEMA exhibited superior mechanical properties in comparison to those containing HEA in the printed parts, primarily attributed to the presence of the methyl group in HEMA. Tensile bars produced with HEA displayed higher elongation values compared to those prepared with HEMA.^{58,59} Furthermore, increasing the weight percentage of HEMA or HEA in the resin formulations resulted in increased tensile strength and Young's modulus for the 3D printed parts.

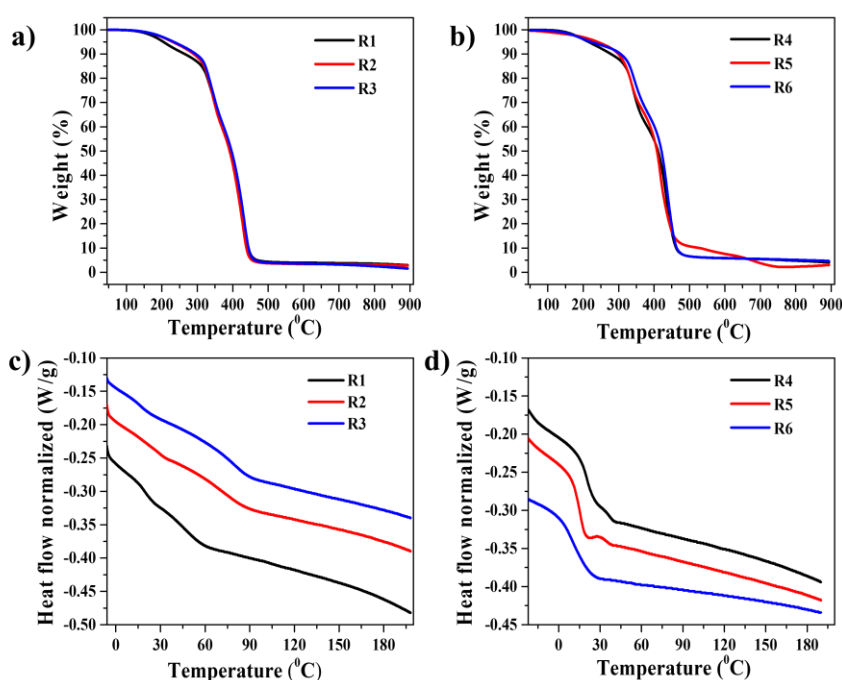


Figure 3.14 (a) TGA thermograms of 3D printed materials using R1, R2, and R3 resins, (b) TGA thermograms of 3D printed materials using R4, R5, and R6 resins, (c) DSC thermograms of 3D printed materials using R1, R2, and R3 resins, (b) DSC thermograms of 3D printed materials using R4, R5, and R6 resins.

The thermal properties of the 3D printed materials were investigated by TGA and DSC experiments (Figure 3.14a to 3.14d). For each of the six resin compositions, the 3D printed components demonstrated good thermal stability with a 10% weight loss indicated in the 260–300 °C range (see Table 3.4 and Figure 3.15a and 3.15b). The DSC analysis revealed the glass transition temperature (T_g) of the HEMA formulations (R 1, R2, and R3) to be 50 °C, 76 °C, and 82 °C respectively (Figure 3.14c), while that for the HEA formulations (R4, R5, and R6) were 20 °C, 14 °C, and 13 °C respectively (Figure 3.14d). It could be observed that increasing the wt. % of HEMA in the resin formulation resulted in higher T_g values making the printed materials stiffer. On the other hand, increasing the HEA content resulted in enhancing the elasticity of the 3D printed objects using the formulations R4 to R6.⁵⁷ The values of T_g and 10 % weight loss temperatures of the 3D printed parts are listed in Table 3.4.

3.3.5 Water uptake and Dye Absorption Study

Experiments were conducted over eight-week time duration to study the water uptake of the 3D printed parts and their degradation. The weight loss and water uptake of the 3D printed samples were monitored each week in phosphate buffer solution (simulating the biological condition) maintaining the pH 7.4 at 37 °C with periodic replenishing of the PBS (details of sample preparation and experimental procedure are given under Materials section). As shown in Figure 3.15a, the water uptake of the 3D printed parts increased in the first two weeks, and on the third week onwards, it reduced and remained constant over a six-week time period. The swelling properties of the crosslinked polymer depend on the composition of the polymeric materials. From the figure 3.15a it can be clearly seen that the HEA based 3D printed samples had higher water uptake compared to the HEMA based 3D printed samples. This could be attributed to the hydrophilic nature of HEA compared to HEMA.⁵⁷ There was an almost 240 % water uptake for the HEA based samples during the first two weeks of incubation after which there was a reduction to about 150 % from the third week onwards, which remained almost constant during the remaining part of the study until the end of eight weeks. The HEMA based 3D printed samples also exhibited increased water uptake until the second week (almost 100 %) after which the water uptake remained steady.

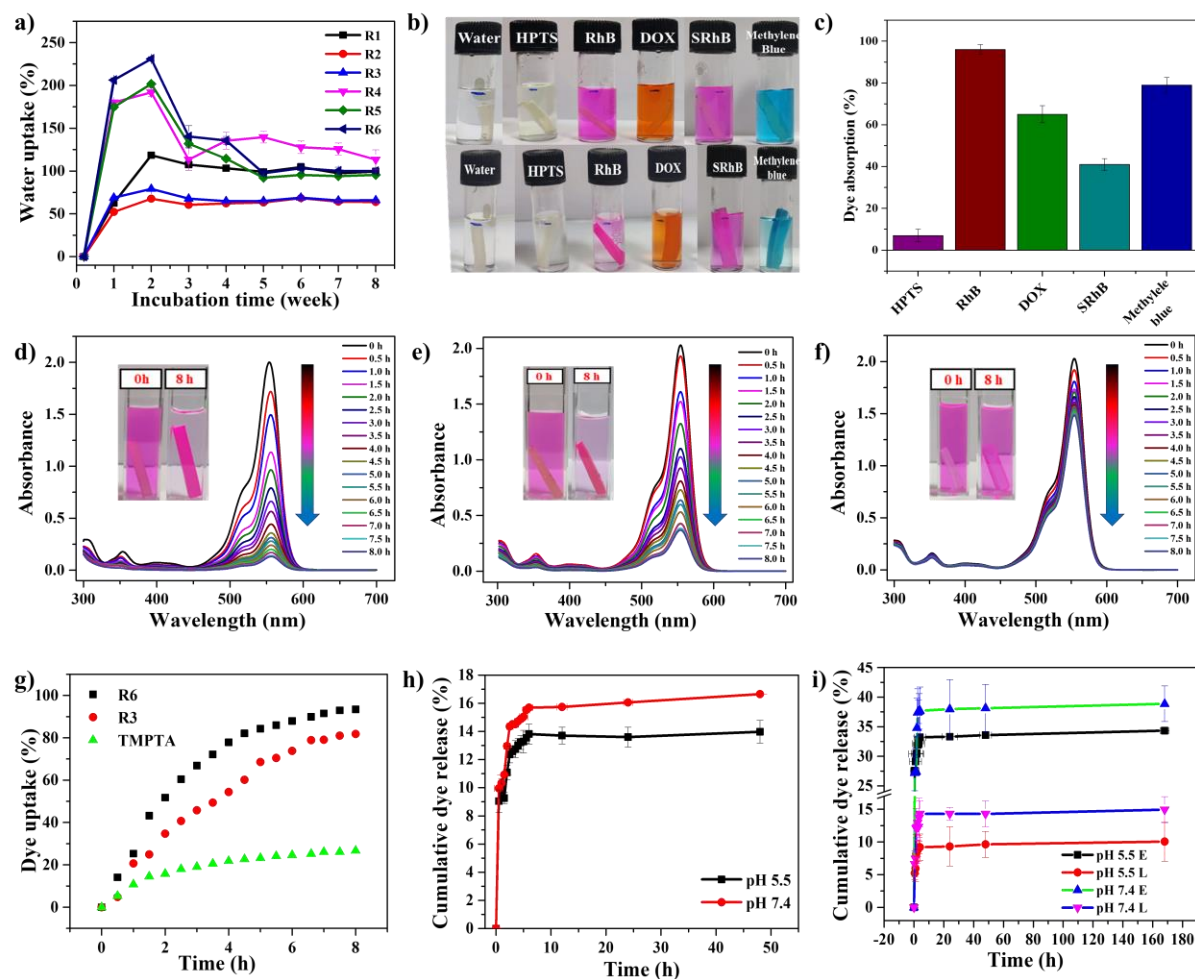


Figure 3.15. a) Water uptake study of the 3D printed parts in PBS solution at 37 °C for 8-week time period. b) Real images of dye absorptions of the resin 6 3D printed part before and after 12 h. c) Dye absorption comparison, d) Absorption plot of R6 resin 3D printed part in RhB over 8 h time period e) absorption plot of R3 resin 3D printed part in RhB over 8 h time period. f) absorption plot of HEA+TMPTA resin 3D printed part in RhB over 8 h time period. (Inset optical image of the cuvette containing dye solution with 3D print part before and after dye absorption). g) Comparison of dye uptake of resin 3, resin 6, and HEA +TMPTA resin 3D printed part. h) and i) Dye release study in different pH at 37 °C and dye release study in different pH in the presence of enzymes (esterase and lipase) at 37 °C.

Following the examination of the swelling characteristics of the 3D printed components, a dye absorption study was conducted. The R6 resin was chosen for its notable water uptake capacity. Five distinct dyes, including HPTS, RhB, DOX, SRhB, and MB, were selected to formulate dye solutions. These solutions were carefully prepared to maintain an optical density (OD) of 2. Subsequently, identical weights of R6 resin 3D printed parts were immersed in 3ml of dye solution each, as illustrated in Figure 3.15b. After 12 hours of dye absorption, it was noted that

the RhB dye exhibited absorption exceeding 95% compared to the other dyes (Figure 3.15c). This distinctive uptake may be attributed to the hydrophobic interaction between the dye and the crosslinked polymer network. Hydrogen bonding interaction between the ester linkage present on the lactic acid and the hydroxyl group present on reactive diluent (HEMA and HEA) also forms a crucial interaction, which can modulate the dye absorption.⁶⁰⁻⁶² Additionally, SEM images revealed the porous nature of the 3D printed part on the surface and cross-section which can aid in the dye absorption (Figure 3.17e)⁶³. To learn more about this phenomenon, a time-dependent study was conducted specifically with the RhB dye. As depicted in Figure 3.15d, a R6 resin 3D printed part was immersed in the RhB dye solution (OD 2), and the dye absorption was monitored by measuring the UV absorption spectra. Comparable results were noted when conducting the same experiment using R3 resin printed part (Figure 3.15e which contains HEMA). A reference resin formulation was prepared by replacing the PVAc-g-PLLA acrylate polymer with 30 wt.% TMPTA (Trimethylolpropane triacrylate), along with 70 wt.% hydroxyethyl acrylate (HEA). The 3D printed part from this resin formulation was subjected to the same RhB dye absorption study as shown in the figure 3.15f. Interestingly, it was observed from the Figure 3.15g, that while the 3D printed part of R6 and R3 exhibited similar dye absorption with more than 95 % and 80 % respectively, whereas the 3D printed part from the TMPTA formulation showed only 20% dye absorption. This observation directly emphasizes the role of the PVA-g-PLLA acrylate polymer in facilitating dye absorption.

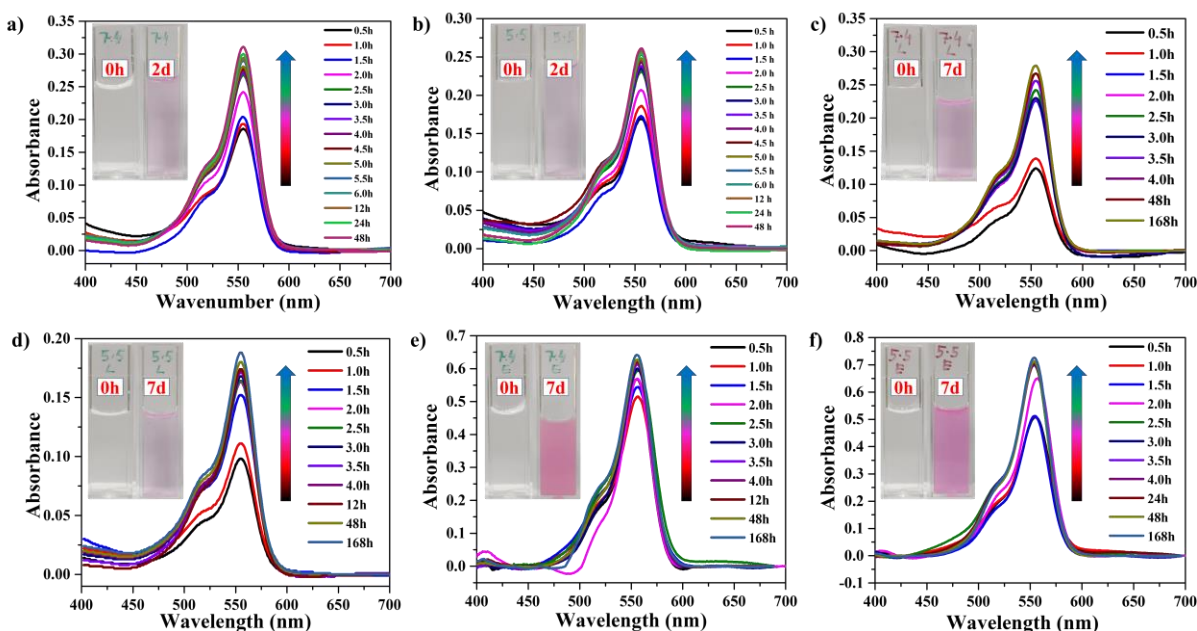


Figure 3.16 Dye release performance of the R6 resin 3D printed part (a) at pH 7.4 and (b) at pH 5.5 at 37 °C without enzyme. Dye release performance of the R6 resin 3D printed part (c)

at pH 7.4 and (d) at pH 5.5 in the presence of Lipase enzyme, (e) at pH 7.4 and (f) at pH 5.5 in the presence of Esterase enzyme.

Additionally, a study on the release of this dye was carried out under different pH and enzyme conditions. After the RhB dye was absorbed from the solution, the 3D printed parts were submerged in two distinct pH solutions at 37 °C for 48 h (pH 7.4 and pH 5.5, as illustrated in Figure 3.16a and 3.16b). As depicted in figure 3.15h, a higher dye release of 16.6% was observed at pH 7.4 compared to the dye release of 14% at pH 5.5, indicating that pH 7.4 facilitated improved dye release. Likewise, dye release experiments were conducted in the presence of Lipase at pH 7.4 and 5.5, and in the presence of Esterase enzyme under the same pH conditions, both at 37 °C for 7 days' time period (refer to Figure 3.16c to Figure 3.16f). From figure 3.15i, it can be seen that the Esterase enzyme proved to be more effective under both pH conditions, yielding 38.8% dye release at pH 7.4 and 34.3% at pH 5.5, possibly due to the hydrolysis of ester bonds present in the crosslinked 3D printed network. The Lipase enzyme resulted in a lower dye release of 14.9% at pH 7.4 and 10% at pH 5.5, indicating its lesser effectiveness in promoting dye release from the 3D printed part. In conclusion, it can be affirmed that the R6 3D printed part exhibits notable swelling properties, demonstrating excellent absorption and release of RhB dye, particularly under pH 7.4 conditions in the presence of Esterase enzyme at 37 °C.

3.3.6 Cell Viability Test and In Vitro Degradation Study

The biocompatibility and cytotoxicity of the 3D-printed network polymers were assessed using the MTT assay. The 3D-printed films from R1 to R6 were incubated with wild-type mouse embryonic (WT-MEF) cells inside the 96 well plates and the cell viability was determined by the MTT assay for 3 different times of incubation (24 h, 48 h, and 72 h). L-lactic acid is the degradation product due to the hydrolytic ester bond cleavage of the PLLA polymer matrix in the 3D printed materials.⁶⁴ In order to avoid the altered pH due to the presence of the L-Lactic acid affecting the experimental observation, the PBS solution was periodically replaced to maintain the pH steady during the course of the experiment. As depicted in Figure 3.17a-c, the 3D-printed films of all resins demonstrated over 90% cell viability after 72 hours of incubation, signifying the non-cytotoxic nature of the PVAc-g-PLLA acrylate polymer in the 3D printed component. This observation suggests the potential use of these 3D-printed parts in biomedical applications.^{65,66} Analysing the weight loss data in Figure 3.17d, it could be observed that the accelerated weight loss also coincided with the accelerated water uptake during the initial two weeks, after which the weight loss remained steady. R6 based samples exhibited the highest

degradability, which was in conformity with its increased water uptake, which could lead to penetration of water into the bulk of the sample accelerating the degradation. Samples R1 and R4 with 50 % PVAc-g-PLLA acrylate showed lower degradability.

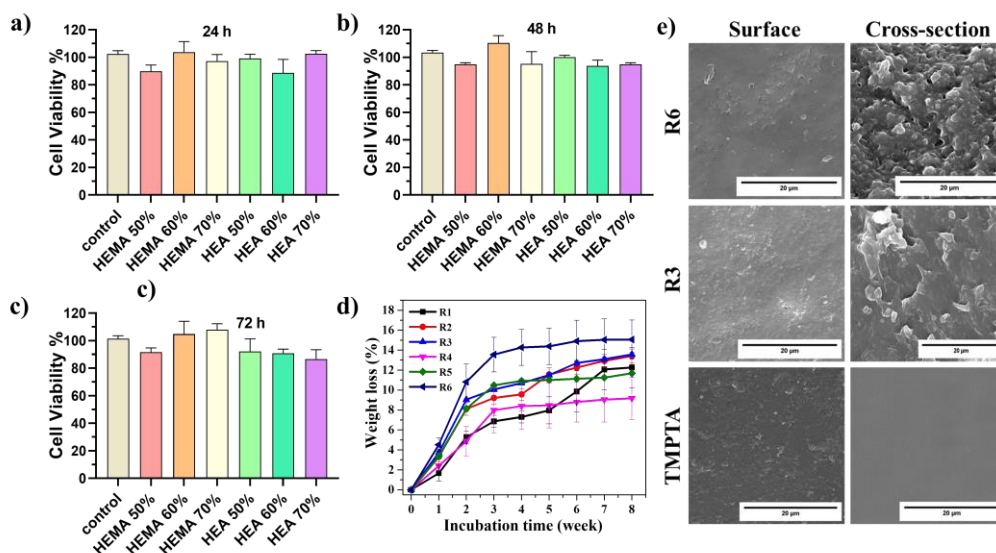


Figure 3.17 Cell viability of the 3D printed parts with different time period a) 24 h, b) 48 h, and c) 72 h wild-type mouse embryonic (WT-MEF) cells, d) In vitro degradation of the 3D printed parts in PBS solution at 37 °C.

3.4 CONCLUSIONS

As a summery it can be concluded that, the novel biobased PVAc-g-PLLA acrylate polymer was designed and synthesized for the preparation of resin formulations with reactive diluents (HEMA and HEA) avoiding the use of any organic solvents. The successful synthesis of all polymers PVAc, partially hydrolysed PVAc, PVA-g-PLLA, and PVA-g-PLLA acrylate were confirmed by the characterizations using NMR and FT-IR spectroscopy. The molecular weights of the polymers were confirmed by GPC in chloroform solvent. The formulated resins were characterized by viscosity and photo-DSC studies. The resins successfully performed 3D printing in DLP 3D printer at room temperature. The complex Elegoo Mars Test Rook and Benchy were printed with very high resolution indicating the potential applicability of the resins. The mechanical properties of the 3D printed parts could be tuned depending on the use of reactive diluent during resin formulation. Additionally, the 3D printed parts showed dye absorption and release properties. The release kinetics of the dye could be optimised depending on the pH and presence of enzymes. Finally, the resin formulations could be 3D printed on any DLP printer and the 3D-printed parts exhibited tuneable mechanical properties which have

immense potential for widespread applications like tissue engineering, soft robotics, tissue culture, biomedical implants, and scaffolds.

3.5 REFERENCES

- (1) Jungst, T.; Smolan, W.; Schacht, K.; Scheibel, T.; Groll, J. *Chem. Rev.* **2016**, *116* (3), 1496–1539.
- (2) Donderwinkel, I.; van Hest, J. C. M.; Cameron, N. R. *Polym. Chem.* **2017**, *8* (31), 4451–4471.
- (3) Mondschein, R. J.; Kanitkar, A.; Williams, C. B.; Verbridge, S. S.; Long, T. E. *Biomaterials* **2017**, *140*, 170–188.
- (4) Ragelle, H.; Tibbitt, M. W.; Wu, S.-Y.; Castillo, M. A.; Cheng, G. Z.; Gangadharan, S. P.; Anderson, D. G.; Cima, M. J.; Langer, R. *Nat. Commun.* **2018**, *9* (1), 1184.
- (5) Stewart, S. A.; Domínguez-Robles, J.; McIlorum, V. J.; Gonzalez, Z.; Utomo, E.; Mancuso, E.; Lamprou, D. A.; Donnelly, R. F.; Larrañeta, E. *Mol. Pharm.* **2020**, *17* (9), 3487–3500.
- (6) Kutlehria, S.; D’Souza, A.; Bleier, B. S.; Amiji, M. M. *Mol. Pharm.* **2022**, *19* (12), 4411–4427.
- (7) Lind, J. U.; Busbee, T. A.; Valentine, A. D.; Pasqualini, F. S.; Yuan, H.; Yadid, M.; Park, S.-J.; Kotikian, A.; Nesmith, A. P.; Campbell, P. H.; Vlassak, J. J.; Lewis, J. A.; Parker, K. K. *Nat. Mater.* **2017**, *16* (3), 303–308.
- (8) Nagarajan, N.; Dupret-Bories, A.; Karabulut, E.; Zorlutuna, P.; Vrana, N. E. *Biotechnol. Adv.* **2018**, *36* (2), 521–533.
- (9) Bhattacharjee, N.; Parra-Cabrera, C.; Kim, Y. T.; Kuo, A. P.; Folch, A. *Adv. Mater.* **2018**, *30* (22), 1800001.
- (10) Wallin, T. J.; Pikul, J.; Shepherd, R. F. *Nat. Rev. Mater.* **2018**, *3* (6), 84–100.
- (11) Sachyani Keneth, E.; Kamyshny, A.; Totaro, M.; Beccai, L.; Magdassi, S. *Adv. Mater.* **2021**, *33* (19), 2003387.
- (12) Bhargav, A.; Sanjairaj, V.; Rosa, V.; Feng, L. W.; Fuh YH, J. *J. Biomed. Mater. Res. Part B Appl. Biomater.* **2018**, *106* (5), 2058–2064.
- (13) Saadi, M. A. S. R.; Maguire, A.; Pottackal, N. T.; Thakur, M. S. H.; Ikram, M. M.; Hart, A. J.; Ajayan, P. M.; Rahman, M. M. *Adv. Mater.* **2022**, *34*, 2108855
- (14) Ligon, S. C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. *Chem Rev* **2017**, *117* (15), 10212–10290.
- (15) Gross, B.; Lockwood, S. Y.; Spence, D. M. *Anal Chem* **2017**, *89* (1), 57–70.

- (16) Guvendiren, M.; Molde, J.; Soares, R. M. D.; Kohn, J. *ACS Biomater. Sci. Eng.* **2016**, 2 (10), 1679–1693.
- (17) Zou, Z.; Chen, Y.; Yuan, S.; Luo, N.; Li, J.; He, Y. *Adv. Funct. Mater.* **2023**, 33 (10), 2213312.
- (18) Jandyal, A.; Chaturvedi, I.; Wazir, I.; Raina, A.; Ul Haq, M. I. *Sustain. Oper. Comput.* **2022**, 3, 33–42.
- (19) Voet, V. S. D.; Strating, T.; Schnelting, G. H. M.; Dijkstra, P.; Tietema, M.; Xu, J.; Woortman, A. J. J.; Loos, K.; Jager, J.; Folkersma, R. *ACS Omega* **2018**, 3 (2), 1403–1408.
- (20) Cohen, J.; Bektas, C. K.; Mullaghy, A.; Perera, M. M.; Gormley, A. J.; Kohn, J. *ACS Biomater. Sci. Eng.* **2021**, 7 (9), 4454–4462.
- (21) Shah, D. M.; Morris, J.; Plaisted, T. A.; Amirkhizi, A. V.; Hansen, C. J. *Addit. Manuf.* **2021**, 37, 101736.
- (22) Melchels, F. P. W.; Feijen, J.; Grijpma, D. W. *Biomaterials* **2009**, 30 (23–24), 3801–3809.
- (23) Seck, T. M.; Melchels, F. P. W.; Feijen, J.; Grijpma, D. W. *J. Control. Release* **2010**, 148 (1), 34–41.
- (24) Pal, S.; S. K., A. *Macromol. Chem. Phys.* **2022**, 223 (22), 2200139.
- (25) Green, B. J.; Worthington, K. S.; Thompson, J. R.; Bunn, S. J.; Rethwisch, M.; Kaalberg, E. E.; Jiao, C.; Wiley, L. A.; Mullins, R. F.; Stone, E. M.; Sohn, E. H.; Tucker, B. A.; Guymon, C. A. *Biomacromolecules* **2018**, 19 (9), 3682–3692.
- (26) Zarek, M.; Layani, M.; Cooperstein, I.; Sachyani, E.; Cohn, D.; Magdassi, S. *Adv. Mater.* **2016**, 28 (22), 4449–4454.
- (27) Kim, E. V.; Petronyuk, Y. S.; Guseynov, N. A.; Tereshchuk, S. V.; Popov, A. A.; Volkov, A. V.; Gorshenev, V. N.; Olkhov, A. A.; Levin, V. M.; Dymnikov, A. B.; Rodionov, V. E.; Tumanyan, G. A.; Ivashkevich, S. G.; Bonartsev, A. P.; Borozdkin, L. L. *Bull. Exp. Biol. Med.* **2021**, 170 (3), 356–359.
- (28) Wilson, J. A.; Luong, D.; Kleinfehn, A. P.; Sallam, S.; Wesdemiotis, C.; Becker, M. L. *J. Am. Chem. Soc.* **2018**, 140 (1), 277–284.
- (29) Luo, Y.; Le Fer, G.; Dean, D.; Becker, M. L. *Biomacromolecules* **2019**, 20 (4), 1699–1708.
- (30) Trivedi, A. K.; Gupta, M. K.; Singh, H. *Adv. Ind. Eng. Polym. Res.* **2023**, 6(4), 382–395.
- (31) Tripathi, N.; Misra, M.; Mohanty, A. K. *ACS Eng. Au* **2021**, 1(1), 7–38.
- (32) Maharana, T.; Pattanaik, S.; Routaray, A.; Nath, N.; Sutar, A. K. *React. Funct. Polym.* **2015**, 93, 47–67.
- (33) Tesfaye, M.; Patwa, R.; Dhar, P.; Katiyar, V. *ACS Omega* **2017**, 2 (10), 7071–7084.

- (34) Yu, S.; Zhang, Y.; Hu, H.; Li, J.; Zhou, W.; Zhao, X.; Peng, S. *RSC Adv.* **2022**, *12* (49), 31629–31638.
- (35) Wu, C.-S. Modulation, *Mater. Sci. Eng. C* **2016**, *69*, 27–36.
- (36) Li, J.; Kong, M.; Cheng, X. J.; Dang, Q. F.; Zhou, X.; Wei, Y. N.; Chen, X. G. *Int. J. Biol. Macromol.* **2012**, *51* (3), 221–227.
- (37) Ma, F. K.; Li, J.; Kong, M.; Liu, Y.; An, Y.; Chen, X. G. *Int. J. Biol. Macromol.* **2013**, *54*, 174–179.
- (38) Guerrouani, N.; Couturaud, B.; Mas, A.; Schué, F.; Robin, J.-J. *Eur. Polym. J.* **2013**, *49* (6), 1621–1633.
- (39) Okuda, T.; Ishimoto, K.; Ohara, H.; Kobayashi, S. *Macromolecules* **2012**, *45* (10), 4166–4174.
- (40) Wallach, J. A.; Huang, S. J. Copolymers of Itaconic Anhydride and Methacrylate-Terminated Poly(Lactic Acid) Macromonomers. *Biomacromolecules* **2000**, *1* (2), 174–179.
- (41) Ding, N.; Shentu, B.; Pan, P.; Shan, G.; Bao, Y.; Weng, Z. *Ind. Eng. Chem. Res.* **2013**, *52*, 12897–12905.
- (42) Ding, J.; Chen, S. C.; Wang, X. L.; Wang, Y. Z. *Ind. Eng. Chem. Res.* **2009**, *48* (2), 788–793.
- (43) Guerrouani, N.; Mas, A.; Schué, F. *J. Appl. Polym. Sci.* **2009**, *113* (2), 1188–1197.
- (44) Jarosz, T.; Gebka, K.; Stolarczyk, A. *Molecules*. **2019**, *24*(16), 3019.
- (45) Mittal, H.; Ray, S. S.; Okamoto, M. *Macromol. Mater. Eng.* **2016**, *301* (5), 496–522.
- (46) Pan, J.; Zhao, M.; Liu, Y.; Wang, B.; Mi, L.; Yang, L. *J Biomed Mater Res A*. **2009**, *89* (1), 160–167.
- (47) Dolatkhah, A.; Wilson, L. D. *ACS Appl. Mater. Interfaces* **2016**, *8* (8), 5595–5607.
- (48) Ghorai, S.; Sarkar, A.; Raoufi, M.; Panda, A. B.; Schönherr, H.; Pal, S. *ACS Appl. Mater. Interfaces* **2014**, *6* (7), 4766–4777.
- (49) Huang, Y.; Xu, J.; Shao, J.; Sun, G.; Li, D.; Fan, Q. *Langmuir* **2020**, *36* (39), 11676–11684.
- (50) Paunović, N.; Bao, Y.; Coulter, F. B.; Masania, K.; Geks, A. K.; Klein, K.; Rafsanjani, A.; Cadalbert, J.; Kronen, P. W.; Kleger, N.; Karol, A.; Luo, Z.; Rüber, F.; Brambilla, D.; von Rechenberg, B.; Franzen, D.; Studart, A. R.; Leroux, J.-C. *Sci. Adv.* **2023**, *7* (6), eabe9499.
- (51) Ghosh, R.; Malhotra, M.; Sathe, R. R. M.; Jayakannan, M. *Biomacromolecules* **2020**, *21* (7), 2896–2912.
- (52) Stenzel, M. H.; Cummins, L.; Roberts, G. E.; Davis, T. P.; Vana, P.; Barner-Kowollik, C. *Macromol. Chem. Phys.* **2003**, *204* (9), 1160–1168.

- (53) Lee, S.-H.; Hyun Kim, S.; Han, Y.-K.; Kim, Y. H. *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39* (7), 973–985. (54) Ghorpade, R. V.; Bhosle, S. M.; Ponrathnam, S.; Rajan, C. R.; Chavan, N. N.; Harikrishna, R. *J. Polym. Res.* **2012**, *19* (2).
- (55) Jansen, J.; Melchels, F. P. W.; Grijpma, D. W.; Feijen, J. *Biomacromolecules* **2009**, *10* (2), 214–220.
- (56) Gastaldi, M.; Cardano, F.; Zanetti, M.; Viscardi, G.; Barolo, C.; Bordiga, S.; Magdassi, S.; Fin, A.; Roppolo, I. *ACS Mater. Lett.* **2021**, *3* (1), 1–17.
- (57) Oucif, A.; Haddadine, N.; Zakia, D.; Bouslah, N.; Benaboura, A.; Beyaz, K.; Guedouar, B.; El-Shall, M. S. *Polym. Bull.* **2022**, *79* (3), 1535–1554.
- (58) Tang, J.; Zhang, J.; Lu, J.; Huang, J.; Zhang, F.; Hu, Y.; Liu, C.; An, R.; Miao, H.; Chen, Y.; Huang, T.; Zhou, Y. *Polymers.* **2020**, *12*(9), 2165.
- (59) Liang, B.; Zhao, J.; Li, G.; Huang, Y.; Yang, Z.; Yuan, T. *Ind. Crops Prod.* **2019**, *138*, 111585.
- (60) Munim, S. A.; Raza, Z. A. *Journal of Porous Materials* **2019**, *26* (3), 881–901.
- (61) Kuo, S. W. *Journal of Polymer Research* **2008**, *15* (6), 459–486.
- (62) Kasprów, M.; MacHnik, J.; Otulakowski, Ł.; Dworak, A.; Trzebicka, B. *RSC Adv.* **2019**, *9* (70), 40966–40974.
- (63) Liu, W.; Erol, O.; Gracias, D. H. *ACS Appl. Mater. Interfaces* **2020**, *12* (29), 33267–33275.
- (64) Zaaba, N. F.; Jaafar, M. A. *Polym. Eng. Sci.* **2020**, *60* (9), 2061–2075.
- (65) Sandmeier, M.; Paunović, N.; Conti, R.; Hofmann, L.; Wang, J.; Luo, Z.; Masania, K.; Wu, N.; Kleger, N.; Coulter, F. B.; Studart, A. R.; Grützmacher, H.; Leroux, J. C.; Bao, Y. *Macromolecules* **2021**, *54* (17), 7830–7839.
- (66) Anindita, S. N.; Conti, R.; Zauchner, D.; Paunović, N.; Qiu, W.; Buzhor, M. G.; Krivitsky, A.; Luo, Z.; Müller, R.; Grützmacher, H.; Qin, X.-H.; Leroux, J.-C.; Bao, Y. *Aggregate* **2023**, e368.

CHAPTER 4

Thiol-Ene-based Degradable 3D Printed Network from Bio Resource Derived Monomers Ethyl-lactate and Isosorbide

4.1 INTRODUCTION

The process of creating objects through additive manufacturing, often known as 3D printing, has opened up new possibilities for creativity and customization across various fields of applications.¹⁻⁶ Among the various 3D printing methods, light-induced polymerization technologies like stereo lithography (SLA) and digital light processing (DLP), offer superior precision of prototype features, mechanical robustness, and layer cohesion when compared to other approaches such as filament deposition modeling (FDM).⁷⁻¹¹ Photo curable polymers are now being used in the creation of 50% of industrial prototypes. The primary materials for 3D printing through photo polymerization predominantly center around acrylate or methacrylate-based formulations, with the choice depending on factors like the quality of chain growth in acrylate polymerization, curing speed, mechanical properties, and costeffectiveness.¹²⁻¹⁴ According to a recent study, commercial acrylate molecules pose toxicity risks due to their existence as residual monomers after polymerization and additionally, they exhibit low degradability after polymerization.¹⁵⁻¹⁷ In an effort to address the significant limitations that are associated with conventional acrylic monomers, researchers have explored the use of thiol-ene-based chemistries.¹⁸⁻¹⁹ Photo-induced thiolene reactions combine the attributes of both photo polymerization and click reactions, including precise control, selectivity, resistance to oxygen and water, and high yields without the formation of by-products.²⁰⁻²³ Unlike chain-growth acrylate polymerizations, thiol-ene reactions proceed via a step-growth mechanism, offering benefits such as delayed gelation, improved monomer conversion, and reduced shrinkage stress.^{24,25} Acrylate-based or thiolene-based thermosets are valued for their thermal and chemical resistance but face environmental concerns due to fossil feedstock usage and increased waste generation. Biomass-derived materials like poly(lactic acid), sucrose, vegetable oil, and eugenol are being incorporated into thermosetting resins to address these issues.^{18, 25-27} Conventional polymer resin-based 3D printing techniques create thermosetting materials that are non-biodegradable and add to the plastic pollution. Therefore, there is an increasing need for 3D printing resins based on renewable and biodegradable ingredients to address this issue. Thiol-ene polymerization producing novel biomaterials possessing unique crosslinking architecture, improved mechanical properties, eco-friendly reaction characteristics, rapid and site-specific polymerization, and the potential of improved degradability are highly sought-after.²⁸⁻³¹ Due to its benefits, thiol-ene photo polymerization is progressively emerging as a viable option for creating resins for additive manufacturing. The recent expansion of literature has shown interest in thiol ene click chemistry in liquid-based

3D printing introducing different thiol and/or ene moieties in polymeric or small molecule fashion.³²⁻³⁴ Andreas Oesterreicher et al and Yimei Wu et al. successfully synthesized thiol-yne small molecules for photo resin formulations to demonstrate biocompatible monomers for UV-based additive manufacturing (DLP 3D printing). They also demonstrated its reduced cytotoxicity and hydrolytic degradability, thereby addressing plastic pollution.^{35,36} Sycks et al. demonstrated the 3D printing of spiro ene molecules with a custom DLP 3D printer, showcasing the tenable mechanical properties through controlled heat treatment and Spiro chemistry.³⁷ Merckle et al. introduced eco-friendly 3D printing resins, comprising 20-40% bio derived monomers from linalool offering high spatial resolution, customizable properties, and also exhibit 4D shape memory effects.³⁸ Eric Constant et al. reported photopolymers derived from natural terpenes, limonene, and β -myrcene that were used for the thiol-ene photo cross-linking via solvent-free DLP 3D printing which exhibited good mechanical properties and cell viability with shape memory effect making them promising for 3D printable photopolymers and structurally robust materials.³² Recently, Porwal et al. extracted Levoglucosan, a bio-based compound, from cellulose biomass through a pyrolysis process. Levoglucosan was subsequently employed to synthesize an ene-containing molecule, which was used to create a thiol-ene network polymer for application in 3D printing technology. The 3D-printed objects exhibited favourable degradability properties in THF/NaOH solution making it a well-suited rapid prototyping application mitigating the waste generation from acrylate-based printing.³⁹ Despite the proliferation of 3D printing resins and processes described in the literature, it is important to note that the mechanical properties of the resulting materials often do not meet the desired standards. The current work outlines the scalable synthesis of ethyl lactate-based polymeric ene and its thiol-ene photochemistry with isosorbide-based thiol and Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) based multifunctional thiol for DLP 3D printing application. Thiol-ene photo kinetics was analysed using photo DSC studies, and the mechanical and thermal properties of the 3D-printed materials were also evaluated. The hydrolytic degradability of the 3D printed parts was showcased in 1 M NaOH solution. Overall, this research presents a promising avenue for the development of new biobased materials that can address the issue of nondegradable acrylate-based 3D print waste. The fast degradability of PAEL-based polymeric thiol-ene 3D print materials has the potential to significantly impact rapid prototyping for mass production applications.

4.2 EXPERIMENTAL SECTION

4.2.1 Materials

Ethyl lactate, allyl bromide, isosorbide, 3-mercapto propionic acid, and 2-hydroxy ethyl acrylate (HEA) were purchased from Sigma Aldrich (India) and used without further purification. Acryloyl chloride, triethyl amine, azobisisobutyronitrile, lithium hydroxide, potassium carbonate, and p-toluene sulphonic acid were purchased from local dealers and used directly without further purification. Phenylbis(2,4,6-trimethyl benzoyl) phosphine oxide (TPO), Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT), Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), and 2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT) dye was purchased from TCI Chemical Pvt. Ltd and used as such. Tetrahydrofuran (THF), chloroform, methanol, isopropyl alcohol, dichloromethane, hexane, and sodium sulfate (anhydrous) were purchased locally. For gel permeation chromatography HPLC-grade THF was purchased from Merck Chemicals (India).

4.2.2 Measurements

^1H and ^{13}C NMR spectra were recorded using Bruker-AVENS 400 and 200 MHz spectrometers and chemical shifts were reported in ppm using CDCl_3 as a solvent with small amounts of Trimethylsilane (TMS) added as an internal standard. The molecular weight of small molecules was recorded on the HRMS (ESI) Thermo Scientific Q-Exactive, Accela 1250 pump. The Fourier transform (FT-IR) spectra were acquired using a BRUKER alpha-E spectrometer. The molecular weights of polymers were determined using size permeation chromatography (SEC) equipped with a Viscotek VE 3580 RI detector. The SEC was calibrated with polystyrene standard and THF (HPLC grade) solvent was used as eluent at a 1 ml/min flow rate. The viscosity of the formulated resins as a function of shear rate was determined using the Anton Paar Physica Modular Compact Rheometer (MCR) 301. The shear rate was performed from 1 to 1000 per second at 30 °C. The thermal stability of all 3D printed parts was analyzed using Thermal Gravimetric Analysis (TGA), TA discover, 550-second generation TGA instrument, at a temperature range of 50 °C to 900 °C under nitrogen atmosphere (25 mL/min), and the heating rate was 10 °C/min. The glass transition temperature (T_g) was determined using TA Discover 250, second generation differential scanning calorimeter under nitrogen atmosphere (50 ml/min) at a heating rate of 10 °C/min. The DSC was calibrated with indium standards before measurement. A photo-DSC experiment was performed using the same DSC instrument equipped with an optical UV light source Omni Cure series 2000.

4.2.3 Methods

A) Thiol-Ene Resin Formulation for 3D Printing

The thiol-ene resin formulations for 3D printing were prepared by mixing different weight percentages of the synthesized allyl PAEL polymer with pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT), and isosorbide bis(3-mercaptopropionate) to target a stoichiometric mixture of 1:1 thiol to alkene functionalities. The TPO photoinitiator weight percentage was examined from the photo DSC kinetic experiment. No organic solvent was added to the 3D printing resin formulation. Allyl PAEL polymer was mixed with TTT and poured into PETMP in cold conditions to avoid premature curing of thiol-ene. The resin was mixed well with a spatula. TPO was separately dissolved in TTT and mixed with the resin just before 3D printing. Considering that the photoinitiator is sensitive to visible light, the glass vial was completely wrapped with a layer of aluminum foil to prevent any pre-polymerization. All resin formulations were prepared following a similar procedure.

B) Photo-Differential Scanning Calorimetry (Photo-DSC)

The Photo-DSC experiments were conducted using a TA Discover 250 second-generation differential scanning calorimeter equipped with a photo calorimetric unit known as the Omni Cure series 2000. The irradiation to the sample chamber was provided by a 200 W high pressure mercury lamp emitting light in the 320-500 nm wavelength range via dual-quartz light guide with neutral density. For the measurement, a precise amount of 5 mg of the prepared resin formulation was carefully weighed and placed into the sample pan, which was then inserted into the DSC cell. The measurements were performed under a consistent flow of nitrogen gas at a rate of 50 ml/min. Before subjecting the sample pan to UV light irradiation, the sample was initially held under isothermal conditions for 2 minutes in a nitrogen atmosphere, with equilibration at 30 °C. Subsequently, the electronic UV light shutter was opened, allowing the sample to be exposed to UV light for a duration of 5 minutes. At the end of the irradiation period, the shutter automatically closed. The peaks in the resulting data were integrated to determine the curing enthalpy.

C) Viscosity Measurement

The viscosity of the resin formulations was determined through Rotational Parallel Plate measurements. The experiment was conducted using the Anton Paar Physica Modular Compact Rheometer (MCR) 301 having a cup and bob. The resin formulation, devoid of any photoinitiator, was carefully poured into the cup up to a specified mark level. Subsequently,

during the experiment the bob was inserted into the resin, and shear was applied by rotating it. The shear rate was systematically increased, ranging from 1 to 1000 per second, to measure the viscosity, which was expressed in units of Pascal-seconds (Pa·s). Throughout the experiment, the temperature of the resin was maintained at a constant 30 °C. The rheology of the resin formulation was measured with the same set of instrumentation. The angular frequency was constant at 1 rad/s and strain was varied from 0.1 to 10.

D) 3D Printing of Thiol-Ene Resin Formulations

Organic solvent-free resin formulations were utilized for DLP (Digital Light Processing) 3D printing using an anycubic photon ultra resin 3D printer. This DLP 3D printer is equipped with a 405 nm LED light source and features a resin bed with dimensions measuring 102.4 x 7.6 x 165 mm. The printing operation was carried out at room temperature. The intensity of the LED light source was precisely measured at 10 mW cm² using a UNO Genetic laser power meter. To initiate the printing process, the resin was carefully poured into the resin bed, filling it up to a designated level. Subsequently, the printing parameters were configured. Each printed layer had a thickness of 100 microns, and for the first 5 layers, the exposure time was set at 12 seconds. Afterwards, each subsequent layer had an exposure time of 5 seconds. Upon completion of the printing process, the printed part underwent a post-processing treatment. This involved washing the printed object with isopropyl alcohol in a resin washer for a duration of 3 minutes. Following the washing step, the printed part was placed in a UV chamber for post-curing, which lasted for 15 minutes.

E) Mechanical Test of 3D Printed Part

The tensile strength analysis of the 3D printed component was conducted using a Universal Testing Machine, specifically the Instron series 33R4204 model, equipped with a 1 KN capacity load cell. This evaluation was carried out at room temperature. For the tensile test, ASTM D638 type V specimens were 3D printed, and an average of five samples were tested to ensure accuracy and consistency in the results. Each sample had a gauge length of 10 mm, and the experiment was conducted at room temperature, employing a stretching rate of 5 mm per minute. Mechanical properties, including tensile strength, Young's modulus, elongation, and toughness, were determined at the point of sample breakage.

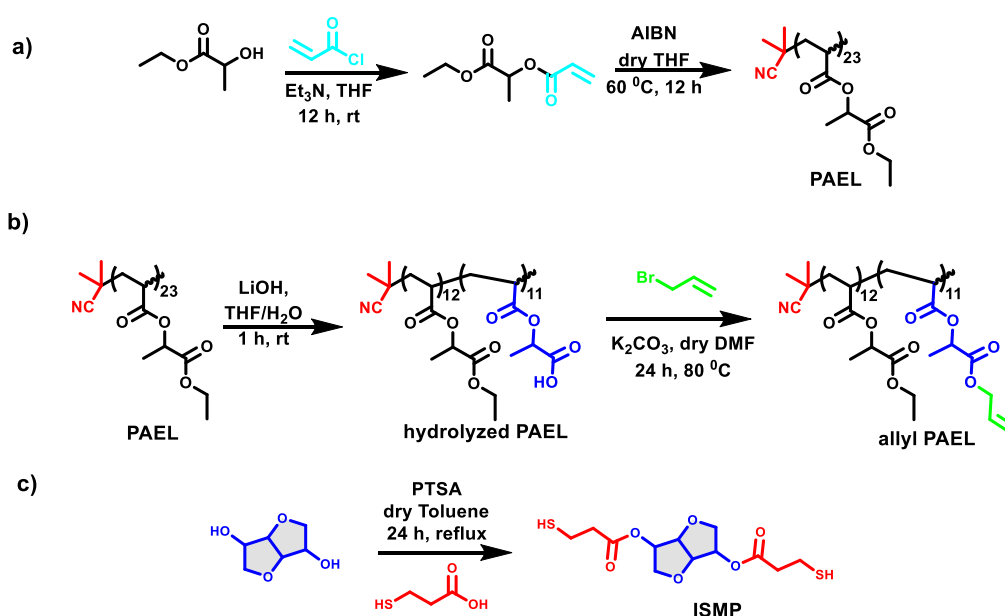
F) Hydrolytic Degradation of 3D Printed Parts

3D-printed dog-bone-shaped specimens were employed as test samples for hydrolytic degradation studies. The procedure began by recording the initial mass of these specimens

before placing them in 20 ml glass vials. Each specimen was then immersed in a 10 ml solution of 0.1 M NaOH to initiate the degradation test, with gentle shaking at 35 °C. Periodic evaluations involved removing the specimens, blotting them dry with tissue paper, and drying them in a vacuum oven at 40–50 °C until constant weight, to record mass loss due to hydrolysis. Subsequently, the dried specimens were re-immersed in the original degradation solution to continue the hydrolysis process. This comprehensive experimental protocol allowed for the continuous monitoring and assessment of the hydrolytic degradation effects on the 3D printed specimens over time. Similarly, a hydrolytic degradation experiment was performed in 0.1 M HCL solution.

4.2.4 Synthesis and Characterization

The low molecular weight allyl functionalized poly(acrylate ethyl lactate) (PAEL) was synthesized from acrylate ethyl lactate monomer by free radical polymerization. The Isosorbide bis-(3mercapto) propionate (ISMP) was prepared according to the literature.⁴¹ The overall scheme of the monomer, polymer, and post modification of the polymer is depicted in the scheme 4.1. The details of synthesis and characterization of the monomers are provided in the section 1 and the synthesis and characterization of polymer and its modifications are provided in the section 2. The molecular weight (M_n and M_w) and the polydispersity index ($\mathcal{D}$) of the PAEL and allyl PAEL polymer were confirmed from the SEC analysis and the values are tabulated in the Table 4.1.



Scheme 4.1 Overall representation of synthesis of PAEL, partially hydrolysed PAEL, allyl PAEL and ISMP

1) Synthesis of the AEL and ISMP

a) Synthesis of Acrylate Ethyl Lactate (AEL) Monomer

Ethyl lactate (15 g, 127 mmol) and triethyl amine (25.7 g, 253 mmol) were taken in a 250 ml two-necked round-bottomed flask containing a magnetic stir bar. 150 ml of dry tetrahydrofuran (THF) was transferred into the flask by syringe under nitrogen atmosphere and acryloyl chloride (18.3 g, 203 mmol) was added slowly at ice-cold conditions during 30 minutes time period. The reaction was run for 12 h at room temperature. After the completion of the reaction, the precipitate was filtered and THF was evaporated. The product was dissolved in ethyl acetate and washed with brine solution three times followed by washing with NaHCO₃ solution three times. The solution was dried over anhydrous sodium sulfate and ethyl acetate was removed by rotary-evaporator. A light-coloured liquid was formed. Yield: 90%.

¹H NMR spectrum (400MHz, CDCl₃) δ in ppm: 6.42-6.51 (dd, 1H), 6.09-6.23 (dd, 1H), 5.85-5.90 (dd, 1H), 5.10 (q, 1H), 4.17 (q, 1H), 1.49 (d, 1H), 1.23 (d, 1H).

¹³C NMR spectrum (100 MHz, CDCl₃) δ in ppm: 169.72, 164.44, 130.80, 126.70, 67.79, 60.39, 15.94, and 13.06. HR-MS mass m/z- C₈H₁₂O₄ Na=195.

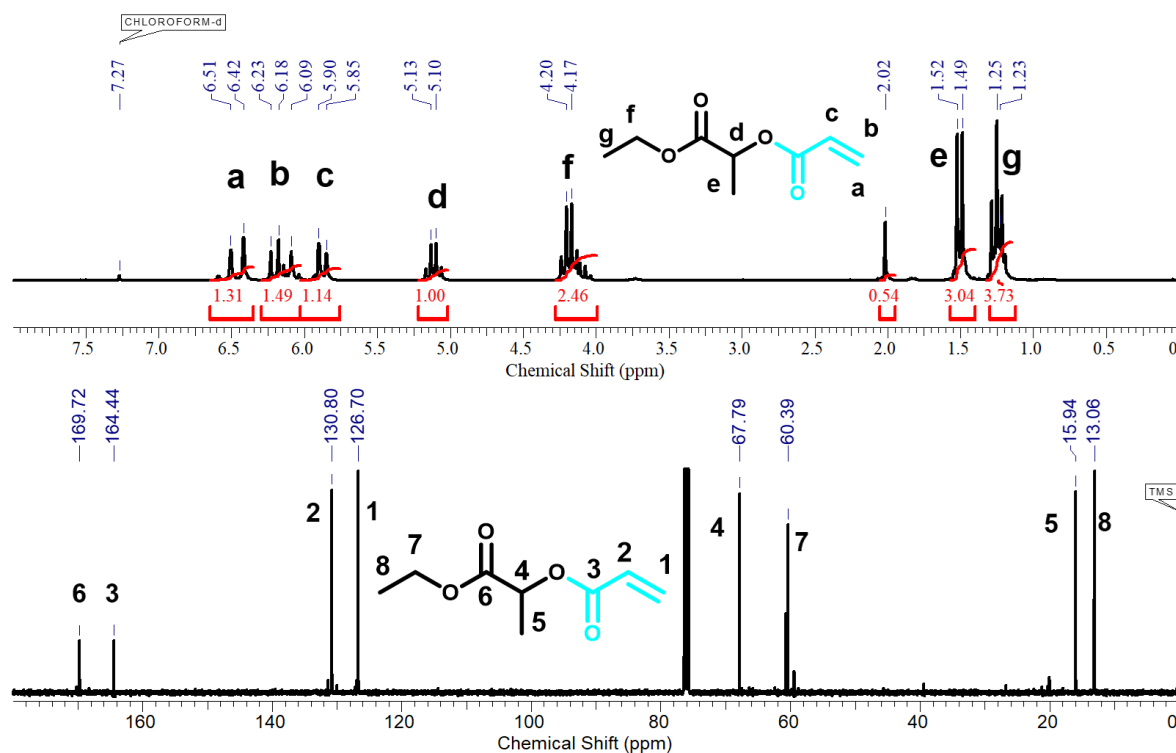


Figure 4.1 ¹H and ¹³C spectra of the acrylate ethyl lactate in CDCl₃

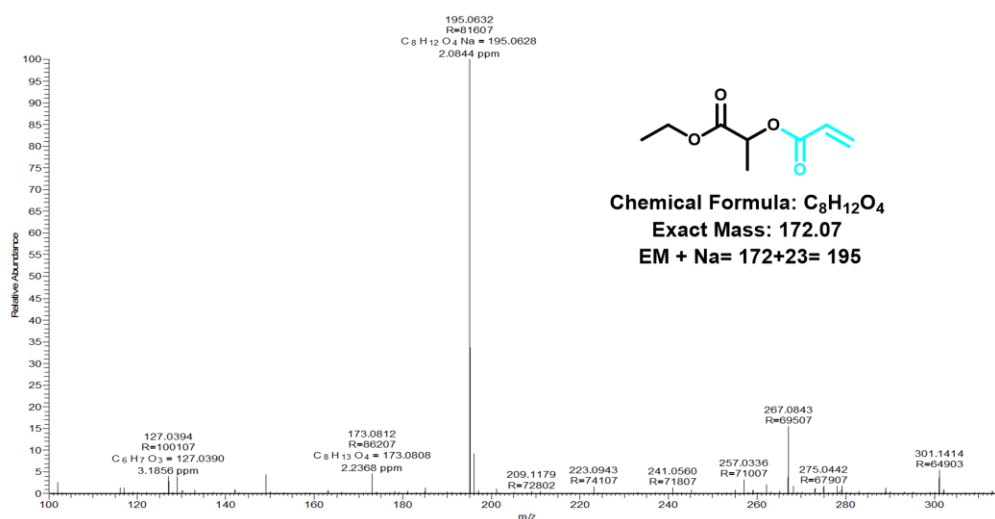


Figure 4.2 HR-MS spectrum of the acrylate ethyl lactate

b) Synthesis of isosorbide bis(3-mercapto) propionate

20 g, (137 mmol) of isosorbide was taken in a two-necked 100 ml round-bottomed flask equipped with a Dean-Stark apparatus, and 100 ml of dry toluene was transferred with a syringe under nitrogen atmosphere. A catalytic amount (0.06 mol %) of p-toluene sulfonic acid was added followed by dropwise addition of 3-mercaptopropionic acid (30.5 g, 287 mmol). The reaction flask was dipped in an oil bath at 130 °C and refluxed for 24 h. The byproduct of the esterification reaction was collected on the Dean-Stark apparatus and removed during the reaction. For workup, the reaction was allowed to cool down to room temperature. The reaction mixture was washed with brine solution several times and three times with $NaHCO_3$ solution. The solution was dried over anhydrous sodium sulphate and the solvent was removed. The product was obtained as a pale-yellow coloured oil. Yield 95 %.

1H NMR spectrum (400MHz, $CDCl_3$) δ in ppm: 5.15-5.24 (m, 2H), 4.84-4.89 (m, 2H), 3.80-3.99 (m, 2H), 2.63-2.88 (m, 8H), 1.59-1.77 (m, 2H)

^{13}C NMR spectrum (100 MHz, $CDCl_3$) δ in ppm: 170.82, 85.76, 80.58, 70.31, 38.06, 19.53.
 HR-MS mass m/z- $C_{12}H_{18}O_6S_2Na$ =345

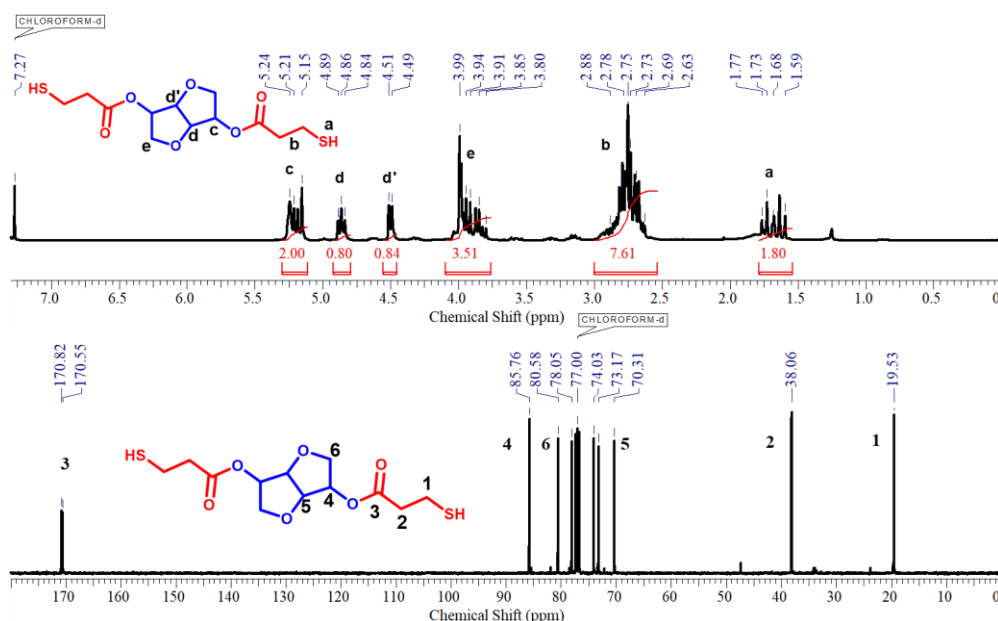


Figure 4.3 ¹H and ¹³C NMR spectra of isosorbide bis(3-mercapto) propionate recorded in CDCl₃

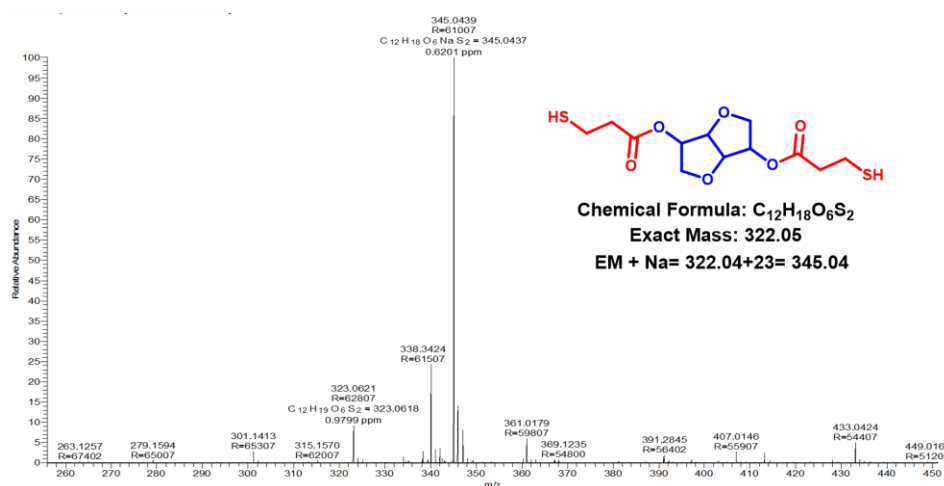


Figure 4.4 HR-MS spectrum of isosorbide bis(3-mercapto) propionate

2) Synthesis of the PAEL, partially hydrolysed PAEL, allyl PAEL polymers

c) Polymerization of Acrylate Ethyl Lactate Monomer

Acrylate ethyl lactate (10g, 58 mmol) and Azobisisobutyronitrile (190 mg, 1.16 mmol) were taken in a one-necked 50 ml round-bottom flask containing a magnetic stir bar. 15 ml of dry THF was transferred into the flask by syringe under nitrogen atmosphere. The flask was immersed in a pre-heated oil bath at 70 °C and continued stirring for 12 h. After polymerization, the reaction was cooled down to room temperature, and the polymer was precipitated into ice-cold pet ether. This process was repeated 2-3 times. The polymer was dried in a vacuum oven at 45 °C for 12 h. Yield 98 %.

^1H NMR spectrum (400MHz, CDCl_3) δ in ppm: 5.01 (q, 1H), 4.16 (q, 2H), 2.59 (m, 1H), 1.82-2.05 (m, 2H), 1.45 (d, 3H), 1.25 (d, 3H).

^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 174.11, 170.56, 68.85, 61.19, 40.91, 33.20, 31.56, 20.38, 16.76, 14.08.

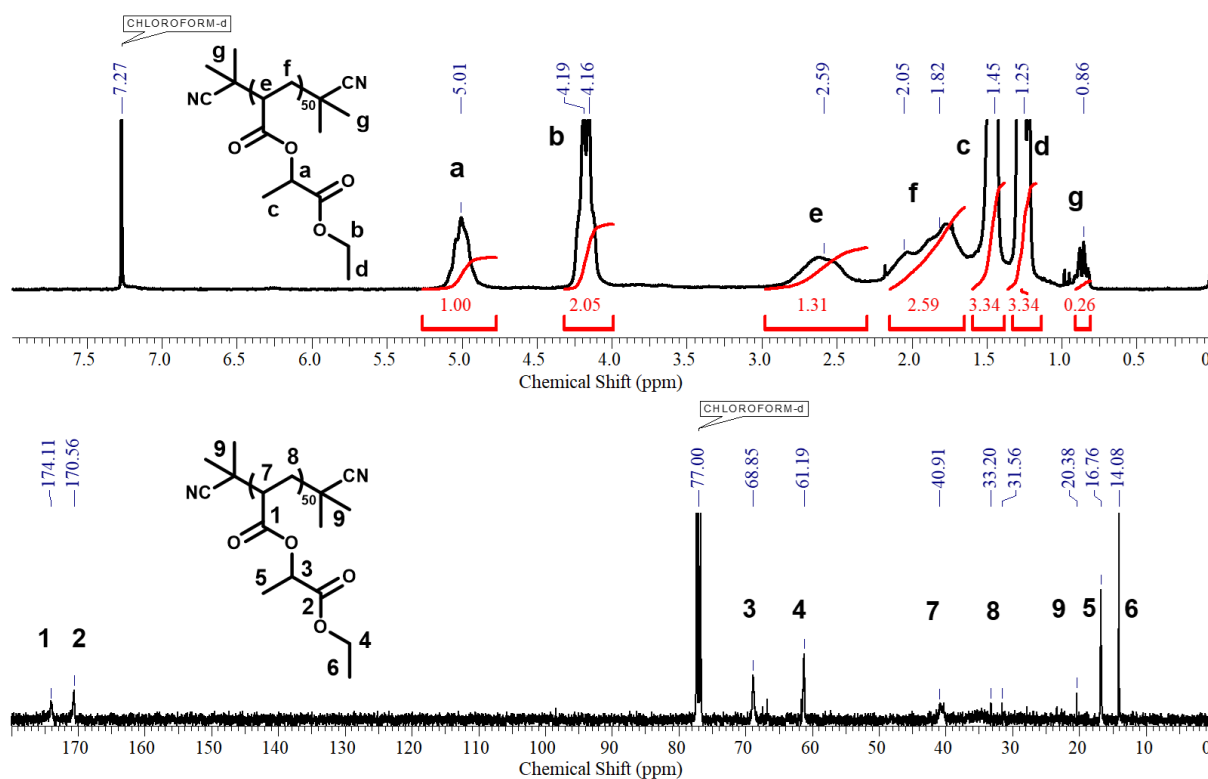


Figure 4.4 ^1H and ^{13}C spectra of poly (acrylate ethyl lactate) recorded in CDCl_3

d) Partial hydrolysis of poly (acrylate ethyl lactate)

Poly(acrylate ethyl lactate) was partially hydrolysed with lithium hydroxide (LiOH). Poly(acrylate ethyl lactate) (5 g, 29 mmol) was taken in a one-necked 100 ml round-bottomed flask and dissolved in 50 ml of THF. LiOH (696 mg, 29 mmol) was dissolved in 5 ml de-ionized water and then added to the reaction mixture. The reaction was stirred at room temperature for 1 h. After that, the THF was removed and the polymer was dissolved in 100 ml methanol. The polymer solution was neutralized with 1 M HCl solution and the partially hydrolysed polymer was collected in ethyl acetate. The polymer solution was further washed with brine solution three times and dried over anhydrous sodium sulfate. The ethyl acetate was removed by rotary-evaporator and a viscous hydrolysed polymer was obtained which was further dried in a vacuum oven at 50 $^{\circ}\text{C}$ for overnight. Yield 90 %.

^1H NMR spectrum (400MHz, CDCl_3) δ in ppm: 4.85-4.92 (m, 1H), 4.10 (m, 1H), 2.16-2.66 (m, 1H), 1.63-1.91 (m, 2H), 1.39 (d, 3H), and 1.11-1.24 (t, 1.5H)

^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 172.28, 170.34, 68.82, 61.10, 21.28, 16.70, 14.10.

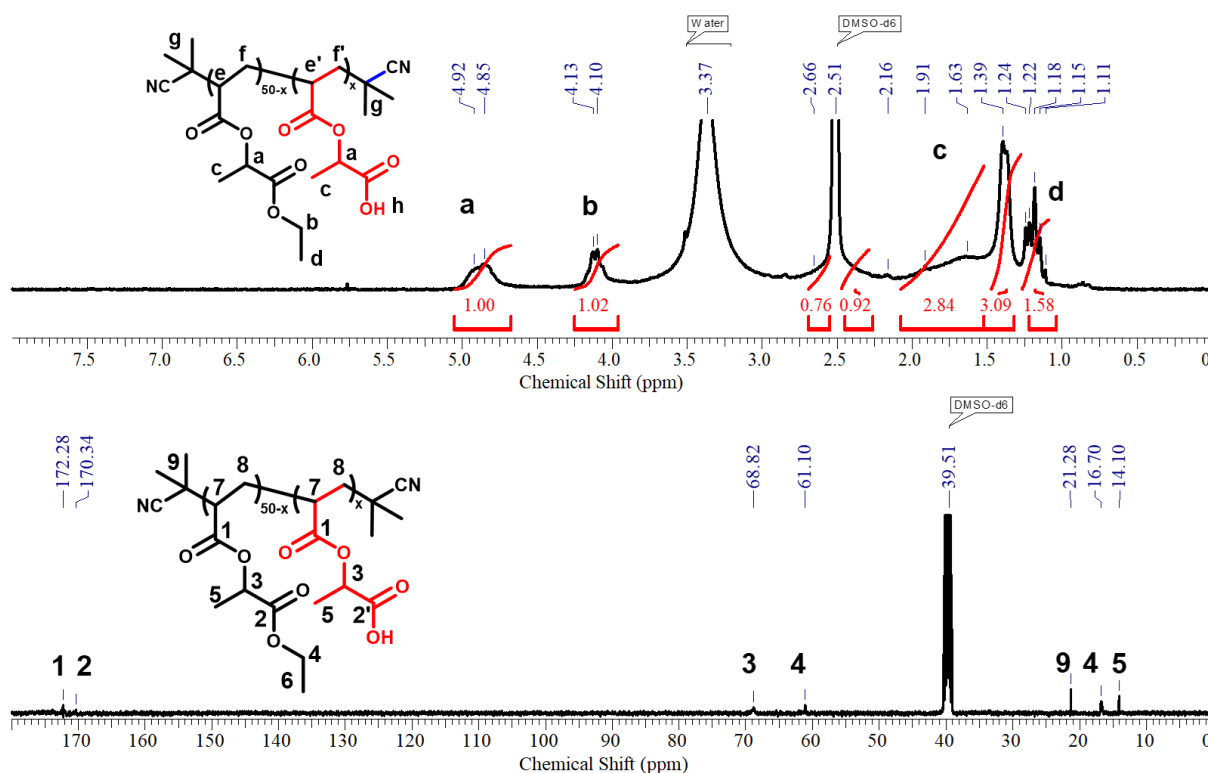


Figure 4.6 ^1H and ^{13}C spectra of hydrolysed poly(acrylate ethyl lactate) in DMSO-d_6

e) Allylation of hydrolysed poly (acrylate ethyl Lactate)

Partially hydrolysed poly (acrylate ethyl lactate) (5 g, 35 mmol) was taken in a two-necked 100 ml round-bottomed flask and 50 ml of dry DMF was transferred into the flask by syringe under nitrogen atmosphere. K_2CO_3 (5.3 g, 38 mmol) was added to the solution and stirred for 30 min at room temperature. Allyl bromide (4.2 g, 35 mmol) was added to the reaction dropwise with constant stirring. The reaction flask was immersed in a pre-heated oil bath at 80°C for 24 h. After the completion of the reaction, the RB was cooled down to room temperature and 80 ml of water was added and stirred for 15 minutes. After that, the reaction mixture was taken in a 1 L separating funnel and the final product was extracted with 400 ml of ethyl acetate by washing with ice-cold brine solution three times. The solution was dried over anhydrous sodium sulfate following which the solvent ethyl acetate was removed. The final polymer was dried in a vacuum oven at 40°C overnight. Yield 85 %.

^1H NMR spectrum (400MHz, CDCl_3) δ in ppm: 5.90 (m, 1H), 5.22-5.34 (m, 1H), 5.02 (m, 1H), 4.55-4.62 (m, 2H), 4.18 (q, 2H), 2.51-2.59 (m, 1H), 1.77 (m, 2H), 1.48 (d, 3H), and 1.26 (t, 1.5 H)

^{13}C NMR spectrum (100 MHz, CDCl_3) δ in ppm: 172.47, 162.78, 132.44, 118.57, 69.19, 61.27, 36.24, 31.23, 21.51, 16.93, 14.30

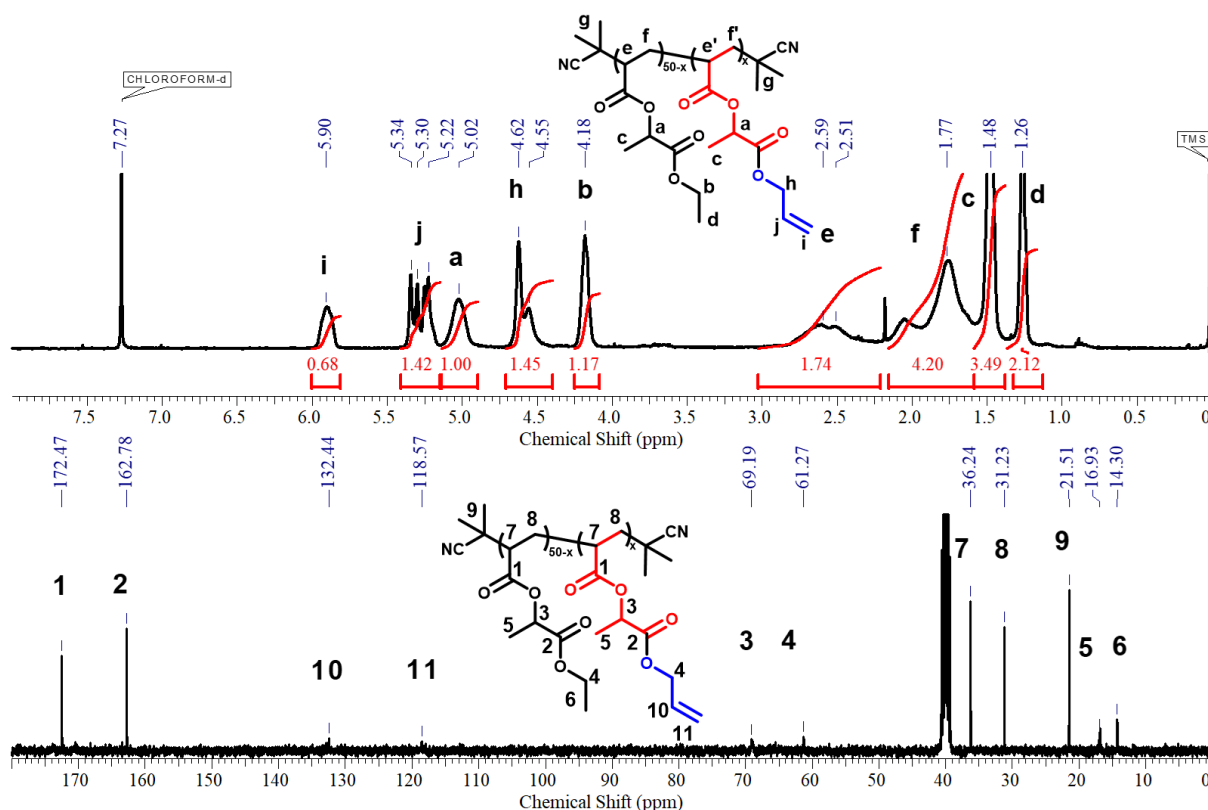


Figure 4.7 ^1H and ^{13}C spectra of allyl poly (acrylate ethyl lactate) recorded in CDCl_3

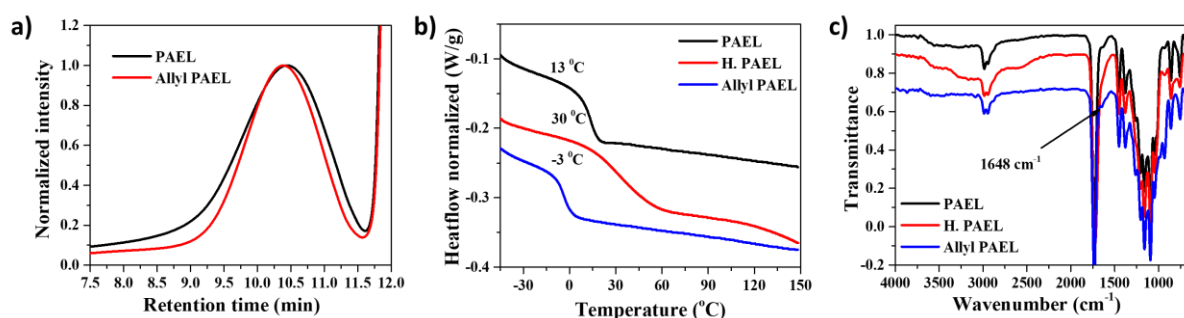


Figure 4.8 a) SEC plot of PAEL and allyl PAEL polymers in THF as eluent and polystyrene (PS) as standard b) FT-IR spectra of PAEL, hydrolyzed PAEL, and allyl PAEL polymer c) DSC thermogram of the PAEL, hydrolyzed PAEL, and allyl PAEL polymers.

Polymers	Mn NMR (gmol^{-1})	Mn ^a GPC (gmol^{-1})	Mw ^a (gmol^{-1})	$\bar{D}^a$ (Mw/Mn)
PAEL	7900	6600	20000	3.11
Allyl PAEL	8100	5600	15000	2.68

Table 4.1 The molecular weight of the PAEL and allyl PAEL polymer calculated from ^1H NMR and SEC analysis.

4.3 RESULT AND DISCUSSION

4.3.1 Synthesis of PAEL, hydrolysed of PAEL, allyl PAEL and ISMP

Acrylate ethyl lactate (AEL) was synthesized according to the literature report as shown in scheme 4.1a using THF as solvent⁴⁰. This reaction could be done on a large scale (30 g) and the resultant AEL monomer could be obtained in high yields (90- 95 %). Briefly, the ethyl lactate was reacted with acryloyl chloride to produce acrylate ethyl lactate at room temperature within 12 h which was purified by simply washing with brine solution several times with no requirement for chromatographic purification. The chemical structure of the synthesized AEL monomer was confirmed by ^1H NMR spectroscopy with the appearance of new peaks from 5.85 to 6.51 ppm corresponding to an acrylate carbon double bond which was also confirmed by the appearance of two peaks in the ^{13}C NMR spectrum at 126 ppm and 130 ppm. HRMS mass data also confirmed the formation of the product. Studies in the literature have explored the polymerization of the AEL monomer, systematically investigating initiator and solvent selection.⁴⁰ In our report, we present a simplified method for synthesizing PAEL polymer. A free radical polymerization approach was employed, utilizing AIBN as the initiator and dry THF as the chosen solvent. A constant monomer-to-initiator ratio was maintained targeting 25 repeat units, and the solvent quantity was maintained at 1.5 times the volume of the monomer. The polymerization reaction was conducted at a temperature of 60 °C for a duration of 12 hours. The structural characterization of the polymer was performed using ^1H NMR spectroscopy and the molecular weight was determined by size exclusion chromatography (SEC). The disappearance of the acrylate peaks of AEL monomer and the formation of two new broad peaks in the 1.82 ppm to 2.59 ppm region corresponding to the methylene protons ($-\text{CHCH}_2$) (*labelled as 'a'*) and methine protons ($-\text{CHCH}_2$) (*labelled as 'b'*) of PAEL polymer repeat units provided structural confirmation for the formation of the polymer. The analysis of ^{13}C NMR spectrum also confirmed the complete conversion by the disappearance of the acrylate carbon double bond at 126 ppm and 130 ppm. The degree of polymerization (X_n) was determined from the ^1H NMR spectra. The integration value of the terminal methyl group of AIBN was utilized to determine the degree of polymerization. The peak at 5.01 ppm corresponds to methine proton ($-\text{C}(\text{OO})\text{CHCH}_3$) (*labelled as 'c'*) of the PAEL polymer repeat unit and the peak at 0.86 ppm corresponds to the terminal AIBN methyl group (*labelled as 'g'*). The calculated integration values of these two peaks revealed a total number of 23 repeat units, which was close to the targeted number of 25 repeat units. The SEC plots of the polymers performed using THF as

eluent are given in Figure 4.8a, which exhibited a monomodal distribution with a polydispersity index (PDI) value of 3.1. The terminal ethyl ester group of the PAEL polymer was hydrolysed with LiOH by base hydrolysis to form a carboxylic functional group in the repeat unit which was further reacted with allyl bromide to introduce the allyl group, as detailed in Scheme 4.1b. The kinetics of the hydrolysis reaction were monitored by NMR spectroscopy using aliquots retrieved at various time intervals. 0.5 equivalents of LiOH were taken with respect to one repeat unit of PAEL polymer for the hydrolysis reaction.

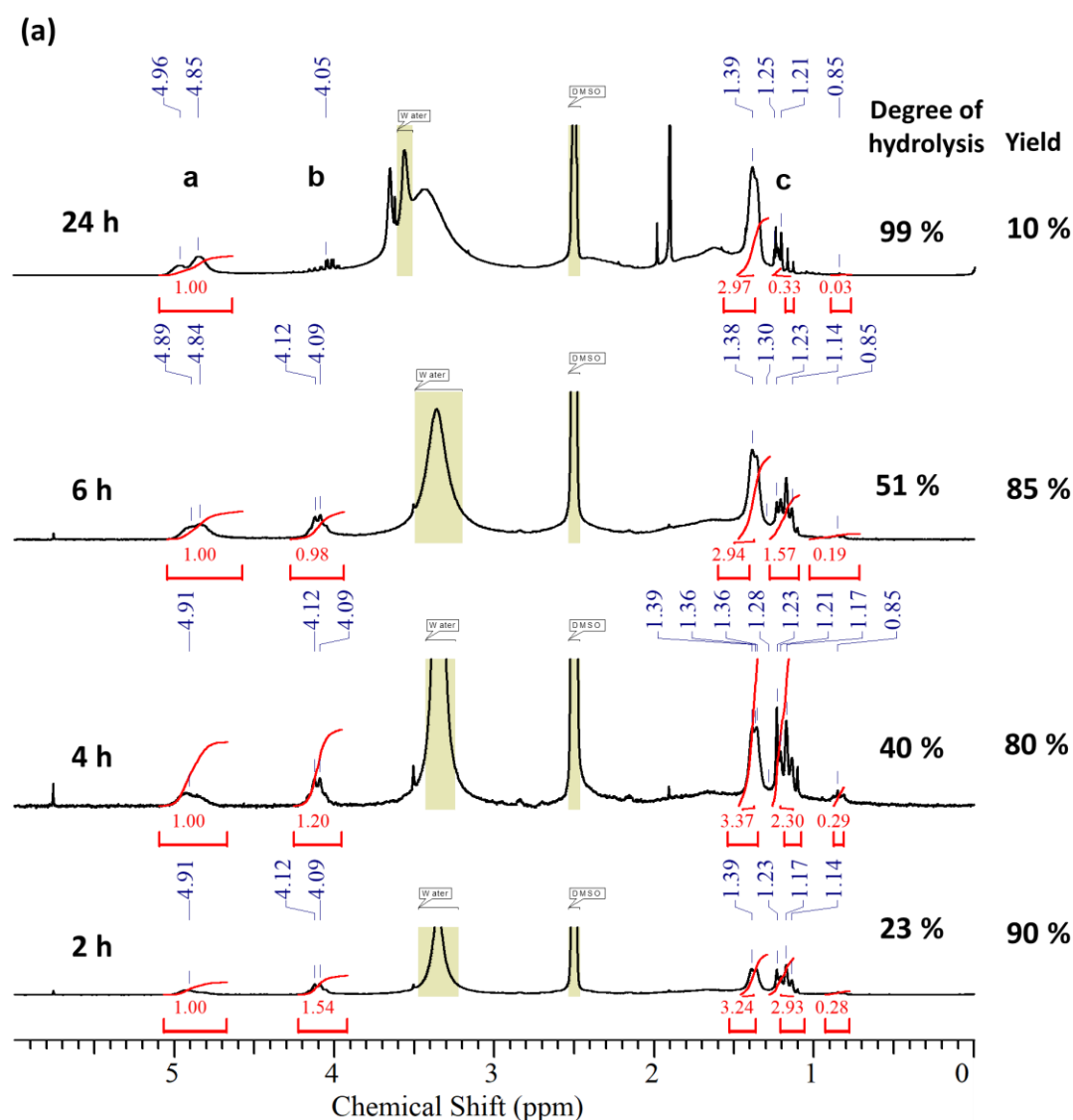


Figure 4.9 Hydrolysis kinetics study of PAEL polymer in 0.5 equivalent of LiOH in different time and the ^1H spectra were recorded in the $\text{DMSO-}d_6$.

The aliquots were collected every two hours and NMR spectra were recorded after purifying the hydrolysed PAEL polymer. The ^1H NMR spectra (recorded in $\text{DMSO-}d_6$) of the hydrolysed PAEL polymers for various time intervals are depicted in figure 4.9. The degree of hydrolysis

was assessed by tracking the decrease in peak areas corresponding to methine proton (labelled as 'e') and methylene proton (labelled as 'f') within the hydrolysed PAEL polymer. It was noted that the degree of hydrolysis of the PAEL polymer increased as the duration of time elapsed. During the initial 6 hours, approximately 50% of the ester groups in the PAEL polymer underwent hydrolysis. After 24 hours, the degree of hydrolysis reached nearly 99%, but the reaction yields significantly declined due to the dissolution of the hydrolysed PAEL polymer in water during the workup process. In order to expedite the hydrolysis reaction of the PAEL polymer, the amount of LiOH was increased to one equivalent with respect to one repeat unit of PAEL, and the reaction time could be shortened to just one hour. Subsequently, analysis of the NMR spectra revealed that approximately 50% of the polymer had undergone hydrolysis within this one-hour timeframe, with a remarkable 90% yield. These revised reaction conditions were deemed optimal for our study.

In the final step of the allyl PAEL polymer synthesis, the 50% hydrolysed PAEL polymer was reacted with allyl bromide in dry DMF for 24 hours, maintaining a temperature of 80 °C (Scheme 4.1b). The confirmation of the successful formation of the allyl PAEL polymer was achieved through the analysis of ^1H and ^{13}C NMR spectra recorded in CDCl_3 . The ^1H NMR spectrum exhibited distinctive peaks at chemical shifts of 5.90 ppm, as well as a cluster of peaks ranging from 5.30 to 5.34 ppm, which were attributed to allyl protons ($-\text{CH}_2\text{C}_2\text{H}_3$) (labelled as 'i,' 'j,'). Additionally, new peaks emerged in the ^1H NMR spectrum at 4.55-4.62 ppm, which corresponded to methylene protons ($-\text{C}(\text{O})\text{O}-\text{CH}_2\text{C}_2\text{H}_3$) of the terminal group, (labelled as 'h'). Similarly, the ^{13}C NMR spectrum analysis showed the appearance of new peaks at chemical shifts of 118 ppm and 132 ppm, which were indicative of the allyl carbon double bond in the resulting polymer. The allyl protons were integrated with respect to the methine proton ($-\text{C}(\text{O})\text{OCHCH}_3$) (labelled as 'c'). As only 50 % of the total repeat unit of PAEL polymer was available in the hydrolysed PAEL for the allylation, the ratio of the integration of allyl proton to the methine proton intensity was half. The disappearance of the hydroxyl peaks as well as matching of the integration values of allyl protons with respect to the methine proton indicated the full conversion of the carboxyl group into the allyl group. Figure 4.8b compares the FT-IR spectra of the polymers before and after modification. The appearance of the peak at 1648 cm^{-1} corresponding to the carbon-carbon double bond in allyl PAEL also confirms the functional group conversion.

The thiol cross linker Isosorbide bis-(3-mercapto) propionate (ISMP) was synthesized according to literature procedure.⁴¹ Isosorbide was reacted with 3-mercapto propionic acid in the presence of p-toluene sulfonic acid as catalyst (Scheme 4.1c). The structure of ISMP was

confirmed by the ^1H , ^{13}C NMR, and HRMS spectra (figure 4.3 and figure 4.4). Differential scanning calorimetry (DSC) analysis (Figure 4.8c) was employed to investigate the thermal characteristics of the polymers. The glass transition temperature (T_g) of polymer PAEL was observed at 13 °C. After undergoing hydrolysis, the T_g increased to 30 °C, attributed to the presence of hydrogen bonding within the hydrolysed acid groups. Upon functional group modification to allyl group, the polymer allyl PAEL exhibited a lower T_g (-3 °C). The lower T_g value of allyl PAEL indicated its soft consistency at room temperature. The Table 4.1 summarizes the molecular weight of the polymer before and after allyl modification.

4.3.2 Resin Formulation and Photo Calorimetric Studies

After the structural characterization of the ene containing polymer- allyl PAEL and thiol cross linker- ISMP, these were used for the formulation of a photo curable resin with Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT). Four resin formulations (F1-F4) were prepared using different weight percentages of allyl PAEL, TTT, PETMP, and ISMP avoiding the use of any non-reactive organic solvent. Figure 4a shows the schematic representation of the preparation of resin formulation. The weight percentages of resin formulations are listed in the table in Figure 4b.

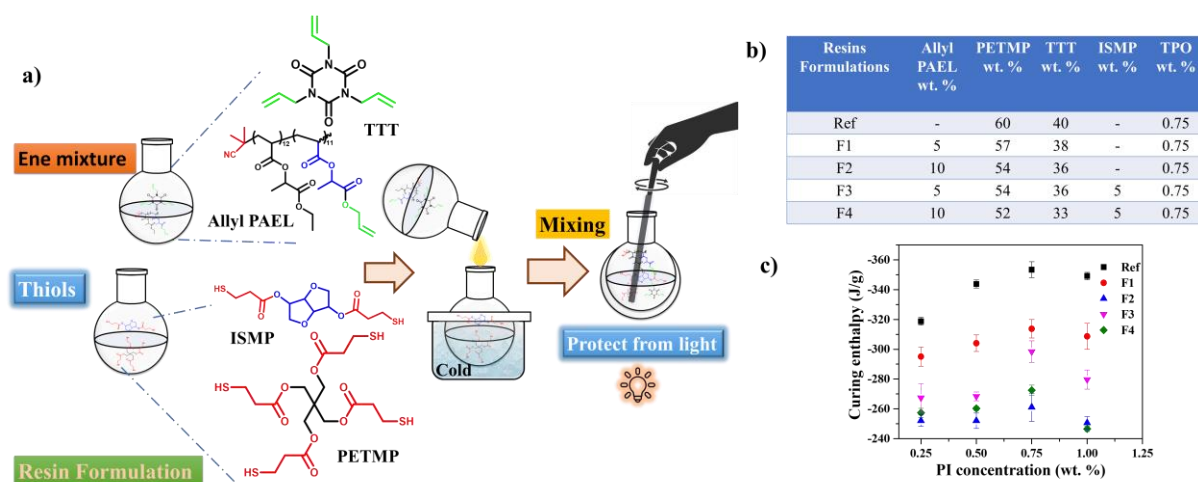


Figure 4.10 (a) Schematic representation of resin formulation of allyl PAEL, TTT, PETMP, and ISMP. (b) Weight percentages of PAEL, TTT, PETMP, and ISMP taken to prepare resin formulations. (c) Optimized curing enthalpies of resin formulations.

The first entry in the table is the reference formulation (Ref) which consists of a stoichiometric blend of the commercial thiol and ene small molecules PETMP and TTT, excluding the synthesized polymer allyl PAEL. This resin serves as a reference material for evaluating the rheological, mechanical, and degradation properties of other resin formulations. The curing kinetics and the specific weight percentage of photoinitiator required for curing the resin

formulations were obtained from photo DSC analysis. Upon reviewing the existing literature, it was found that the kinetics of free radical network polymerization of thiol-ene click chemistry is influenced by the specific structures of the alkenes and thiol. The chemical reactions involving alkane thiols and terminal alkenes, resulting in the formation of linear thioethers, were found to be exothermic with an approximate heat change (ΔH) of around -19 kcal/mol.²⁰ The mechanism governing the radical-initiated thiol-ene formation can be described as a step-growth pathway, which can be divided into two distinct steps following the initial formation of the thiyl radical through its reaction with the photoinitiator. The thiyl radical then reacts with the alkene, leading to the creation of a stable carbon-centered radical intermediate. Subsequently, this intermediate undergoes chain transfer to another thiol molecule. The curing enthalpies of the resin formulations were examined by altering the weight percentage of the TPO photoinitiator within the range of 0.25 to 1.0 wt. % of the total weight of a specific resin formulation (Figure 4c). The photo DSC plots and table listing the curing enthalpies of all formulations as a function of varying photoinitiator concentrations are given in Figure 4.11 and Table 4.2.

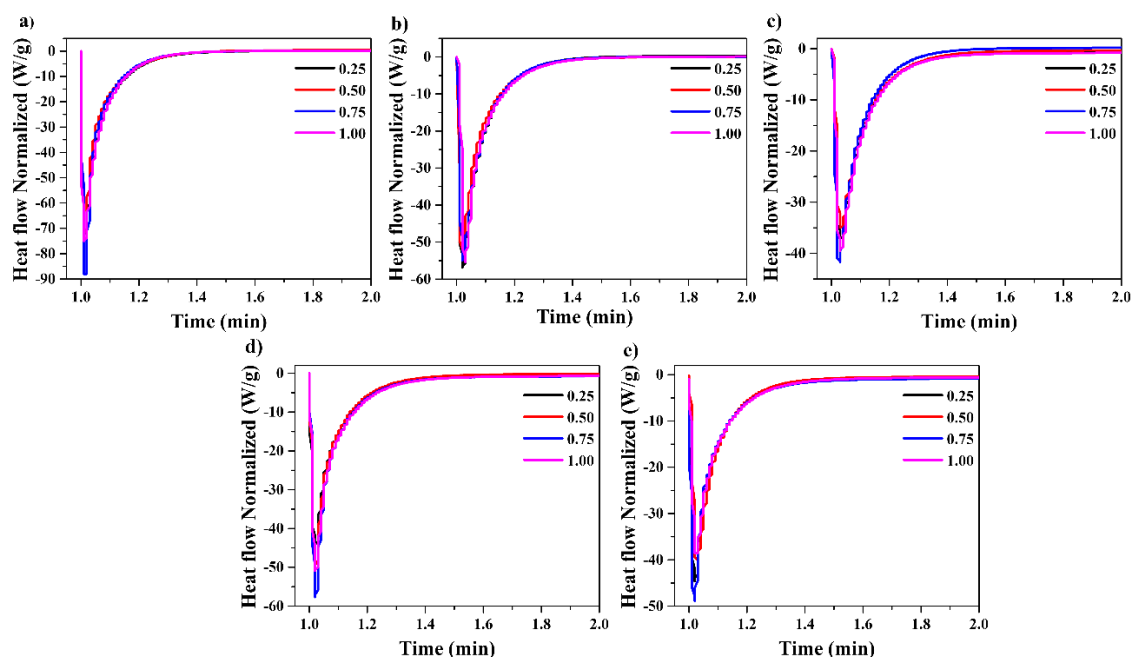


Figure 4.11 PhotoDSC spectra of (a) Reference, (b) F1, (c) F2, (D) F3, (E) F4 in different weight percentages ranging from 0.25 to 1.0 wt. % of TPO photoinitiator.

Resin formulations	Curing enthalpies (J/g) with different TPO Photo initiator wt. %			
	0.25	0.5	0.75	1.0
Ref	343±6	318±7	353±5	349±3
F1	304±6	295±5	313±5	308±8
F2	252±3	256±5	261±9	250±4
F3	267±9	268±2	298±7	279±6
F4	257±3	260±2	272±4	246±2

Table 4.2 Curing Enthalpies of each resin formulation

The rate of thiol-ene network polymerization was increased (indicated by the larger heat flow peaks) when the concentration of TPO was increased. For all formulations, the curing enthalpies increased with increasing photoinitiator concentration from 0.25 wt. % to 0.75 wt. %, though reduction was observed in the curing enthalpy for 1 wt. % photoinitiator concentration. This phenomenon could be attributed to either the self-absorption of UV light by the photoinitiator or the possibility of network polymerization being quenched due to the recombination of radicals (such as thiyl or carbon-centered radicals) resulting in dead-polymerization beyond the optimized concentration of photoinitiator.⁴² Further, the thiol-ene network formation was followed using FTIR spectroscopy (shown in figure 4.12) as a function of varying exposure time.

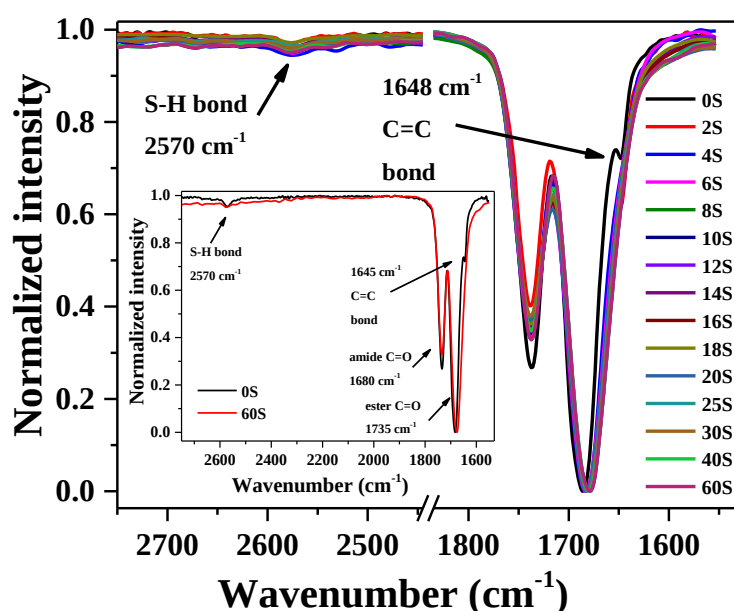


Figure 4.12 FT-IR analysis of thiol-ene network conversion of F2 resin with different exposure times. Inset showed the FT-IR spectra of before the UV exposure (0S) and after 60 S exposure.

Formulation F2 was subjected to this FTIR analysis, by tracing the disappearance of the carbon-carbon double bond peak at 1648 cm^{-1} (for TTT and allyl PAEL) and sulfur hydrogen bond at 2570 cm^{-1} present in PETMP. The disappearance of these peaks upon irradiation also gave additional support for the thiol-ene network formation.

4.3.3 Rheology and Viscosity of Prepared Resin Formulations

The stability of thiol-ene resin formulations poses a significant challenge due to the rapid reactivity of the thiol reaction.⁴³ As a result, the viscosity of the thiol-ene resin formulations increased with time even at ambient temperature.⁴⁴ In our study, we conducted measurements of viscosity and rheology for the thiol-ene resin formulation at a temperature of $30\text{ }^{\circ}\text{C}$, with a focus on assessing its suitability for room-temperature Digital Light Processing (DLP) 3D printing. To achieve optimal results, including smooth, high-resolution, and pristine printed objects, it is essential that the resin's viscosity remains below $10\text{ Pa}\cdot\text{s}$.⁴⁵ The viscosity of the resin formulations was measured using cup and bob set up and the viscosity was observed between $0.23\text{ Pa}\cdot\text{s}$ and $0.61\text{ Pa}\cdot\text{s}$, (Figure 4.13a and Table 4.3). As seen from the Figure 4.13b, no significant change was observed with higher shear rates, indicating its Newtonian fluid-like behaviour. However, when the weight percentage of PAEL polymer increased from 5 wt. % to 10 wt. %, the viscosity of the resins also increased. To prevent the thiol-ene mixture from curing prematurely and leading to an undesirable increase in viscosity, which could pose difficulties in DLP 3D printing, we combined the thiols and enes immediately just before commencing the 3D printing process. The rheology of the resin formulations was examined to prove the liquid-like behavior. The higher values of loss modulus (G'') compared to storage modulus (G') indicated the stability of the liquid form of resin formulations (Figure 4 13c).

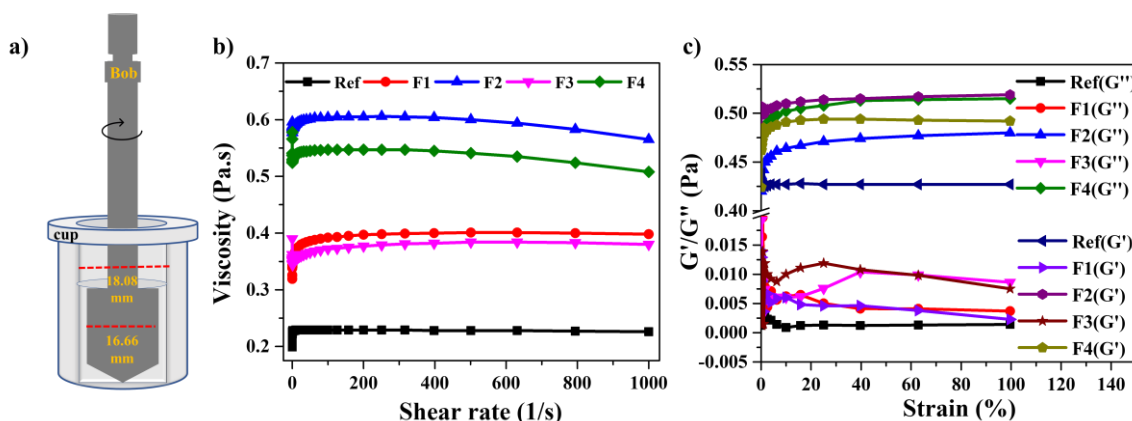


Figure 4.13 (a) Schematic representation of Cup and Bob for viscosity and rheology measurement (b) Measurement of viscosity of resin formulations (c) Storage modulus (G') and loss modulus (G'') of resin formulations.

Table 4.3 Viscosity, mechanical properties, and thermal properties of resin formulations.

Resin formulations	Viscosity ^a (Pa.s)	Tensile strength MPa	Elongation %	Young's modulus GPa	T _g ^b (°C)	T _{d10%} (°C)
Ref	0.23	11.0±2.8	11±1.5	0.9±0.02	58	372
F1	0.38	28.1±3.1	3±1.6	1.8±0.03	54	375
F2	0.61	21.4±1.1	8±1.6	1.1±0.02	44	364
F3	0.40	25.0±4.2	6±1.5	1.4±0.04	51	366
F4	0.55	19.1±2.2	10±1.0	1.0±0.01	47	355

a) viscosity of resin formulation at 30 °C b) T_g of printed parts from DSC.

4.3.4 3D Printing of Thiol-Ene Resins

The thiol–ene photo polymerization is quite attractive for 3D printing due to its low shrinkage derived from the step-growth mechanism. Spot cure studies were carried out to get the estimate of the time required for the curing of the resin formulation. Spot curing of the resin formulation was executed on a glass plate to ensure that the resins achieved complete curing within a rapid timeframe of 4-8 seconds. The printability of allyl PAEL thiol-ene resin formulation was demonstrated with a DLP 3D printer (schematically depicted in Figure 4.14a) to explore the creation of intricate 3D printed objects that exhibited controlled degradation for sustainable end-of-life. All prepared resin formulations were used to demonstrate the 3D printing. The images of the 3D-printed parts are shown in Figure 4.14b and 4.14d. The 3D printed component depicted in Figure 4.14d (bottom) corresponds to a conventional Amara Labs Town CAD file employed for calibrating DLP 3D printers and testing resin formulations. The successful printing of this standardized CAD file serves as validation for the printing capabilities of the thiol-ene resins. Additional images from various angles of viewing can be found in Figure 4.15. Figure 4.14e shows a 3D-printed highly porous complex structure that once again proves the fidelity of thiol-ene resin printability. For 3D printing using the anycubic DLP 3D printer, the exposure time of the bottom layer was intentionally set slightly higher at 12 sec to secure the attachment of the cured layer to the aluminum build platform, thereafter subsequent layers were printed at 5s exposure. To improve the resolution of the 3D-printed part 0.03 wt. % of (2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene) (BBOT) a fluorescent dye was mixed with the thiol-ene resin formulation.

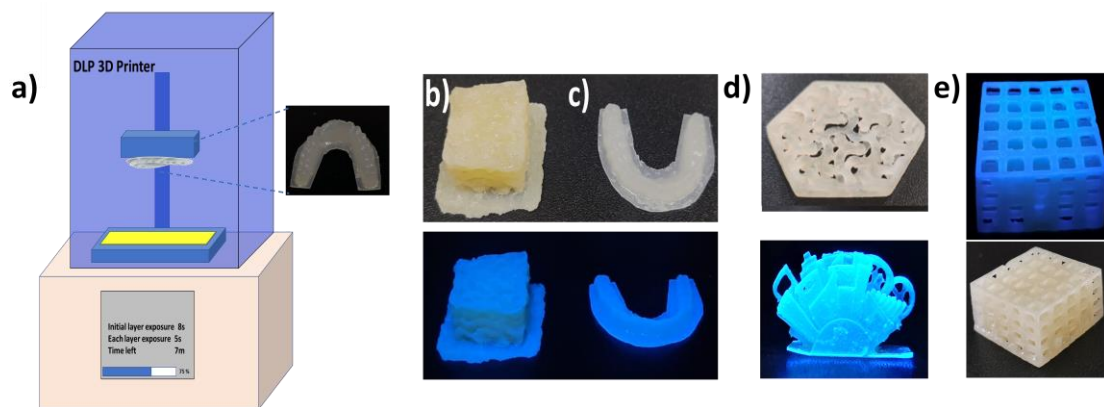


Figure 4.14 (a) Schematic depiction of the DLP 3D printing process. (b) Picture of 3D printed part of a filled gyrometric square structure. (c) 3D printed teeth model in visible light and under UV light. (d) Hexagonal 3D model with complex design inside, an Ameralabs Town (standard stl. file) 3D printed part with high resolution. (e) a highly porous complex CAD file 3D printed structure showing the fidelity of thiol ene resin printability.

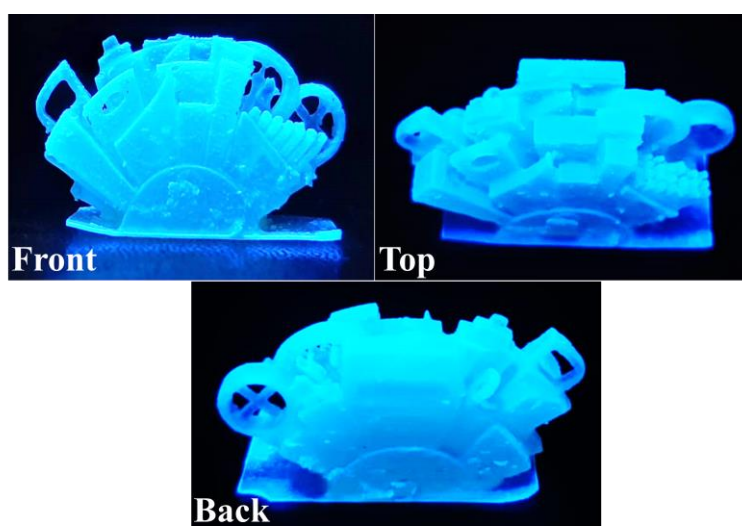


Figure 4.15 Photograph of 3D printed part of Standard Amera Labs Town CAD file from different sides.

4.3.5 Mechanical and Thermal Properties of The Thiol-Ene Polymer Network

Mechanical testing, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were performed to elucidate the impact of the weight percentage of biobased allyl PAEL polymer and isosorbide thiol in the 3D printed thiol-ene network. Figure 5.16a illustrates a typical stress-strain curve for the 3D-printed thiol-ene network. The mechanical properties such as tensile strength, Young's modulus, and elongation at break were obtained from the stress-strain curve and these results are summarized in Table 4.3.

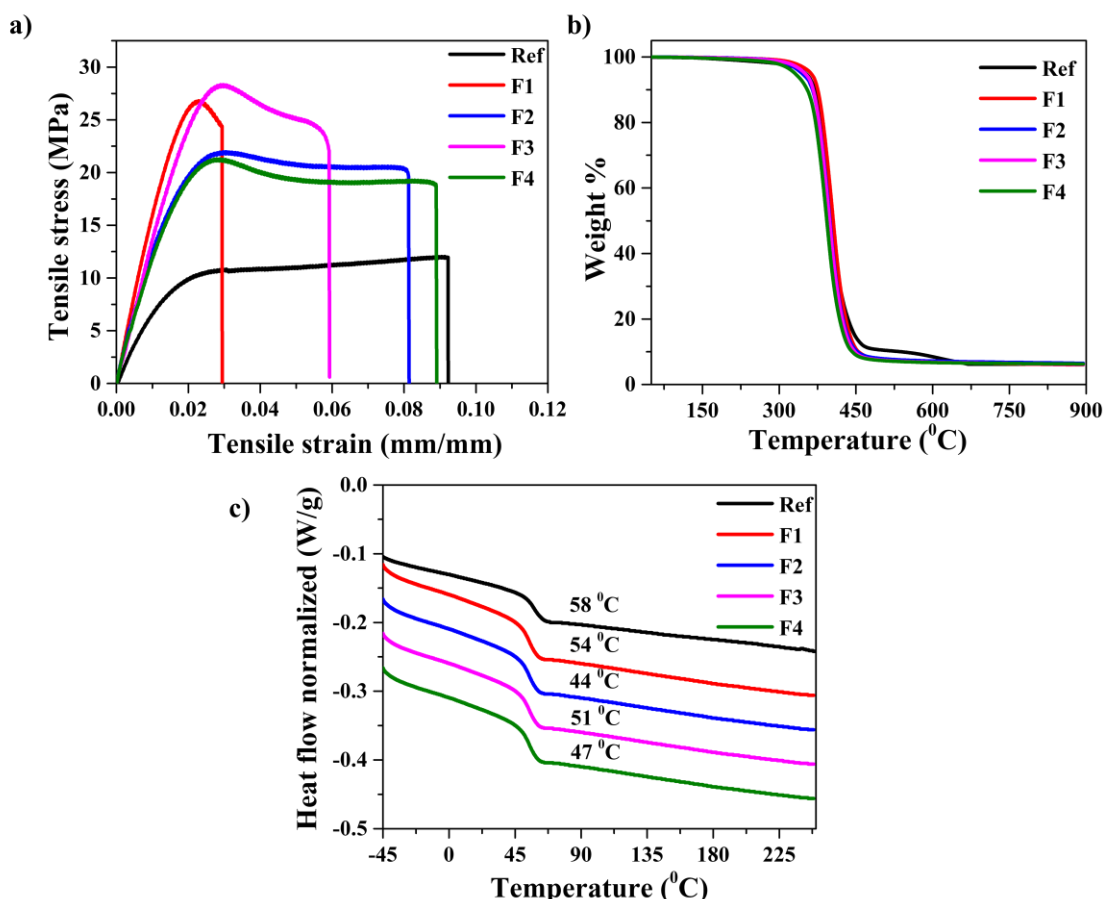


Figure 4.16 (a) Tensile stress-strain plots of 3D printed thiol-ene network of different resin formulations (b) TGA plots of 3D printed thiol-ene network of different resin formulations (c) DSC plots of 3D printed thiol-ene network of different resin formulations

The introduction of allyl PAEL polymer had a significant positive effect on the mechanical properties of the reference material, which was much higher than the literature reports^{39,46,47}. Specifically, there was a notable improvement in both tensile strength, which increased from 11 ± 2.8 MPa to 28.1 ± 3.1 MPa, and Young's modulus, which increased from 0.9 ± 0.02 GPa to 1.8 ± 0.03 GPa for F1 (5 wt. % allyl PAEL polymer) when compared with reference material. The reference resin is composed of small molecules only- tetra functional thiol and trifunctional ene whereas all the other resin formulations incorporated a polymeric 'ene' component of the PAEL polymer, which forms a higher crosslinking network during 3D printing than the reference resin formulation. As a result, the mechanical properties like the tensile strength were much higher for the resin formulation compared to the 'ref' resin. However, it has to be noted that this enhancement in mechanical properties was accompanied by a reduction in elongation. The elongation of the F1 resin was 3% compared to the 11% elongation for the 'ref'. This reduction can be attributed to the higher crosslinking network formed during the 3D printing

process which makes it less flexible. While the increased crosslinking enhances strength and modulus, it tends to limit the material's ability to deform before reaching failure, as evidenced by the decrease in elongation. The formulation F2 was prepared with 10 wt. % of branched allyl PAEL polymer and the mechanical properties of the 3D printed parts showed lower tensile strength than F1 (28 MPa for F1 to about 21 MPa for F2) and the modulus also decreased from 1.8 GPa to 1.1 GPa. As the polymer content in the F2 resin formulation increased, the branching side chain in the 3D printed part also increased, leading to disruptions in the formation of the printed network structure. This disruption results in a less favourable distribution of molecular segments, leading to changes in tensile strength and modulus and improved flexibility as observed from the increase in elongation from 3 to 8 %.^{48,49} Similarly, the observed mechanical properties of the F3 and F4 resin formulations followed a similar trend.

All resin formulations F1 to F4 exhibited improvement in tensile and Young's modulus compared to the reference material. The inclusion of isosorbide thiol in the resin formulation did not notably enhance the mechanical properties, but it exhibited significant improvement in degradation behaviour, which will be discussed in the section 4.3.6.

The thermal stability of the thiol-ene 3D printed parts is shown in Fig. 5b and the values are summarized in Table 1. The thermal decomposition of the thiol-ene network in all resin formulations followed a single-step process. Importantly, all of the 3D printed thiol-ene networks demonstrated outstanding thermal stability, as indicated by a T_d , 10% (the temperature at which 10% weight loss occurs) exceeding 350 °C. The glass transition temperature (T_g) determined from the DSC thermogram ranged from 44 to 54 °C. The plots are shown in Fig. 5c and the T_g values are reported in Table 1. The absence of any endothermic peaks in the DSC thermogram indicated the amorphous nature of the network formed.

4.3.6 Degradation of thiol-ene polymer network

The hydrolytic degradation of the 3D printed crosslinked thiol-ene network polymer was investigated both under acidic and basic conditions. Different reports studied the degradation mechanism of the ester bond present in thiol ene network thermoset polymer.^{50,51} Han Shih et. al.⁵² showed the ester bond hydrolysis of thiol-ene hydrogels for base-catalyzed hydrolytic degradation and changes in degradation behaviour by manipulating the degree of thiol-ene network cross-linking. Mayuri et al.³⁹ reported the degradation of the thiol-ene network in different NaOH base strengths with an organic solvent which promotes the swelling of the thiol-ene network and enhances the degradation. Figure 4.16 shows the degradation studies of the 3D printed thiol-ene network polymer performed in 10 ml of 1 M NaOH solution and 1 M HCl solution for each resin formulation at room temperature. As shown in Figure 4.17a, there

was a noticeable escalation in the degradation rate of 3D printed components in 1 M NaOH over time. The reference materials, which consisted of a stoichiometric blend of PETMP and TTT, displayed minimal degradation, measuring just 10 % in a two-day timeframe. In contrast, 3D printed parts composed of other resins containing allyl polymer and isosorbide thiol exhibited significantly higher levels of degradation during 48 h. The 3D printed component from formulation F1, which included 5 wt. % of PAEL polymer exhibited a degradation of 30 %. Meanwhile, formulation F3, comprising 5 wt. % of PAEL polymer and an additional 5 wt. % of isosorbide experienced a higher degradation reaching 60% at the end of 48 h. The 3D printed components from formulation F2, which included 10 wt. % of PAEL polymer, and formulation F4, which contained 10 wt. % of PAEL polymer along with 5 wt. % isosorbide demonstrated significantly higher degradation. Specifically, F2 showed almost 95 % degradation, while F4 exhibited complete degradation, reaching 100 %. The elevated degradation observed in the resin formulations, in contrast to the reference material, can be attributed to the inclusion of allyl polymer, specifically ethyl lactate ester. This particular component is notably susceptible to ester hydrolysis, particularly in the presence of a potent base like NaOH.

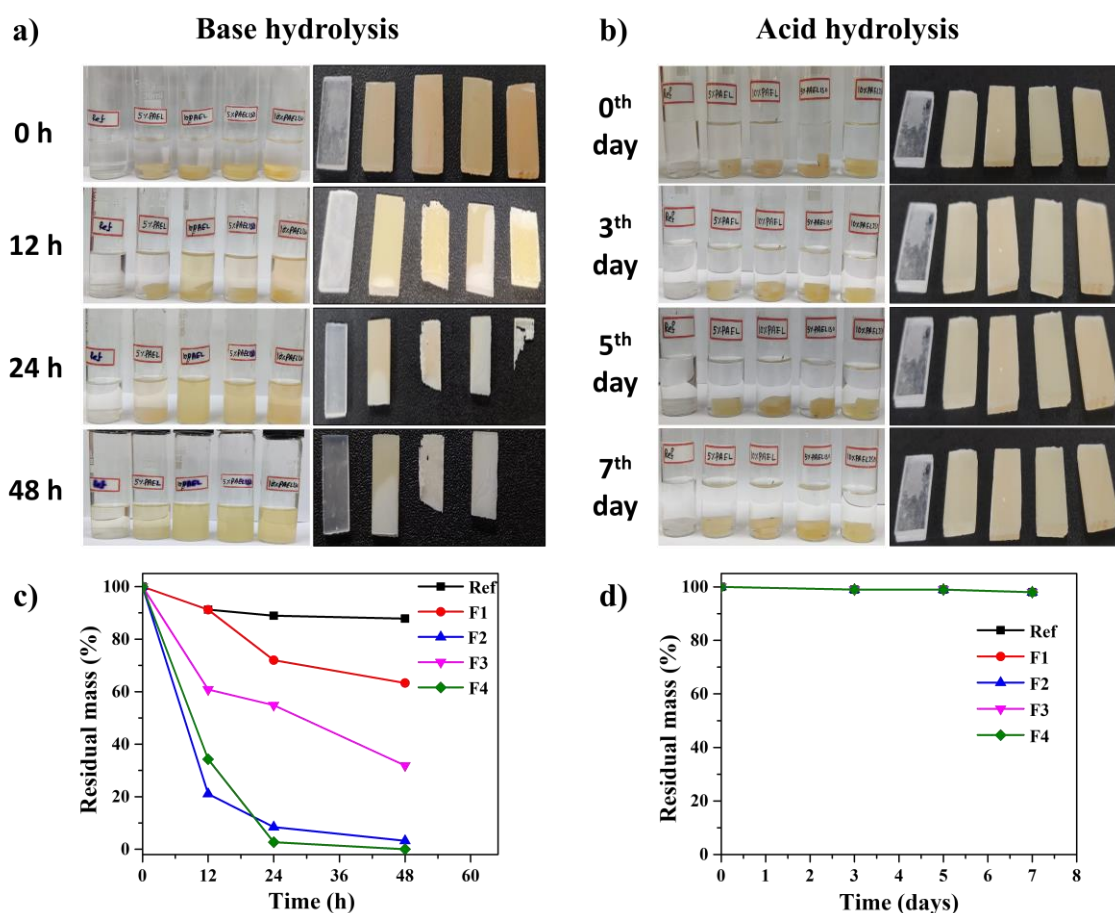


Figure 4.17 Real-time photographs of degradation of the different 3D printed parts in (a) 10 ml 1 M NaOH solution over 48 h (b) 10 ml 1M HCL solution for 7 days (c) degradation plot of 3D printed parts in 1 M NaOH solution for 48 h (d) degradation plot of 3D printed parts in 1 M HCl solution for one week.

The degradation process was replicated in a solution with 1 M HCl solution. Surprisingly, even after a consistent week-long experiment, there was no significant degradation observed (Figure 4.17b). These findings suggest that the thiol-ene 3D printed network, featuring allyl PAEL, displays remarkable stability in an aqueous acidic environment, whereas it readily degrades in a basic medium. The degradation study involving the allyl PAEL-containing thiol-ene network highlighted the rapid degradation efficiency of 3D printed parts within a span of 2 days. This characteristic renders it an exceptionally appealing material for various prototype applications, especially those focusing on renewable sources and a sustainable end-of-life cycle.

4.4 Conclusions

In conclusion, this study has successfully demonstrated a scalable and sustainable approach for developing 3D printing materials via thiol-ene photochemistry, utilizing ethyl lactate-based polymeric ene and isosorbide-based thiol. The synthesis of the ethyl lactate-based polymeric ene component was achieved by free radical polymerization of acrylate ethyl lactate monomer, followed by partial hydrolysis and subsequent reaction with allyl bromide. The thiol-ene photo kinetics was analysed through photo DSC experiments, shedding light on the underlying chemical reactions that occur during the curing process. The mechanical and thermal property analysis provided valuable insights into the potential applications and performance of these novel biobased thiol-ene materials. The practical application of the developed materials was showcased through 3D printing using a commercial DLP 3D printer, highlighting their feasibility for manufacturing and prototyping purposes. Notably, the hydrolytic degradability of the 3D printed parts was demonstrated in a 1 M NaOH solution, underlining the eco-friendly aspect of these materials and their potential to mitigate the issue of nondegradable acrylate-based 3D printed waste. This research paves the way for the development of environmentally responsible materials that have the potential to revolutionize the 3D printing industry. The fast degradability of PAEL-based polymeric thiol-ene 3D print materials opens new possibilities for rapid prototyping in mass production applications, making it a promising avenue for addressing the sustainability challenges associated with traditional acrylate-based materials. By combining the benefits of biobased sourcing, scalability, and degradability, these materials

represent a significant step towards a more sustainable and environmentally conscious future in the field of 3D printing.

4.5 REFERENCES

- (1) T.J. Wallin, J. Pikul, R.F. Shepherd, *Nat. Rev. Mater.* **2018**, *3*, 84–100.
- (2) Y. Li, S. Peng, K. Li, D. Qin, Z. Weng, J. Li, L. Zheng, L. Wu, C.-P. Yu, *Addit. Manuf.* **2022**, *60*, 103268.
- (3) G. Zhou, M.-C. Li, F. Wang, C. Liu, C. Mei, *Addit. Manuf.* **2022**, *59*, 103124.
- (4) Y. Zhang, Y. Gao, L. Michelin, L. Josien, L. Vidal, G. Schrodj, A. Simon-Masseron, J. Lalevée, *Eur. Polym. J.* **2022**, *179*, 111552.
- (5) N.B. Palaganas, J.O. Palaganas, S.H.Z. Doroteo, J.C. Millare, *Addit. Manuf.* **2023**, *61*, 103295.
- (6) F. Kabirian, M. Mozafari, P. Mela, R. Heying, *ACS Biomater. Sci. Eng.* **2023**, *9*, *11*, 5953–5967
- (7) H. Kadry, S. Wadnap, C. Xu, F. Ahsan, *Eur. J. Pharm. Sci.* **2019**, *135*, 60–67.
- (8) C. Yu, J. Schimelman, P. Wang, K.L. Miller, X. Ma, S. You, J. Guan, B. Sun, W. Zhu, S. Chen, *Chem. Rev.* **2020**, *120*, 10695–10743.
- (9) A. Schwab, R. Levato, M. D’Este, S. Piluso, D. Eglin, J. Malda, *Chem. Rev.* **2020**, *120*, 11028–11055.
- (10) K.L. Sampson, B. Deore, A. Go, M.A. Nayak, A. Orth, M. Gallerneault, P.R.L. Malenfant, C. Paquet, *ACS Appl. Polym. Mater.* **2021**, *3*, 4304–4324.
- (11) V. Shanmugam, M.V. Pavan, K. Babu, B. Karnan, *Polym. Compos.* **2021**, *3*, 4304–4324.
- (12) M. Guvendiren, J. Molde, R.M.D. Soares, J. Kohn, *ACS Biomater. Sci. Eng.* **2016**, *2*, 1679–1693.
- (13) J. Zhang, P. Xiao, *Polym. Chem.* **2018**, *9*, 1530–1540.
- (14) A. Atala, *Chem. Rev.* **2020**, *120*, 10545–10546.
- (15) M.A. Pemberton, B.S. Lohmann, *Regul. Toxicol. Pharmacol.* **2014**, *69*, 467–475.
- (16) B.J. Black, M. Ecker, A. Stiller, R. Rihani, V.R. Danda, I. Reed, W.E. Voit, J.J. Pancrazio, *J. Biomed. Mater. Res. Part A.* **2018**, *106*, 2891–2898.
- (17) R. Ding, Y. Du, R.B. Goncalves, L.F. Francis, T.M. Reineke, *Polym. Chem.* **2019**, *10*, 1067–1077.
- (18) W.D. Cook, S. Chausson, F. Chen, L. Le Pluart, C.N. Bowman, T.F. Scott, *Polym. Int.* **2008**, *57*, 469–478.
- (19) B.H. Northrop, R.N. Coffey, *J. Am. Chem. Soc.* **2012**, *134*, 13804–13817.

- (20) C.E. Hoyle, T.Y. Lee, T. Roper, *J. Polym. Sci. Part A Polym. Chem.* **2004**, *42*, 5301–5338.
- (21) A.K. O'Brien, N.B. Cramer, C.N. Bowman, *J. Polym. Sci. Part A Polym. Chem.* **2006**, *44*, 2007–2014.
- (22) C.E. Hoyle, C.N. Bowman, *Angew. Chemie Int. Ed.* **2010**, *49*, 1540–1573.
- (23) N.B. Cramer, C.N. Bowman, *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39*, 3311–3319.
- (24) C.J. Kloxin, T.F. Scott, C.N. *Macromolecules.* **2009**, *42*, 2551–2556.
- (25) R.A. Ortiz, A.E. Garcia Valdéz, M.G. Martinez Aguilar, M.L. Berlanga Duarte, *Carbohydr. Polym.* **2009**, *78*, 282–286.
- (26) T. Yoshimura, T. Shimasaki, N. Teramoto, M. Shibata, *Eur. Polym. J.* **2015**, *67*, 397–408.
- (27) S. Briede, M. Jurinovs, S. Nechausov, O. Platnieks, S. Gaidukovs, *Mol. Syst. Des. Eng.* **2022**, *7*, 1434–1448.
- (28) D.G. Sycks, T. Wu, H.S. Park, K. Gall, *J. Appl. Polym. Sci.* **2018**, *135*, 46259.
- (29) R. Ohno, K. Sugane, M. Shibata, *Eur. Polym. J.* **2021**, *159*, 110738.
- (30) Y. Wu, M.C. Simpson, J. Jin, *Macromol. Chem. Phys.* **2021**, *222*, 2000435.
- (31) E. Constant, O. King, A.C. Weems, *Biomacromolecules.* **2022**, *23*, 2342–2352.
- (32) S. Bertlein, G. Brown, K.S. Lim, T. Jungst, T. Boeck, T. Blunk, J. Tessmar, G.J. Hooper, T.B.F. Woodfield, J. Groll, *Adv. Mater.* **2017**, *29*, 1703404.
- (33) P. Marx, A. Romano, I. Roppolo, A. Chemelli, I. Mühlbacher, W. Kern, S. Chaudhary, T. Andritsch, M. Sangermano, F. Wiesbrock, *Macromol. Mater. Eng.* **2019**, *304*, 1900515.
- (34) C.C. Cook, E.J. Fong, J.J. Schwartz, D.H. Porcincula, A.C. Kaczmarek, J.S. Oakdale, B.D. Moran, K.M. Champley, C.M. Rackson, A. Muralidharan, R.R. McLeod, M. Shusteff, *Adv. Mater.* **2008**, *32*, 2003376.
- (35) A. Oesterreicher, J. Wiener, M. Roth, A. Moser, R. Gmeiner, M. Edler, G. Pinter, T. Griesser, *Polym. Chem.* **2016**, *7*, 5169–5180.
- (36) Y. Wu, M.C. Simpson, J. Jin, *Macromol. Chem. Phys.* **2021**, *222*, 1–7.
- (37) D.G. Sycks, T. Wu, H.S. Park, K. Gall, *J. Appl. Polym. Sci.* **2018**, *135*, 1–12.
- (38) D. Merckle, E. Constant, A.C. Weems, *ACS Sustain. Chem. Eng.* **2021**, *9*, 12213–12222.
- (39) M.K. Porwal, M.M. Hausladen, C.J. Ellison, T.M. Reineke, *Green Chem.* **2023**, *25*, 1488–1502.
- (40) N. Bensabeh, A. Moreno, A. Roig, O.R. Monaghan, J.C. Ronda, V. Cádiz, M. Galià, S.M. Howdle, G. Lligadas, V. Percec, *Biomacromolecules.* **2019**, *20*, 2135–2147.
- (41) H. Seker, E. Cakmakci *J. Polym. Sci.* **2020**, *58*, 1105–1114
- (42) W.D. Cook, S. Chausson, F. Chen, L. Le Pluart, C.N. Bowman, T.F. Scott, *Polym. Int.* **2008**, *57*, 469–478.

- (43) J. Yue, J. Nie, X. Zhu, *J. Photochem. Photobiol. A Chem.* **2023**, 436, 114417.
- (44) L. Chen, Q. Wu, G. Wei, R. Liu, Z. Li, *J. Mater. Chem. C* **2018**, 6, 11561–11568.
- (45) Y. Luo, G. Le Fer, D. Dean, M.L. Becker, *Biomacromolecules*. **2019**, 20, 1699–1708.
- (46) D.B. Larsen, R. Sønderbæk-Jørgensen, J.Ø. Duus, A.E. Daugaard, *Eur. Polym. J.* **2018**, 102, 1–8.
- (47) J. Dai, S. Ma, L. Zhu, S. Wang, L. Yang, Z. Song, X. Liu, J. Zhu, *Polymer*. **2017**, 108, 215–222.
- (48) V.A. Bobrin, Y. Yao, X. Shi, Y. Xiu, J. Zhang, N. Corrigan, C. Boyer, *Nat. Commun.* **2022**, 13, 1–10.
- (49) D.P. Street, A.H. Mah, W.K. Ledford, S. Patterson, J.A. Bergman, B.S. Lokitz, D.L. Pickel, J.M. Messman, G.E. Stein, S.M. Kilbey, *ACS Appl. Polym. Mater.* **2020**, 2, 1312–1324.
- (50) A.T. Metters, K.S. Anseth, C.N. Bowman, *J. Phys. Chem. B*. **2001**, 105, 8069–8076.
- (51) A.T. Metters, C.N. Bowman, K.S. Anseth, *J. Phys. Chem. B*. **2000**, 104, 7043–7049.
- (52) H. Shih, C.-C. Lin, *Biomacromolecules*. **2012**, 13, 2003–2012

CHAPTER 5

Room Temperature Photocurable PEEK Polymer Formulations for High-Performance 3D Printing Applications

5.1 INTRODUCTION

3D printing can be applied in diverse fields such as tissue engineering, the fabrication of medical devices, soft robotics, dentistry, and many more.¹⁻⁵ The utilization of photocurable bio-based polymers has become prevalent in DLP 3D printing. However, a persistent challenge lies in processing High-Performance Polymers (HPPs) such as polyether ether ketone (PEEK) and polyimide under ambient conditions.^{6,7} High-performance polymers exhibit notable mechanical (commercial PEEK polymer has a reported tensile strength of 90-100 MPa and Young's Modulus of 4 GPa) and thermal properties (glass transition temperature of 143 °C and stable up to 450 °C with only 5 % weight loss) owing to a substantial concentration of aromatic rings within the polymer chain, contributing to strong bonds and inter-chain interactions.⁸ The remarkable physical properties of PEEK polymers make them highly attractive for a diverse range of applications. PEEK is extensively utilized in fields such as the automotive industry, where its unique combination of strength and heat resistance is valuable.⁹ Additionally, PEEK finds crucial applications in the medical field, serving as a material for implants due to its biocompatibility and durability.^{10,11} Despite facing challenges in processing PEEK polymer, several research groups have dedicated considerable efforts to 3D printing this polymer.¹² Tan. K. H et. al. performed direct energy deposition system using a CO₂ laser beam to form a circular disc of PEEK polymer after blending with hydroxyapatite powder. Through the analysis of micrographs of sintered specimens and careful examination of part bed temperature they concluded that the optimized 3D printing parameters were 140 °C and 16-21 W for direct energy deposition (DED) of PEEK polymer.¹³ Thereafter, other research groups have employed the same printing parameters for processing PEEK polymer or PEEK polymer composites with bio-active additives. The resulting materials demonstrated non- toxicity and porosity, making them suitable for applications in porous scaffolds.^{10,14} An alternative method involves melt material extrusion (MME), wherein PEEK filament materials are extruded through a heated extruder head (maintained above 360 °C) for 3D printing human bone structures.^{15,16} The processing of the PEEK polymer was further examined in terms of adhesion between print layers, printing temperature, printing speed and post curing parameters.¹¹ Rinaldi et al. demonstrated variations in the Young's Modulus of 3D printed PEEK materials based on the infill percentage of printed materials.¹⁷ The 100% infilled parts revealed remarkably high mechanical strength at 4 GPa, while parts with 20% or 50% infilling showed comparatively lower values. Hu et al. documented an additional heat control treatment implemented during

3D printing to mitigate layer warping, thereby enhancing interlayer connectivity.¹⁸ In a recent development, Lee et al. demonstrated the room temperature 3D printing of PEEK materials through the direct ink writing (DIW) 3D printing process.¹⁹ They created a novel epoxy-functionalized PEEK paste using commercial PEEK powder and fenchone (colorless oily liquid used to make the PEEK paste). The resulting 3D printed parts exhibited outstanding thermal and chemical stability, achieving 62% of the mechanical strength observed in commercial PEEK materials. In another report, 3D printing was carried out for polyimide using vat polymerization after synthesizing photo-cross-linkable acrylate-functionalized polyamic acid derivatives in NMP solvent.²⁰ As far as we are aware, the exploration of liquid-based 3D printing for PEEK polymer has not been undertaken to date.

The current work reports the synthesis of urethane acrylate-based polyether ether ketone (PEEK) and its successful demonstration for room temperature DLP 3D printing. The urethane methacrylate end capped PEEK polymers were incorporated into resin formulations with varying percentages of reactive diluents. The resin formulations were characterized for viscosity and curing kinetics using rheology and photo-differential scanning calorimetry (photo-DSC) analysis. The thermal and mechanical properties of the DLP 3D printed parts were assessed. Overall, our research reports for the first-time room temperature DLP 3D printing of functionalized PEEK polymers which achieved comparable Young's modulus and thermal properties with a promising synthetic approach to modify PEEK polymers, addressing the specific requirements for high mechanical strength in DLP 3D-printed parts intended for end-use product fabrication.

5.2 EXPERIMENTAL SECTION

5.2.1 Materials

4,4'-difluoro benzophenone, 2,2-Bis(4-hydroxyphenyl) propane, 4-fluoro benzoic acid and dibutyltin dilaurate (DBTDL), 3-Pentadecyl phenol, and tetrakis(triphenylphosphine) palladium were purchased from Aldrich and used as such. Bromo ethanol, Methacryloyloxyethyl isocyanate, Tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate (TCDDA), 4-methoxy phenyl boronic acid, Bisphenol A ethoxylate dimethacrylate (BPAEDMA), N-bromo succinimide, and boron tribromide were purchased from TCI chemicals and used without purification. The following items were bought locally: sodium sulfate (anhydrous), dichloromethane, toluene, methanol, isopropyl alcohol (IPA), potassium carbonate, diethyl amine, dimethyl sulfate, tetrahydrofuran, acetone, CHCl₃, and hydrochloric

acid. For gel permeation chromatography HPLC-grade THF was purchased from Merck Chemicals.

5.2.2 Measurements

The ^1H and ^{13}C NMR spectra were collected using Bruker-AVENS 400 and 200 MHz spectrometers, respectively, with chemical shifts reported in ppm. CDCl_3 was used as the solvent, and small amounts of Trimethylsilane (TMS) served as an internal standard. Molecular weights of small molecules were determined with Thermo Scientific Q-Exactive HRMS (ESI). Fourier transform (FT-IR) spectra were obtained using a BRUKER alpha-E spectrometer. Molecular weights of polymers were measured using gel permeation chromatography (GPC) with a Viscotek VE 3580 RI detector. The GPC system was calibrated using polystyrene standards, and THF (HPLC grade) was used as the eluent at a flow rate of 1 ml/min. The viscosity of formulated resins was assessed in relation to shear rate using the Anton Paar Physica Modular Compact Rheometer (MCR) 301. The test involved cup and bob components with diameters of 18.08 mm and 16.66 mm, respectively. Shear rates ranged from 1 to 1000 per second at a temperature of 30 °C. Thermal stability of 3D printed parts was evaluated through Thermal Gravimetric Analysis (TGA) using a TA Discover 550-second generation TGA instrument. The analysis spanned a temperature range of 50 °C to 900 °C under a nitrogen atmosphere (25 mL/min) with a heating rate of 10 °C/min. Glass transition temperature (T_g) was determined using a TA Discover 250 second generation differential scanning calorimeter (DSC) under a nitrogen atmosphere (50 ml/min). The measurement involved heating from -50 °C to 180 °C at a rate of 10 °C/min, and the DSC instrument was calibrated with indium standards before each measurement. Additionally, a photo-DSC experiment was conducted using the same DSC instrument equipped with an optical UV light source Omni Cure series 2000.

5.2.3 Methods

A) Resin Preparation for DLP 3D Printing of Urethane Methacrylate PEEK Polymers

The UMPEEK resin formulations were prepared by blending different concentration of UMPEEK and UMmPEEK polymers with Tricyclo[5.2.1.0^{2,6}] decanedimethanol diacrylate (TCDDA) and Bisphenol A ethoxylate dimethacrylate (BPAEDMA) as a reactive diluent. Initially, the polymer was placed in a 50 ml vial, followed by the addition of reactive diluents. The contents of the vial were subjected to sonication for 1 hour to ensure complete miscibility of the polymer. Throughout the sonication, the water bath temperature was maintained at 30 °C. The weight percentage of the TPO photoinitiator was determined through a photo DSC

experiment. The 3D printing resin formulation excluded any organic solvents. The glass vial was completely covered in aluminum foil to protect the photoinitiator from light and to avoid pre-polymerization. The resin formulations reported herein were prepared following a similar protocol.

B) Curing Kinetics of Resin Formulations (Photo-DSC)

A TA Discover 250 second-generation differential scanning calorimeter fitted to an Omni Cure series 2000 photo calorimetric unit was used to conduct the Photo-DSC studies. A 200 W high-pressure mercury lamp with a range of 320–500 nm was used to irradiate the sample. The light from the lamp was directed through a dual-quartz light support with balanced intensity into the material's container. Sample preparation involved the precise weighing of 5 mg resin formulation samples and placing them into the sample pan. After that, the sample pan was placed inside the DSC cell. Nitrogen gas was continuously supplied at a rate of 50 milliliters per minute during the measurements. The sample pans were initially maintained at isothermal temperatures (30 °C) for two minutes under nitrogen atmosphere, before being exposed to UV light. The specimen was exposed to UV light for five minutes after the electronic UV light shutter was opened. The shutter closed on its own when the irradiation period ended. The curing enthalpy was calculated by integrating the peaks in the generated data.

C) Measurement of Resin Viscosity

Rotational Parallel Plate measurements were used to evaluate the viscosity of the resin compositions; photoinitiator was not used in this test. Anton Paar Physica Modular Compact Rheometer (MCR) 301 was used in the experiment with a cup and bob. The photoinitiator-free resin formulation was poured carefully into the cup until it reached the predetermined mark. The bob was then rotated to provide shear during the experiment after it had been placed into the resin. The viscosity, measured in Pascal-seconds (Pa·s), was determined by methodically increasing the shear rate between 1 and 1000 per second. The resin temperature was kept constant during the experiment at 30 °C.

D) DLP 3D Printing of Urethane Methacrylate PEEK Polymer Resins

Anycubic Photon Ultra resin 3D printer was used for the DLP 3D printing of the resin compositions without organic solvents. The resin bed of the DLP printer had a dimension of 102.4 x 57.6 x 165 mm³, and a 405 nm LED light source. A UNO Genetic laser power meter was used for recording the LED light source's intensity of 10 mW cm⁻². The printing process was started by carefully adding resin to the resin bed until it reached a predetermined level.

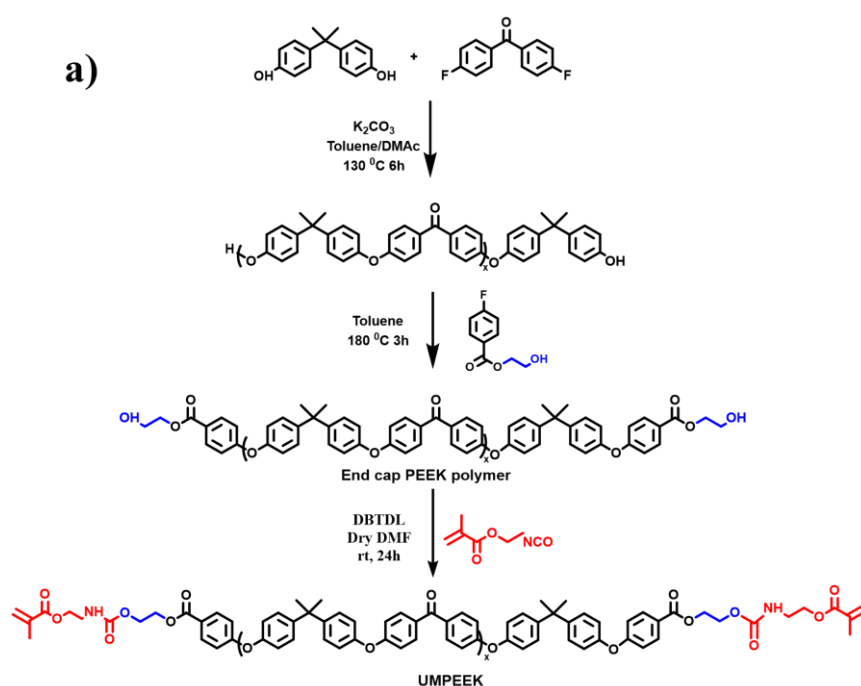
The printing of the resin formulation was performed at room temperature. The dimension of each printed layer was 100 microns, and the exposure time for the first five layers was set at 30 seconds. Each succeeding layer were exposed for ten seconds. The printed object was subjected to post-processing treatment after washing with IPA in a resin washer for 3 minutes followed by post-cure for fifteen minutes under UV light in a 360o rotating curing platform fitted with 12 UV lights of wavelength 405 nm covered with plastic cage.

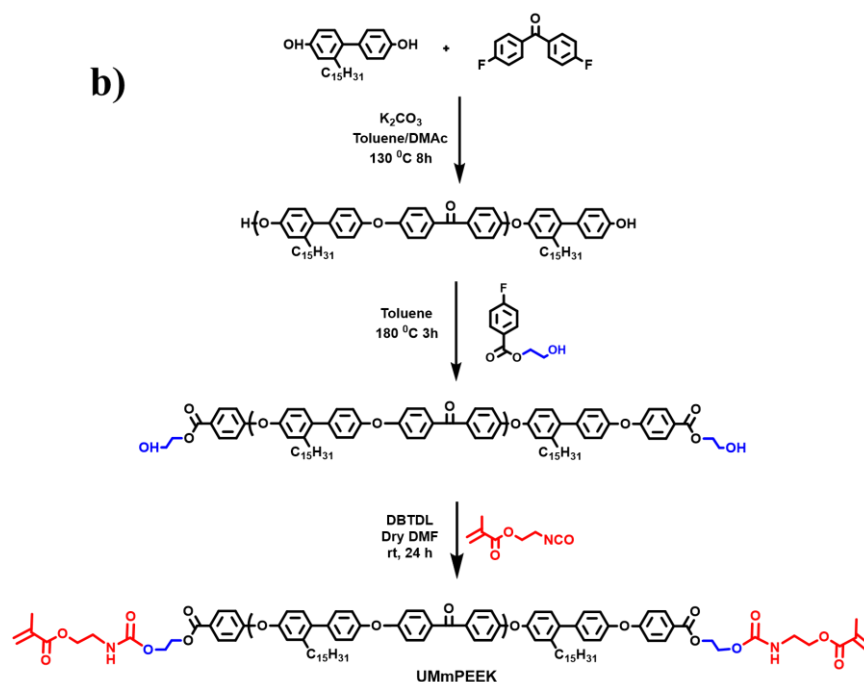
E) Mechanical Test of 3D Printed Part

The tensile strength of the 3D printed part was examined using the Instron series 33R4204 model of the Universal Testing Machine, which has a 1 KN capacity load cell. 3D-printed ASTM D638 type V specimens were used for the tensile test and 5 specimens were tested for each set of samples. Each specimen in the experiment had a gauge length of 10 mm, and the stretching rate was 5 mm per minute at room temperature. Mechanical properties such as toughness, elongation, Young's modulus, and tensile strength were determined.

5.2.4 Synthesis and Characterization

Specifically, regular polyether ether ketone (PEEK) and modified poly ether ether ketone incorporating pendant pentadecyl chains (mPEEK) were synthesized and further end functionalized with photocurable moieties. Scheme 1 shows the synthesis of PEEK and mPEEK and their further modification by introduction of photo curable urethane methacrylate group. Size exclusion chromatography (SEC) and proton NMR spectroscopy were used to determine the degree of polymerization for the PEEK and mPEEK polymers.



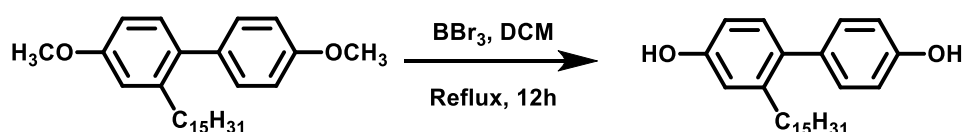


Scheme 1. Synthetic scheme for the terminal functionalized a) urethane methacrylate PEEK b) urethane methacrylate mPEEK polymers.

1) Synthesis of 3-pentadecyl 4,4'-biphenol and Synthesis of 2-hydroxyethyl 4-fluorobenzoate

a) Synthesis of 3-pentadecyl 4,4'-biphenol

Synthesis of the 3-pentadecyl 4,4'-biphenol was done according to the literature [1] with some modification in the deprotection step. The details of the deprotection of 4,4'-dimethoxy-2-pentadecyl-1,1'-biphenyl is given below.



4,4'-dimethoxy-2-pentadecyl-1,1'-biphenyl (6 g, 14.13 mmol) was taken in a 250 ml two necked round bottom flask with magnetic stirring bar fitted with condenser and addition funnel. A two head take-off was fitted on the condenser with double nitrogen balloon. BBr_3 (7.08g, 28.26 mmol) was mixed with DCM and poured into the addition funnel. After that BBr_3 DCM mixture was added dropwise into the reaction at ice cold condition. The reaction was run for 12 h and then ice-cold water was added to stop the reaction. The product was collected in DCM after washing with water 4-5 times. The final product was crystalline in DCM/pet ether solvent mixture. The crystalline product was filtered and dried in vacuum oven at $40\text{ }^\circ\text{C}$ for overnight. Yield-72 %.

^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 7.15 (d, 2H), 7.04 (d, 1H), 6.85 (d, 2H), 6.76 (d, 1H), 6.70 (d, 1H), 4.1 (s, 1H), 4.83 (s, 1H), 2.52 (d, 2H), 1.45 (dd, 2H), 1.26-1.19 (m, 24H), 0.89 (d, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ in ppm: 154.7, 154.4, 142.5, 134.46, 131.56, 130.93, 115.93, 115.08, 112.57, 33.35, 31.17, 31.38, 29.94, 29.6, 22.94, 14.36.

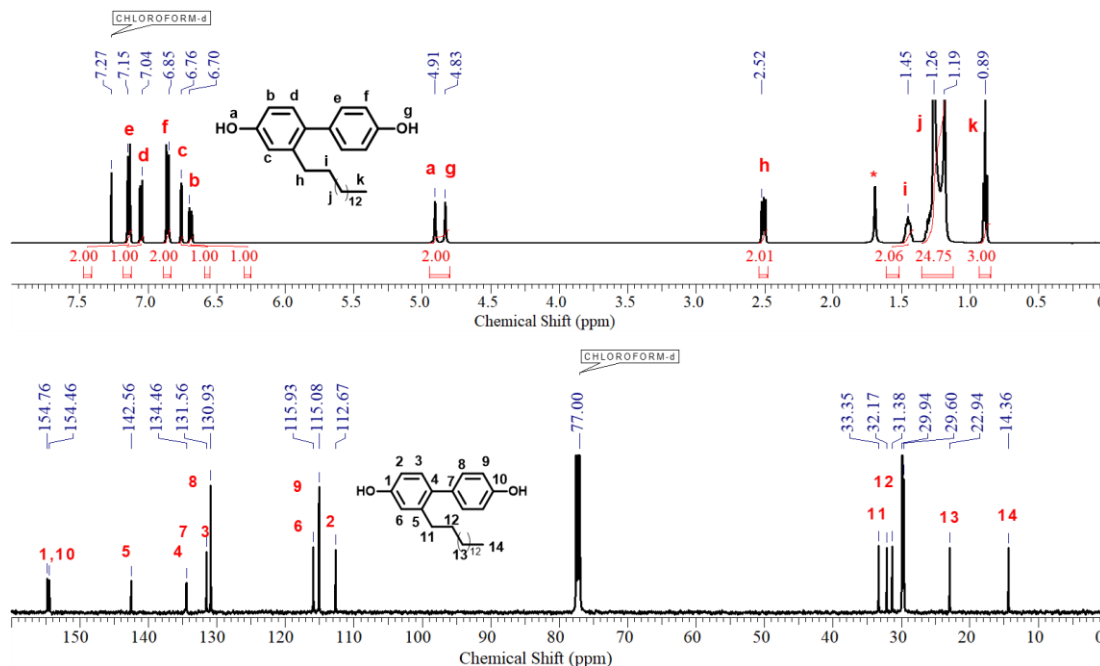
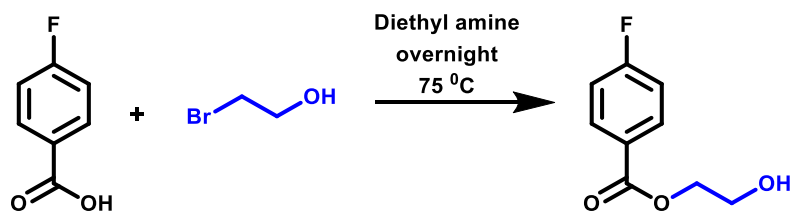


Figure 5.1 ^1H and ^{13}C NMR spectra of 3-pentadecyl 4,4'-biphenol

b) Synthesis of 2-hydroxyethyl 4-fluorobenzoate



4-Fluoro benzoic acid (5 g, 35.7 mmol) and Bromo ethanol (5.8 g, 46.4) were taken in a two-necked round bottom flask equipped with a magnetic stirring bar. 150 ml of acetonitrile was added to the reaction mixture and stirred for 10 minutes. N, N-Diisopropylethylamine (5.5 g, 42.84 mmol) was added to the reaction and immersed into a pre-heated oil bath at 75 °C for 12 h. The reaction mixture was removed from the oil bath and allowed to cool to room temperature. The solvent was removed with the aid of a rotary evaporator. Finally, the crude residue was dissolved in ethyl acetate and washed with 1 M HCl solution three times, saturated NaHCO_3 three times, followed by brine solution. The organic part was dried over sodium sulfate and the solvent was evaporated in a rotary evaporator. Yield 78 %.

^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 8.05 (d, 2H), 7.11 (d, 2H), 4.44 (d, 2H), 3.94 (d, 2H), 2.16 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ in ppm: 165.65, 164.29, 131.97, 125.77, 115.14, 66.41, 61.02

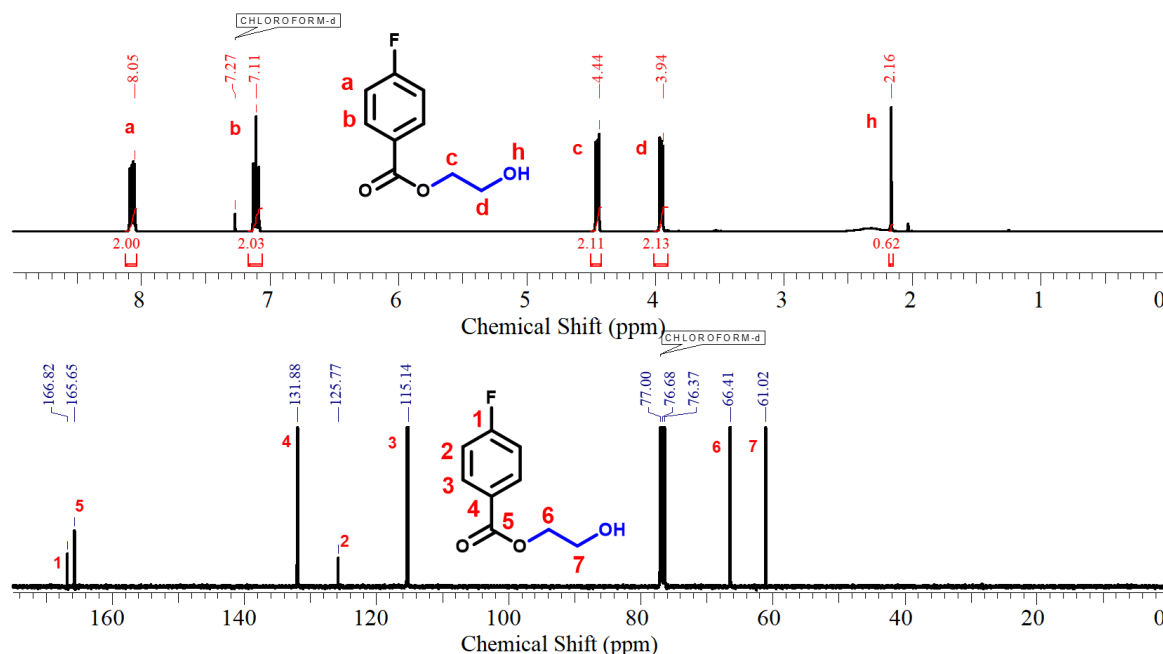
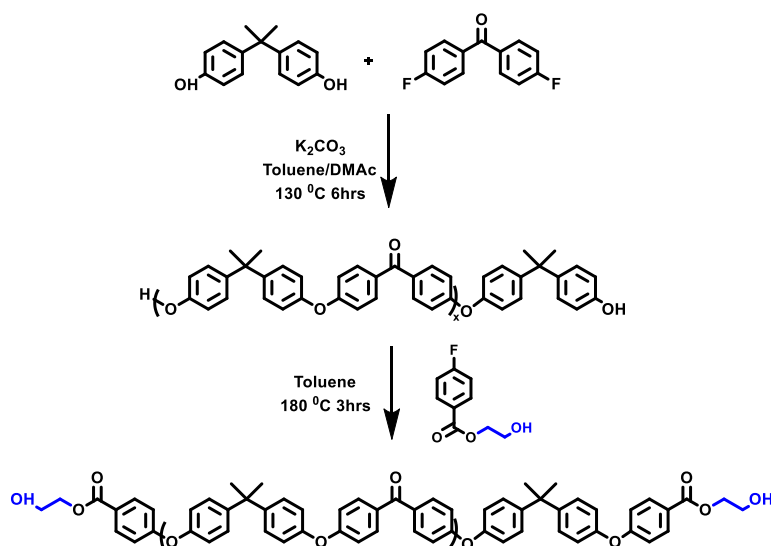


Figure 5.2 ^1H and ^{13}C NMR spectra of 2-hydroxyethyl 4-fluorobenzoate

2) Synthesis of PEEK, mPEEK, and urethane methacrylate of PEEK, and mPEEK

c) Synthesis of polyether ether ketone (PEEK) polymer



Bisphenol A (3.45 g, 15.1 mmol), 4,4'-difluoro benzophenone (3 g, 13.7 mmol), and potassium carbonate (4.6 g, 33.2 mmol) were taken in a three-necked round bottom flask equipped with a reflux condenser, Dean-Stark trap, and magnetic stirring bar at nitrogen atmosphere. 20 ml

of dimethyl acetamide and 20 ml of toluene were added to the reaction mixture and immersed into the pre-heated oil bath at 130 °C for 3 h. After that, the temperature was raised to 180 °C to remove water and toluene by azeotropic distillation and the reaction was continued for another 3 h. Subsequently, a solution of 2-hydroxyethyl 4-fluoro benzoate (1.26 g, 6.8 mmol) in toluene was added to the reaction mixture and the reaction was continued for another 3 h. After cooling, the obtained viscous reaction mixture was poured into the methanol to precipitate the polymer, which was filtered, and washed with water 2-3 times to remove the salt. Again, dissolved in chloroform and precipitated in methanol, filtered, and dried under a vacuum at 50 °C for 24 h. Yield 80 %.

^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 8.04 (d, 4H), 7.77-7.78 (m, 193H), 7.25-7.29 (m, 222H), 6.98-7.05 (m, 407H), 4.43-4.48 (m, 4H), 3.95-3.98 (m, 4H), and 1.72 (m, 293H)

^{13}C NMR (100 MHz, CDCl_3) δ in ppm: 186.18, 161.43, 153.49, 146.73, 132.19, 128.33, 119.53, 117.16, 66.92, 60.93, 42.37, 31.01

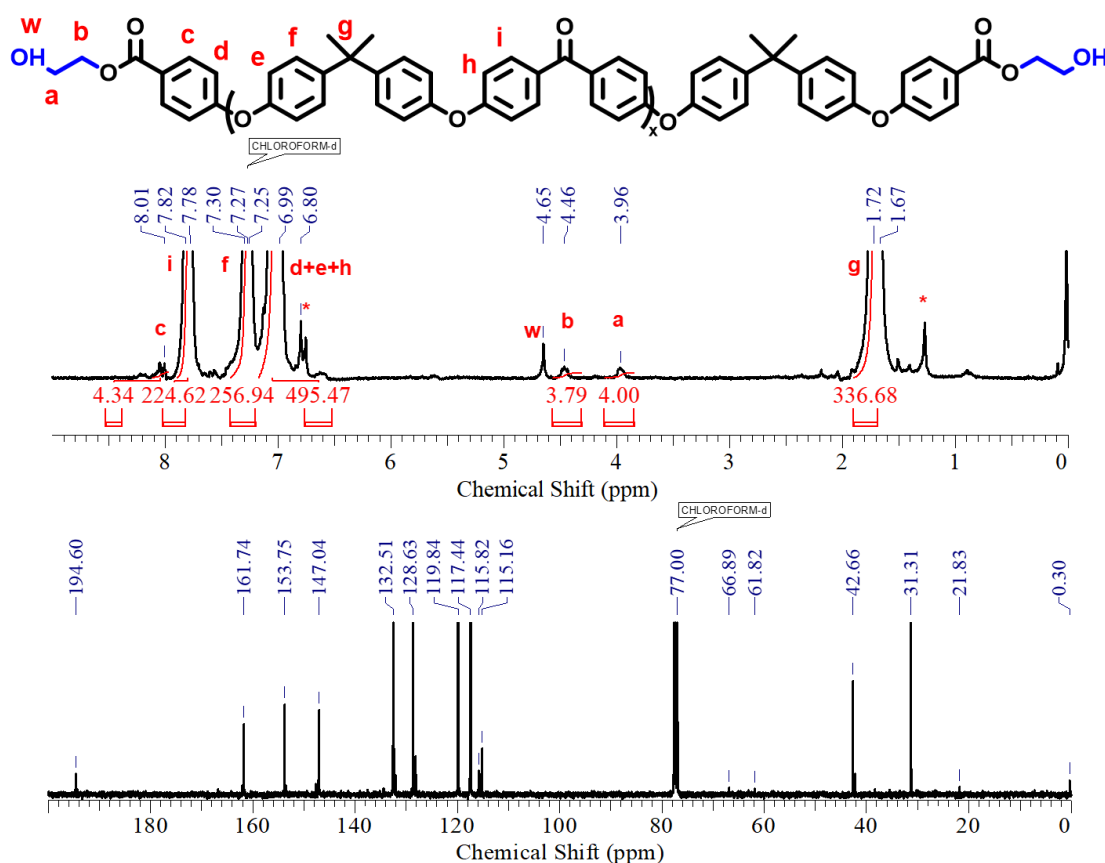
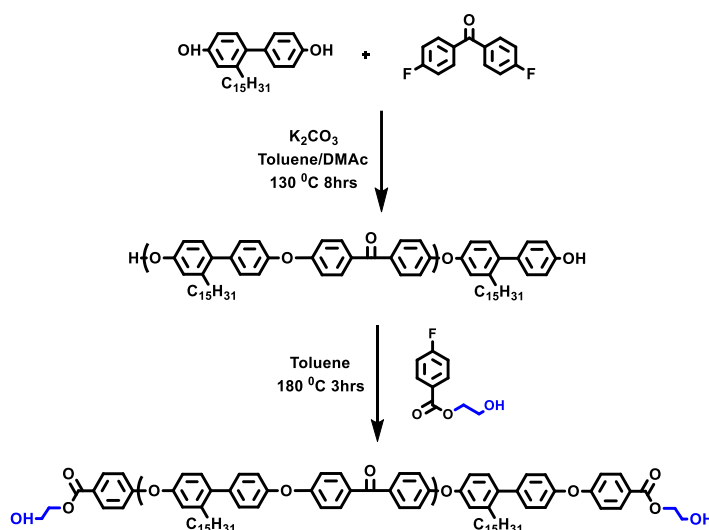


Figure 5.3 ^1H and ^{13}C NMR spectra of polyether ether ketone (PEEK) polymer.

d) Synthesis of modified polyether ether ketone (mPEEK) polymer



3-pentadecyl 4,4'-biphenol was synthesized according to the literature report. 3-pentadecyl 4,4'-biphenol (2.99 g, 7.56 mmol), 4,4'-difluoro benzophenone (1.5 g, 6.87 mmol), and potassium carbonate (2.3 g, 16.6 mmol) were taken in a three-necked round bottom flask equipped with a reflux condenser, Dean-Stark trap, and magnetic stirring bar at nitrogen atmosphere. 15 ml of Dimethyl acetamide and 15 ml of toluene were added to the reaction mixture and immersed into the pre-heated oil bath at 130 °C for 3 h. After that, the temperature was raised to 180 °C to remove water and toluene by azeotropic distillation and the reaction was continued for another 8 h. After that, a solution of 2-hydroxyethyl 4-fluoro benzoate (1.26 g, 6.8 mmol) in toluene was added to the reaction mixture and the reaction was continued for another 3 h. After cooling, the obtained viscous reaction mixture was poured into methanol to precipitate the polymer. The methanol was then decanted, and the polymer was washed with water 2-3 times to remove the salt. Again, dissolved in chloroform, precipitated in methanol, and dried under a vacuum at 50 °C for 24 h. Yield 75%.

¹H NMR spectrum (400 MHz, CDCl₃) δ in ppm: 8.08 (d, 4H), 7.84-7.88 (m, 130H), 7.37 (m, 68H), 6.95-7.09 (m, 313H), 4.47 (m, 4H), 3.98 (m, 4H), 2.59 (m, 65H), 1.23-1.49 (m, 960H), 0.87 (m, 118H)

¹³C NMR (100 MHz, CDCl₃) δ in ppm: 194.29, 191.31, 161.25, 154.72, 142.82, 137.52, 132.28, 130.97, 119.59, 117.41, 70.29, 65.19, 33.16, 31.92, 29.69, 22.69, 14.13.

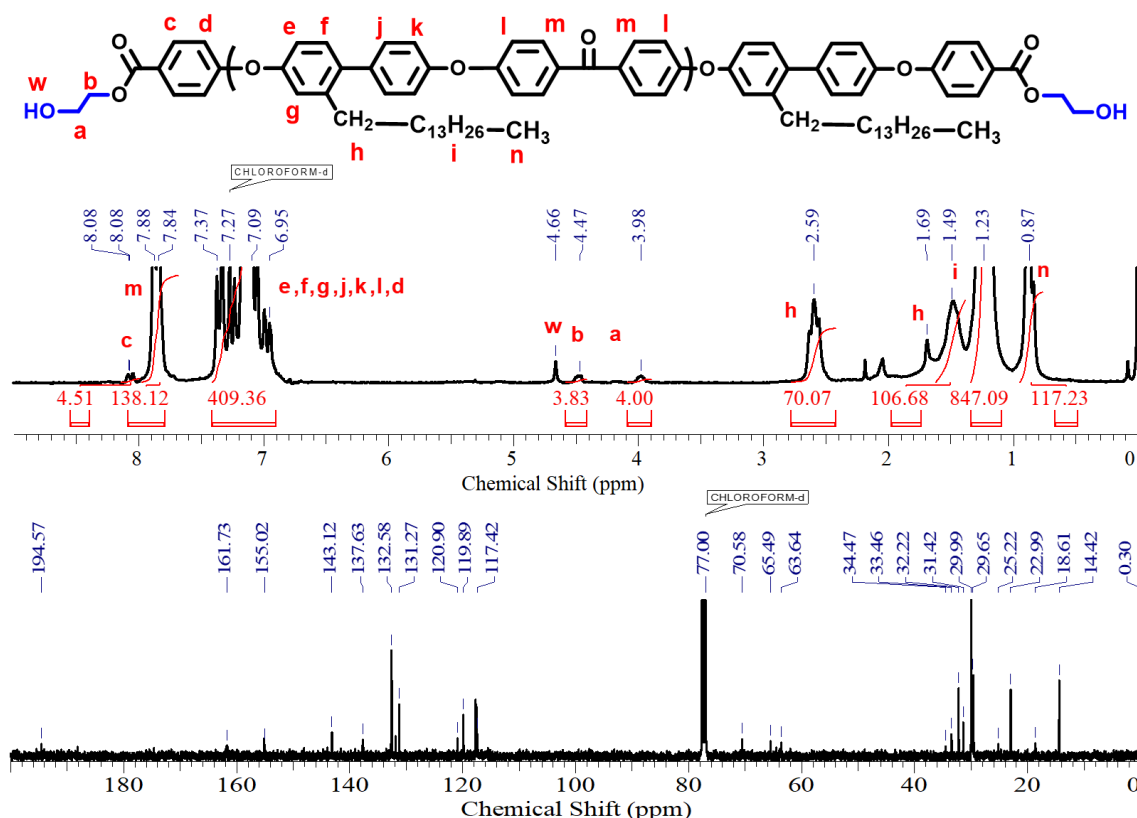
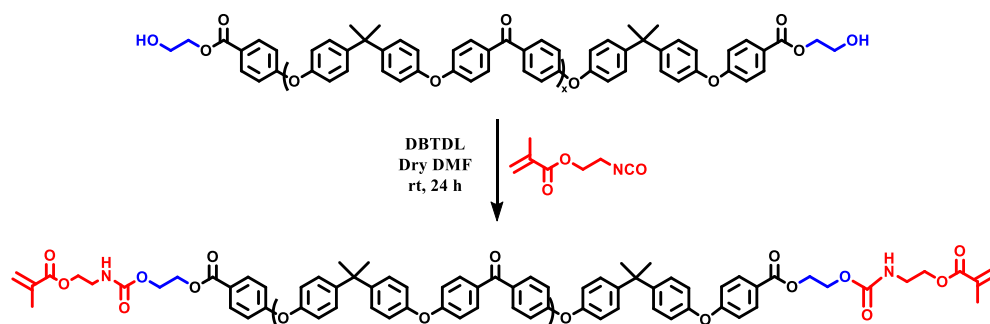


Figure 5.4 ¹H and ¹³C NMR spectra of modified polyether ether ketone (mPEEK) polymer.

e) Synthesis of urethane methacrylate polyether ether ketone (UMPEEK) polymer



PEEK polymer (average MW 23200 g/mol, 0.086 mmol) was dissolved in 30 ml of dry dimethyl formamide in a 50 ml two-necked round bottom flask under a nitrogen atmosphere and cooled under an ice bath. Two drops of dibutyltindilaurate (DBTDL) were added as a catalyst followed by dropwise addition of 2-isocyanatoethyl methacrylate (160 mg, 1.03 mmol) in 2 ml of dry DMF within 30 minutes of time period. The reaction was stirred at cold conditions for 2 h and further left for 12 h at room temperature. After that, the reaction was poured into methanol to precipitate the acrylate PEEK polymer and filtered. Again, the polymer was dissolved in chloroform and reprecipitated in methanol 2-3 times to completely remove

any unreacted product. The white power polymer was dried under vacuum at room temperature for 24 h. Yield 75 %.

^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 8.04 (d, 4H), 7.82 (m, 203H), 7.25-7.27 (m, 240H), 6.98 (m, 424H). 6.11 (s, 2H), 5.57 (s, 2H), 4.47 (m, 8H), 4.24 (m, 8H), 2.04 (s, 6H), 1.67 (m, 288H).

^{13}C NMR (100 MHz, CDCl_3) δ in ppm: 194.32, 161.46, 153.47, 146.75, 132.23, 128.35, 119.56, 117.16, 66.61, 61.54, 42.38, 31.03.

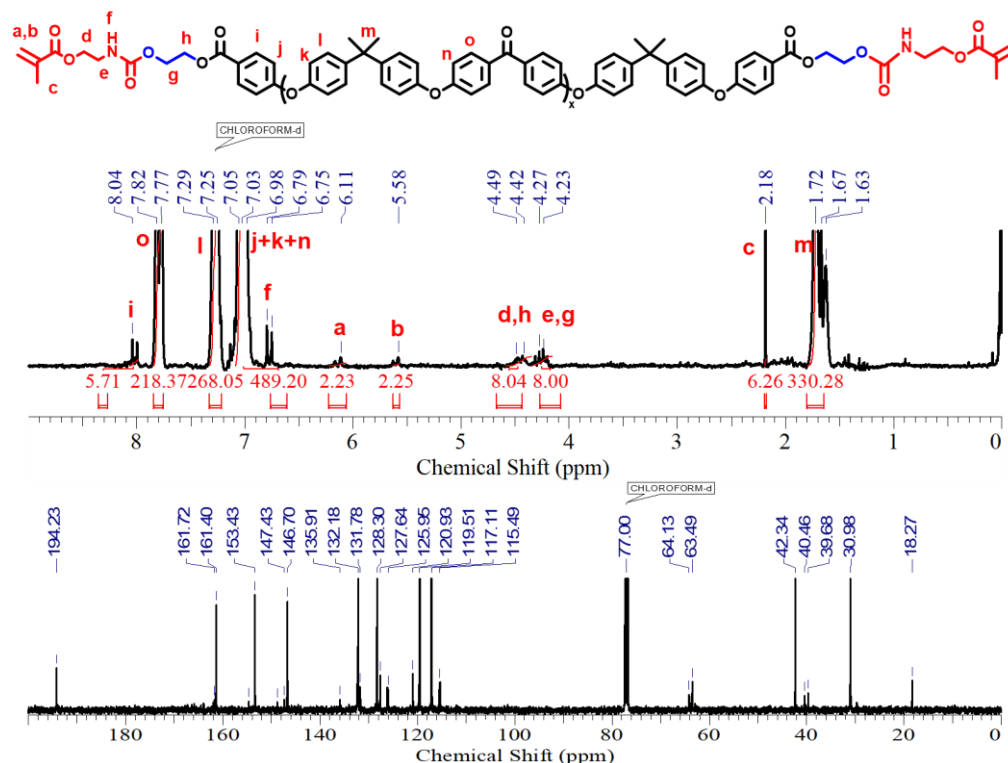
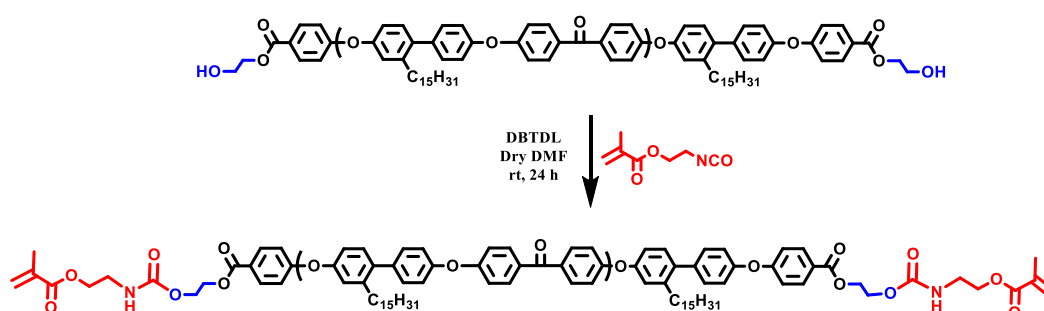


Figure 5.5 ^1H and ^{13}C NMR spectra of urethane methacrylate polyether ether ketone (UMPEEK) polymer

f) Synthesis of urethane methacrylate modified polyether ether ketone (UMmPEEK) polymer



A similar procedure was followed for the synthesis of urethane acrylate-modified PEEK polymer. Modified PEEK (17500 g/mol, 0.11 mmol) was dissolved in 30 ml of dry DMF and two drops of DBTDL were added at the nitrogen atmosphere. 2-isocyanatoethyl methacrylate (202 mg, 1.3 mmol) in 2 ml of dry DMF was added to the polymer solution within 30 minutes of time period under ice-cold conditions. The reaction was stirred at cold conditions for 2 h and further left for 12 h at room temperature. After that, the reaction mixture was poured into methanol to precipitate the polymer. Methanol was decanted and the polymer was dissolved in chloroform and reprecipitated in methanol 2-3 times to remove any unreacted product. The semi-solid polymer was dried under vacuum at room temperature for 24 h. Yield 75 %.

^1H NMR spectrum (400 MHz, CDCl_3) δ in ppm: 8.05 (d, 4H), 7.84 (m, 121H), 6.98-7.33 (m, 392H), 6.12 (s, 2H), 5.59 (s, 2H), 4.48 (m, 8H), 4.22 (m, 8H), 2.59 (m, 64H), 2.20 (s, 6H), 1.49-1.63 (m, 165H), 1.23 (m, 828H), 0.87 (m, 122H).

^{13}C NMR (100 MHz, CDCl_3) δ in ppm: 194.27, 187.86, 161.25, 154.90, 142.82, 137.33, 132.28, 131.56, 130.97, 120.60, 119.59, 117.25, 70.29, 65.19, 31.92, 29.35, 22.69, 18.31, 14.12.

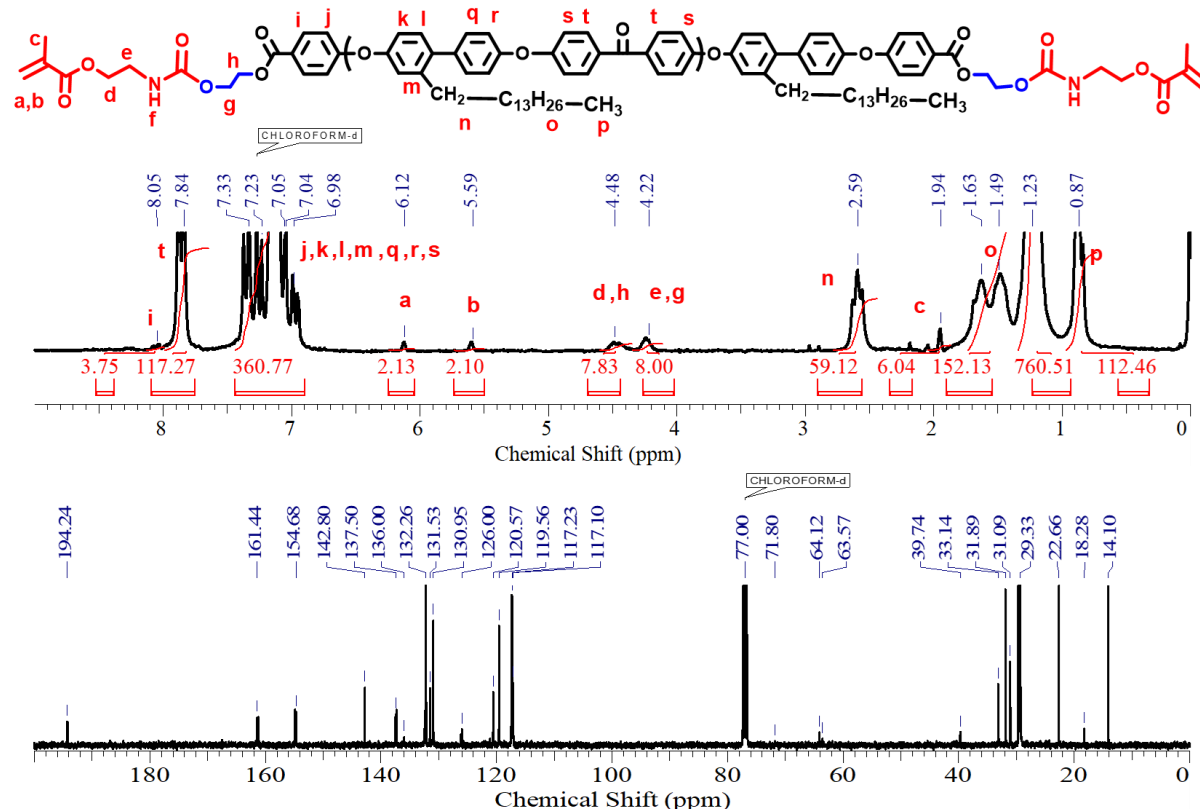


Figure 5.6 ^1H and ^{13}C NMR spectra of urethane methacrylate mPEEK (UMmPEEK) polymer

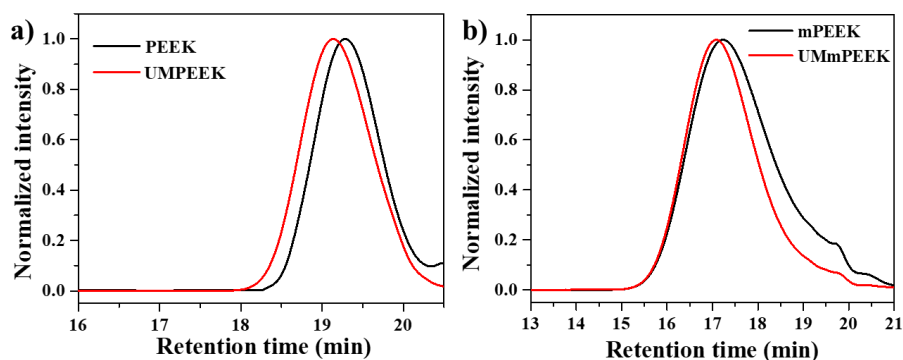


Figure 5.7 SEC plots of the PEEK, UMPEEK, mPEEK and UMmPEEK polymers

Polymers	Mn ^a (g/mol)	Mn ^b (g/mol)	Mw ^b (g/mol)	Đ ^b
PEEK	23200	8100	14200	1.7
UMPEEK	23400	9700	19000	1.9
mPEEK	17500	18400	23000	1.3
UMmPEEK	17800	16300	27300	1.7

a) NMR, b) GPC in THF eluent, PS standard

Table 5.1 Molecular weight of PEEK, UMPEEK, mPEEK and UMmPEEK polymers from NMR and SEC analysis.

5.3 RESULT AND DISCUSSION

5.3.1 Synthesis and characterization of urethane methacrylate PEEK (UMPEEK) and urethane methacrylate mPEEK (UMmPEEK) polymers

Figure 5.8 summarizes the main goals of creating a photocurable resin formulation with PEEK/mPEEK polymer. The synthesis of the modified PEEK with appended pentadecyl chain was adopted with some modifications from the literature (mentioned in the synthesis and characterization section a and figure 5.1).²¹ Briefly, the synthesis of PEEK (or mPEEK) involved the polycondensation reaction of bisphenol A (or 3-pentadecyl 4,4'-biphenol) with 4,4'-difluoro benzophenone in a solvent mixture of toluene and dimethyl acetamide in presence of anhydrous potassium carbonate. After three hours of reaction at 130 °C, the temperature was increased to 180 °C to remove water and toluene as an azeotropic mixture. Afterwards, 2-hydroxyethyl 4-fluoro benzoate was added to end cap the formed polymer. A moderate molecular weight was targeted for the polymerization so as to enable processing the polymer in a photocurable resin formulation. The precipitated polymer was structurally characterized by NMR spectroscopy and molecular weight determined by size exclusion chromatography. (Figure 5.3, figure 5.4, figure 5.7 and table 5.1).

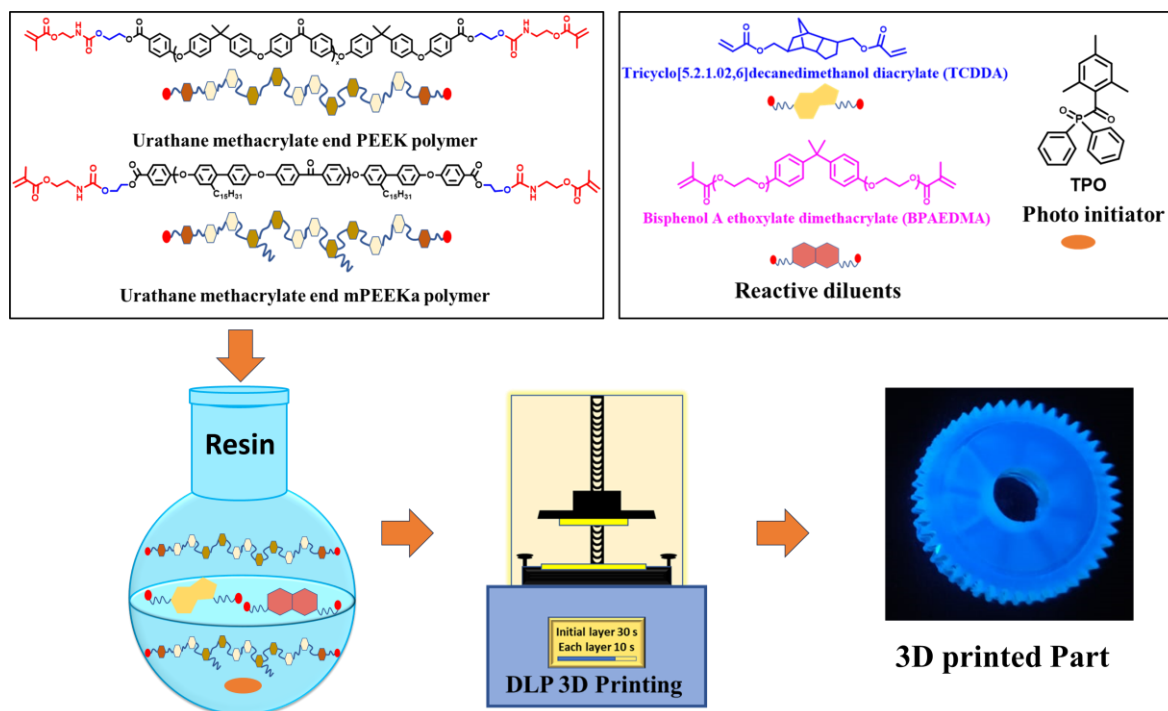


Figure 5.8 Overall representation summarizing the preparation of the 3D printable photocurable resins of UMPEEK/UMmPEEK polymers into 3D printed physical objects using DLP 3D printer.

The methacrylate modification of the end groups was accomplished by reacting the hydroxyl terminated PEEK and mPEEK polymer by reacting with 2-isocyanatoethyl methacrylate in presence of dibutyltindilaurate (DBTDL) as catalyst.²² The final photocurable PEEK polymers were obtained by precipitation from chloroform into methanol at least 2-3 times. Figure 5.5 and figure 5.6 compares the labeled proton NMR spectra of the UMPEEK and UMmPEEK polymers. The terminal methacrylate protons were observed as two doublets at 6.12 and 5.59 ppm respectively. By integrating the intensity of the methacrylate protons with respect to the aromatic protons (especially the isolated peak near the ketone labeled as ‘o’ for UMPEEK and ‘t’ for UMmPEEK) at 7.82-7.84 ppm, the number of repeat units was obtained as 56 for UMPEEK and 30 for UMmPEEK polymer respectively. The molecular weights of the polymers were measured using GPC with THF as eluent and polystyrene as standard. The molecular weights of the PEEK polymers are given on the figure 5.7 and table 5.1. The molecular weight of the PEEK polymers should not be taken as absolute as it is taken with respect to the polystyrene standard.^{23,24} Additionally, the introduction of long pentadecyl group in the mPEEK polymer altered the hydrodynamic volume resulting in changes in the molecular weight.²⁵

5.3.2 Resin formulations and photocuring experiments

Following the structural characterization, the PEEK polymers were used to formulate a photocurable resin mixture. The formulations incorporated Tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate (TCDDA) and Bisphenol A ethoxylate dimethacrylate (BPAEDMA) as reactive diluents.

Resin formulations	TCDDA wt. %	BPAEDMA wt. %	UMPEEK wt. %	UMm PEEK wt. %	TPO wt. %	Viscosity (Pa.s)
Ref	49.5	49.5	-	-	1	0.17
UMPEEK5	47	47	5	-	1	0.32
UMPEEK10	44.5	44.5	10	-	1	0.57
UMmPEEK5	47	47	-	5	1	0.54
UMmPEEK10	44.5	44.5	-	10	1	1.03

Table 5.2 Weight percentages of the UMPEEK, UMmPEEK, TCDDA, BPAEDMA, and PI taken to prepare resin formulations and their measured viscosity.

Table 5.2 lists the weight percentages of polymers and reactive diluents used in the resin composition. Two formulations each were prepared using 5 and 10 weight percentage of UMPEEK and UMmPEEK polymers respectively in the resin mixture of equal weight percentage of TCDDA and BPAEDMA. The solid polymer was sonicated for one hour in the

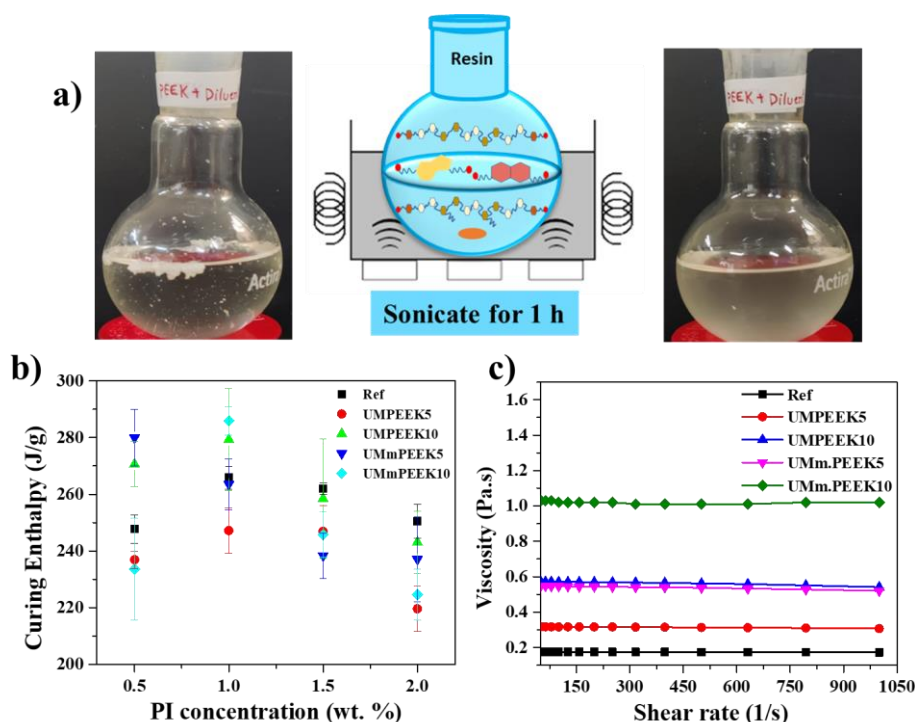


Figure 5.9 a) UMPEEK polymer with reactive diluent and sonicated for the resin formulation b) selection of the photo initiator weight percentage by photo curing study, c) Measurement of viscosity of the resin formulations and reference resin.

resin mixture to dissolve completely (see figure 5.9a). A formulation of only TCDDA and BPAEDMA was also prepared without the PEEK polymer as a reference system. The weight percentage of the photoinitiator TPO required for the curing was determined using isothermal photo DSC analysis at 30 °C. In this process, resin formulations underwent solidification upon exposure to UV light, and accurate measurements of curing enthalpies were obtained. The curing mechanism involves the initiation of radicals by the cleaving the photoinitiator in presence of UV light, resulting in the formation of a crosslinked network polymer. To examine the curing enthalpies in the resin compositions, the TPO photoinitiator's weight percentage was varied between 0.5 and 2 wt. %. (figure 5.9b). Figure 5.10 shows photo-DSC graphs for the resin formulations at various percentages of PI. Analysis of the curing enthalpies revealed increase in enthalpy with increase in concentration of PI up till a concentration of 1 wt. %, after which, the enthalpy decreased with further increase in the PI concentration. Based on this observation the ideal PI concentration was fixed at of 1 wt. % for maximum conversion.

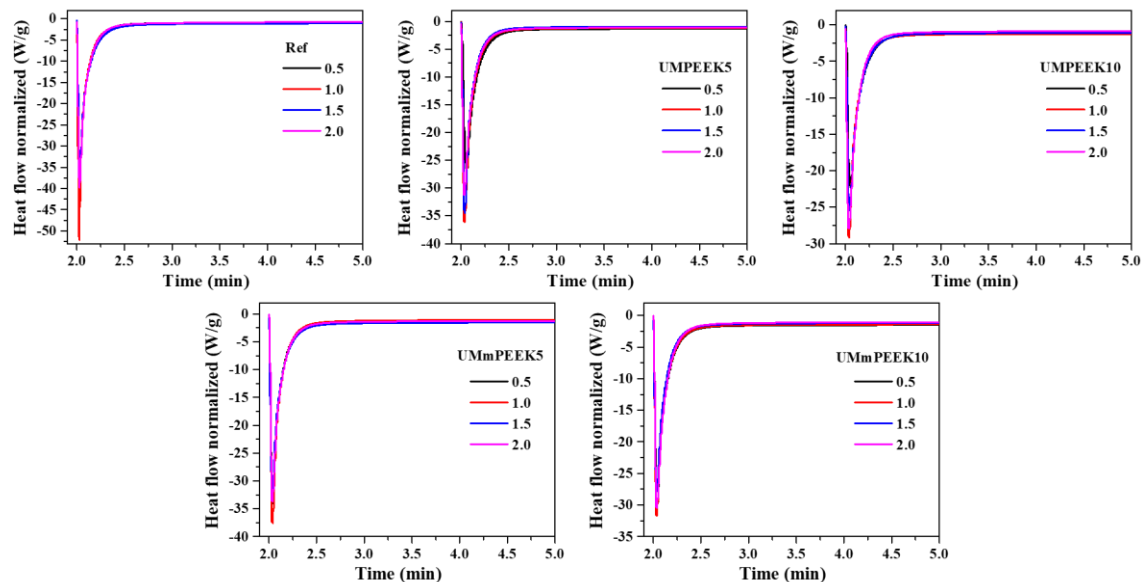


Figure 5.10 Photo-DSC plots of resin formulations with different PI weight percentages

It is reported that insufficient amounts of PI concentration may be inadequate for complete curing. However, higher concentrations of PI can result in increased light absorption, potentially leading to insufficient light penetration for the comprehensive curing of the resin samples.²⁶

5.3.3 Viscosity Measurement

A key factor in room temperature DLP 3D printing is the viscosity of the resin formulation. For a 3D printing process to be smooth and distortion-free, the resin must flow easily. The resin used in room temperature DLP 3D printing should ideally have a viscosity of no more than 10 Pa.s.²⁷ Figure 5.9c compares the viscosity as a function of increasing shear rate for the different resin formulations at 30 °C. There was no significant change observed in the viscosity of the resin with increasing shear rates, indicating Newtonian behavior. On the other hand, the viscosity of the resin rose from 0.32 to 0.57 Pa.s and from 0.54 to 1.03 Pa.s respectively with an increase in the weight proportion of UMPEEK/UMmPEEK polymer. Despite the resin formulations exhibiting low viscosity, they were found to be entirely adequate for room temperature 3D printing. All the prepared resins demonstrated suitability for DLP 3D printing, ensuring a smooth and successful printing process. The viscosity of the UMmPEEK containing resin is higher than the UMPEEK because the higher mol percentage incorporation of the UMmPEEK in the same weight of resin formulation.²⁸

5.3.4 DLP 3D printing of PEEK resin formulations

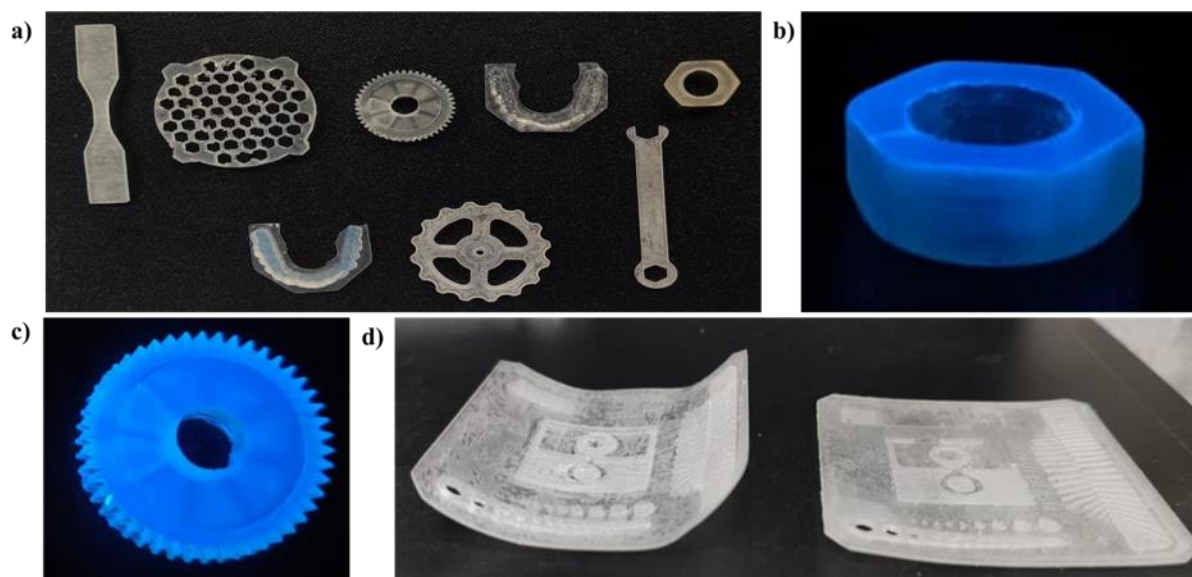


Figure 5.11 a) Top view of different 3D printed parts of acrylate UMPEEK/UMmPEEK polymers. b) & c) high resolution 3D printed parts. d) left side 3D print part of resin validation Xp2 Standard Triangle Language file of 10 wt. % UMPEEK polymer (distorted due to warpage), right side 3D printed part of same with 10 wt. % UMmPEEK polymers (no distortion).

3D Printing of PEEK polymer at room temperature presents a challenge, but this challenge was addressed by utilizing a miscible (meth)acrylate PEEK polymer as the resin at room temperature. Spot curing studies were conducted to estimate curing time of the resins. Spot curing involved applying the resins onto a glass plate and exposing it to UV light from a home-made setup utilizing six UV-LED lights. A single drop of resin solidified within 10 seconds, as confirmed by tilting the glass plate without any observable resin flow. The printing capabilities of PEEK (meth)acrylate resin formulations were assessed using the Anycubic Photon Ultra resin 3D printer (Schematically represented in Figure 5.8). The printing parameters of the DLP 3D printer involved 30 s for the initial 5 layers followed by 10 s for each succeeding layers. The longer irradiation time for the initial layers is required to make the layer stick on the build plate, otherwise the succeeding layers will collapse under its own weight. All resins were employed to showcase their 3D printing capabilities, and it was noted that each resin produced prints with sharply defined edges. In order to achieve high-resolution 3D printed parts (shown in figure 5.12), 0.02 weight percent of a fluorescent dye (2,5-Bis(5-tert-bustyl-benzoxazol-2-yl)thiophene (BBOT) was added to the resin compositions. Figure 5.11a displays top-view images of the intricate 3D printed part using UMPEEK/UMmPEEK resin formulations.



Figure 5.12 High-resolution 3D printed parts with BBOT dye

Figure 5.11b and 5.11c exhibits sharp edges of the 3D printed parts. Some issues of warpage were observed during post cure treatment for 3D printed parts using UMPEEK resin formulations, which were not observed while using the UMmPEEK resin formulations. The

UMPEEK acrylate 3D printed part (resin validation Xp2 Standard Triangle Language) displayed a distorted structure after post. However, it is noteworthy that this distortion was not observed when printing thicker 3D parts, as depicted in the first three images of Figure 5.11. In contrast, the 3D printed parts using the UMmPEEK resin formulation exhibited a precisely flat structure according to the resin validation Xp2 Standard Triangle Language, even after a 15-minute post-curing period (figure 5.11d right). This occurrence can be attributed to the presence of the long alkyl chain within the 3D printed crosslinked network, which effectively reduced the overall crosslinked density and created space between the extended polymer chains.²⁹ This was also reflected in the mechanical properties which are mentioned below.²¹

5.3.5 Mechanical and Thermal Properties of 3D Printed Parts

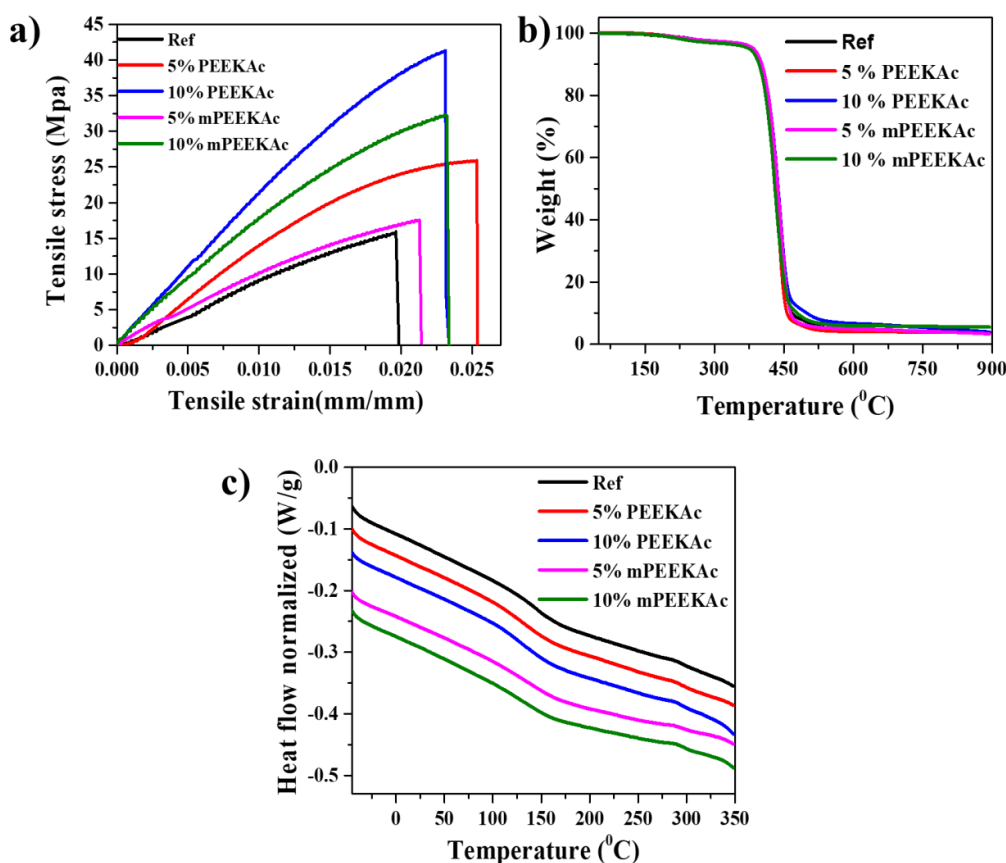


Figure 5.13 (a) The Tensile stress-strain graph of 3D printed parts of different resins (b)

TGA graph of all 3D printed parts (c) DSC graph of all resin's 3D printed parts.

3D printed parts were subjected to mechanical testing, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) to investigate the effect of varying weight percentage of UMPEEK/UMmPEEK polymer in the resin formulation. The mechanical properties were assessed by employing 3D printed dumbbell-shaped specimens of ASTM D638 type V for each resin formulation. Tensile strength values were obtained by averaging the results from a total

of five specimens. Figure 5.13a depicts the stress-strain plot of the 3D printed PEEK polymer, while Table 5.3 provides a summary of mechanical properties, including tensile strength, Young's modulus, and elongation at break. Analysis of the mechanical properties revealed a notable positive impact of the UMPEEK polymer on the reference materials.

Resin formulations	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (GPa)	T _g (°C)	T _{d10} % (°C)
Ref	15±2	2.0±0.3	0.9±0.01	145	398
5% UMPEEK	27±3	2.4±0.1	1.6±0.01	140	399
10% UMPEEK	39±2	2.2±0.2	2.1±0.02	140	401
5% UMmPEEK	18±3	2.2±2.7	0.9±0.01	140	402
10% UMmPEEK	25±4	2.2±0.3	1.7±0.02	139	396

Table 5.3 Mechanical and thermal properties of the 3D printed parts

The 3D reference resin printed part which is a mixture of aromatic acrylate (TCDDA) and cyclic(meth)acrylate (BPAEDMA), exhibited a tensile strength of 15±2 MPa and Young's modulus of 0.9±0.01 GPa with 2±0.3% elongation. Upon increasing the UMPEEK polymer content from 5 wt. % to 10 wt. % in reference resin, the tensile strength improved from 27±3 MPa to 39±2 MPa, and Young's modulus increased from 1.6±0.01 GPa to 2.1±0.02 GPa, while maintaining similar elongation values. Following a similar trend, the inclusion of the UMmPEEK polymer elevated the mechanical properties of the 3D printed part. The increase of UMmPEEK polymer from 5 wt. % to 10 wt. % resulted in an increase of tensile strength from 18±3 MPa to 25±4 MPa. Concurrently, the Young's modulus also improved from 0.9±0.01 GPa to 1.7±0.02 GPa, while maintaining a consistent elongation. Based on the mechanical properties, it could be deduced that the tensile strength and Young's modulus of the 10 wt.% UMPEEK resin 3D printed part surpassed those of the other resin-printed parts. The enhanced mechanical properties in the 10 wt.% UMPEEK resin printed part were attributed to the rigid aromatic ring of the PEEK polymer and the formation of crosslinks with the terminal methacrylate group. In contrast, the 10 wt.% UMmPEEK resin 3D printed part exhibited lower tensile strength and Young's modulus compared to the 10 wt.% UMPEEK resin 3D printed part. This difference was linked to the presence of the long-alkylated chain in each repeat unit of the former, which potentially disrupted the crosslinked network polymer, creating space between the extended polymer chains.^{30,31} The modulus of the 10 wt. % UMPEEK 3D printed part could attain almost 60 % of the tensile values of commercial PEEK polymer.⁸

Thermal properties of the PEEK polymer 3D printed materials are depicted in the Figure 5.13b and 5.13c, and the values are summarized in the Table 5.3. In Figure 5.13c, it was observed that all the 3D printed parts showed a one-step degradation. The temperature at which a 10% loss in weight occurs, or $T_{d10wt\%}$, is more than 390 °C, demonstrating that all of the PEEK polymer 3D printed parts exhibit high thermal stability. In Figure 5.13c, it was observed that the glass transition temperature values for all resin 3D printed parts ranged from 140 °C to 145 °C. Notably, no melting temperature was observed even at high temperatures, due to the crosslinked PEEK 3D network structure of printed parts.

5.4 CONCLUSION

In conclusion, in this study we report for the first time DLP 3D printing of functionalized PEEK polymer at room temperature which exhibited almost 55 % of Young's modulus of commercial PEEK polymer. The end capped PEEK polymers and its reaction with methacryloyloxyethyl isocyanate were successfully accomplished and characterized with NMR spectroscopy. A new modified PEEK polymer with long alkyl chain in repeat unit was synthesized and further reacted to introduce methacrylate group. The methacrylate PEEK polymer was used for the resin formulation up to 10 wt. % and further used for the room temperature DLP 3D printing. The printed part of the PEEK resins showed very good resolution and high mechanical values (39 ± 2 MPa tensile strength and 2.2 ± 0.2 GPa Young's modulus). The incorporation of the long alkyl chain in the 3D printed crosslinked network removed the warpage problem after the post curing of 3D printed part. Thermal analysis revealed a higher value of 10 wt. % degradation temperature (400 °C) and high glass transition temperature (140 °C) which is an excellent result for DLP 3D printed PEEK polymer. This study is a first report of the room temperature DLP 3D printing of functionalized PEEK polymers which achieved comparable Young's modulus and thermal properties.

5.5 REFERENCES

- (1) R.J. Mondschein, A. Kanitkar, C.B. Williams, S.S. Verbridge, T.E. Long, *Biomaterials*. **2017**, *140*, 170–188.
- (2) S. Kutlehria, A. D'Souza, B.S. Bleier, M.M. Amiji, *Mol. Pharm.* **2022**, *19*, 4411–4427.
- (3) S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, *Chem. Rev.* **2017**, *117*, 10212–10290.
- (4) P. Vasamsetty, T. Pss, D. Kukkala, M. Singamshetty, S. Gajula, *Mater. Today Proc.* **2019**, *26*, 838–841.
- (5) P. Boyraz, G. Runge, A. Raatz, *Actuators*, **2018**, *7*, 48.

- (6) J.W. Stansbury, M.J. Idacavage, *Dent. Mater.* **2016**, 32, 54–64.
- (7) A. Das, C.A. Chatham, J.J. Fallon, C.E. Zawaski, E.L. Gilmer, C.B. Williams, M.J. Bortner, *Addit. Manuf.* **2020**, 34, 101218.
- (8) P.J. Rae, E.N. Brown, E.B. Orler, *Polymer*. **2007**, 48, 598–615.
- (9) L. Lin, A.K. Schlarb, *Tribol. Int.* **2016**, 101, 218–225.
- (10) M. Roskies, J.O. Jordan, D. Fang, M.-N. Abdallah, M.P. Hier, A. Mlynarek, F. Tamimi, S.D. Tran, *J. Biomater. Appl.* **2016**, 31, 132–139.
- (11) Y. Wang, W.-D. Müller, A. Rumjahn, A. Schwitalla, *Materials (Basel)*. **2020**, 13, 466.
- (12) A.J. Boydston, J. Cui, C.-U. Lee, B.E. Lynde, C.A. Schilling, *ACS Macro Lett.* **2020**, 9, 1119–1129.
- (13) K.H. Tan, C.K. Chua, K.F. Leong, C.M. Cheah, P. Cheang, M.S. Abu Bakar, S.W. Cha, *Biomaterials* **2003**, 24, 3115–3123.
- (14) D. Pohle, S. Ponader, T. Rechtenwald, M. Schmidt, K.A. Schlegel, H. Münstedt, F.W. Neukam, E. Nkenke, C. von Wilmowsky, *Macromol. Symp.* **2007**, 253, 65–70.
- (15) M. Vaezi, S. Yang, *Virtual Phys. Prototyp.* **2015**, 10, 123–135.
- (16) L. Deng, Y. Deng, K. Xie, *Colloids Surfaces B Biointerfaces.* **2017**, 160, 483–492.
- (17) M. Rinaldi, T. Ghidini, F. Cecchini, A. Brandao, F. Nanni, *Compos. Part B Eng.* **2018**, 145, 162–172.
- (18) B. Hu, X. Duan, Z. Xing, Z. Xu, C. Du, H. Zhou, R. Chen, B. Shan, *Mech. Mater.* **2019**, 137, 103139.
- (19) C.-U. Lee, J. Vandenbrande, A.E. Goetz, M.A. Ganter, D.W. Storti, A.J. Boydston, *Addit. Manuf.* **2019**, 28, 430–438.
- (20) M. Hegde, V. Meenakshisundaram, N. Chartrain, S. Sekhar, D. Tafti, C.B. Williams, T.E. Long, *Adv. Mater.* **2017**, 29, 1701240.
- (21) B. V. Tawade, S. V. Shaligram, N.G. Valsange, U.K. Kharul, P.P. Wadgaonkar, *Polym. Int.* **2016**, 65, 567–576.
- (22) N. Rekha, S.K. Asha, *J. Polym. Sci. Part A Polym. Chem.* **2009**, 47, 2996–3009.
- (23) N. V. Sadavarte, M.R. Halhalli, C. V. Avadhani, P.P. Wadgaonkar, *Eur. Polym. J.* **2009**, 45, 582–589.
- (24) P.N. Honkhambe, S.K. Pasale, N.S. Bhairamadgi, K.P. Kumbhar, M.M. Salunkhe, P.P. Wadgaonkar, *J. Appl. Polym. Sci.* **2011**, 122, 1607–1613.
- (25) D. Schmaljohann, L. Häußler, P. Pötschke, B.I. Voit, T.J.A. Loontjens, *Macromol. Chem. Phys.* **2000**, 201, 49–57.

- (26) P. Castell, M. Wouters, H. Fischer, G. De With, *J. Coatings Technol. Res.* **2007**, *4*, 411–423.
- (27) T. Kuhnt, F.L.C. Morgan, M.B. Baker, L. Moroni, *Addit. Manuf.* **2021**, *46*, 102102.
- (28) H.M. Quackenbos, *J. Appl. Polym. Sci.* **1980**, *25*, 1435–1442.
- (29) L. Jiafeng, Z. Qin, F. Tiantang, G. Li, Y. Wuyou, F. Zhongyong, C. Lu, L. Qing, *CrystEngComm.* **2020**, *22*, 728–739.
- (30) A.S. More, S.K. Pasale, P.P. Wadgaonkar, *Eur. Polym. J.* **2010**, *46*, 557–567.
- (31) S. Poongavalappil, P. Svoboda, R. Theravalappil, D. Svobodova, T. Ougizawa, T. Sedlacek, *Polym. J.* **2013**, *45*, 651–658.

CHAPTER 6

Conclusion and Future Perspective

6.1 CONCLUSIONS

The thesis entitled, “**Structure Property Correlation of Novel Photocurable Polymers for Light-Based 3D Printing Application**” described the synthesis and characterization of photocurable bio-based and high-performance polymeric materials for the liquid-based DLP 3D printing technology. Creating tailored polymeric materials through synthesis was essential for enhancing the properties of the DLP printing materials. Commercial resin materials are accessible for rapid prototyping production, but they fail to meet the desired 3D printing standards and generate considerable waste due to their non-degradability. Polymeric resin materials offer the flexibility to fulfil these criteria and adjust properties accordingly. Polymer synthesis and modification represents an intriguing field within polymer research. Various characterization techniques are employed in this thesis to elucidate the structure and physical properties of polymers. This thesis primarily aimed to synthesize tailor-made bio-based polymers and employ them in light-based DLP 3D printing. DLP 3D printing stands out as a widely favoured additive manufacturing technology due to its rapid production, design flexibility, and high-resolution capabilities. Its widespread adoption facilitates the seamless fabrication of intricate structures. The work was also focused on the properties of the 3D printed materials like- degradability, mechanical properties, and 3D printing resolution. These 3D printed materials are useful in different fields of applications.

In the first working chapter, two different linear and star architectures of PLLA polymers were synthesized by the ring opening polymerization (ROP) of L-lactide. For the ROP two initiators - 1,6-hexane diol and pentaerythritol were used. The synthesized low molecular weight polymer was further reacted with acryloyl chloride to introduce photo curable groups in the terminal positions. The polymers were characterized by the NMR, FTIR spectroscopies and the molecular weight of the polymer was measured from the GPC analysis. The photocurable modified polymer was used for three different resin formulations depending on the different weight percentage of the polymer and HEMA as reactive diluents. The photo initiator concentration was measured by the photoDSC experiments. The prepared resin formulations showed good printability with DLP 3D printer at room temperature. The 3D printed parts showed moderate mechanical and degradable properties in PBS solution.

In the second chapter, the focus was to enhance both the printability and mechanical properties of the 3D printed materials. vinyl acetate was polymerised to polyvinyl acetate using the RAFT polymerization method. Subsequently, the polymer underwent partial hydrolysis to introduce hydroxyl groups into the PVAc polymer backbone. This partially

hydrolysed PVAc polymer served as a macro initiator for the Ring-Opening Polymerization (ROP) of L-lactide, resulting in the formation of a graft polymer PVAc-g-PLLA. Further, the terminal hydroxyl group of the PVAc-g-PLLA polymer was reacted with acryloyl chloride to introduce acrylate photoreactive groups. Characterization of all polymers was conducted using NMR and FTIR spectroscopy, while their molecular weight was determined through GPC analysis. Different weight percentages of the grafted acrylate PVAc-g-PLLA were combined with HEMA and HEA as reactive diluents to formulate resins. The prepared resins exhibited promising DLP 3D printing capabilities with tunable mechanical properties. Moreover, the 3D printed parts displayed notable swelling and degradation characteristics. Remarkably, these 3D printed parts demonstrated dye absorption properties from solutions containing various dyes, thus expanding their potential applications across different fields.

In the third working chapter, utilizing ethyl lactate-based polymeric ene and isosorbide-based thiol, a scalable and sustainable approach for developing 3D printing materials through thiol-ene photochemistry was demonstrated. The synthesis of the ethyl lactate-based polymeric ene component involved free radical polymerization of acrylate ethyl lactate monomer, followed by partial hydrolysis and subsequent reaction with allyl bromide. Mechanical and thermal property analysis provided insights into the potential applications and performance of these novel biobased thiol-ene materials. Showcasing practical application, 3D printing was conducted using a commercial DLP 3D printer, highlighting their feasibility for manufacturing and prototyping purposes. The hydrolytic degradability of the 3D printed parts was demonstrated in 1 M NaOH solution, emphasizing the eco-friendly aspect of these materials and their potential to mitigate nondegradable acrylate-based 3D printed waste. This research lays the foundation for the development of environmentally responsible materials poised to revolutionize the 3D printing industry. The fast degradability of PAEL-based polymeric thiol-ene 3D printed materials opens new possibilities for rapid prototyping in mass production applications, addressing sustainability challenges associated with traditional acrylate-based materials. By amalgamating biobased sourcing, scalability, and degradability, these materials represent a significant stride towards a more sustainable and environmentally conscious future in 3D printing.

In the fourth working chapter, the innovative achievement of DLP 3D printing of functionalized PEEK polymer was successfully demonstrated at room temperature, exhibiting approximately 55% of the Young's modulus of commercial PEEK polymer. The synthesis and characterization of end-capped PEEK polymers, along with their reaction with

methacryloyloxyethyl isocyanate, were successfully carried out and analysed using NMR spectroscopy. Additionally, a novel modified PEEK polymer with a long alkyl chain in the repeat unit was synthesized and further modified to introduce methacrylate groups. The methacrylate-modified PEEK polymer was incorporated into the resin formulation up to 10 wt. % and utilized for room temperature DLP 3D printing. The printed parts exhibited exceptional resolution and mechanical properties, with a tensile strength of 39 ± 2 MPa and a Young's modulus of 2.2 ± 0.2 GPa. The inclusion of the long alkyl chain in the crosslinked network of the 3D prints effectively addressed warpage issues after post-curing. Thermal analysis revealed impressive results, including a higher degradation temperature of 400 °C and a high glass transition temperature of 140 °C, which are exceptionally favourable for DLP 3D printing of PEEK polymer. This study marks the first successful demonstration of room temperature DLP 3D printing of functionalized PEEK polymers, achieving comparable Young's modulus and thermal properties.

6.2 FUTURE PERSPECTIVE

Advances in 3D printing technology, continuous research on materials development, and the varied demands of different sectors for different applications are driving the development of photocurable polymer resins for Digital Light Processing (DLP) 3D printing. The DLP 3D printing is a technology which provides the fast and high precision 3D printed products with improved resolution among the other existing 3D printing technology. Advancements in resin formulation based on polymeric material makes the DLP printing method more reliable and production of biocompatible end use products. Besides, a range of functional resin materials have been developed by improving toughness and durability of the 3D printed materials for the specific application like soft robotics model, prototypes, dental, and medical implants. Biocompatible polymeric resins are making expandable demand for the bio-medical applications. Polymeric photo resins are suitable in terms of strength, biocompatibility, and non-toxicity. Choosing polymeric materials that are degradable increases their demand, as they contribute to waste reduction after use. In summary, the use of photocurable polymeric resin formulations broadens the the possibilities in DLP 3D printing and enhances the potential for sustainable material innovation. Bio-based polymeric materials are dependable for creating 3D printed end-use products, especially in bio-medical application. In this regard some future objectives are mentioned here-

1. To improve the resolution of the DLP 3D printed materials an external dye was mixed with the resin which can potentially leach out during use of the 3D printed material for particular applications. To overcome this problem a simple synthetic pathway can be designed, which incorporates a light absorbing group in the curable and degradable polymeric chain. Employing minimal amounts of this modified polymer will enhance the resolution of DLP 3D printing with minimum possibility of dye leaching.

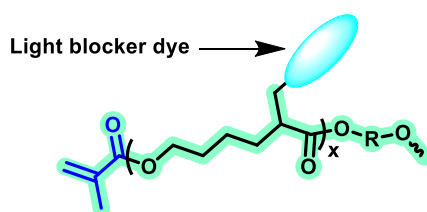


Figure 6.1 Dye-containing bio-based photo-crosslinker

2. To improve the mechanical properties of the 3D printed product, an aromatic repeat unit can be introduced in the polymeric backbone. The polymer can be further modified in the telechelic position to introduce the cross-linkable group either acrylate or 'ene-containing'

group to take part in the thiol-ene crosslinking network formation during DLP 3D printing. The thiol-ene chemistry will improve the curing kinetics of the resin formulations as well as the toughness of the printed parts.

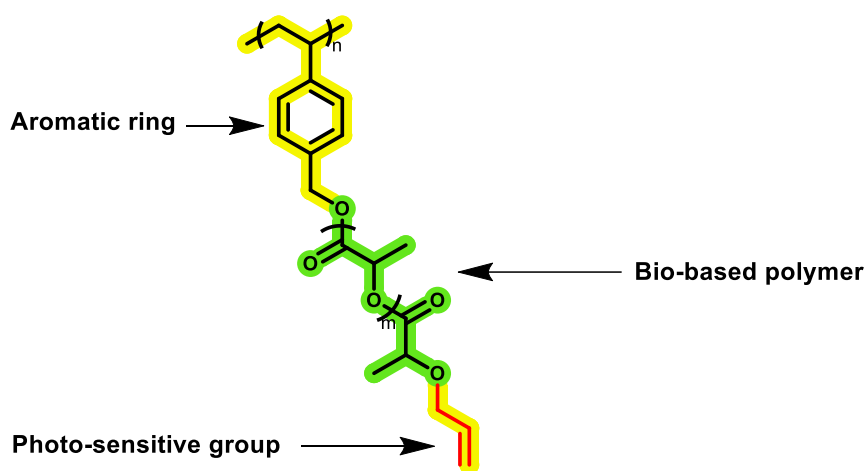


Figure 6.2 Aromatic backbone and bio-based polymer with photo-sensitive group

3. The presence of the polymeric styrene and polylactide or poly caprolactone makes the 3D printed materials non-toxic and biocompatible for the use in biomedical applications.
4. The presence of the degradable ester linkage in the network makes the 3D printed materials prone to degradation in the presence of appropriate stimuli either presence of enzymes or presence of acid or base.
5. The mechanical properties of the DLP 3D printed materials can be improved by introducing photocurable group in the PEEK polymer repeat unit pendent group so as to have polymerizable moieties in every repeat unit, rather than limited to the terminal positions.

ABSTRACT

Name of the Student: Shibam Pal	Registration Number.: 10CC18A26013
Faculty of Study: Chemical Science	Year of Submission: 2024
AcSIR academic centre/CSIR Lab: CSIR-National Chemical Laboratory	Name of the Supervisor: Dr. Asha S.K
Title of the thesis: Structure Property Correlation of Novel Photocurable Polymers for Light-Based 3D Printing Applications.	

The thesis work focused on the importance of developing bio-based polymeric materials for liquid-based DLP 3D printing technology. DLP 3D printing stands as a widely utilized additive manufacturing technology, offering rapid production, design flexibility, and high-resolution outputs. Its adoption allows for the creation of complex structures with ease. However, a significant challenge lies in the development of bio-based polymeric resin materials suitable for DLP 3D printing. Polymeric materials have garnered attention due to their favourable processability and the ability to adjust curing properties to achieve desired mechanical properties. The primary objective of the thesis is to develop different types of photocurable crosslinkers to be utilized in the development of resin formulations. After that, the prepared resins will be used in light-based DLP 3D printing technology. The thesis also focuses on the properties of the 3D printed materials like- degradability, mechanical properties, and 3D printing resolution. These 3D printed materials are useful in different fields of applications.

Chapter 2 focuses on developing linear and star PLLA polymers functionalized with photocurable methacrylate groups for resin formulation and DLP 3D printing. Chapter 3 improves printability and mechanical properties by grafting PLLA onto a Poly(vinyl acetate) backbone, resulting in tunable mechanical properties and interesting dye absorption capabilities. Chapter 4 incorporates thiol-ene chemistry into bio-based polymers for DLP 3D printing, resulting in high modulus and degradability in basic solutions. Chapter 5 develops high-performance polymer resin formulations using PEEK derivatives with urethane acrylate groups, achieving high modulus and tensile strength in 3D printed parts.

List of Publications Emanating from the Thesis Work

1. **Shibam Pal**, and Asha SK. Biodegradable, Solvent-Free Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing. *Macromolecular Chemistry and Physics*. **2022**, *223 (22)*, 2200139.
2. **Shibam Pal**, and Asha SK. Thiol-ene-based degradable 3D printed network from bio resource derived monomers ethyl-lactate and isosorbide. *European Polymer Journal*. **2024**, *205*, 112761.
3. **Shibam Pal**, Yogesh Gaikwad, and Asha SK. Room Temperature Photocurable PEEK Polymer Formulations for High-Performance 3D Printing Applications. *ACS Applied Engineering Materials*. **2024**, *2, 6*, 1450-1459.

Patent

1. **Shibam Pal**, and Asha SK. Acrylated Polyvinyl-grafted-poly(l-lactide) (PVAc-g-PLLA) Based Compound and Compositions Thereof for 3D Printing (*Provisional patent Application number 202311061154*).
2. **Shibam Pal**, and Asha SK. Modified Photocurable Peek Photopolymer for 3D Printing and Preparations Thereof. (*Provisional patent Application number 202411004776*)

List of poster presentation with details

1. National Science Day 2020 Poster Presentation at CSIR-National Chemical Laboratory, Pune (India), February 2020.

Title: Biodegradable Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing

Abstract: The aim of the current project is to develop resin formulations based on thermoplastic polymer like PLA (poly Lactic acid). PLA filaments are used for additive manufacturing using fused deposition modeling (FDM). PLA is biodegradable, biocompatible and has excellent processability; in addition, it is derived from natural resources. However, it absorbs moisture as it is hygroscopic in nature, which is a disadvantage in storing PLA filaments for FDM application. Photocrosslinkable PLA could be an alternative to the PLA filaments as it would enable 3D printing using alternate techniques like the DLP (digital light processing). The resin printing has the added advantage of better resolution of the printed object compared to a FDM printed object. Thus, the first objective of the project is to develop telechelic PLA resin formulation by either end functionalization of oligoPLA or transesterification of high molecular weight PLA using crosslinkable acrylates.

2. CASM 2022, Poster Presentation at International Conference on Chemistry and Applications of Soft Materials, CSIR-NIIST, Thiruvananthapuram, (India), July 2022

Title: Biodegradable, Solvent-Free Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing

Abstract: We've developed acrylate end-functionalized linear and star poly l-lactide (PLLA)-based aliphatic, photocurable oligomeric crosslinkers. These crosslinkers are formulated with hydroxyl (ethyl)methacrylate (HEMA) as a biodegradable reactive diluent. We successfully demonstrate their application for solvent-less 3D printing using digital light processing (DLP) technique, as well as a custom-designed direct ink writing 3D printer. To optimize the resin formulation for 3D printing, we utilized spot curing, photodifferential scanning calorimetry, and cure depth analysis. The resulting 3D printed parts exhibit promising mechanical properties, along with improved hydrophilicity and biodegradability. This development of new photocurable resin formulations is anticipated to meet the increasing demand for raw materials suitable for creating custom-designed bio-implantable objects.

3. 5th NCL RF Student Conference 2023 Oral Presentation at CSIR-National Chemical Laboratory, Pune (India), November 2023.

Title: Biocompatible PVAc-g-PLLA Resin Formulations with tunable mechanical properties for DLP/SLA 3D Printing.

Abstract: The technological advancement of Additive Manufacturing has enabled the fabrication of various customized artefacts and devices, which has prompted a huge demand for multilaterals that can cater to the stringent mechanical, chemical and other functional property requirements. Photocurable formulations that are widely used for Digital Light Processing (DLP) / Stereolithography (SLA) 3D printing applications are now expected to meet these new challenges of hard and soft or stretchable structural requirements in addition to good resolution in multiple scales. Here we present a biocompatible photocurable resin formulation with tunable mechanical properties that can produce hard or stretchable elastomeric 3D printed materials in a graded manner. Acrylated poly(lactic acid) (PLA) grafted poly vinyl acetate (PVAc) polymer was mixed with hydroxyl methyl methacrylate (HEMA) and hydroxyl ethyl acrylate (HEA) as reactive diluents in various compositions to form a series of photocurable resin formulations. Depending on the nature of the reactive diluent (HEMA or HEA) and their weight percentage, the mechanical properties of the 3D-printed parts could be fine-tuned from hard to soft materials. The printed materials exhibited cell viability for mouse embryonic (WT-MEF) cells and degradability in the PBS solution. These bio-based 3D printing resins have the potential for a variety of applications, including the development of bio-cellular matrix, tissue engineering, soft robotics, and elastomeric actuators.

4. 3DGEM-2023, Poster Presentation, 3d Graphy Engineering & Medical 2024 at Indian Institute of Technology Mumbai, Maharashtra, (India) December 2023.

Title: DLP 3D Printing with High Mechanical Properties PEEK Polymer

Abstract: We report our efforts toward 3D printing of polyether ether ketone (PEEK) at room temperature by Digital Light Processing (DLP) technology. The room-temperature DLP printing method was enabled by a unique formulation comprised of synthesized urethane acrylate PEEK polymer with acrylate reactive diluent. This combination formed a flowable resin that could be printable using a readily available DLP printer. The terminal position of the PEEK was modified with a urethane acrylate group to make a crosslinked network structure during DLP 3D printing. A similar modified PEEK polymer was synthesized with

long alkyl chain in the backbone to enhance the elongation properties. The structural properties of the PEEK polymers were characterized by NMR spectroscopy whereas, the curing kinetics of the resin formulations were performed by photoDSC. The mechanical properties of the 3D printed part were increased with increasing the wt. % PEEK polymer from 5 wt. % and 10 wt. % in the resin formulations. The final 3D printed part has excellent thermal properties with glass transition temperature of 140 °C and 10 % degradation temperature around 400 °C. The resins are good in printability with high resolution even a dental complex material with a complex shape can be easily printable. The printed materials are useful in different fields of applications like dentistry, automobile, and robotics.

5. SPSI-MACRO-2023, Oral Presentation 17th International Conference on Polymer Science and Technology at Indian Institute of Technology Guwahati, Assam, (India), December, 2023

Title: Degradable Thiol-ene Networks from Ethyl Lactate-based Polymer for 3D Printing Applications

Abstract: Ethyl lactate is a biobased material obtained naturally or chemically in high yields in the form of ethyl ester of lactic acid. Here, we report an efficient and scalable method for creating a biobased thiol-ene network from allyl poly (acrylate ethyl lactate) (PAEL) and multifunctional thiol via DLP 3D printing. The thiol used in this report is also synthesized from isosorbide, the dehydration form of D-sorbitol, contributing to the overall eco-friendly nature of the resulting thiol-ene network. The properties of these networks can be customized based on the specific type and stoichiometric ratio of the thiol crosslinker employed. This customization allows for a wide range of tunability in both Young's modulus (ranging from 1.75 GPa to 1.03 GPa) and glass transition temperature (ranging from 44 °C to 54 °C) for the PAEL-based networks. Furthermore, these PAEL-based thermosets exhibit good thermal stability, with decomposition temperature ($T_{d,10\%}$) above 350 °C for all the networks studied. Additionally, the research demonstrates the suitability of these resin formulations for resin-based 3D printing, producing 3D-printed parts with good resolution. The study also highlights the hydrolytic degradation properties of these 3D printed parts through ester hydrolysis, showing that PAEL-based resins are highly promising for sustainable rapid prototyping and mass production applications. Overall, this work demonstrates the immense potential of PAEL-based materials as a sustainable source of bio-based resins, providing the

prospect of the development of specialized thermosetting compounds required for a variety of applications, such as 3D printing and biomaterials.

List of Conferences Attended with details

- 1. SPSI-MACRO-2023**, 17th International Conference on Polymer Science and Technology at Indian Institute of Technology Guwahati, Assam, (India), December,10-13 **2023**
- 2. SPSI-MACRO-2022**, 16th International Conference on Polymer Science and Technology at CSIR- National Chemical Laboratory (CSIR-NCL), Pune (India), Indian Institute of Science Education and Research (IISER) Pune, and Savitribai Phule Pune University. November, 2-4, **2022**
- 3. SPSI-Macro-2018**, 15th International Conference on Polymer Science and Technology Department of Chemistry, Indian Institute of Science Education and Research (IISER) Pune, CSIR- National Chemical Laboratory (CSIR-NCL), and Savitribai Phule Pune University. December 19-22, 2018, December 19-22, **2018**.
- 4. ICDDMAP- 2019, 3rd International Conference on Direct Digital Manufacturing and Polymers**, Department of Chemistry, Karnataka University Dharwad, Karnataka, India. February, 20-23, **2019**.
- 5. National Symposium of Polymer and Technology, Academia and Industry Perspectives**. at Somaiya Vidyapith University, Mumbai, (India) May, 6-7, **2022**.
- 6. Workshop attended at CSIR-National Chemical Laboratory, Pune (India), on “Global Climate Clock Assembly and Demonstration” April 2023.**
- 7. Internship with Kashtakari Panchayat (KP) for the Plastic waste flow mapping study, specifically in a waste audit. December 2021 to May 2022.**

ABOUT THE AUTHOR



Mr. Shibam Pal was born to shri. Sudeb Pal and smt. Prajapati Palin in 1995 at Gachha, a village in Nadia district of West Bengal (India). The author started his primary schooling at Gachha primary school and completed secondary education from Bethuadahari J. C. M. high school, moved to Krishnagar govt. college under the University of Kalyani for graduation in 2016. The author pursued his master's degree in chemistry (Organic Chemistry) from the Banaras Hindu University. During the post-graduation, author qualified CSIR-National Eligibility Test examination with AIR 134 in December 2017. Then he joined CSIR- National Chemical Laboratory, Pune, India for the Ph.D. programme under the supervision of Prof. Dr. Asha S.K, chief Scientist in polymer science and engineering division. He has received a research fellowship (JRF and SRF) from the Council of Scientific & Industrial Research to carry out the Ph.D. thesis work.

Biodegradable, Solvent-Free Photocrosslinkable PLLA Resin Formulations for Additive Manufacturing

Shibam Pal and Asha S. K.*

Acrylate end-functionalized linear and star poly L-lactide (PLLA) based aliphatic, photocurable oligomeric crosslinkers are developed, which are formulated with hydroxyl (ethyl)methacrylate (HEMA) as a biodegradable reactive diluent to demonstrate successful application for solvent-less 3D printing using digital light processing (DLP) technique as well as a custom-designed direct ink writing 3D printer. The resin formulation for 3D printing is optimized using spot curing, photodifferential scanning calorimetry and cure depth analysis. The 3D printed parts exhibit promising mechanical property along with improved hydrophilicity and biodegradability. The development of new photocurable resin formulations are expected to meet the growing demand for raw materials that can be applied for developing custom designed bio implantable objects.

materials that meets the functional requirements of customized 3D printing technologies.^[12,13] The examples of some of the most commonly used biopolymers are polylactide (PLA), polycaprolactone (PCL), and polyglycolide (PGL), which are all derived from natural resources such as starch, sugar cane, corn, wheat straw, and wood chip.^[14,15] These polymers are characterized by the ester linkage that is amenable to hydrolytic cleavage to form small molecules.^[16,17] PLA and its composite or petroleum-based polymers with bio fillers are available in the form of solid fillaments that can be used directly in additive manufacturing.^[18,19]

1. Introduction

In recent years there is an increasing demand for biodegradable materials for fabricating complex 3D biomedical patient specific implants.^[1–3] The additive manufacturing (AM) or 3D printing technology has been trying to meet these requirements for custom-designed device fabrication using various technologies like the selective laser sintering (SLS), fused deposition modeling (FDM), light based technologies like the stereolithography (SLA) and digital light processing (DLP), extrusion-based 3D printing, inkjet printing, etc.^[4–9] The challenge for suitable biomaterial selection is uphill with severe limitation in the availability of materials that can meet all the mechanical and processing requirements of device fabrication and at the same time meet the stringent requirements acceptable for medical application.^[10] The rapid progress in technological development of machinery for AM achieved in the recent decade has also spurred the search for suitable materials that could meet the requirements of these applications.^[11] With the on-going focus on research in bio 3D printing, there is a need for the development of more new

Photocuring based 3D printing technologies like the DLP is very amenable for bio 3D printing as they offer many advantages like high resolution and gentle processing conditions compared to the extrusion-based AM technologies.^[20–22] Moreover, the print speed can be controlled by adjusting the intensity of light or the exposure time.^[23,24] Compared to filament extrusion-based 3D printing technologies, the photocuring based 3D printing has the added advantage of enhanced bonding across the layers as the polymerization can continue even in the absence of light thereby connecting polymer chains across the different layers.^[25,26] Although many natural polymers satisfy the biological function requirements, they seldom possess the mechanical properties and structural integrity that are required to develop printable resin formulations.^[27] One approach to improve the mechanical integrity is to incorporate crosslinking strategy. Among the available biopolymers, PLA is the most promising one for 3D printing due to its biocompatibility and biodegradability. Photocurable PLA can be developed by end functionalization with acrylate or by transesterification reactions to obtain oligomeric crosslinkers.^[28–31] Recent work has also reported 3D printing using photocurable monomer incorporating trithiocarbonate that could undergo photo-Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization.^[32,33] Melchels et al. reported photocurable formulations based on methacrylate end functionalized star shaped poly(D,L-lactide) diluted with ethyl lactate as a nonreactive diluent for 3D printing by SLA technique. They demonstrated porous 3D printed scaffolds that exhibited around 10% isotropic shrinkage upon removal of the nonreactive diluent. The 3D printed scaffold exhibited excellent mechanical properties and was compatible for cell attachment and proliferation.^[34] Seck et al. reported synthesis and formulation of an aqueous photo-curable resin based on methacrylate-functionalized poly(ethylene glycol) / poly(D,L-lactide), which was demonstrated

S. Pal, A. S. K.
 Polymer Science and Engineering Division
 CSIR-National Chemical Laboratory
 Dr. Homi Bhabha Road, Pashan, Pune 411008, India
 E-mail: sk.asha@ncl.res.in

S. Pal, A. S. K.
 Academy of Scientific and Innovative Research
 Sector 19, Kamla Nehru Nagar, Ghaziabad, Uttar Pradesh 201002, India

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/macp.202200139>

DOI: 10.1002/macp.202200139

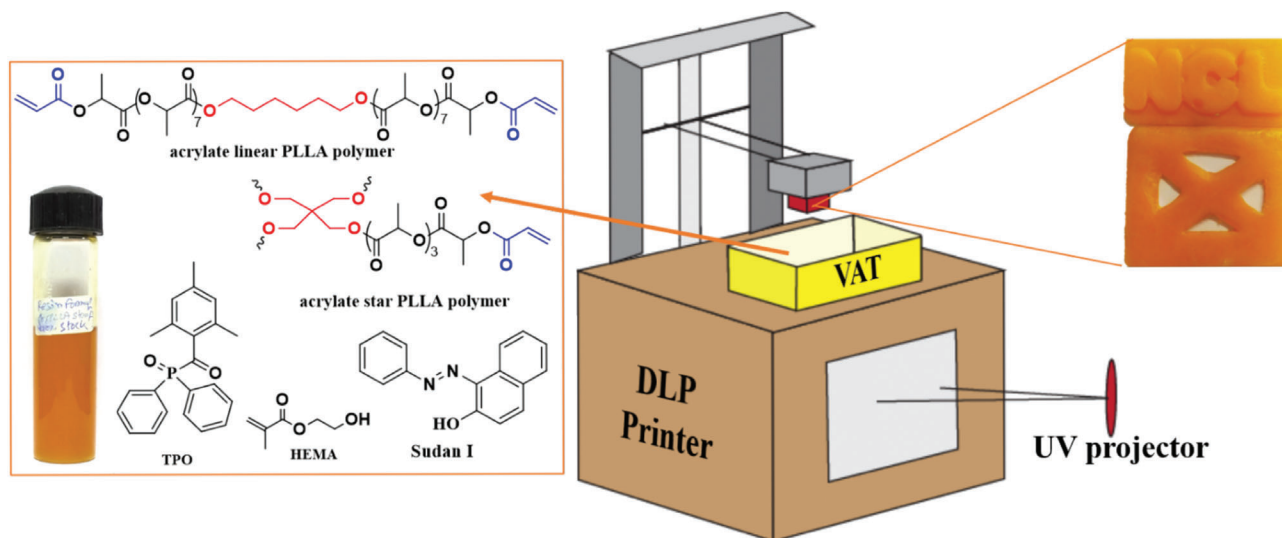


Figure 1. Schematic representation summarizing the conversion of 3D printable photocurable resin formulation based on PLLA into solid objects using a DLP printer.

for printing porous scaffolds using SLA technique with pore size in the range of 400–500 microns that was compatible for cell seeding.^[35] Ronca et al. prepared a composite resin formulation with methacrylate end capped poly(D, L-lactide) macromer and nano-hydroxyapatite which was dispersed with N-methyl-2-pyrrolidone (NMP) as nonreactive diluent and demonstrated for 3D printing schwarz pore network structure with the help of micro-stereolithography.^[36] Arvin et al. reported the synthesis of methacrylic end-functionalized PLLA which was formulated into a photocurable resin by adding 20 wt% 2-ethyl-2-hydroxymethyl-trimethacrylate as crosslinker, 20 wt% of NMP as nonreactive diluent along with 4 wt% phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) as photoinitiator (PI). This formulation was used to 3D print gyroid scaffold with interconnected pores using a DLP 3D printer; the 3D printed part exhibited good cell viability although it had comparatively feeble mechanical strength to be applicable for actual bone grafting.^[37] In most of the reported PLA based literature, nonreactive solvents are used as diluent for the preparation of resin formulation in order to avoid the use of nondegradable reactive diluents like methyl methacrylate. However, the nonreactive diluents lead to shrinkage of the printed object upon its removal with solvent after 3D printing. Recently, Sandmeier et al. reported the solvent free resin formulation to 3D print biodegradable elastomer using heat-assisted DLP 3D printer.^[38] This was achieved by covalently incorporating the photoinitiator bisacylphosphane oxide (BAPO) as part of macro-photoinitiator into random copolymers of D,L-lactide, and ϵ -caprolactone, resulting in viscous liquid polymers that were 3D printed using customized DLP printer equipped with heating facility.

In this work, we demonstrate the development of solvent-free resin formulations based on star and linear PLLA polymer crosslinkers, which was utilized to generate 3D network structure using DLP 3D printer at room temperature. Two different resin formulations were developed by diluting the linear and star PLLA acrylate crosslinkers with 50% by weight of biodegradable hydroxy ethyl methacrylate (HEMA) as a reactive diluent. A third

resin formulation with a 50 wt% of PLLA oligomer (50:50 wt% of mixture of linear and star PLLA acrylate crosslinkers) and 50 wt% of HEMA, had optimum viscosity for DLP 3D printing and exhibited compatible tensile strength, Young's modulus and elongation for 3D printing tissue engineering scaffold. The photocuring kinetics of formulated resins with respect to photoinitiator concentration was studied using photodifferential scanning calorimetry (photo-DSC). The PLLA based formulation is anticipated to add to the palette of photocurable materials for DLP printing that do not exhibit shrinkage after printing and are also biodegradable.

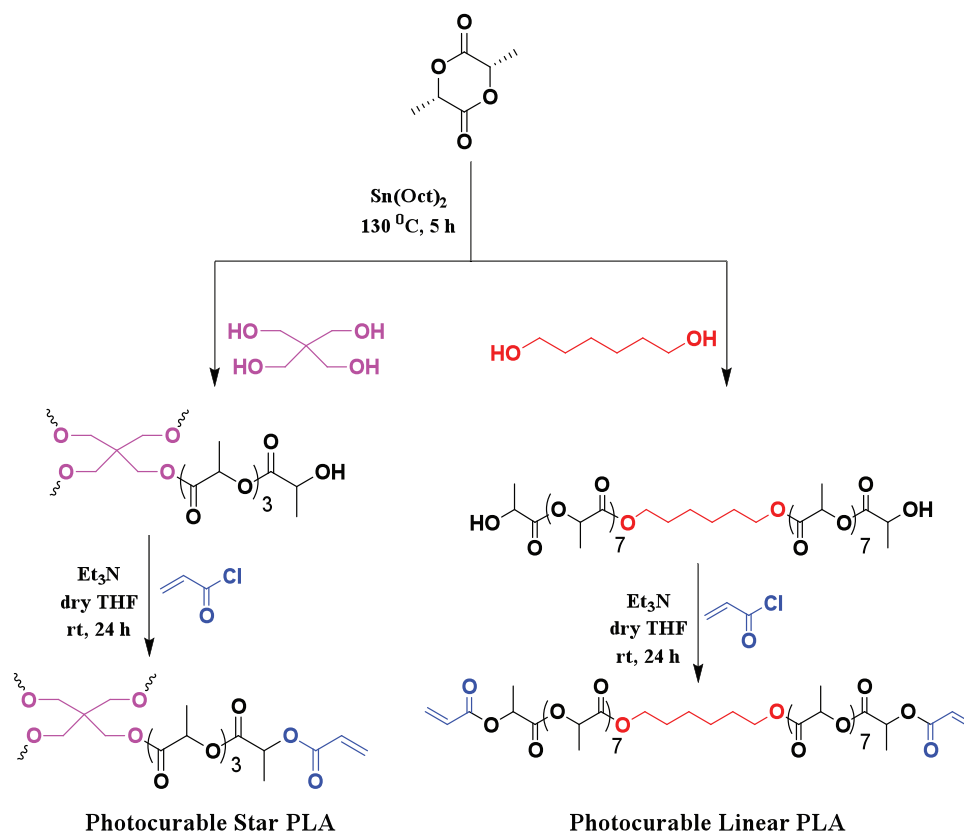
2. Results and Discussion

2.1. Synthesis and Characterization

Figure 1 summarizes the overall objectives of developing photocurable resin formulations using biodegradable PLLA-based crosslinkers and the demonstration of 3D printing using the same. Low molecular weight linear and star PLLA polymers were synthesized by the ring opening polymerization of L-Lactide with stannous 2-ethylhexanoate as the catalyst and 1,6-hexane diol as initiator for the linear and pentaerythritol as the initiator for the star PLLA respectively as detailed in **Scheme 1**.

The details of synthesis and structural characterization of the polymers are provided in Sections S1–S5 and Figures S1–S10 (Supporting Information). The degree of polymerization for the linear and star PLLA was obtained from the proton NMR spectra by integrating the peak area for the terminal methine protons versus chain methylene protons. **Figure 2** compares the expanded region in the proton NMR spectra of (a) linear and (b) star PLLA before and after acrylation.

The entire range of the proton and ^{13}C NMR spectra of all samples is provided in the supporting information file in Figures S3–S10 (Supporting Information). In **Figure 2a**, the two terminal methine protons of linear PLLA labeled “e” appeared at 4.38 ppm, while the methine protons in the repeat unit labeled



Scheme 1. Overall synthetic scheme for acryloyl functionalized linear and star PLLA crosslinkers.

“c” (on either side of the central hexamethylene chain), appeared at 5.15 ppm. From the ratio of these two peak areas, the number of repeat units on either side of the central hexamethylene spacer could be assigned as 8 for the linear PLLA in accordance with the theoretical calculation. In the case of the star PLLA, shown in Figure 2b, the central methylene (CH_2) protons of the initiator (labeled “a”) was integrated for 8 protons for the four arms. The methine proton of the terminal (total 4 for four arms, labeled “e”) was also partially merged with the “a” protons. So, the total integration of the peaks in the range 4.19 to 4.38 ppm was taken as 12. The integration for the methine protons of the repeat units at 5.19 ppm was obtained as 16. Taking the ratio of this peak area with respect to the e+a protons, the average number of repeat units per arm was obtained as 4 which match with the theoretical monomer to initiator ratio. The linear and star PLLA was reacted with acryloyl chloride in presence of triethyl amine as base to convert the terminal hydroxyl units into acryloyl functionality. This reaction was optimized in THF as solvent to obtain reasonable yields in the range of 80 to 85%.^[39,40] The introduction of the acryloyl functionality was confirmed by the appearance of the new peak corresponding to the acryloyl double bond in the range of 5.8–6.63 in the proton NMR spectra (top spectra in Figure 2a,b). The formation of the acryloyl double bond could be further confirmed with ^{13}C NMR and FT-IR spectroscopy as well. Comparing the ^{13}C NMR spectra of linear (Figure S4, Supporting Information) and star PLLA (Figure S8, Supporting Information) polymers with their respective PLLA acrylate polymer (Figures S6 and S10, respectively, Supporting Information), it was observed

that two new peaks appeared at 131 ppm and 127 ppm in linear PLLA acrylate, 135 and 127 ppm in star PLLA acrylate due to the presence of carbon–carbon double bond. Similarly, the stack plot of the FTIR spectra of linear and star PLLA before and after acrylation (Figure S11, Supporting Information), clearly indicated the appearance of new peaks at 1629 cm^{-1} in case of linear and 1627 cm^{-1} for star PLLA corresponding to $\text{C}=\text{C}$ stretching frequency respectively. The molecular weights of the polymers were determined using size exclusion chromatography recorded in THF using polystyrene standards. The SEC plot is provided in supporting Figure S12 (Supporting Information) and the molecular weight is tabulated in Table S1 (Supporting Information). The GPC data revealed almost similar molecular weight for the linear and star PLLA, and their acrylated derivatives. The polydispersity index for all four polymers was in the range of 1.17–1.37. The number average molecular weight of linear and star PLLA were 2.6 and 2.7 KDa respectively while that after their modification with acrylate moieties were 2.3 and 2.6 KDa respectively.

2.2. Photocalorimetric Studies

Isothermal (at $30\text{ }^\circ\text{C}$) photo-DSC studies under nitrogen atmosphere were undertaken to extract information regarding the enthalpy of double bond conversion.

Figure 3 compares the specific heat flow obtained for HEMA, Linear PLLA acrylate and Star PLLA acrylate with 1 wt% of PI. The theoretical heat of polymerization (ΔH_p) of HEMA was

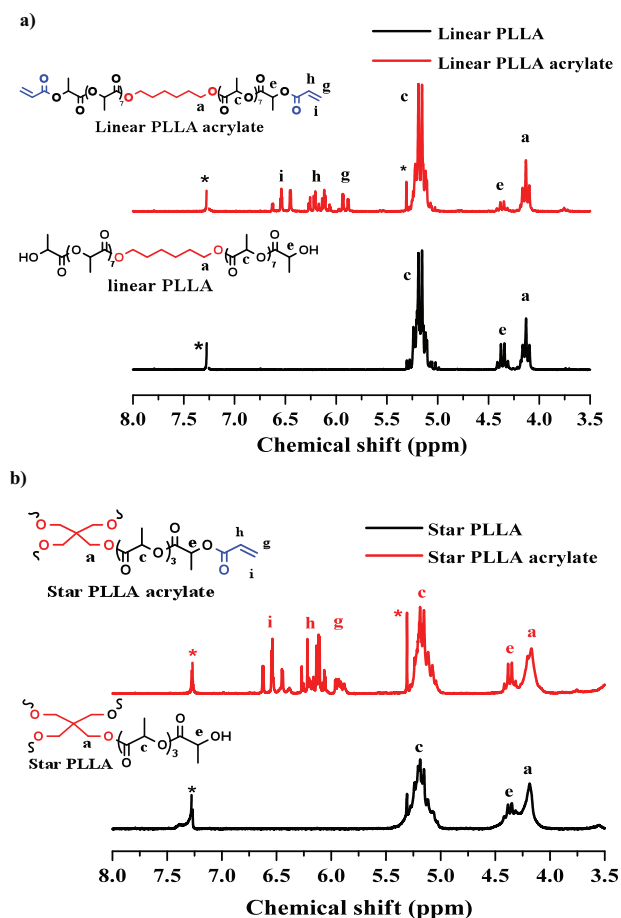


Figure 2. Comparison of the expanded region (3.5 to 8.0 ppm) in the ^1H NMR spectra in CDCl_3 of a) linear PLLA and linear PLLA acrylate; b) star PLLA and star PLLA acrylate

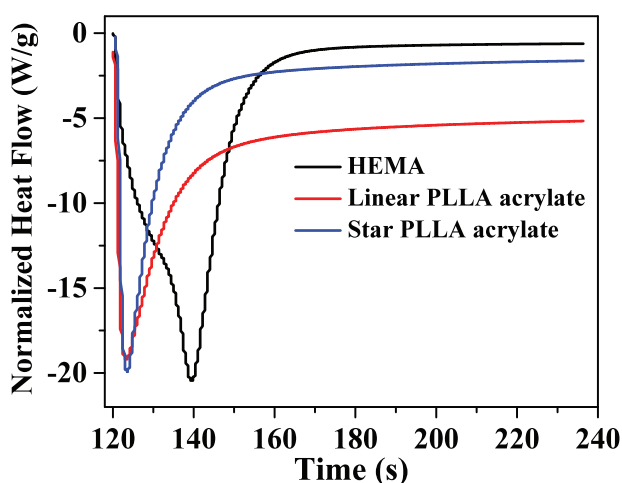


Figure 3. Specific heat flow obtained from photo-DSC measurements at $30\text{ }^\circ\text{C}$ for HEMA, Linear PLLA acrylate and Star PLLA acrylate with 1 wt% of PI.

Table 1. Photocuring enthalpy (J g^{-1}) of 1 wt% of TPO as photoinitiator.

Materials	Curing enthalpy [J g^{-1}]	Theoretical heat of polymerization (ΔH_p) [J g^{-1}]	Cure (%)
HEMA	391.47	421.16	92.9
Acrylate Linear PLLA	77.71	125.09	62.1
Acrylate Star PLLA	113.37	229.24	49.5

Table 2. Composition of the resin formulations used for 3D printing.

Sl. No.	Linear PLLA [wt%]	Star PLLA [wt%]	HEMA [wt%]	TPO [wt%]
Resin A	49.5	-	49.5	1
Resin B	-	49.5	49.5	1
Resin C	24.75	24.75	49.5	1

estimated as 421.16 J g^{-1} based on literature value for heat of polymerization of $13.1\text{ Kcal mol}^{-1}$ per methacrylate double bond.^[41] Similarly theoretical heat of polymerization was calculated for the linear and star PLLA oligomers based on literature values of $20.6\text{ Kcal mol}^{-1}$ per acrylate double bond. The calculated ΔH_p values were 125.09 J g^{-1} for the linear PLLA acrylate and 229.24 J g^{-1} for the star PLLA acrylate. Here due consideration was taken to account for two acrylate double bonds for the linear PLLA acrylate and 4 double bonds for the star PLLA acrylate. The details of the calculation are provided in Supporting Information S6. From the theoretical heat of polymerization for 100% double bond conversion the extent of cure achieved for HEMA was estimated to be 92.9% while the percentage cure for the linear and star acrylate oligomers were 62.1% and 49.5% respectively at 1 wt% of PI concentration.^[42] Table 1 lists the curing parameters determined for HEMA, Linear PLLA acrylate and star PLLA acrylate. A shoulder peak was observed in the reaction rate curve for HEMA, which has been attributed to fast reaction leading to microgel formation in the bulk material as reported in the literature.^[43] However, it did not impact the final conversion rate achieved for HEMA. The lower cure rate observed for the acrylate compared to the methacrylate double bond (HEMA) is due to the higher viscosity of the oligomeric acrylates – linear as well as star PLLA.

Table 2 lists the composition of the three resin formulations that were prepared by mixing 50 wt% HEMA with equal weight percentage of linear PLLA acrylate (Resin A), star PLLA acrylate (Resin B), and the third formulation Resin C with 50 wt% HEMA and 50 wt% each of linear and star PLLA acrylate. Prior to 3D printing, screening experiment was designed by varying the amounts of the PI TPO used for the three resin formulations A, B and C. A drop each of these formulations was placed on a clear glass slide and irradiated for 60 s using a set of 6 commercial LEDs of wavelength 365 nm fitted into a circular holder in a homemade setup. The detail of the homemade setup is provided under the experimental section and the photo of the setup is provided in the supporting information (Figure S13, Supporting Information). At the end of the specified time of irradiation, the glass slide was tilted to observe if the formulation had solidified or exhibited liquid-like flow behavior. Figure S14 (Supporting Information) shows the image of glass slides for

Table 3. Photocuring enthalpy [J g^{-1}] of Resin A, Resin B, and Resin C with different weight % of PI (TPO).

Resin formulations	Curing enthalpy [J g^{-1}] at different PI wt%				
	0.5	1.0	1.5	2.0	2.5
Resin A	−237	−283	−279	−272	−256
Resin B	−244	−284	−256	−250	−242
Resin C	−251	−309	−277	−275	−273

three formulations. The weight % of the PI TPO was varied from 0.5 to 2.5 wt% for each of the 3 resin formulations. From these screening experiments, it could be observed that formulations with PI concentration >1 wt% exhibited incomplete curing with the sample flowing at the end of the 60 s irradiation, while those with 0.5 and 1 wt% PI formed solid films. At higher PI concentration, the rate of recombination also increased resulting in reduced conversion.^[44]

Isothermal photo-DSC analysis was carried out for the 3 resin formulations, i.e., Resin A with 50–50 wt% of HEMA and linear PLLA acrylate, Resin B having 50–50 wt% of HEMA and star PLLA acrylate and Resin C having 50 wt% HEMA and 25–25 wt% linear and star PLLA acrylate each.

Figure S15 (Supporting Information) shows the Photo-DSC plots for the 3 resins at various PI concentrations ranging from 0.5 to 2.5 wt% and the corresponding enthalpy values are listed in Table 3. From the values of enthalpies listed in the table, it could be observed that for all 3 resin formulations the heat of photopolymerization increased initially from 0.5 to 1 wt%, after which it continuously decreased with an increase in the concentration of PI. This indicated that the highest cure conversion was obtained at the optimum PI concentration of 1 wt%. This was in corroboration with the screening studies carried out on the glass slides. Insufficient amounts of PI can lead to incomplete curing, while larger amounts of PI can lead to higher absorption of the incident light. This would result in insufficient light for the bulk of the sample leading to incomplete curing. Therefore, an optimum concentration of PI is necessary for photocurable formulations.^[45] Thus, the resin formulations were optimized with 1 wt% of TPO as PI for the 3D printing (the formulation used for 3D printing is given in Table 2).

2.3. Viscosity Measurement

For DLP 3D printing, the viscosity of the photocurable resin is a critical parameter to ensure easy flow as well as smooth, warpage-free printed material at room temperature. Ideally, the viscosity of photo resin used in room temperature DLP 3D printing should not exceed 5 Pa s.^[46,47] Figure 4a compares the increase in viscosity of resin formulation with increasing wt% addition of linear or star acrylate PLLA in HEMA which were determined using an isothermal parallel plate rotational rheometer.

From the figure, it could be seen that the linear polymer exhibited slightly higher viscosity compared to the star polymer for all the studied compositions in HEMA. Figure 4b shows the plot of viscosity of resin formulations versus shear rate for the three

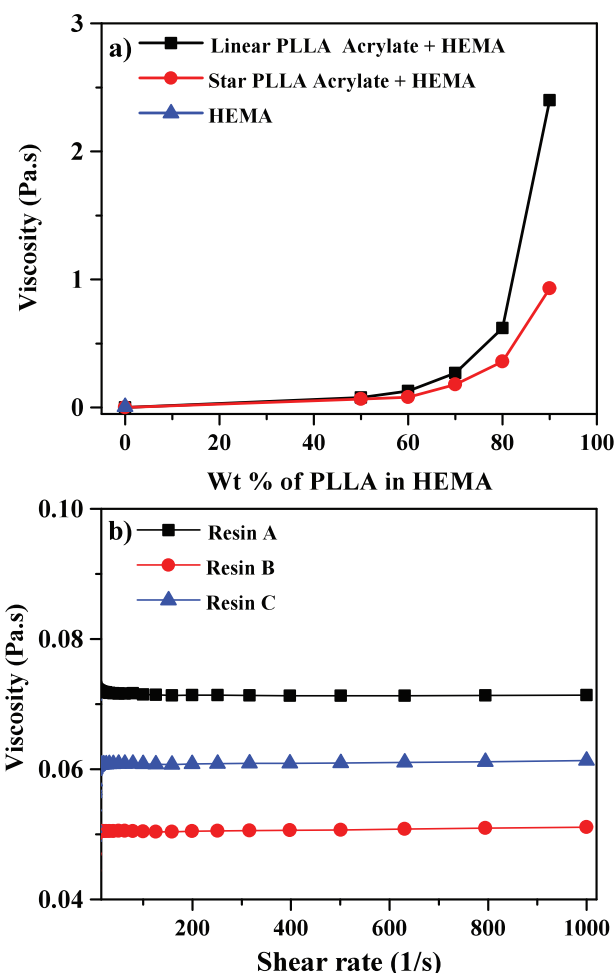


Figure 4. a) Viscosity as a function of increased weight percentage of the oligomer (linear or star PLLA acrylate) in HEMA; b) plot of complex viscosity of resin formulations (without photoinitiator) versus shear rate (s^{-1}).

Table 4. Viscosity of the three resins formulations.

Resin formulations	Viscosity [Pa s]
Resin A	0.072
Resin B	0.051
Resin C	0.060

resin formulations (without added PI) from which the viscosity was calculated. From Figure 4a,b, it could be observed that the formulated resins exhibited viscosity in the range of 0.051 to 0.072 Pascal-second (Pa s) with resin A having the highest viscosity at 0.072 Pa s, Resin B lowest at 0.051 Pa s, and Resin C exhibiting viscosity value in between that of Resin A and Resin B at 0.060 Pa s (Table 4). The viscosity at 30°C remained constant with increasing shear rate, indicating the Newtonian fluid-like behavior of the materials. Although the viscosity values of the 3 resin formulations were lower than those reported in the open literature, it was adequate for 3D printing using a commercial DLP 3D printer at room temperature.

Table 5. Critical energy and penetration depth obtained from the working curve for all three resin formulations.

Resin formulations	Critical energy (E_c) [mJ cm ⁻²]	Penetration depth (D_p) [μm]
Resin A	631	686
Resin B	251	685
Resin C	501	581

2.4. Resin Cure Characteristics

Figure S16 (Supporting Information) compares the cure depths of the resins as a function of increasing energy density. From the plot, it could be observed that the cure depth gradually increased with increasing exposure time from 20 to 60 sec for all three resin formulations (the photograph of the cured square objects with different exposure times is shown in Figure S17, Supporting Information). Extrapolation of the trend line on the x-axis provided the critical exposure energy and the slope of the trend line provided the depth of penetration of light into the resin formulation. Table 5 summarizes the critical energy and penetration depth of the 3 resin formulations determined from the working curve and Equation (1).

Higher penetration depth indicated that the resin allowed more photons to enter deeper inside, which could result in crosslinking of regions outside the required area leading to poor resolution. From Table 5, it could be seen that the penetration depth of both resin A and resin B were similar but the critical energy of resin B was lower compared to resin A. This could be attributed to the higher concentration of crosslinkable groups in resin B—the star PLLA acrylate with four terminal acrylate groups, which facilitated the formation of a larger polymer network structure and easy solidification under low exposure of light energy compared to Resin A (only two terminal acrylate curable groups of linear PLLA acrylate). On the other hand, Resin C which is a mixture of 50:50 wt% of resin A and resin B, showed curing behavior which was in between that of resin A and resin B. Based on this evaluation of the curing characteristics, the printing parameter like the layer thickness of the 3D printed object was fixed at 50 μm. The exposure time required for each layer was calculated from the cure-depth experiment. For instance, the exposure time required for each layer for the DLP 3D printing using resin C was estimated by dividing the critical energy of resin C –501 mJ cm⁻² by the DLP projector light intensity of 31.67 mJ cm⁻² to get the critical exposure time of 16 s. The critical exposure time indicates the time required to start the curing of the resin using the DLP printer. Therefore, the exposure time was set higher than the critical exposure time to ensure complete curing. The printing was performed at room temperature, with layer thickness of 50 μm and exposure time 40 s for initial 5 layers to enable proper adherence to the aluminum build platform followed by 25 s for the rest of the layers.

2.5. 3D Printing of Formulated Resins

The printing ability of the three formulated resins was evaluated using a DLP 3D printer at room temperature. The designed structures could be successfully printed without any organic solvent.

All three resins could successfully print films of 500 micrometers thickness which were further used for the mechanical test measurements. Resin C was taken up for further optimization for complex structure 3D printing. Resin C was further mixed with Sudan I dye to improve the resolution of the printed object. Absorbers like Sudan dyes have good spectral overlap with the light source (LED lamp of 405 nm normally used in DLP 3D printers), which helps to limit the penetration depth of the light from the LED and thus control the cure depth of the resin.^[48,49] In the absence of the dye, the light from the source LED will penetrate deeper causing unwanted polymerization inside voids, around edges etc. resulting in loss of resolution of the 3D printed object. Figure S18 (Supporting Information) compares the absorption spectra of Sudan dye I and TPO photoinitiator recorded in chloroform. Sudan dye has good absorption in the 405 nm thereby ensuring its usefulness for improving resolution in DLP-based 3D printing.^[50] Figure 5a shows the 3D printed structures, where without dye incorporation the areas with triangular holes are also filled and the object has a larger dimension because areas beyond the edges also got polymerized. Figure 5 also shows 3D print of the institute name tag (b) NCL: National Chemical Laboratory and (c) some 3D printed objects demonstrating 3D printing ability of vertical designs with intricate holes and patterns using the resin.

Visual evaluation of the print quality like sharp edges and the designed holes demonstrated very good build geometry and resolution of the printed object using the newly developed PLLA resin formulation. The resin could also be customized to print using a Direct Ink Writing custom-designed 3D printer fitted with a UV light source. The consistency of the resin required for the extrusion-based 3D printer is much more viscous compared to the DLP-based printing technique. The viscosity could be adjusted by reducing the wt% of HEMA as the diluent. Thus, 80 wt% of a 50:50 mixture of the linear and star PLLA was mixed with only 20 wt% of HEMA and used as the resin for the custom-built Direct Ink 3D printer. The details of the printing parameters are provided under the experimental section. The image of the printed object is given in Figure S19 (Supporting Information). A video of the printing process is provided in the Supporting Information. The resolution of the printed object was not as good as that obtained from the DLP printer; nevertheless, the process demonstrated the versatility of the photocurable resin formulation.

2.6. Mechanical and Thermal Properties of 3D Printed Parts

The mechanical properties of thin dog bone-shaped samples which were prepared from the 3D printed film of three different resin formulations were measured at room temperature. The results obtained for uniaxial tensile testing using the three resin formulations is plotted in Figure 6. Table 6 lists the tensile strength, Young's modulus, and elongation at break for the samples.

3D printed film using Resin A exhibited the lowest tensile strength (3.7 MPa) and highest elongation (220%) compared to the other two formulations. Resin B printed part exhibited tensile strength at 4.8 MPa and elongation up to 156%. 3D printed film using Resin C exhibited the highest tensile strength (6.6 MPa) as well as highest Young's modulus (60 Mpa) along with good

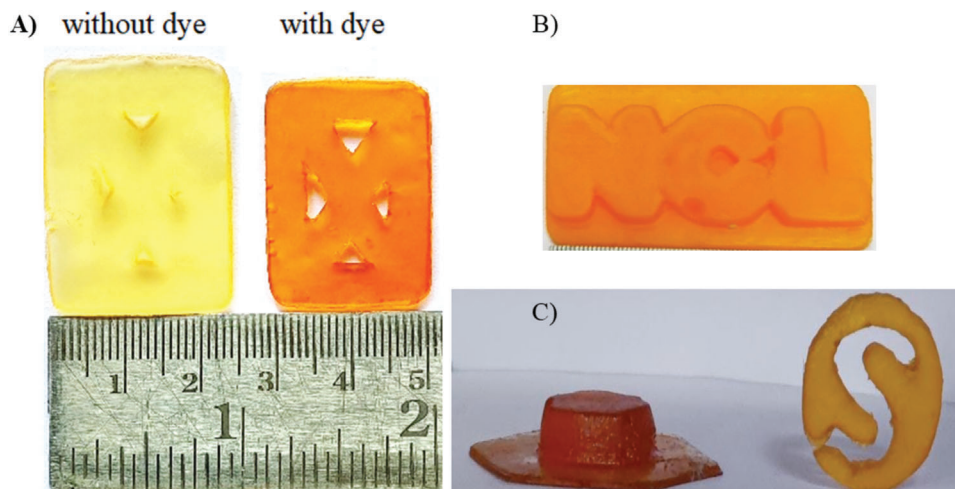


Figure 5. Image of 3D printed objects made using Resin C incorporating Sudan I dye.

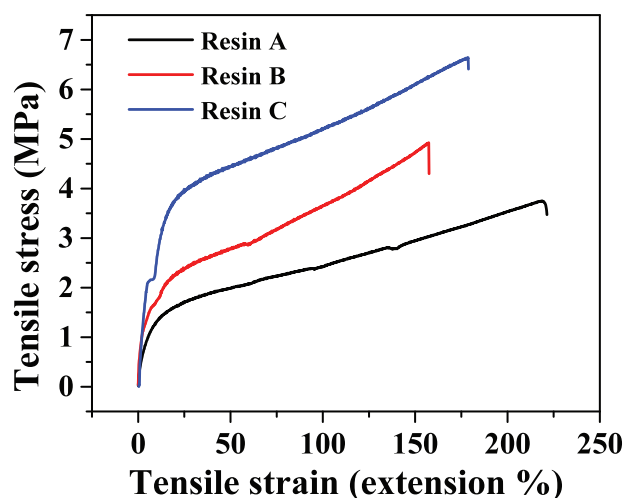


Figure 6. Tensile–strain curves of 3D printed part of resin A, resin B, and Resin C formulations.

elongation (178%). Compared to resin A printed part, the printed part of resin B reflected higher tensile strength and Young's modulus due to the formation of higher polymer network structure as the latter possessed higher density of crosslinking group. The reason for the highest tensile strength and Young's modulus for 3D printed parts from resin C could be a synergistic effect of physical interlocking along with chemical crosslinking upon mixing resin A and resin B.^[51,52] Generally, PLA is a brittle

material with less than 10% elongation at break;^[53] the design of PLLA as star and linear acrylate crosslinkers endowed the 3D printed object with stretchable characteristics.

Thermogravimetric analysis was carried out to study the thermal stability of the 3D printed parts (Figure S20a, Supporting Information). The 3D printed parts exhibited good thermal stability with 10% weight loss observed above 250 °C for all samples. Glass Transition Temperature (T_g) of the 3D printed parts were observed in the range of 20–26 °C which indicated the soft nature of the polymers (Figure S20b, Supporting Information). The values of 10% weight loss and T_g of the 3D printed parts are tabulated in Table 5.

2.7. In Vitro Degradation Studies

The degradation profile of 3D printed parts was evaluated by carrying out degradation studies of 3D printed films cut into square specimens and immersed in PBS solution (comparable to biological conditions) maintained at a pH of 7 at 25 °C and monitored over a period of 90 d. An initial fast weight loss was followed by the slowdown of the degradation with an almost steady state beyond 30 d. The 3D printed film from Resin B exhibited a slightly lower extent of weight loss at around 22% compared to around 30% weight loss exhibited by 3D printed films from resin A and resin C. This could be attributed to the higher extent of crosslinking present in the star polymer-based formulation (4 acrylic units) (B), which slows down the degradation. Attempts to extract the products of degradation from the buffer solution for

Table 6. Tensile strength, Young's modulus, elongation, glass transition, and 10 weight % degradation temperature of 3D printed parts along with their weight loss over a period of 90 d in phosphate buffer solution (PBS).

Printed film	Tensile strength [Mpa]	Young's Modulus [Mpa]	Elongation (%)	T_g [°C]	$T_{d10\%}$ [°C]	Weight Loss % (from in vitro degradation studies)
Resin A	3.7±0.92	13.10±2.10	220 ±9.87	24	256	32
Resin B	4.8±0.23	23.63±2.06	156±6.28	26	260	22
Resin C	6.6±0.42	60.29±9.74	178±7.32	20	264	33

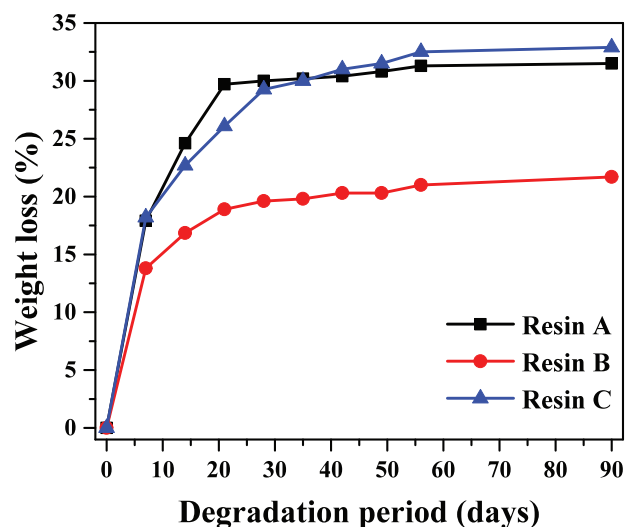


Figure 7. Weight loss of the three different 3D printed parts over a period of 90 d in PBS solution.

characterization using FTIR or proton NMR studies were not very fruitful as the concentration of degraded products was below the detection limit for these techniques. However, there is ample evidence in the literature suggesting the formation of L-lactic acid as the product of degradation of PLLA, which was measured by an enzymatic method using an L-lactic acid assay kit.^[54] As degradation sets in, the pH of the solution changes from neutral to acidic due to the presence of degraded by-products of PLLA. The PBS solutions were replaced periodically to maintain the pH throughout the course of the study. The weight loss percentage observed for the 3D printed objects in the PBS solution is shown in **Figure 7** and the values are listed in Table 6.

Scanning electron microscopy (SEM) images were recorded for the 3D printed samples before degradation and after 28 d of degradation, which is shown in **Figure 8**. The images on the top (Figure 8a–c) were for the fresh 3D printed samples of resin A, resin B, and resin C before they were subjected to degradation in the PBS solution. The images on the bottom panel (Figure 8d–f) which were recorded after 28 d of degradation, demonstrate the presence of microcracks and surface roughness due to the onset of degradation. The ester linkage present on the backbone of the PLLA resin formulation undergoes hydrolytic degradation leading to the formation of the microcracks that are observed in the SEM images.^[55,56] SEM was performed to reveal the qualitative information of connectivity across adjacent layers of the 3D printed parts. SEM images of the gold-coated cross-section of 3D printed materials are shown in Figure S21 (Supporting Information). From these cross-section images of 3D printed parts, no clear boundary could be observed at 50 micrometer thickness (each layer thickness during printing) length scales, which indicated the chemical interconnection across the different layers of the 3D printed objects.

3. Conclusions

In summary, we report the synthesis and formulation of a solvent-free photocrosslinkable PLLA-based resin and its application in room temperature 3D printing using a commercial DLP 3D printer as well as direct ink writing 3D printer. Oligomeric linear and star PLLA acrylate crosslinkers were synthesized and characterized and photocurable resin formulations were prepared by mixing with HEMA as the diluent and 1 wt% TPO as the photoinitiator. The 3D printed parts exhibited promising mechanical properties with biodegradability in phosphate buffer solution highlighting the potential of the new PLLA-based

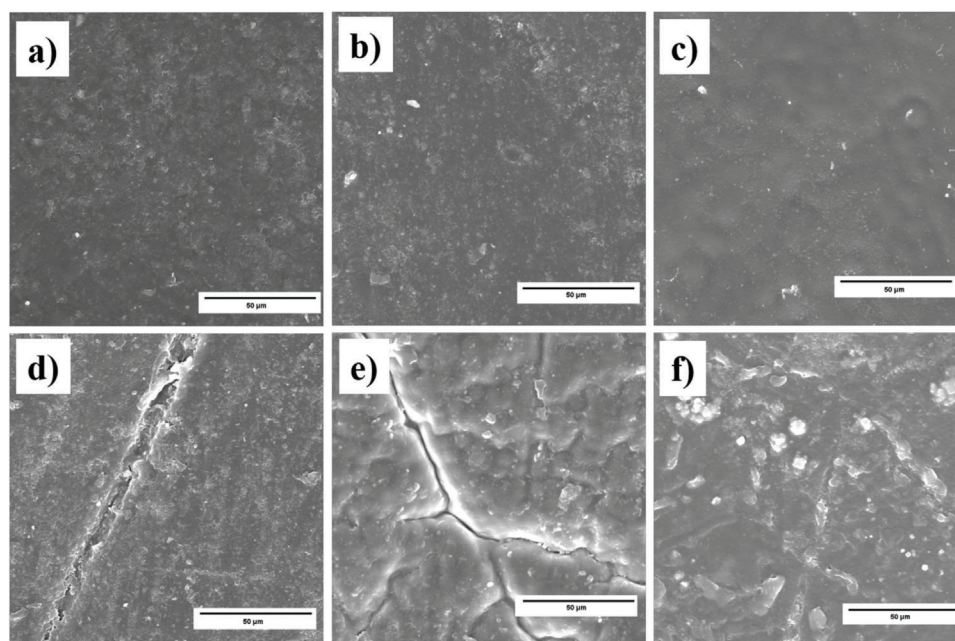


Figure 8. SEM images of the surface of 3D printed film a–c) before degradation of resins A, B, and C, respectively, and after 28 d degradation of resins A, B, and C respectively.

biodegradable photocurable formulation for 3D printing prototypes as well as for medical application, bone tissue engineering, etc.

4. Experimental Section

Materials: (3S, 6S)-3, 6-dimethyl-1, 4-dioxane-2, 5-dione, 1, 6-hexanediol, pentaerythritol, stannous 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$), Hydroxyethylmethacrylate were purchased from Sigma-Aldrich (India) and used as such without further purification. Acrylic acid was purchased from Sigma Aldrich and purified by distillation. Phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide was purchased from TCI chemical (India) Pvt. Ltd and used as such. Thionyl chloride (SOCl_2), Tetrahydrofuran (THF), Chloroform (CHCl_3), Methanol (MeOH), Dichloromethane (DCM) and Sodium sulphate (Na_2SO_4) were purchased locally. For gel permeation chromatography HPLC grade THF was purchased from Merck Chemicals (India).

Measurements: Proton NMR spectra were recorded using 400 MHz Bruker-AVENS NMR spectrophotometer using CDCl_3 as solvent with small amounts of Trimethylsilane (TMS) added as an internal standard. BRUKER alpha-E Fourier transform (FTIR) spectrometer was used to record the FTIR spectra. The molecular weights of polymers were determined using gel permeation chromatography (GPC) equipped with Viscotek VE 3580 RI detector. The GPC was calibrated with polystyrene standard and THF solvent as eluent at 1 mL min^{-1} flow rate. The thermal properties of all polymers were analyzed using thermal gravimetric analysis (TGA), TA discover 550 second-generation TGA instrument, under nitrogen atmosphere by heating from 50 to 900°C at the heating rate of $10^\circ\text{C min}^{-1}$. The glass transition temperature (T_g) was determined using TA Discover 250 second-generation differential scanning calorimeter under nitrogen atmosphere by heating from -30 to 180°C at the heating rate of $10^\circ\text{C min}^{-1}$. The DSC was calibrated with indium standards before measurement. 2–3 mg of sample was taken in an aluminum pan, sealed, and measured at the same heating rate.

Resin Formulation: Photocurable resin formulations were prepared by mixing 50 wt% of PLLA acrylate crosslinker (linear or star; resin A and resin B, respectively) in HEMA as a reactive diluent with 1% by weight of TPO as a photoinitiator in a 30 mL vial. The third formulation—resin C was prepared by mixing a 50:50 wt% mixture of the linear and star PLLA acrylate crosslinkers with 50 wt% of HEMA along with 1 wt% of TPO. The vial was sonicated for 1 h at room temperature while covered with an aluminum foil and stored in the fridge until the time of 3D printing. Just before use for DLP 3D printing, the resin was shaken in a vortex mixer for 5 min at room temperature. To print in custom-built 3D printer one more resin formulation was prepared by mixing of 80 wt% of 50:50 mixture of linear and star acrylate PLLA, 19 wt% of HEMA and 1 wt% of TPO. The materials were taken in a round bottom flask and sonicated for 1 h at room temperature after covering the flask with aluminum foil to protect from light.

Spot Curing: For the spot curing experiment, a homemade setup having six commercial LED lights positioned in a circular fashion was made use of. The wavelength of light was 365 nm and the intensity of the light was measured to be 35 mW cm^{-2} , with the help of UNO Gentec laser power meter (from a distance that was approximately equal to the space between the projector and the lower part of the vat in the 3D printer). Five samples each of resin A, resin B, or resin C (without the PI) were taken in 5 mL vials to which different weight percentages of TPO (from 0.5 to 2.5 wt%) were added. The resin mixtures were sonicated for a period of 30 min. After that one drop of resin was taken on a glass slide and kept under the homemade light setup at a specific distance and irradiated for 60 s. After 60 s the glass slide was tilted to visually inspect if the drop had solidified into a film or still exhibited liquid nature by flowing.

Photodifferential Scanning Calorimetry: The photo-DSC studies were carried out in a TA Discover 250 second-generation differential scanning calorimeter equipped with a photo calorimetric unit (Onni cure series 2000). A 200 W high pressure mercury lamp which transmits the light of wavelength 320–500 nm, provides the irradiation to the sample chamber via dual-quartz light guide with neutral density.^[57] The sample preparation

was similar to that described for the spot cure studies. 5.5 mg of samples were weighed out exactly into the sample pan and measurement was carried out under constant nitrogen flow rate of 60 mL min^{-1} . For the photo DSC experiment, the sample was initially held in isothermal condition for 2 min under nitrogen atmosphere and equilibrated at 30°C , following which the electronic UV light shutter was opened and sample was exposed to UV light for 2 min of irradiation. The shutter was closed automatically at the end of irradiation time and the baseline was recovered. The peaks were integrated to get the curing enthalpy from a plot of normalized heat flow as a function of irradiation time.

Viscosity Measurement: Rotational parallel plate measurements of formulations without added photoinitiator were performed on a Brookfield DV-II+ pro viscometer using Spindle CPE-42 and CPE-52 to analyze viscosity of the resins. The gap between the upper and lower plate was 1 mm; the amount of sample was 0.5 and 1 mL for the CPE-52 and CPE-42 spindle respectively. The temperature was constant at 30°C throughout the experiment and the rotation was 0.3 to 12 rpm. The evaluation of viscosity as a function of shear rate was determined using the Anton Paar Physica Modular Compact Rheometer (MCR) 301. The test was performed in cup and bob with the diameter of 18.08 mm and 16.66 mm respectively. The shear rate was performed from 1 to 1000 s^{-1} .

Cure Depth: In light-based 3D printing, the cure depth is a critical parameter that provides a rough estimate of the curing time required to print each layer.

This parameter can be obtained using the Jacob's equation based on the Beer-Lambert law shown in Equation (1)^[58,59]

$$C_d = D_p \ln \frac{E_0}{E_c} \quad (1)$$

Here, C_d is the thickness of the printed part, D_p is the penetration depth or the depth to which the light can cure inside the liquid resin, E_c is the critical exposure energy required for starting the curing process of the resin at room temperature, E_0 is the energy of the incident light at the surface. Photocuring properties of the formulated resin like penetration depth and critical energy dose were determined using a Solus DLP 3D printer. The resin was irradiated in a square-shaped area on the vat of the 3D printer with different exposure times ranging from 20 to 60 s. The thickness of the crosslinked part was measured using a micrometer caliper. The value of the E_c and D_p was evaluated from the slope of the working curve and x-axis intercept, respectively.

3D Printing: The prepared solvent-free resin formulations were printed using the commercial Solus DLP 3D printer at room temperature. The DLP 3D printer was connected with a projector having light source of H1186HD projector. The intensity of the projector light was 31.67 mW cm^{-2} measured using UNO Gentec laser power meter. The printing was performed at room temperature, with layer thickness of 50 μm and exposure time 40 s for initial 5 layers to enable proper adherence to the aluminum build platform followed by 25 s for the rest of the layers. After 3D printing, the printed objects were washed with isopropyl alcohol three times.

Custom Built 3D Printer: A direct ink writing 3D printer was custom built (Manufacturer: Utpal3dsystems, U3DS, Gujarat, India) to additionally have a UV light source attached to it so as to cure the resin as it was deposited on the substrate bed. The viscous resin was taken in a 25 cm diameter syringe connected with an 18 gauge diameter needle and fitted to the 3D printer. For the extrusion of the resin from the syringe through the needle, controlled pneumatic pressure (almost 50 psi) was applied and the printing speed was 8 mm s^{-1} . The resin formulation was taken in the syringe and each layer thickness was set at 200 μm and filling density was 100%. The printer was connected with a 365 nm UV light source which cured the photo curable resin. The intensity of the light was 35 mW cm^{-2} . After supplying the CAD file information to the printer through the software, the printer recognized the bed leveling automatically and printed the file. To print an object from this printer, the parameters like layer thickness, printing speed, and pressure of the air could be controlled. After printing, the object was kept in a UV chamber for 1 h to ensure complete curing of the printed part.

Mechanical Test: The tensile test measurements of the 3D printed parts were obtained using a Universal Testing Machine (Instron, Series 5943) with a 500 N capacity load cell at room temperature. Tensile tests were performed on dog bone-shaped objects which were cut from 3D printed films. The size of the testing sample was approximately $30 \times 10 \times 0.5$ mm³ and the gauge length was 5 mm with the stretching rate of 5 mm min⁻¹. 5 samples were tested for each resin formulation. The tensile strength, Young's modulus, and elongation at break were determined.

In Vitro Degradation Study: 3D printed square specimens of each resin formulation were immersed in 150 ml of neutral PBS solution (pH 7) at 25 °C. The buffer solution (Sørensen solution) was prepared by mixing two different concentrations of salt solution. The first solution was prepared by dissolving 1/15 mol (9.078 g) of potassium dihydrogen phosphate (KH₂PO₄) in 1 L of de-ionized water. The second solution was prepared by dissolving 1/15 mol (11.876 g) of disodium phosphate (Na₂HPO₄) in 1 L of de-ionized water. The PBS solution was prepared by mixing 18.2 v/v % of first solution and 81.8 v/v % of the second solution.^[60] The printed samples were weighed to obtain the initial weight and then kept inside a 2k dialysis tube inside the PBS solution with constant stirring at 25 °C. The first weight loss reading was taken by removing the samples from the tube, wiping it gently with soft tissue paper and drying under a vacuum at 50 °C for overnight. The PBS solutions were replaced every week keeping the pH level same as before.

Scanning Electron Microscopy Imaging: A cross-section of the 3D printed part was examined using FE-SEM with an FEI Nova Nano SEM 450. The surface of the 3D printed films before and after degradation were examined with the same instrumentation. To examine the cross-section the samples were prepared by cutting the 3D printed film with a sharp blade and the cross-section part was mounted on the measurement stub vertically with the black carbon tape. Similarly, all three samples were mounted on a single stub. To examine the surface of 3D printed film before degradation, a small part of the fresh 3D printed film was cut and washed with deionized water and dried in vacuum oven. After 28 d of degradation, the film was removed from the dialysis tube and a small part was cut, washed and dried in vacuum oven. After that, the samples were mounted on the stub with carbon tape. All the samples were coated with gold prior to the SEM analysis.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the Center of Excellence (CoE) (F.No. 25014/2/2015-PC-II (FTS: 14428)) supported by the Ministry of Chemical and Fertilizers, Department of Chemicals and Petrochemicals, Government of India and Facility Creation Project (FCP; No. 34/FCP/NCL/2019-RPPBDD) supported by the Council of Scientific and Industrial Research, Project Planning & Business Development Directorate, New Delhi. S.P. thanks CSIR for senior research fellowship (SRF). The authors would like to acknowledge Dr. Arun Torris and Dr. Kadiravan Shanmuganathan CSIR-NCL, Pune, for help in the characterization of 3D printed film.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

3D printing, biodegradable materials, digital light processing, L-lactide, photocurable materials

Received: May 4, 2022

Revised: August 12, 2022

Published online: October 20, 2022

- [1] R. Du, Y. X. Su, Y. Yan, W. S. Choi, W. F. Yang, C. Zhang, X. Chen, J. P. Curtin, J. Ouyang, B. A. Zhang, *Engineering* **2020**, *6*, 1291.
- [2] H. Saniei, S. Mousavi, *Polymer* **2020**, *196*, 122467.
- [3] H. Zhao, F. Yang, J. Fu, Q. Gao, A. Liu, M. Sun, Y. He, *ACS Biomater. Sci. Eng.* **2017**, *3*, 3083.
- [4] C. Yu, J. Schimelman, P. Wang, K. L. Miller, X. Ma, S. You, J. Guan, B. Sun, W. Zhu, S. Chen, *Chem. Rev.* **2020**, *120*, 10695.
- [5] S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, *Chem. Rev.* **2017**, *117*, 10212.
- [6] R. Ajdary, N. Kretzschmar, H. Baniasadi, J. Trifol, J. V. Seppälä, J. Partanen, O. J. Rojas, *ACS Sustainable Chem. Eng.* **2021**, *9*, 2727.
- [7] K. L. Sampson, B. Deore, A. Go, M. A. Nayak, A. Orth, M. Gallerneault, P. R. L. Malenfant, C. Paquet, *ACS Appl. Polym. Mater.* **2021**, *3*, 4304.
- [8] V. Shanmugam, M. V. Pavan, K. Babu, B. Karnan, *Polym. Compos.* **2021**, *42*, 5656.
- [9] A. Schwab, R. Levato, M. D'este, S. Piluso, D. Eglin, J. Malda, *Chem. Rev.* **2020**, *120*, 11028.
- [10] J. Zhang, P. Xiao, *Polym. Chem.* **2018**, *9*, 1530.
- [11] M. Guvendiren, J. Molde, R. M. D. Soares, J. Kohn, *ACS Biomater. Sci. Eng.* **2016**, *2*, 1679.
- [12] A. Atala, *Chem. Rev.* **2020**, *120*, 10545.
- [13] M. Shahbazi, H. Jäger, *ACS Appl. Bio Mater.* **2021**, *4*, 325.
- [14] A. Haryńska, H. Janik, M. Sienkiewicz, B. Mikolaszek, J. Kucińska-Lipka, *ACS Sustainable Chem. Eng.* **2021**, *9*, 6923.
- [15] J. R. Rocca-Smith, O. Whyte, C.-H. Brachais, D. Champion, F. Pisante, E. Marcuzzo, A. Sensidoni, F. Debeaufort, T. Karbowiak, *ACS Sustainable Chem. Eng.* **2017**, *5*, 2751.
- [16] W. K. Lee, J. A. Gardella, *Langmuir* **2000**, *16*, 3401.
- [17] H. J. Kim, M. A. Hillmyer, C. J. Ellison, *J. Am. Chem. Soc.* **2021**, *143*, 15784.
- [18] S. Wasti, S. Adhikari, *Front. Chem.* **2020**, *8*, 315.
- [19] N. Tripathi, M. Misra, A. K. Mohanty, *ACS Eng. Au* **2021**, *1*, 7.
- [20] Z. Fang, Y. Shi, Y. Zhang, Q. Zhao, J. Wu, *ACS Appl. Mater. Interfaces* **2021**, *13*, 15584.
- [21] X. Li, R. Yu, Y. He, Y. Zhang, X. Yang, X. Zhao, W. Huang, *ACS Macro Lett.* **2019**, *8*, 1511.
- [22] V. S. D. Voet, T. Strating, G. H. M. Schnelting, P. Dijkstra, M. Tietema, J. Xu, A. J. J. Woortman, K. Loos, J. Jager, R. Folkersma, *ACS Omega* **2018**, *3*, 1403.
- [23] S. Barone, P. Neri, A. Paoli, A. V. Rationale, F. Tamburrino, *Procedia Manuf.* **2019**, *38*, 1017.
- [24] J. Zhang, Q. Hu, S. Wang, J. Tao, M. Gou, *Int. J. Bioprint.* **2020**, *6*, 12.
- [25] S. T. Jaber, M. Y. Hajeer, T. Z. Khattab, L. Mahaini, *Clin. Exp. Dent. Res.* **2021**, *7*, 591.
- [26] B. Gross, S. Y. Lockwood, D. M. Spence, *Anal. Chem.* **2017**, *89*, 57.
- [27] G. Tafuro, A. Costantini, G. Baratto, S. Francescato, A. Semenzato, *ACS Omega* **2020**, *5*, 15280.
- [28] F. Chen, G. Hochleitner, T. Woodfield, J. Groll, P. D. Dalton, B. G. Amsden, *Biomacromolecules* **2016**, *17*, 208.
- [29] F. P. W. Melchels, A. M. C. Barradas, C. A. Van Blitterswijk, J. De Boer, J. Feijen, D. W. Grijpma, *Acta Biomater.* **2010**, *6*, 4208.
- [30] S. Moeinzadeh, S. N. Khorasani, J. Ma, X. He, E. Jabbari, *Polymer* **2011**, *52*, 3887.

- [31] G. 'R. Coullerez, C. Lowe, P. Pechy, H. H. Kausch, J. N. Hilborn, *J. Mater. Sci. Mater. Med.* **2000**, *11*, 505.
- [32] A. Bagheri, K. E. Engel, C. W. A. Bainbridge, J. Xu, C. Boyer, J. Jin, *Polym. Chem.* **2020**, *11*, 641.
- [33] A. Bagheri, H. Ling, C. W. A. Bainbridge, J. Jin, *ACS Appl. Polym. Mater.* **2021**, *3*, 2921.
- [34] F. P. W. Melchels, J. Feijen, D. W. Grijpma, *Biomaterials* **2009**, *30*, 3801.
- [35] T. M. Seck, F. P. W. Melchels, J. Feijen, D. W. Grijpma, *J. Controlled Release* **2010**, *148*, 34.
- [36] A. Ronca, L. Ambrosio, D. W. Grijpma, *Acta Biomater.* **2013**, *9*, 5989.
- [37] A. Bagheri Saed, A. H. Behraves, S. Hasannia, B. Akhoundi, S. K. Hedayati, F. Gashtasbi, *Eur. Polym. J.* **2020**, *141*, 110057.
- [38] M. Sandmeier, N. Paunović, R. Conti, L. Hofmann, J. Wang, Z. Luo, K. Masania, N. Wu, N. Kleger, F. B. Coulter, A. R. Studart, H. Grütz-macher, J. C. Leroux, Y. Bao, *Macromolecules* **2021**, *54*, 7830.
- [39] M. Danko, J. Libiszowski, T. Biela, M. Wolszczak, A. Duda, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4586.
- [40] A. Kulkarni, A. Lele, S. Sivaram, P. R. Rajamohanan, S. Velankar, A. Chatterji, *Macromolecules* **2015**, *48*, 6580.
- [41] R. V. Ghorpade, S. M. Bhosle, S. Ponrathnam, C. R. Rajan, N. N. Cha-van, R. Harikrishna, *J. Polym. Res.* **2012**, *19*, 9811.
- [42] J. Wei, R. Lu, F. Liu, *J. Polym. Res.* **2011**, *18*, 1001.
- [43] L. Ling, L. J. Lee, *Kobunja Kwahak Kwa Kisul* **2005**, *46*, 11540.
- [44] P. Castell, M. Wouters, H. Fischer, G. De With, *J. Coat. Technol. Res.* **2007**, *4*, 411.
- [45] B. Steyrer, P. Neubauer, R. Liska, J. Stampfl, *Materials* **2017**, *10*, 1445.
- [46] G. A. Appuhamillage, N. Chartrain, V. Meenakshisundaram, K. D. Feller, C. B. Williams, T. E. Long, *Ind. Eng. Chem. Res.* **2019**, *58*, 15109.
- [47] K. Pooput, S. Channasanon, P. Tesavibul, P. Pittayavinai, W. Taweelue, *J. Polym. Res.* **2020**, *27*, 322.
- [48] H. Quan, T. Zhang, H. Xu, S. Luo, J. Nie, X. Zhu, *Bioact Mater* **2020**, *5*, 110.
- [49] C. Kolb, N. Lindemann, H. Wolter, G. SEXTL, *J. Appl. Polym. Sci.* **2021**, *138*, 49691.
- [50] M. P. Lee, G. J. T. Cooper, T. Hinkley, G. M. Gibson, M. J. Padgett, L. Cronin, *Sci. Rep.* **2015**, *5*, 9875.
- [51] S. Nouri, C. Dubois, P. G. Lafleur, *J. Rheol.* **2015**, *59*, 1045.
- [52] P. E. Theodorakis, A. Avgeropoulos, J. J. Freire, M. Kosmas, C. Vlahos, *J. Chem. Phys.* **2007**, *126*, 174904.
- [53] N. Kiuna, C. J. Lawrence, Q. P. V. Fontana, P. D. Lee, T. Selerland, P. D. M. Spelt, *Composites, Part A* **2002**, *33*, 1497.
- [54] A. Göpferich, *Biomater. Silver Jubilee Compend.* **1996**, *17*, 117.
- [55] N. F. Zaaba, M. Jaafar, *Polym. Eng. Sci.* **2020**, *60*, 2061.
- [56] I. Grizzi, H. Garreau, S. Li, M. Vert, *Biomaterials* **1995**, *16*, 305.
- [57] Y. Huang, J. Xu, J. Shao, G. Sun, D. Li, Q. Fan, *Langmuir* **2020**, *36*, 11676.
- [58] J.-T. Miao, S. Peng, M. Ge, Y. Li, J. Zhong, Z. Weng, L. Wu, L. Zheng, *ACS Sustainable Chem. Eng.* **2020**, *8*, 9415.
- [59] S. Peng, Y. Li, L. Wu, J. Zhong, Z. Weng, L. Zheng, Z. Yang, J.-T. Miao, *ACS Appl. Mater. Interfaces* **2020**, *12*, 6479.
- [60] A. Bagheri Saed, A. H. Behraves, S. Hasannia, S. A. Alavinasab Arde-bili, B. Akhoundi, M. Pourghayoumi, *J. Manuf. Process.* **2020**, *56*, 550.



Thiol-ene-based degradable 3D printed network from bio resource derived monomers ethyl-lactate and isosorbide

Shibam Pal^{a,b}, S.K. Asha^{a,b,*}

^a Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008, India

^b Academy of Scientific and Innovative Research, Sector 19, Kamlia Nehru Nagar, Ghaziabad 201002, Uttar Pradesh, India

ARTICLE INFO

Keywords:

Poly (acrylate ethyl lactate)

Degradation

Thiol-ene

3D printing

Digital light processing

ABSTRACT

A polymeric ene-based thiol-ene network is reported that was demonstrated for light-based 3D printing. Allyl poly (acrylate ethyl lactate) (PAEL) was synthesized starting from ethyl lactate in an efficient and scalable manner. Ethyl lactate is a biobased material obtained naturally or chemically in high yields in the form of ethyl ester of lactic acid. Isosorbide, which is also a bio based resource was converted into thiol derivative and was used along with Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) as multifunctional thiol. The polymeric nature of the ene (i.e. PAEL) imparted exceptionally high mechanical properties like Young's modulus of 1.75 GPa as well as high thermal stability with a decomposition temperature ($T_{d,10\%}$) exceeding 350 °C for all the networks studied. The properties could also be customized by fine tuning the type and stoichiometric ratio of the thiol crosslinked employed. For instance, the Young's modulus range from 1.75 GPa to 1.03 GPa and glass transition temperature range from 44 °C to 54 °C could be achieved. DLP 3D printing was used to demonstrate the printability of the resins with high resolution and structural fidelity. The study also highlights the base-mediated rapid hydrolytic degradation efficiency of the 3D printed parts, demonstrating the applicability of these novel polymeric ene based thiol-ene for sustainable and eco-friendly 3D printable formulations.

1. Introduction

The process of creating objects through additive manufacturing, often known as 3D printing, has opened up new possibilities for creativity and customization across various fields of applications. [1–6] Among the various 3D printing methods, light-induced polymerization technologies like stereo lithography (SLA) and digital light processing (DLP), offer superior precision of prototype features, mechanical robustness, and layer cohesion when compared to other approaches such as filament deposition modeling (FDM). [7–11] Photo curable polymers are now being used in the creation of 50 % of industrial prototypes. The primary materials for 3D printing through photo polymerization predominantly center around acrylate or methacrylate-based formulations, with the choice depending on factors like the quality of chain growth in acrylate polymerization, curing speed, mechanical properties, and cost-effectiveness. [12–14] According to a recent study, commercial acrylate molecules pose toxicity risks due to their existence as residual monomers after polymerization and additionally, they exhibit low degradability after polymerization. [15–17] In an effort to address the significant limitations that are associated with conventional acrylic monomers,

researchers have explored the use of thiol-ene-based chemistries. [18,19] Photo-induced thiol-ene reactions combine the attributes of both photo polymerization and click reactions, including precise control, selectivity, resistance to oxygen and water, and high yields without the formation of by-products. [20–23] Unlike chain-growth acrylate polymerizations, thiol-ene reactions proceed via a step-growth mechanism, offering benefits such as delayed gelation, improved monomer conversion, and reduced shrinkage stress. [24,25] Acrylate-based or thiol-ene-based thermosets are valued for their thermal and chemical resistance but face environmental concerns due to fossil feedstock usage and increased waste generation. Biomass-derived materials like poly (lactic acid), sucrose, vegetable oil, and eugenol are being incorporated into thermosetting resins to address these issues. [18,25–27] Conventional polymer resin-based 3D printing techniques create thermosetting materials that are non-biodegradable and add to the plastic pollution. Therefore, there is an increasing need for 3D printing resins based on renewable and biodegradable ingredients to address this issue. Thiol-ene polymerization producing novel biomaterials possessing unique cross-linking architecture, improved mechanical properties, eco-friendly reaction characteristics, rapid and site-specific polymerization, and the

* Corresponding author at: Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008, India.
E-mail address: sk.asha@ncl.res.in (S.K. Asha).

potential of improved degradability are highly sought-after. [28–31] Due to its benefits, thiol-ene photo polymerization is progressively emerging as a viable option for creating resins for additive manufacturing. The recent expansion of literature has shown interest in thiol ene click chemistry in liquid-based 3D printing introducing different thiol and/or ene moieties in polymeric or small molecule fashion. [32–34] Andreas Oesterreicher *et al* and Yimei Wu *et al* successfully synthesized thiol-yne small molecules for photo resin formulations to demonstrate biocompatible monomers for UV-based additive manufacturing (DLP 3D printing). They also demonstrated its reduced cytotoxicity and hydrolytic degradability, thereby addressing plastic pollution. [35,36] Sycks *et al* demonstrated the 3D printing of spiro ene molecules with a custom DLP 3D printer, showcasing the tenable mechanical properties through controlled heat treatment and Spiro chemistry. [37] Merckle *et al* introduced eco-friendly 3D printing resins, comprising 20–40 % bio derived monomers from linalool offering high spatial resolution, customizable properties, and also exhibit 4D shape memory effects. [38] Eric Constant *et al* reported photopolymers derived from natural terpenes, limonene, and β -myrcene that were used for the thiol-ene photo cross-linking via solvent-free DLP 3D printing which exhibited good mechanical properties and cell viability with shape memory effect making them promising for 3D printable photopolymers and structurally robust materials. [32] Recently, Porwal *et al* extracted Levoglucosan, a bio-based compound, from cellulose biomass through a pyrolysis process. Levoglucosan was subsequently employed to synthesize an ene-containing molecule, which was used to create a thiol-ene network polymer for application in 3D printing technology. The 3D-printed objects exhibited favorable degradability properties in THF/NaOH solution making it a well-suited rapid prototyping application mitigating the waste generation from acrylate-based printing. [39] Despite the proliferation of 3D printing resins and processes described in the literature, it is important to note that the mechanical properties of the resulting materials often do not meet the desired standards. The current work outlines the scalable synthesis of ethyl lactate-based polymeric ene and its thiol-ene photochemistry with isosorbide-based thiol and Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) based multifunctional thiol for DLP 3D printing application. Thiol-ene photo kinetics was analyzed using photo DSC studies, and the mechanical and thermal properties of the 3D-printed materials were also evaluated. The hydrolytic degradability of the 3D printed parts was showcased in 1 M NaOH solution. Overall, this research presents a promising avenue for the development of new biobased materials that can address the issue of nondegradable acrylate-based 3D print waste. The fast degradability of PAEL-based polymeric thiol-ene 3D print materials has the potential to significantly impact rapid prototyping for mass production applications.

2. Materials and methods

2.1. General information

Ethyl lactate, allyl bromide, isosorbide, 3-mercaptopropionic acid, and 2-hydroxy ethyl acrylate (HEA) were purchased from Sigma Aldrich (India) and used without further purification. Acryloyl chloride, triethyl amine, azobisisobutyronitrile, lithium hydroxide, potassium carbonate, and p-toluene sulphonic acid were purchased from local dealers and used directly without further purification. Phenylbis(2,4,6-trimethyl benzoyl) phosphine oxide (TPO), Triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione (TTT), Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), and 2,5-Bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene (BBOT) dye was purchased from TCI Chemical Pvt. Ltd and used as such. Tetrahydrofuran (THF), chloroform, methanol, isopropyl alcohol, dichloromethane, hexane, and sodium sulfate (anhydrous) were purchased locally. For gel permeation chromatography HPLC-grade THF was purchased from Merck Chemicals (India). ^1H and ^{13}C NMR spectra were recorded using Bruker-AVENS 400 and 200 MHz spectrometers

and chemical shifts were reported in ppm using CDCl_3 as a solvent with small amounts of Trimethylsilane (TMS) added as an internal standard. The molecular weight of small molecules was recorded on the HRMS (ESI) Thermo Scientific Q-Exactive, Accela 1250 pump. The Fourier transform (FT-IR) spectra were acquired using a BRUKER alpha-E spectrometer. The molecular weights of polymers were determined using size permeation chromatography (SEC) equipped with a Viscotek VE 3580 RI detector. The SEC was calibrated with polystyrene standard and THF (HPLC grade) solvent was used as eluent at a 1 ml/min flow rate. The viscosity of the formulated resins as a function of shear rate was determined using the Anton Paar Physica Modular Compact Rheometer (MCR) 301. The shear rate was performed from 1 to 1000 per second at 30 °C. The thermal stability of all 3D printed parts was analyzed using Thermal Gravimetric Analysis (TGA), TA discover, 550-second generation TGA instrument, at a temperature range of 50 °C to 900 °C under nitrogen atmosphere (25 ml/min), and the heating rate was 10 °C/min. The glass transition temperature (T_g) was determined using TA Discover 250, second generation differential scanning calorimeter under nitrogen atmosphere (50 ml/min) at a heating rate of 10 °C/min. The DSC was calibrated with indium standards before measurement. A photo-DSC experiment was performed using the same DSC instrument equipped with an optical UV light source Omni Cure series 2000.

2.2. Thiol-ene resin formulation for 3D printing

The thiol-ene resin formulations for 3D printing was prepared by mixing different weight percentages of allyl PAEL polymer with pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT), and isosorbide bis(3-mercaptopropionate) to target a stoichiometric mixture of 1:1 thiol to alkene functionalities. The TPO photoinitiator weight percentage was examined from the photo DSC kinetic experiment. No organic solvent was added to the 3D printing resin formulation. Allyl PAEL polymer was mixed with TTT and poured into PETMP in cold conditions to avoid premature curing of thiol-ene. The resin was mixed well with a spatula. TPO was separately dissolved in TTT and mixed with the resin just before 3D printing. Considering that the photoinitiator is sensitive to visible light, the glass vial was completely wrapped with a layer of aluminum foil to prevent any pre-polymerization. All resin formulations were prepared following a similar procedure.

2.3. Photo-differential scanning calorimetry (Photo-DSC)

The Photo-DSC experiments were conducted using a TA Discover 250 s-generation differential scanning calorimeter equipped with a photo calorimetric unit known as the Omni Cure series 2000. The irradiation to the sample chamber was provided by a 200 W high-pressure mercury lamp emitting light in the 320–500 nm wavelength range via dual-quartz light guide with neutral density. For the measurement, a precise amount of 5 mg of the prepared resin formulation was carefully weighed and placed into the sample pan, which was then inserted into the DSC cell. The measurements were performed under a consistent flow of nitrogen gas at a rate of 50 ml/min. Before subjecting the sample pan to UV light irradiation, the sample was initially held under isothermal conditions for 2 min in a nitrogen atmosphere, with equilibration at 30 °C. Subsequently, the electronic UV light shutter was opened, allowing the sample to be exposed to UV light for a duration of 5 min. At the end of the irradiation period, the shutter automatically closed. The peaks in the resulting data were integrated to determine the curing enthalpy.

2.4. Viscosity measurement

The viscosity of the resin formulations was determined through Rotational Parallel Plate measurements. The experiment was conducted using the Anton Paar Physica Modular Compact Rheometer (MCR) 301

having a cup and bob. The resin formulation, devoid of any photoinitiator, was carefully poured into the cup up to a specified mark level. Subsequently, during the experiment the bob was inserted into the resin, and shear was applied by rotating it. The shear rate was systematically increased, ranging from 1 to 1000 per second, to measure the viscosity, which was expressed in units of Pascal-seconds (Pa·s). Throughout the experiment, the temperature of the resin was maintained at a constant 30 °C. The rheology of the resin formulation was measured with the same set of instrumentation. The angular frequency was constant at 1 rad/s and strain was varied from 0.1 to 100.

2.5. 3D printing of thiol-ene resin formulations

Organic solvent-free resin formulations were utilized for DLP (Digital Light Processing) 3D printing using an anycubic photon ultra resin 3D printer. This DLP 3D printer is equipped with a 405 nm LED light source and features a resin bed with dimensions measuring 102.4 × 57.6 × 165 mm. The printing operation was carried out at room temperature. The intensity of the LED light source was precisely measured at 10 mW cm² using a UNO Genetic laser power meter. To initiate the printing process, the resin was carefully poured into the resin bed, filling it up to a designated level. Subsequently, the printing parameters were configured. Each printed layer had a thickness of 100 µm, and for the first 5 layers, the exposure time was set at 12 s. Afterwards, each subsequent layer had an exposure time of 5 s. Upon completion of the printing process, the printed part underwent a post-processing treatment. This involved washing the printed object with isopropyl alcohol in a resin washer for a duration of 3 min. Following the washing step, the printed part was placed in a UV chamber for post-curing, which lasted for 15 min.

2.6. Mechanical test of 3D printed part

The tensile strength analysis of the 3D printed component was conducted using a Universal Testing Machine, specifically the Instron series 33R4204 model, equipped with a 1 KN capacity load cell. This evaluation was carried out at room temperature. For the tensile test, ASTM D638 type V specimens were 3D printed, and an average of five samples were tested to ensure accuracy and consistency in the results. Each sample had a gauge length of 10 mm, and the experiment was conducted at room temperature, employing a stretching rate of 5 mm per minute. Mechanical properties, including tensile strength, Young's modulus, elongation, and toughness, were determined at the point of sample breakage.

2.7. Hydrolytic degradation of 3D printed parts

3D-printed dog-bone-shaped specimens were employed as test samples for hydrolytic degradation studies. The procedure began by recording the initial mass of these specimens before placing them in 20 ml glass vials. Each specimen was then immersed in a 10 ml solution of 0.1 M NaOH to initiate the degradation test, with gentle shaking at 35 °C. Periodic evaluations involved removing the specimens, blotting them dry with tissue paper, and drying them in a vacuum oven at 40–50 °C until constant weight, to record mass loss due to hydrolysis. Subsequently, the dried specimens were re-immersed in the original degradation solution to continue the hydrolysis process. This comprehensive experimental protocol allowed for the continuous monitoring and assessment of the hydrolytic degradation effects on the 3D printed specimens over time. Similarly, a hydrolytic degradation experiment was performed in 0.1 M HCL solution.

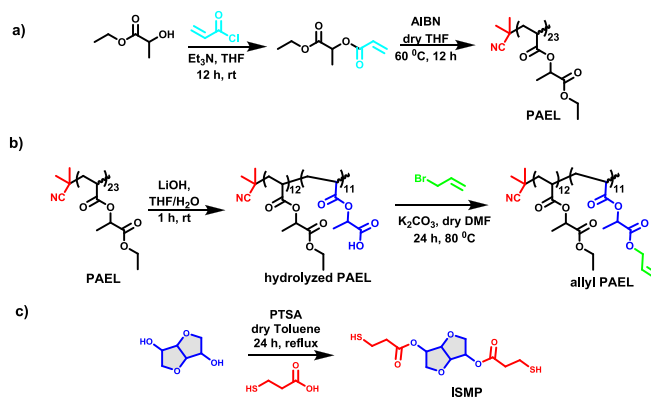
3. Results and discussions

3.1. Synthesis of PAEL and hydrolysis of PAEL, allyl PAEL and ISMP

Acrylate ethyl lactate (AEL) was synthesized according to the literature report as shown in [scheme 1a](#) using THF as solvent [40].

This reaction could be done on a large scale (30 g) and the resultant AEL monomer could be obtained in high yields (90–95 %). Briefly, the ethyl lactate was reacted with acryloyl chloride to produce acrylate ethyl lactate at room temperature within 12 h which was purified by simply washing with brine solution several times with no requirement for chromatographic purification. The chemical structure of the synthesized AEL monomer was confirmed by ¹H NMR spectroscopy (Fig. S1) with the appearance of new peaks from 5.85 to 6.51 ppm corresponding to an acrylate carbon double bond which was also confirmed by the appearance of two peaks in the ¹³C NMR spectrum at 126 ppm and 130 ppm. HRMS mass data also confirmed the formation of the product (Fig. S2). Studies in the literature have explored the polymerization of the AEL monomer, systematically investigating initiator and solvent selection [40]. In our report, we present a simplified method for synthesizing PAEL polymer. A free radical polymerization approach was employed, utilizing AIBN as the initiator and dry THF as the chosen solvent. A constant monomer-to-initiator ratio was maintained targeting 25 repeat units, and the solvent quantity was maintained at 1.5 times the volume of the monomer. The polymerization reaction was conducted at a temperature of 60 °C for a duration of 12 h. The structural characterization of the polymer was performed using ¹H NMR spectroscopy (Fig. S3) and the molecular weight was determined by size exclusion chromatography (SEC). The disappearance of the acrylate peaks of AEL monomer and the formation of two new broad peaks in the 1.82 ppm to 2.59 ppm region corresponding to the methylene protons (–CHCH₂) (labeled as 'a') and methine protons (–CHCH₂) (labeled as 'b') of PAEL polymer repeat units provided structural confirmation for the formation of the polymer. The ¹³C NMR spectrum (Fig S3) also confirmed the complete conversion by the disappearance of the acrylate carbon double bond at 126 ppm and 130 ppm. The degree of polymerization (X_n) was determined from the ¹H NMR spectra. The integration value of the terminal methyl group of AIBN was utilized to determine the degree of polymerization. The peak at 5.01 ppm corresponds to methine proton (–C(OO)CHCH₃) (labeled as 'c') of the PAEL polymer repeat unit and the peak at 0.86 ppm corresponds to the terminal AIBN methyl group (labeled as 'g'). The calculated integration values of these two peaks revealed a total number of 23 repeat units, which was close to the targeted number of 25 repeat units. The SEC plots of the polymers performed using THF as eluent are given in [Fig. 1b](#), which exhibited a monomodal distribution with a polydispersity index (PDI) value of 3.1.

The terminal ethyl ester group of the PAEL polymer was hydrolyzed with LiOH by base hydrolysis to form a carboxylic functional group in



Scheme 1. Synthesis of PAEL, partially hydrolyzed PAEL, allyl PAEL, and ISMP.

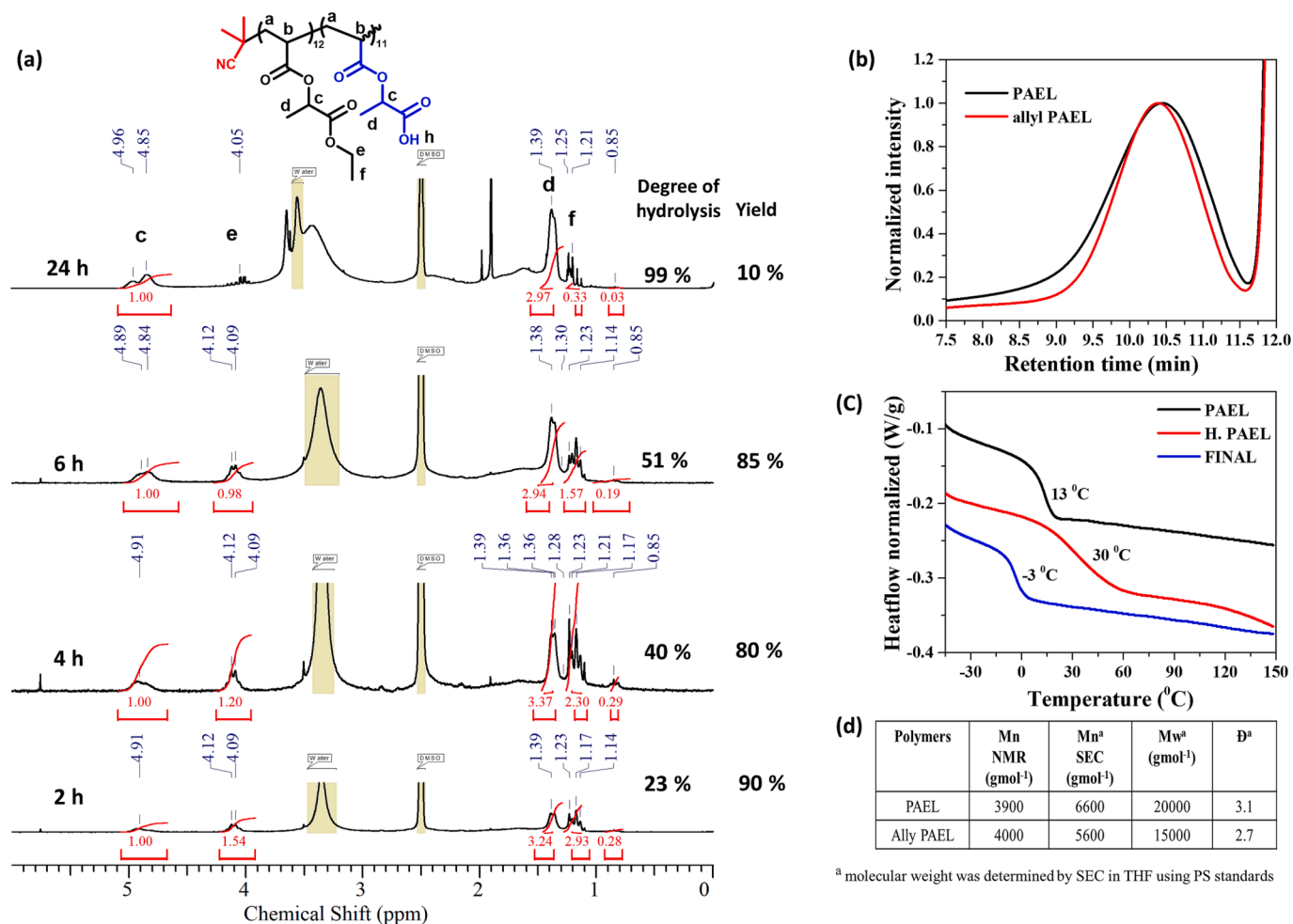


Fig. 1. (a) Hydrolysis kinetics study of PAEL polymer in 0.5 eq. of LiOH followed by ^1H NMR spectra recorded in DMSO-d_6 (b) SEC plot of PAEL and Allyl PAEL in THF as eluent and Polystyrene (PS) as standard (c) DSC thermogram of PAEL, hydrolyzed, and allyl PAEL polymers (d) Table of the molecular weight of the polymer PAEL and allyl PAEL calculated from ^1H NMR and SEC.

the repeat unit which was further reacted with allyl bromide to introduce the allyl group, as detailed in Scheme 1b. The kinetics of the hydrolysis reaction were monitored by NMR spectroscopy using aliquots retrieved at various time intervals. 0.5 equivalents of LiOH were taken with respect to one repeat unit of PAEL polymer for the hydrolysis reaction. The aliquots were collected every two hours and NMR spectra were recorded after purifying the hydrolyzed PAEL polymer. The ^1H NMR spectra (recorded in DMSO-d_6) of the hydrolyzed PAEL polymers for various time intervals are depicted in Fig. 1a. The degree of hydrolysis was assessed by tracking the decrease in peak areas corresponding to methine proton (labeled as 'e') and methylene proton (labeled as 'f') within the hydrolyzed PAEL polymer. It was noted that the degree of hydrolysis of the PAEL polymer increased as the duration of time elapsed. During the initial 6 h, approximately 50 % of the ester groups in the PAEL polymer underwent hydrolysis. After 24 h, the degree of hydrolysis reached nearly 99 %, but the reaction yield significantly declined due to the dissolution of the hydrolyzed PAEL polymer in water during the workup process. In order to expedite the hydrolysis reaction of the PAEL polymer, the amount of LiOH was increased to one equivalent with respect to one repeat unit of PAEL, and the reaction time could be shortened to just one hour. Subsequently, NMR spectra (Fig. S4) analysis revealed that approximately 50 % of the polymer had undergone hydrolysis within this one-hour timeframe, with a remarkable 90 % yield. These revised reaction conditions were deemed optimal for our study.

In the final step of the allyl PAEL polymer synthesis, the 50 %

hydrolyzed PAEL polymer was reacted with allyl bromide in dry DMF for 24 h, maintaining a temperature of 80 °C (Scheme 1b). The confirmation of the successful formation of the allyl PAEL polymer was achieved through the analysis of ^1H and ^{13}C NMR spectra recorded in CDCl_3 (Fig. S5). The ^1H NMR spectrum exhibited distinctive peaks at chemical shifts of 5.90 ppm, as well as a cluster of peaks ranging from 5.30 to 5.34 ppm, which were attributed to allyl protons ($-\text{CH}_2\text{C}_2\text{H}_3$) (labeled as 'i,' 'j,'). Additionally, new peaks emerged in the ^1H NMR spectrum at 4.55–4.62 ppm, which corresponded to methylene protons ($-\text{C}(\text{O})\text{O}-\text{CH}_2\text{C}_2\text{H}_3$) of the terminal group, (labeled as 'h'). Similarly, the ^{13}C NMR spectrum showed the appearance of new peaks at chemical shifts of 118 ppm and 132 ppm (labeled as 10, 11 in Fig. S5), which were indicative of the allyl carbon double bond in the resulting polymer. The allyl protons were integrated with respect to the methine proton ($-\text{C}(\text{O})\text{OCHCH}_3$) (labeled as 'c'). As only 50 % of the total repeat unit of PAEL polymer was available in the hydrolyzed PAEL for the allylation, the ratio of the integration of allyl proton to the methine proton intensity was half. The disappearance of the hydroxyl peaks as well as matching of the integration values of allyl protons with respect to the methine proton indicated the full conversion of the carboxyl group into the allyl group. Fig. S6 compares the FT-IR spectra of the polymers before and after modification. The appearance of the peak at 1648 cm^{-1} corresponding to the carbon–carbon double bond in allyl PAEL also confirms the functional group conversion.

The thiol cross linker Isosorbide bis-(3-mercapto) propionate (ISMP) was synthesized according to literature procedure.[41] Isosorbide was

reacted with 3-mercapto propionic acid in the presence of p-toluene sulfonic acid as catalyst (Scheme 1c). The structural confirmation of ISMP was confirmed by the ^1H , ^{13}C NMR, and HRMS spectra (Fig. S7 and S8).

Differential scanning calorimetry (DSC) analysis (Fig. 1c) was employed to investigate the thermal characteristics of the polymers. The glass transition temperature (T_g) of polymer PAEL was observed at 13 °C. After undergoing hydrolysis, the T_g increased to 30 °C, likely due to the presence of hydrogen bonding within the hydrolyzed acid groups. Upon functional group modification to allyl group, the polymer allyl PAEL exhibited a lower T_g (-3 °C). The lower T_g value of allyl PAEL indicated its soft consistency at room temperature. The table in Fig. 1d summarizes the molecular weight of the polymer before and after allyl modification.

3.2. Resin formulation and photo calorimetric studies

After the structural characterization of the ene containing polymer - allyl PAEL and thiol cross linker - ISMP, these were used for the formulation of a photo curable resin with Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and Triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione (TTT). Four resin formulations (F1-F4) were prepared using different weight percentages of allyl PAEL, TTT, PETMP, and ISMP avoiding the use of any non-reactive organic solvent. Fig. 2a shows the schematic representation of the preparation of resin formulation. The weight percentages of resin formulations are listed in the table in Fig. 2(b).

The first entry in the table is the reference formulation (Ref) which consists of a stoichiometric blend of the commercial thiol and ene small molecules PETMP and TTT, excluding the synthesized polymer allyl PAEL. This resin serves as a reference material for evaluating the rheological, mechanical, and degradation properties of other resin formulations. The curing kinetics and the specific weight percentage of photoinitiator required for curing the resin formulations were obtained from photo DSC analysis. Upon reviewing the existing literature, it was found that the kinetics of free radical network polymerization of thiol-ene click chemistry is influenced by the specific structures of the alkenes and thiol. The chemical reactions involving alkane thiols and terminal alkenes, resulting in the formation of linear thioethers, were found to be exothermic with an approximate heat change (ΔH) of around -19 kcal/mol. [20] The mechanism governing the radical-initiated thiol-ene formation can be described as a step-growth pathway, which can be divided into two distinct steps following the

initial formation of the thiyl radical through its reaction with the photoinitiator. The thiyl radical then reacts with the alkene, leading to the creation of a stable carbon-centered radical intermediate. Subsequently, this intermediate undergoes chain transfer to another thiol molecule. The curing enthalpies of the resin formulations were examined by altering the weight percentage of the TPO photoinitiator within the range of 0.25 to 1.0 wt% of the total weight of a specific resin formulation (Fig. 2c). The photo DSC plots and table listing the curing enthalpies of all formulations as a function of varying photoinitiator concentrations are given in Fig S9 and Table S1. The rate of thiol-ene network polymerization was increased (indicated by the larger heat flow peaks) when the concentration of TPO was increased. For all formulations, the curing enthalpies increased with increasing photoinitiator concentration from 0.25 wt% to 0.75 wt%, though reduction was observed in the curing enthalpy for 1 wt% photoinitiator concentration. This phenomenon could be attributed to either the self-absorption of UV light by the photoinitiator or the possibility of network polymerization being quenched due to the recombination of radicals (such as thiyl or carbon-centered radicals) resulting in dead-polymerization beyond the optimized concentration of photoinitiator. [42] Further, the thiol-ene network formation was followed using FTIR spectroscopy (shown in Fig. S10) as a function of varying exposure time. Formulation F2 was subjected to this FTIR analysis, by tracing the disappearance of the carbon-carbon double bond peak at 1648 cm^{-1} (for TTT and allyl PAEL) and sulfur hydrogen bond at 2570 cm^{-1} present in PETMP. The disappearance of these peaks upon irradiation also gave additional support for the thiol-ene network formation.

3.3. Rheology and viscosity of prepared resin formulations

The stability of thiol-ene resin formulations poses a significant challenge due to the rapid reactivity of the thiol reaction. [43] As a result, the viscosity of the thiol-ene resin formulations increased with time even at ambient temperature. [44] In our study, we conducted measurements of viscosity and rheology for the thiol-ene resin formulation at a temperature of 30 °C, with a focus on assessing its suitability for room-temperature Digital Light Processing (DLP) 3D printing. To achieve optimal results, including smooth, high-resolution, and pristine printed objects, it is essential that the resin's viscosity remains below 10 Pa-s. [45] The viscosity of the resin formulations was observed between 0.23 Pa-s and 0.61 Pa-s, (Fig. 3a and Table 1).

As seen from the Fig. 3b, no significant change was observed with higher shear rates, indicating its Newtonian fluid-like behavior.

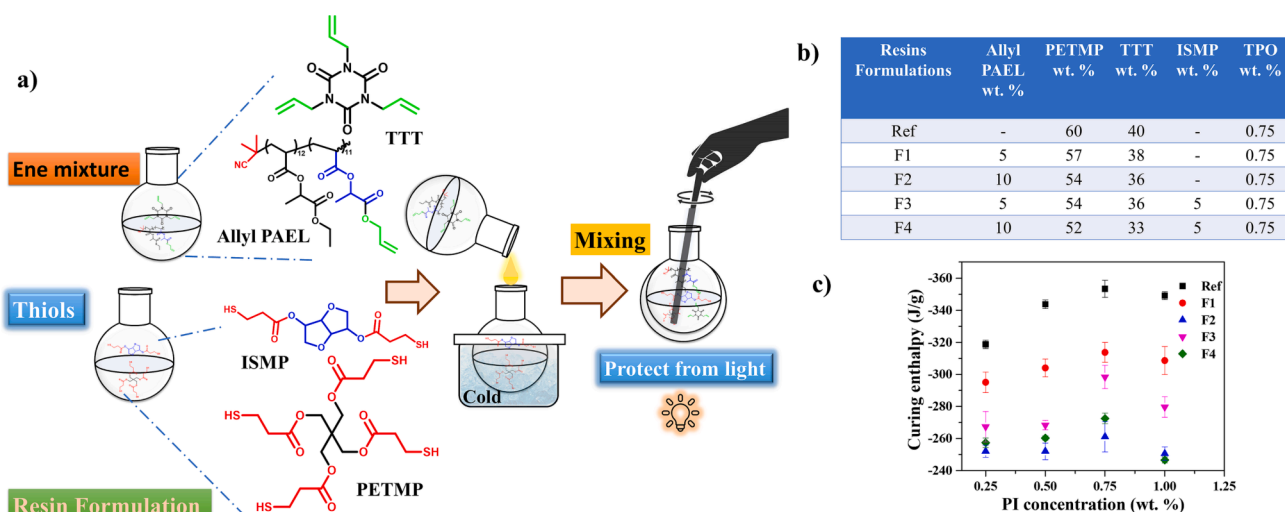


Fig. 2. (a) Schematic representation of resin formulation of allyl PAEL, TTT, PETMP, and ISMP. (b) Weight percentages of PAEL, TTT, PETMP, and ISMP taken to prepare resin formulations. (c) Optimized curing enthalpies of resin formulations.

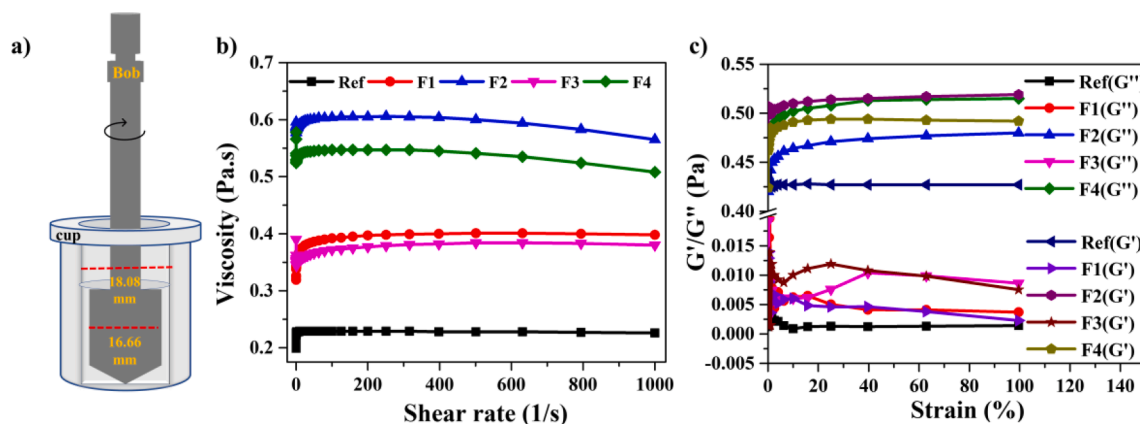


Fig. 3. (a) Schematic representation of Cup and Bob for viscosity and rheology measurement (b) Measurement of viscosity of resin formulations (c) Storage modulus (G') and loss modulus (G'') of resin formulations.

Table 1

Viscosity, mechanical properties, and thermal properties of resin formulations.

Resin formulations	Viscosity ^a (Pa.s)	Tensile strength MPa	Elongation %	Young's modulus GPa	T _g ^b (°C)	T _{d10%} (°C)
Ref	0.23	11.0 ± 2.8	11 ± 1.5	0.9 ± 0.02	58	372
F1	0.38	28.1 ± 3.1	3 ± 1.6	1.8 ± 0.03	54	375
F2	0.61	21.4 ± 1.1	8 ± 1.6	1.1 ± 0.02	44	364
F3	0.40	25.0 ± 4.2	6 ± 1.5	1.4 ± 0.04	51	366
F4	0.55	19.1 ± 2.2	10 ± 1.0	1.0 ± 0.01	47	355

a) viscosity of resin formulation at 30 °C b) T_g of printed parts from DSC.

However, when the weight percentage of PAEL polymer increased from 5 wt% to 10 wt%, the viscosity of the resins also increased. To prevent the thiol-ene mixture from curing prematurely and leading to an undesirable increase in viscosity, which could pose difficulties in DLP 3D printing, we combined the thiols and enes immediately just before commencing the 3D printing process. The rheology of the resin formulations was examined to prove the liquid-like behavior. The higher values of loss modulus (G'') compared to storage modulus (G') indicated the stability of the liquid form of resin formulations (Fig. 3c).

3.4. 3D printing of thiol-ene resins

The thiol-ene photo polymerization is quite attractive for 3D

printing due to its low shrinkage derived from the step-growth mechanism. Spot cure studies were carried out to get the estimate of the time required for the curing of the resin formulation. Spot curing of the resin formulation was executed on a glass plate to ensure that the resins achieved complete curing within a rapid timeframe of 4–8 s. The printability of allyl PAEL thiol-ene resin formulation was demonstrated with a DLP 3D printer (schematically depicted in Fig. 4a) to explore the creation of intricate 3D printed objects that exhibited controlled degradation for sustainable end-of-life.

All the prepared resin formulations were used to demonstrate the 3D printing. To improve the resolution of the 3D-printed part 0.03 wt% of (2,5-Bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene) (BBOT) a fluorescent dye was mixed with the thiol-ene resin formulation. The images of the

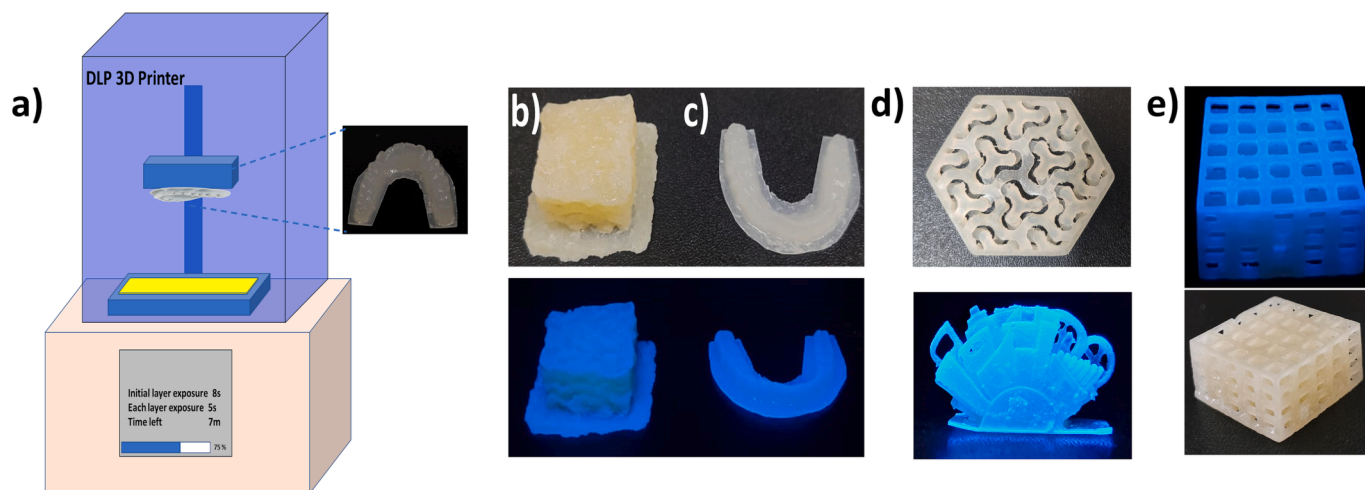


Fig. 4. (a) Schematic depiction of the DLP 3D printing process. (b) Picture of 3D printed part of a filled gyrometric square structure. (c) 3D printed teeth model in visible light and under UV light. (d) (top) Hexagonal 3D model with complex design inside, (bottom) an Ameralabs Town (standard stl. file) 3D printed part with high resolution. (e) a highly porous complex CAD file 3D printed structure showing the fidelity of thiol ene resin printability.

3D-printed parts are shown in Fig. 4b-e. Fig. 4b, 4c and 4d (top) depicts 3D printed gyrometric square, teeth model and a hexagonal 3D model with complex internal design respectively. The 3D printed component depicted in Fig. 4d (bottom) corresponds to a conventional AmeraLabs Town CAD file employed for calibrating DLP 3D printers and testing resin formulations. The successful printing of this standardized CAD file serves as validation for the printing capabilities of the thiol-ene resins. Additional images from various angles of viewing can be found in Fig. S11. Fig. 4e shows a 3D-printed highly porous complex structure that once again proves the fidelity of thiol-ene resin printability. For 3D printing using the anycubic DLP 3D printer, the exposure time of the bottom layer was intentionally set slightly higher at 12 sec to secure the attachment of the cured layer to the aluminum build platform, thereafter subsequent layers were printed at 5 s exposure.

3.5. Mechanical and thermal properties of the thiol-ene polymer network

Mechanical testing, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were performed to elucidate the impact of the weight percentage of biobased allyl PAEL polymer and isosorbide thiol in the 3D printed thiol-ene network. Fig. 5a illustrates a typical stress-strain curve for the 3D-printed thiol-ene network. The mechanical properties such as tensile strength, Young's modulus, and elongation at break were obtained from the stress-strain curve and these results are summarized in Table 1. The introduction of allyl PAEL polymer had a significant positive effect on the mechanical properties of the reference material, which was much higher than the literature reports (Table S2). [39,46,47] Specifically, there was a notable improvement in both tensile strength, which increased from 11 ± 2.8 MPa to 28.1 ± 3.1 MPa, and Young's modulus, which increased from 0.9 ± 0.02

GPa to 1.8 ± 0.03 GPa for F1 (5 wt% allyl PAEL polymer) when compared with reference material. The reference resin (Ref) is composed of small molecules only- tetra functional thiol and trifunctional 'ene' whereas all the other resin formulations incorporated a polymeric 'ene' component – the PAEL polymer, which forms a higher crosslinking network during 3D printing than the reference resin formulation. As a result, the mechanical properties like the tensile strength were much higher for the resin formulation compared to the 'Ref' resin. However, it has to be noted that this enhancement in mechanical properties was accompanied by a reduction in elongation. The elongation of the F1 resin was 3 % compared to the 11 % elongation for the 'Ref'. This reduction can be attributed to the higher crosslinking network formed during the 3D printing process which makes it less flexible. While the increased crosslinking enhances strength and modulus, it tends to limit the material's ability to deform before reaching failure, as evidenced by the decrease in elongation. The formulation F2 was prepared with 10 wt % of branched allyl PAEL polymer and the mechanical properties of the 3D printed parts showed lower tensile strength than F1 (28 MPa for F1 and 21 MPa for F2) and the modulus also decreased from 1.8 GPa to 1.1 GPa. As the polymer content in the F2 resin formulation increased, the branching side chain in the 3D printed part also increased, leading to disruptions in the formation of the printed network structure. This disruption results in a less favorable distribution of molecular segments, leading to changes in tensile strength and modulus and improved flexibility as observed from the increase in elongation from 3 to 8 %. [48,49] Similarly, the observed mechanical properties of the F3 and F4 resin formulations followed a similar trend. All resin formulations F1 to F4 exhibited improvement in tensile and Young's modulus compared to the reference material. The inclusion of isosorbide thiol in the resin formulation did not notably enhance the mechanical properties, but it

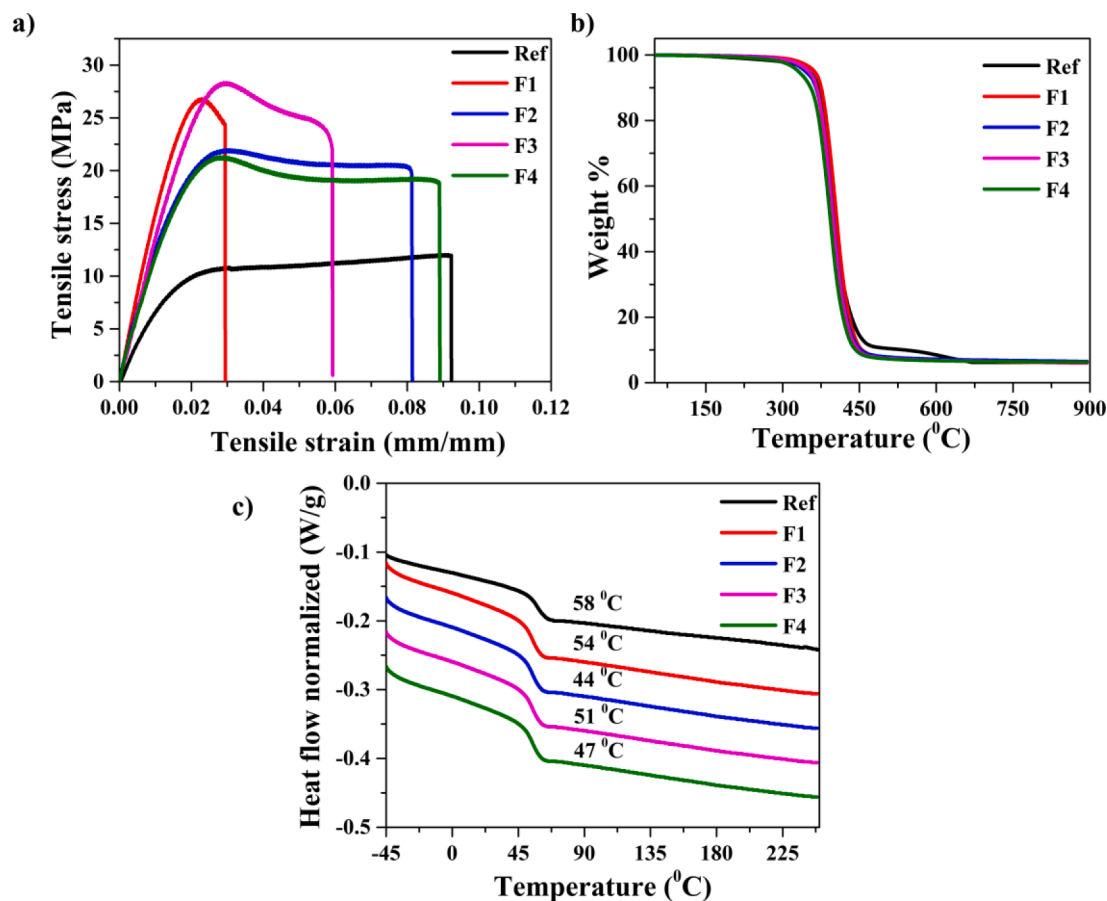


Fig. 5. (a) Tensile stress-strain plots of 3D printed thiol-ene network of different resin formulations (b) TGA plots of 3D printed thiol-ene network of different resin formulations (c) DSC plots of 3D printed thiol-ene network of different resin formulations.

exhibited significant improvement in degradation behaviour, which will be discussed in the later section.

The thermal stability of the thiol-ene 3D printed parts is shown in Fig. 5b and the values are summarized in Table 1. The thermal decomposition of the thiol-ene network in all resin formulations followed a single-step process. Importantly, all of the 3D printed thiol-ene networks demonstrated outstanding thermal stability, as indicated by a T_d , 10 % (the temperature at which 10 % weight loss occurs) exceeding 350 °C. The glass transition temperature (T_g) determined from the DSC thermogram ranged from 44 to 54 °C. The plots are shown in Fig. 5c and the T_g values are reported in Table 1. The absence of any endothermic peaks in the DSC thermogram indicated the amorphous nature of the network formed

3.6. Degradation of thiol-ene polymer network

The hydrolytic degradation of the 3D printed crosslinked thiol-ene network polymer was investigated both under acidic and basic conditions. Different reports studied the degradation mechanism of the ester bond present in thiol ene network thermoset polymer. [50,51] Han Shih et. al [52] showed the ester bond hydrolysis of thiol-ene hydrogels for base-catalyzed hydrolytic degradation and changes in degradation

behavior by manipulating the degree of thiol-ene network cross-linking. Mayuri et al. [39] reported the degradation of the thiol-ene network in different NaOH base strengths with an organic solvent which promotes the swelling of the thiol-ene network and enhances the degradation. Fig. 6a shows the degradation studies of the 3D printed thiol-ene network polymer performed in 10 ml of 1 M NaOH solution and 1 M HCl solution for each resin formulation at room temperature. As shown in Fig. 6a, there was a noticeable escalation in the degradation rate of 3D printed components in 1 M NaOH over time. The reference materials, which consisted of a stoichiometric blend of PETMP and TTT, displayed minimal degradation, measuring just 10 % in a two-day timeframe. In contrast, 3D printed parts composed of other resins containing allyl polymer and isosorbide thiol exhibited significantly higher levels of degradation during 48 h. The 3D printed component from formulation F1, which included 5 wt% of PAEL polymer exhibited a degradation of 30 %. Meanwhile, formulation F3, comprising 5 wt% of PAEL polymer and an additional 5 wt% of isosorbide experienced a higher degradation reaching 60 % at the end of 48 h. The 3D printed components from formulation F2, which included 10 wt% of PAEL polymer, and formulation F4, which contained 10 wt% of PAEL polymer along with 5 wt% isosorbide demonstrated significantly higher degradation. Specifically, F2 showed almost 95 % degradation, while F4 exhibited complete

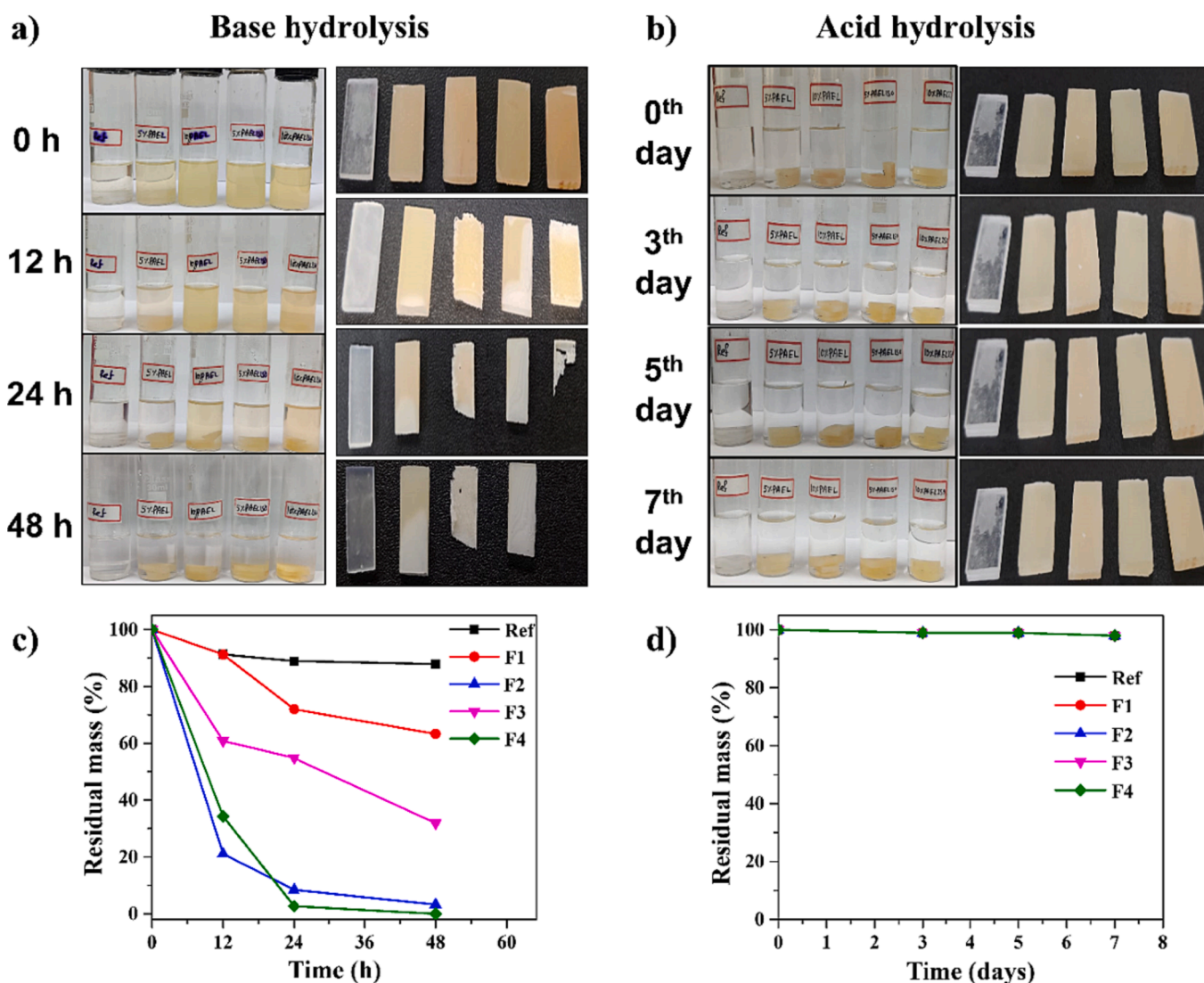


Fig. 6. Real-time photographs of degradation of the different 3D printed parts in (a) 10 ml 1 M NaOH solution over 48 h (b) 10 ml 1 M HCL solution for 7 days (c) degradation plot of 3D printed parts in 1 M NaOH solution for 48 h (d) degradation plot of 3D printed parts in 1 M HCl solution for one week.

degradation, reaching 100 %. The elevated degradation observed in the resin formulations, in contrast to the reference material, can be attributed to the inclusion of allyl polymer, specifically ethyl lactate ester. This particular component is notably susceptible to ester hydrolysis, particularly in the presence of a potent base like NaOH. The degradation process was replicated in a solution with 1 M HCl solution. Surprisingly, even after a consistent week-long experiment, there was no significant degradation observed. These findings suggest that the thiol-ene 3D printed network, featuring allyl PAEL, displays remarkable stability in an aqueous acidic environment, whereas it readily degrades in a basic medium. The degradation study involving the allyl PAEL-containing thiol-ene network highlighted the rapid degradation efficiency of 3D printed parts within a span of 2 days. This characteristic renders it an exceptionally appealing material for various prototype applications, especially those focusing on renewable sources and a sustainable end-of-life cycle.

4. Conclusions

In conclusion, this study has successfully demonstrated a scalable and sustainable approach for developing 3D printing materials via thiol-ene photochemistry, utilizing ethyl lactate-based polymeric ene and isosorbide-based thiol. The synthesis of the ethyl lactate-based polymeric ene component was achieved by free radical polymerization of acrylate ethyl lactate monomer, followed by partial hydrolysis and subsequent reaction with allyl bromide. The thiol-ene photo kinetics was analyzed through photo DSC experiments, shedding light on the underlying chemical reactions that occur during the curing process. The mechanical and thermal property analysis provided valuable insights into the potential applications and performance of these novel bio based thiol-ene materials. The practical application of the developed materials was showcased through 3D printing using a commercial DLP 3D printer, highlighting their feasibility for manufacturing and prototyping purposes. Notably, the hydrolytic degradability of the 3D printed parts was demonstrated in a 1 M NaOH solution, underlining the eco-friendly aspect of these materials and their potential to mitigate the issue of nondegradable acrylate-based 3D printed waste. This research paves the way for the development of environmentally responsible materials that have the potential to revolutionize the 3D printing industry. The fast degradability of PAEL-based polymeric thiol-ene 3D print materials opens new possibilities for rapid prototyping in mass production applications, making it a promising avenue for addressing the sustainability challenges associated with traditional acrylate-based materials. By combining the benefits of bio based sourcing, scalability, and degradability, these materials represent a significant step towards a more sustainable and environmentally conscious future in the field of 3D printing.

CRedit authorship contribution statement

Shibam Pal: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **S.K. Asha:** Conceptualization, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Resources, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dr Asha SK reports financial support was provided by Ministry of Chemical and Fertilizers, Department of Chemicals and Petrochemicals, Government of India. Dr Asha SK reports financial support was provided by Council of Scientific and Industrial Research, Project Planning & Business Development Directorate, New Delhi. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

This work has been financially supported by the Center of Excellence (CoE) (F.No. 25014/2/2015-PC-II (FTS: 14428)) supported by the Ministry of Chemical and Fertilizers, Department of Chemicals and Petrochemicals, Government of India and Facility Creation Project (FCP; No. 34/FCP/NCL/2019-RPPBDD) supported by Council of Scientific and Industrial Research, Project Planning & Business Development Directorate, New Delhi. Shibam Pal thanks CSIR for the senior research fellowship (SRF).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2024.112761>.

References

- [1] T.J. Wallin, J. Pikul, R.F. Shepherd, 3D printing of soft robotic systems, *Nat. Rev. Mater.* 3 (2018) 84–100.
- [2] Y. Li, S. Peng, K. Li, D. Qin, Z. Weng, J. Li, L. Zheng, L. Wu, C.-P. Yu, Material extrusion-based 3D printing for the fabrication of bacteria into functional biomaterials: The case study of ammonia removal application, *Addit. Manuf.* 60 (2022) 103268.
- [3] G. Zhou, M.-C. Li, F. Wang, C. Liu, C. Mei, 3D printing of cellulose nanofiber monoliths for thermal insulation and energy storage applications, *Addit. Manuf.* 59 (2022) 103124.
- [4] Y. Zhang, Y. Gao, L. Michelin, L. Josien, L. Vidal, G. Schrodj, A. Simon-Masseron, J. Lalevée, Photopolymerization of ceramic/zeolite reinforced photopolymers: Towards 3D/4D printing and gas adsorption applications, *Eur. Polym. J.* 179 (2022) 111552.
- [5] N.B. Palaganas, J.O. Palaganas, S.H.Z. Doroteo, J.C. Millare, Covalently functionalized cellulose nanocrystal-reinforced photocurable thermosetting elastomer for 3D printing application, *Addit. Manuf.* 61 (2023) 103295.
- [6] F. Kabirian, M. Mozafari, P. Mela, R. Heying, Incorporation of controlled release systems improves the functionality of biodegradable 3D printed cardiovascular implants, *ACS Biomater. Sci. Eng.* (2023), <https://doi.org/10.1021/acsbiomaterials.3c00559>.
- [7] H. Kadrý, S. Wadnap, C. Xu, F. Ahsan, Digital light processing (DLP) 3D-printing technology and photoreactive polymers in fabrication of modified-release tablets, *Eur. J. Pharm. Sci.* 135 (2019) 60–67.
- [8] C. Yu, J. Schimelman, P. Wang, K.L. Miller, X. Ma, S. You, J. Guan, B. Sun, W. Zhu, S. Chen, Photopolymerizable biomaterials and light-based 3D printing strategies for biomedical applications, *Chem. Rev.* 120 (2020) 10695–10743.
- [9] A. Schwab, R. Levato, M. D'Este, S. Piluso, D. Eglín, J. Malda, Printability and shape fidelity of bioinks in 3D bioprinting, *Chem. Rev.* 120 (2020) 11028–11055.
- [10] K.L. Sampson, B. Deore, A. Go, M.A. Nayak, A. Orth, M. Gallerneault, P.R. L. Malenfant, C. Paquet, Multimaterial vat polymerization additive manufacturing, *ACS Appl. Polym. Mater.* 3 (2021) 4304–4324.
- [11] V. Shanmugam, M.V. Pavan, K. Babu, B. Karnan, Fused deposition modeling based polymeric materials and their performance: a review, *Polym. Compos.* 3 (2021) 4304–4324.
- [12] M. Guvendiren, J. Molde, R.M.D. Soares, J. Kohn, Designing biomaterials for 3D printing, *ACS Biomater. Sci. Eng.* 2 (2016) 1679–1693.
- [13] J. Zhang, P. Xiao, 3D printing of photopolymers, *Polym. Chem.* 9 (2018) 1530–1540.
- [14] A. Atala, Introduction: 3D printing for biomaterials, *Chem. Rev.* 120 (2020) 10545–10546.
- [15] M.A. Pemberton, B.S. Lohmann, Risk Assessment of residual monomer migrating from acrylic polymers and causing Allergic Contact Dermatitis during normal handling and use, *Regul. Toxicol. Pharmacol.* 69 (2014) 467–475.
- [16] B.J. Black, M. Ecker, A. Stiller, R. Rihani, V.R. Danda, I. Reed, W.E. Voit, J. J. Pancrazio, In vitro compatibility testing of thiol-ene/acrylate-based shape memory polymers for use in implantable neural interfaces, *J. Biomed. Mater. Res. Part A* 106 (2018) 2891–2898.
- [17] R. Ding, Y. Du, R.B. Gonçalves, L.F. Francis, T.M. Reineke, Sustainable near UV-curable acrylates based on natural phenolics for stereolithography 3D printing, *Polym. Chem.* 10 (2019) 1067–1077.
- [18] W.D. Cook, S. Chausson, F. Chen, L. Le Pluart, C.N. Bowman, T.F. Scott, Photopolymerization kinetics, photorheology and photoplasticity of thiol-ene-allylic sulfide networks, *Polym. Int.* 57 (2008) 469–478.

- [19] B.H. Northrop, R.N. Coffey, Thiol-ene click chemistry: computational and kinetic analysis of the influence of alkene functionality, *J. Am. Chem. Soc.* 134 (2012) 13804–13817.
- [20] C.E. Hoyle, T.Y. Lee, T. Roper, Thiol-enes: chemistry of the past with promise for the future, *J. Polym. Sci. Part A Polym. Chem.* 42 (2004) 5301–5338.
- [21] A.K. O'Brien, N.B. Cramer, C.N. Bowman, Oxygen inhibition in thiol-acrylate photopolymerizations, *J. Polym. Sci. Part A Polym. Chem.* 44 (2006) 2007–2014.
- [22] C.E. Hoyle, C.N. Bowman, Thiol-ene click chemistry, *Angew. Chem. Int. Ed.* 49 (2010) 1540–1573.
- [23] N.B. Cramer, C.N. Bowman, Kinetics of thiol-ene and thiol-acrylate photopolymerizations with real-time fourier transform infrared, *J. Polym. Sci. Part A Polym. Chem.* 39 (2001) 3311–3319.
- [24] C.J. Kloxin, T.F. Scott, C.N. Bowman, Stress relaxation via addition-fragmentation chain transfer in a thiol-ene photopolymerization, *Macromolecules* 42 (2009) 2551–2556.
- [25] R.A. Ortiz, A.E. García Valdéz, M.G. Martínez Aguilar, M.L. Berlanga Duarte, An effective method to prepare sucrose polymers by Thiol-Ene photopolymerization, *Carbohydr. Polym.* 78 (2009) 282–286.
- [26] T. Yoshimura, T. Shimasaki, N. Teramoto, M. Shibata, Bio-based polymer networks by thiol-ene photopolymerizations of allyl-etherified eugenol derivatives, *Eur. Polym. J.* 67 (2015) 397–408.
- [27] S. Briede, M. Jurinovs, S. Nechausov, O. Platnieks, S. Gaidukovs, State-of-the-art UV-assisted 3D printing via a rapid syringe-extrusion approach for photoactive vegetable oil acrylates produced in one-step synthesis, *Mol. Syst. Des. Eng.* 7 (2022) 1434–1448.
- [28] D.G. Sycks, T. Wu, H.S. Park, K. Gall, Tough, stable spiroacetal thiol-ene resin for 3D printing, *J. Appl. Polym. Sci.* 135 (2018) 46259.
- [29] R. Ohno, K. Sugane, M. Shibata, Thermal and mechanical properties of polymer networks prepared by the thiol-ene reaction of a vanillin/acetone condensate and its related compounds, *Eur. Polym. J.* 159 (2021) 110738.
- [30] Y. Wu, M.C. Simpson, J. Jin, Fast hydrolytically degradable 3D printed object based on aliphatic polycarbonate thiol-yne photoresins, *Macromol. Chem. Phys.* 222 (2021) 2000435.
- [31] E. Constant, O. King, A.C. Weems, Bioderived 4D printable terpene photopolymers from limonene and β -myrcene, *Biomacromolecules* 23 (2022) 2342–2352.
- [32] S. Bertlein, G. Brown, K.S. Lim, T. Jungst, T. Boeck, T. Blunk, J. Tessmar, G. J. Hooper, T.B.F. Woodfield, J. Groll, Thiol-ene clickable gelatin: a platform bioink for multiple 3D biofabrication technologies, *Adv. Mater.* 29 (2017) 1703404.
- [33] P. Marx, A. Romano, I. Roppolo, A. Chemelli, I. Mühlbacher, W. Kern, S. Chaudhary, T. Andritsch, M. Sangermano, F. Wiesbrock, 3D-printing of high- κ thiol-ene resins with spiro-orthoesters as anti-shrinkage additive, *Macromol. Mater. Eng.* 304 (2019) 1900515.
- [34] C.C. Cook, E.J. Fong, J.J. Schwartz, D.H. Porcincula, A.C. Kaczmarek, J.S. Oakdale, B.D. Moran, K.M. Champley, C.M. Rackson, A. Muralidharan, R.R. McLeod, M. Shusteff, Highly tunable thiol-ene photoresins for volumetric additive manufacturing, *Adv. Mater.* 32 (2020) 2003376.
- [35] A. Oesterreicher, J. Wiener, M. Roth, A. Moser, R. Gmeiner, M. Edler, G. Pinter, T. Griesser, Tough and degradable photopolymers derived from alkyne monomers for 3D printing of biomedical materials, *Polym. Chem.* 7 (2016) 5169–5180.
- [36] Y. Wu, M.C. Simpson, J. Jin, Fast hydrolytically degradable 3D printed object based on aliphatic polycarbonate thiol-yne photoresins, *Macromol. Chem. Phys.* 222 (2021) 1–7.
- [37] D.G. Sycks, T. Wu, H.S. Park, K. Gall, Tough, stable spiroacetal thiol-ene resin for 3D printing, *J. Appl. Polym. Sci.* 135 (2018) 1–12.
- [38] D. Merckle, E. Constant, A.C. Weems, Linalool derivatives for natural product-based 4D printing resins, *ACS Sustain. Chem. Eng.* 9 (2021) 12213–12222.
- [39] M.K. Porwal, M.M. Hausladen, C.J. Ellison, T.M. Reineke, Biobased and degradable thiol-ene networks from levoglucosan for sustainable 3D printing, *Green Chem.* 25 (2023) 1488–1502.
- [40] N. Bensabeh, A. Moreno, A. Roig, O.R. Monaghan, J.C. Ronda, V. Cádiz, M. Galià, S.M. Howdle, G. Lligadas, V. Percec, Polyacrylates derived from biobased ethyl lactate solvent via SET-LRP, *Biomacromolecules* 20 (2019) 2135–2147.
- [41] *Journal of Polymer Science - 2020 - eker - Fully bio-based thiol-ene photocured thermosets from isosorbide and tung oil.* *J. Polym. Sci.* 58 (2020) 1105–1114.
- [42] W.D. Cook, S. Chausson, F. Chen, L. Le Pluart, C.N. Bowman, T.F. Scott, Photopolymerization kinetics, photorheology and photoplasticity of thiol-ene-allylic sulfide networks, *Polym. Int.* 57 (2008) 469–478.
- [43] J. Yue, J. Nie, X. Zhu, Thiol-divinylbenzene: A thiol-ene system with high storage stability, *J. Photochem. Photobiol. A Chem.* 436 (2023) 114417.
- [44] L. Chen, Q. Wu, G. Wei, R. Liu, Z. Li, Highly stable thiol-ene systems: From their structure-property relationship to DLP 3D printing, *J. Mater. Chem. C* 6 (2018) 11561–11568.
- [45] Y. Luo, G. Le Fer, D. Dean, M.L. Becker, 3D printing of poly(propylene fumarate) oligomers: evaluation of resin viscosity, printing characteristics and mechanical properties, *Biomacromolecules* 20 (2019) 1699–1708.
- [46] D.B. Larsen, R. Sønderbæk-Jørgensen, J.Ø. Duus, A.E. Daugaard, Investigation of curing rates of bio-based thiol-ene films from diallyl 2,5-furandicarboxylate, *Eur. Polym. J.* 102 (2018) 1–8.
- [47] J. Dai, S. Ma, L. Zhu, S. Wang, L. Yang, Z. Song, X. Liu, J. Zhu, UV-thermal dual cured anti-bacterial thiol-ene networks with superior performance from renewable resources, *Polymer* 108 (2017) 215–222.
- [48] V.A. Bobrin, Y. Yao, X. Shi, Y. Xiu, J. Zhang, N. Corrigan, C. Boyer, Nano- to macro-scale control of 3D printed materials via polymerization induced microphase separation, *Nat. Commun.* 13 (2022) 1–10.
- [49] D.P. Street, A.H. Mah, W.K. Ledford, S. Patterson, J.A. Bergman, B.S. Lokitz, D. L. Pickel, J.M. Messman, G.E. Stein, S.M. Kilbey, Tailoring interfacial interactions via polymer-grafted nanoparticles improves performance of parts created by 3D printing, *ACS Appl. Polym. Mater.* 2 (2020) 1312–1324.
- [50] A.T. Metters, K.S. Anseth, C.N. Bowman, A statistical kinetic model for the bulk degradation of PLA-b-PEG-b-PLA hydrogel networks: incorporating network non-idealities, *J. Phys. Chem. B* 105 (2001) 8069–8076.
- [51] A.T. Metters, C.N. Bowman, K.S. Anseth, A statistical kinetic model for the bulk degradation of PLA-b-PEG-b-PLA hydrogel networks, *J. Phys. Chem. B* 104 (2000) 7043–7049.
- [52] H. Shih, C.-C. Lin, Cross-linking and degradation of step-growth hydrogels formed by thiol-ene photoclick chemistry, *Biomacromolecules* 13 (2012) 2003–2012.

Room Temperature Photocurable PEEK Polymer Formulations for High-Performance 3D Printing Applications

Published as part of ACS Applied Engineering Materials *virtual special issue* “Celebrating the 25th Anniversary of the Chemical Research Society of India”.

Shibam Pal, Yogesh Gaikwad, and Asha S. K.*



Cite This: *ACS Appl. Eng. Mater.* 2024, 2, 1450–1459



Read Online

ACCESS |



Metrics & More



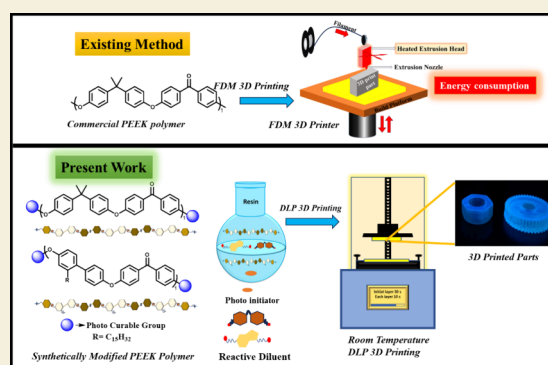
Article Recommendations



Supporting Information

ABSTRACT: Digital light processing (DLP) technology was employed to 3D print acrylate-modified poly(ether ether ketone) (PEEK). PEEK and modified PEEK (mPEEK incorporating pendant pentadecyl chain) polymers were synthesized and end-capped with urethane acrylate units. These end-modified PEEK polymers were combined with commercially available (meth)acrylic cross-linkers and photoinitiator to create photocurable resin formulations suitable for DLP 3D printing. The resulting 3D-printed parts exhibited remarkable mechanical strength, with a Young's modulus of 2.1 GPa. This surpassed the mechanical properties of commercial acrylate resin 3D-printed parts and achieved approximately 55% of the Young's modulus of reported commercial PEEK polymer. Notably, the thermal properties of the 3D-printed materials were impressive, including a high glass transition temperature of 140 °C and stability with only around 10% weight degradation occurring at approximately 400 °C. These innovative resins demonstrated excellent printability with high resolution, enabling the fabrication of intricate shapes, including complex dental materials by DLP 3D printing. Their versatility extends to potential applications in dentistry, automobile manufacturing, and robotics.

KEYWORDS: additive manufacturing, polyether ether ketone, digital light processing, acrylate PEEK, 3D printing



INTRODUCTION

3D printing has garnered significant interest due to its ability to facilitate rapid prototyping and on-demand production of materials. This innovative technique involves constructing objects layer-by-layer, effectively transforming computer-aided designs into tangible three-dimensional models. Beyond prototyping, these methodologies are now envisioned for directly fabricating intricate structures as end-use components.

In diverse fields, 3D printing finds applications ranging from tissue engineering and medical device fabrication to soft robotics, dentistry, and sensor development among many others.^{1–6} The methods used in 3D printing are classified based on printing techniques and material utilization. Extrusion-based 3D printing, including melt material extrusion (MME) and direct ink writing (DIW), is commonly employed for the fabrication of high-performance polymer (HPP) structures from filaments or shear thinning inks.^{7–9} Photocuring technologies, such as stereolithography (SLA) and digital light processing (DLP), utilize photochemical curing of liquid acrylate or cationically polymerizable resin materials to produce 3D-printed components.^{10,11} Compared to extrusion-based methods, DLP 3D printing offers higher precision in manufacturing, improved mechanical toughness, and better

layer unity.^{12,13} Despite these advancements, a persistent challenge lies in processing high-performance polymers (HPPs) such as polyether ether ketone (PEEK) and polyimide under ambient conditions.^{14,15} HPPs exhibit remarkable mechanical and thermal properties due to the concentration of aromatic rings within their polymer chains, resulting in strong bonds and interchain interactions.^{16,17} PEEK, in particular, stands out for its strength and heat resistance, making it valuable in fields like the automotive industry and medical implants.^{18–20} Commercial PEEK polymer has a reported tensile strength of 90–100 MPa and Young's modulus of 4 GPa with a glass transition temperature of 143 °C and stability up to 450 °C with only 5% weight loss.

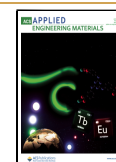
While processing PEEK polymer remains challenging, research groups have made significant efforts to 3D print this material.²¹ For instance, Tan et al. used direct energy

Received: April 24, 2024

Revised: May 25, 2024

Accepted: May 28, 2024

Published: June 10, 2024



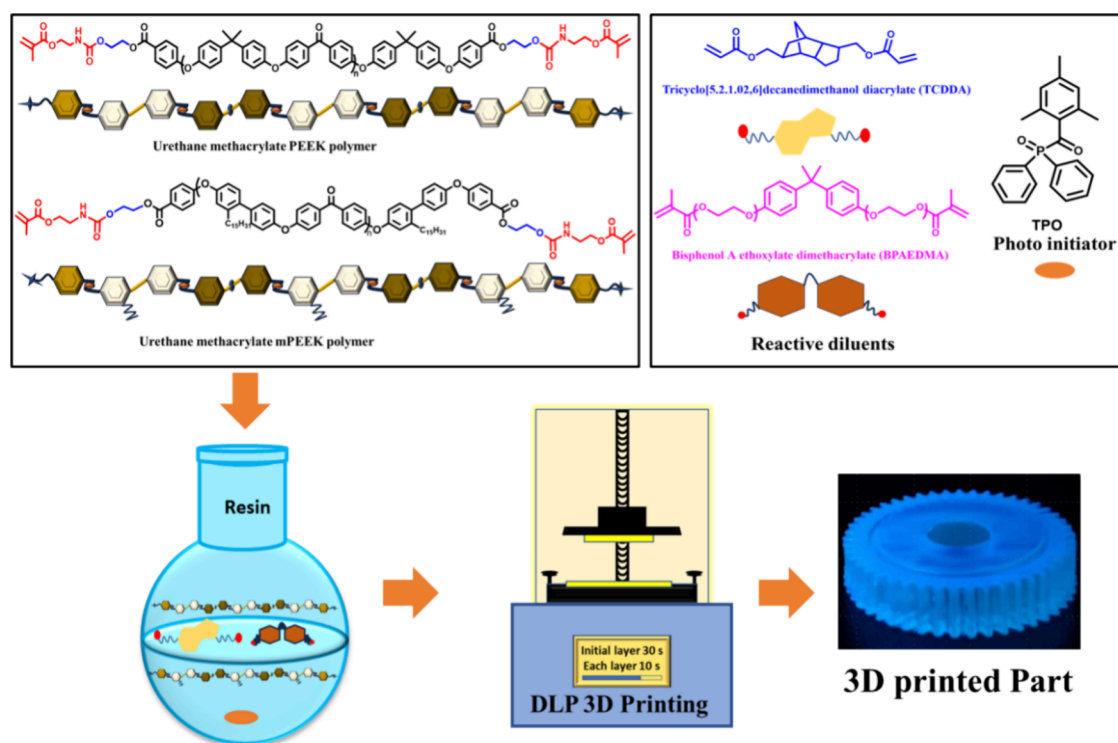


Figure 1. Overall representation summarizing the preparation of the 3D printable photocurable resins of UMPEEK/UMmPEEK polymers into 3D-printed physical objects using a DLP 3D printer.

deposition with a CO₂ laser beam to create circular PEEK polymer discs blended with hydroxyapatite powder. Optimized printing parameters included a temperature of 140 °C and 16–21 W for direct energy deposition (DED).²² Other studies have explored PEEK polymer composites with bioactive additives, resulting in nontoxic and porous materials suitable for applications like porous scaffolds.^{19,23} Another approach involves MME, where PEEK filament materials are extruded through a heated extruder head (maintained above 360 °C) for 3D printing human bone structures.^{24,25} Researchers have also investigated factors like adhesion between print layers, printing temperature, speed, and postcuring parameters.^{7,20} Notably, Rinaldi et al. observed variations in the Young's modulus of 3D-printed PEEK materials based on the infill percentage with 100% infilled parts exhibiting a remarkable mechanical strength at 4 GPa.²⁶ Hu et al. documented an additional heat control treatment implemented during 3D printing to mitigate layer warping, thereby enhancing interlayer connectivity.²⁷ In a recent development, Lee et al. demonstrated the room temperature 3D printing of PEEK materials through the DIW 3D printing process.²⁸ They created a novel epoxy-functionalized PEEK paste using commercial PEEK powder and fenchone (a colorless oily liquid used to make the PEEK paste). The resulting 3D-printed parts exhibited outstanding thermal and chemical stability, achieving 62% of the mechanical strength observed in commercial PEEK materials. In yet another report, 3D printing was carried out for polyimide using vat polymerization after synthesizing photocross-linkable acrylate-functionalized polyamic acid derivatives in NMP solvent.²⁹ As far as we are aware, the exploration of liquid-based 3D printing for the PEEK polymer has not been undertaken to date.

The current work details the synthesis of urethane methacrylate-based poly(ether ether ketone) (PEEK) and its

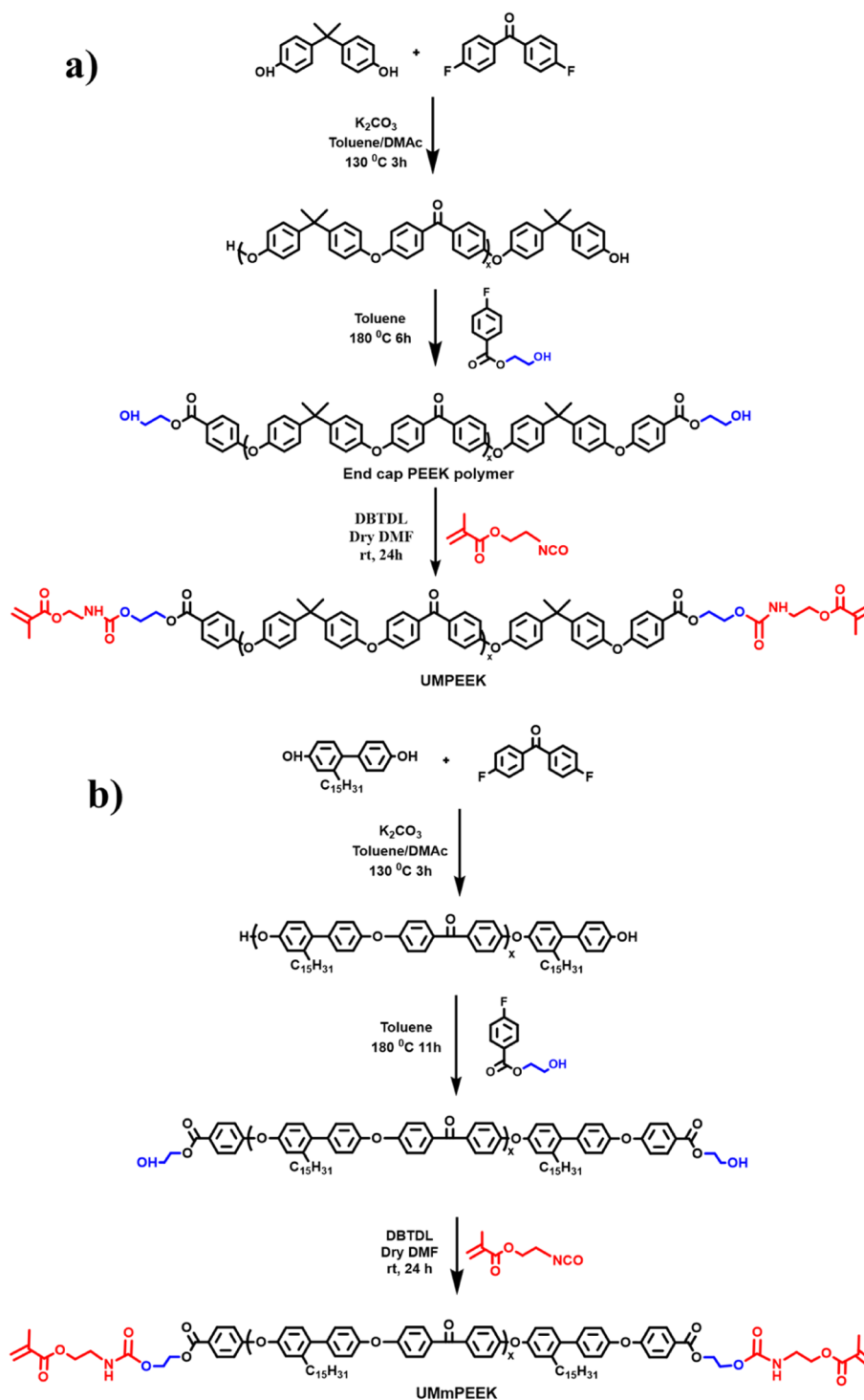
successful application in room temperature DLP 3D printing. The urethane methacrylate end-capped PEEK polymers were incorporated into resin formulations, adjusting the proportions of reactive diluents. The viscosity and curing kinetics of these resin formulations were characterized using rheology and photodifferential scanning calorimetry (photo-DSC) analysis. Additionally, the thermal and mechanical properties of the DLP 3D-printed parts were evaluated. Notably, our research marks the first instance of room temperature DLP 3D printing of functionalized PEEK polymers. These 3D-printed PEEK parts exhibit comparable Young's modulus and thermal properties, demonstrating a promising synthetic approach to enhance PEEK polymers for high mechanical strength in end-use product fabrication.

RESULTS AND DISCUSSIONS

Synthesis and Characterization of Urethane Methacrylate PEEK (UMPEEK) and Urethane Methacrylate-Modified PEEK (UMmPEEK) Polymers

Figure 1 summarizes the main goals of creating a photocurable resin formulation with the UMPEEK/UMmPEEK polymer. Specifically, regular polyether ether ketone (PEEK) and modified polyether ether ketone incorporating pendant pentadecyl chains (mPEEK) were synthesized and further end-functionalized with photocurable moieties. Scheme 1 shows the synthesis of PEEK and mPEEK and their further modification by introduction of a photocurable urethane methacrylate group. The synthesis of the modified PEEK with an appended pentadecyl chain was adopted with some modifications from the literature (mentioned in the Supporting Information S2).³⁰ The sections S3–S7 and Figures S1–S6 of the Supporting Information provide the details of the synthesis and structural analysis of the polymers. Size exclusion

Scheme 1. Synthetic Scheme for the Terminal-Functionalized Urethane Methacrylate PEEK Polymers: (a) UMPEEK and (b) UMmPEEK



chromatography (SEC) and proton NMR spectroscopy were used to determine the degree of polymerization for the PEEK and mPEEK polymers.

Briefly, the synthesis of PEEK (or mPEEK) involved the polycondensation reaction of bisphenol A (or 3-pentadecyl 4,4'-biphenol) with 4,4'-difluorobenzophenone in a solvent mixture of toluene and dimethylacetamide in the presence of anhydrous potassium carbonate. After a 3 h of reaction at 130 °C, the temperature was increased to 180 °C to remove water and toluene as an azeotropic mixture. Afterward, 2-

hydroxyethyl 4-fluorobenzoate was added to end-cap the formed polymer. A moderate molecular weight was targeted for the polymerization to enable processing of the polymer in a photocurable resin formulation. The precipitated polymer was structurally characterized by NMR spectroscopy, and molecular weight was determined by size exclusion chromatography (Figures S3, S4, and S7). The methacrylate modification of the end groups was accomplished by reacting the hydroxyl terminated PEEK and mPEEK polymer with 2-isocyanatoethyl methacrylate in the presence of dibutyltin dilaurate (DBTDL)

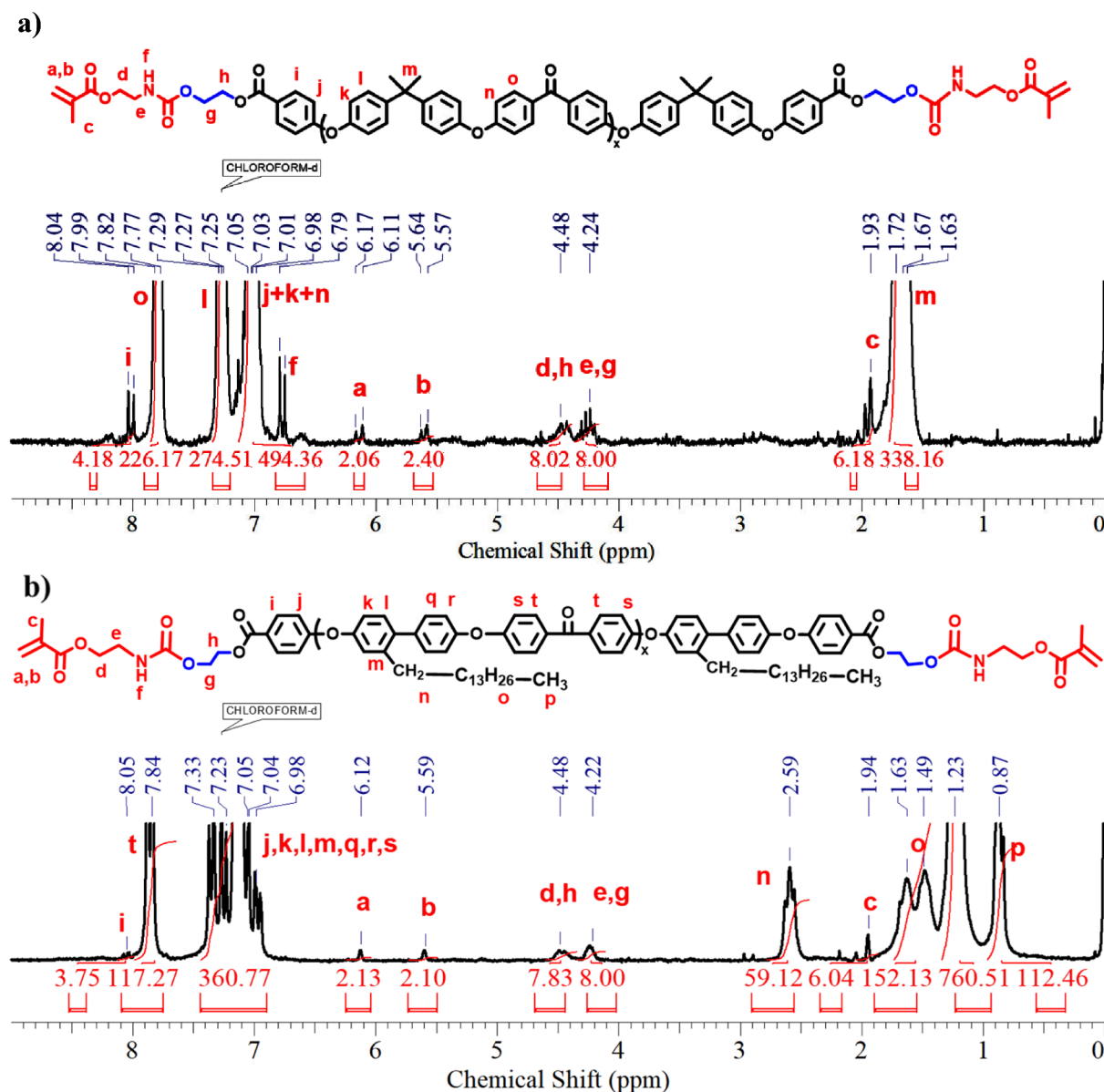


Figure 2. ^1H NMR spectra of (a) UMPEEK polymer and (b) UMmPEEK polymer.

as a catalyst.³¹ The final photocurable PEEK polymers were obtained by precipitation from chloroform into methanol at least 2–3 times.

Figure 2 compares the proton NMR spectra of the methacrylate end-capped PEEK and mPEEK polymers, which were named as urethane methacrylate PEEK (UMPEEK) and urethane methacrylate-modified PEEK (UMmPEEK). The terminal methacrylate protons were observed as two doublets at 6.12 and 5.59 ppm respectively. By integrating the intensity of the methacrylate protons with respect to the aromatic protons (especially the isolated peak near the ketone labeled as ‘o’ for UMPEEK and ‘t’ for UMmPEEK) at 7.82–7.84 ppm, the average number of repeat units was obtained as 56 for UMPEEK and 30 for the UMmPEEK polymer respectively. Table 1 lists the number-average molecular weight determined from proton NMR spectroscopy.

The molecular weights of the polymers were measured using GPC with THF as eluent and polystyrene as a standard. The GPC chromatograms are given in Figure S7, and the values are listed in Table 1. The number-average molecular weights

Table 1. Molecular Weight of the PEEK Polymers Was Determined from NMR Spectroscopy and GPC Analysis

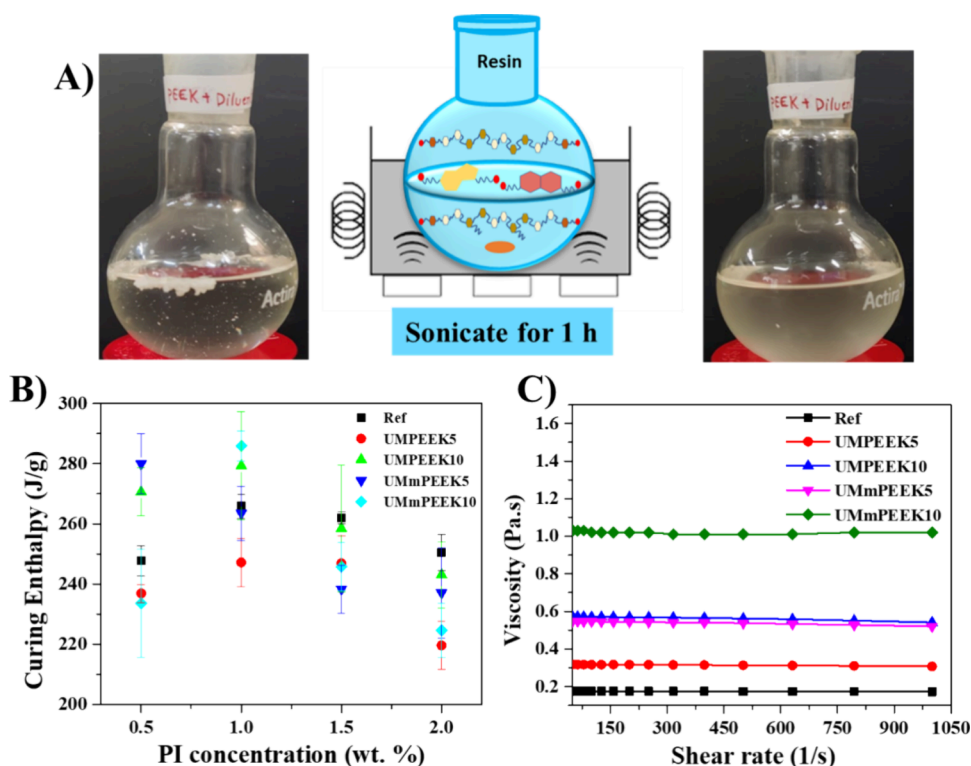
Polymers	M_n^a (g/mol)	M_n^b (g/mol)	M_w^b (g/mol)	$\bar{D}^b$
PEEK	23 200	8100	14 200	1.7
UMPEEK	23 400	9700	19 000	1.9
mPEEK	17 500	18 400	23 000	1.3
UMmPEEK	17 800	16 300	27 300	1.7

^aNMR. ^bGPC in THF eluent, PS standard.

determined from GPC were much lower compared with that determined from NMR spectroscopy for the UMPEEK polymer. On the other hand, the corresponding values for UMmPEEK seemed to exhibit a reverse trend, with the GPC molecular weights on the higher side compared to that determined from proton NMR spectroscopy. The molecular weights determined by proton NMR spectroscopy are more reliable than that obtained using GPC for these aromatic polymers, as the latter measurement is taken with respect to polystyrene standards.^{32,33} Additionally, the introduction of a

Table 2. Weight Percentages of UMPEEK, UMmPEEK, TCDDA, BPAEDMA, and PI Taken to Prepare Resin Formulations and Their Measured Viscosity

Resin formulations	TCDDA wt %	BPAEDMA wt %	UMPEEK wt %	UMmPEEK wt %	TPO wt %	Viscosity (Pa·s)
Ref	49.5	49.5	-	-	1	0.17
UMPEEK5	47	47	5	-	1	0.32
UMPEEK10	44.5	44.5	10	-	1	0.57
UMmPEEK5	47	47	-	5	1	0.54
UMmPEEK10	44.5	44.5	-	10	1	1.03

**Figure 3.** (A) UMPEEK polymer with reactive diluents before and after sonication, (B) selection of the photoinitiator weight percentage by photocuring study, (C) measurement of viscosity of the resin formulations.

long pentadecyl group in the mPEEK polymer altered the hydrodynamic volume resulting in the much higher values for the molecular weight.³⁴

Resin Formulations and Photocuring Experiments

Following structural characterization, the PEEK polymers were used to formulate a photocurable resin mixture. The formulations incorporated tricyclo[5.2.1.0^{2,6}]-decanedimethanol diacrylate (TCDDA) and bisphenol A ethoxylate dimethacrylate (BPAEDMA) as reactive diluents. Table 2 lists the weight percentages of polymers and reactive diluents used in the resin composition. Two formulations each were prepared using 5 and 10 wt % of UMPEEK and UMmPEEK polymers, respectively, in the resin mixture of equal weight percentages of TCDDA and BPAEDMA. Figure S8 illustrates the attempts made to increase the weight percentage of the UMPEEK and UMmPEEK polymers in the resin formulation. Unfortunately, due to dissolution problems, it was not feasible to create resin formulations with a higher weight percentage incorporation of the PEEK polymers. As a result, the resin could not be formulated for printing at higher PEEK concentrations.

The solid polymer was sonicated for 1 h in the resin mixture to let it dissolve completely (Figure 3A). A formulation of only

TCDDA and BPAEDMA was also prepared without the PEEK polymer as a reference system. The weight percentage of the photoinitiator TPO required for the curing was determined using isothermal photo-DSC analysis at 30 °C. In this process, resin formulations underwent solidification upon exposure to UV light, and accurate measurements of curing enthalpies were obtained. The curing mechanism involves the initiation of radicals by cleaving the photoinitiator in the presence of UV light, resulting in the formation of a cross-linked network polymer. To examine the curing enthalpies in the resin compositions, the weight percentage of TPO photoinitiator was varied between 0.5 and 2 wt % (Figure 3B). Figure S9 in the Supporting Information shows photo-DSC graphs for the resin formulations at various percentages of PI. Analysis of the curing enthalpies revealed an increase in enthalpy with an increase in concentration of PI until a concentration of 1 wt %, after which, the enthalpy decreased with further increase in the PI concentration. Based on this observation, the ideal PI concentration was fixed at 1 wt % for maximum conversion. It is reported that insufficient amounts of PI concentration may be inadequate for complete curing. However, higher concentrations of PI can result in increased light absorption, potentially leading to insufficient light penetration for the comprehensive curing of the resin samples.³⁵

Viscosity Measurement. A key factor in room temperature DLP 3D printing is the viscosity of the resin formulation. For a 3D printing process to be smooth and distortion-free, the resin must flow easily. The resin used in room temperature DLP 3D printing should ideally have a viscosity less than 10 Pa·s.^{35,36} Figure 3C compares the viscosity as a function of increasing shear rate for the different resin formulations at 30 °C. There was no significant change observed in the viscosity of the resin with increasing shear rates, indicating Newtonian behavior. On the other hand, the viscosity of the resin rose from 0.32 to 0.57 Pa·s and from 0.54 to 1.03 Pa·s, respectively, with an increase in the weight proportion of UMPEEK/UMmPEEK polymer. Despite the low viscosity exhibited by the resin formulations, they were found to be entirely adequate for room temperature DLP 3D printing, ensuring a smooth and successful printing process. Despite their comparatively lower molecular weight, the formulations incorporating UMmPEEK exhibited higher viscosities. One reason for this could be the presence of the long C15 alkyl side chains in each repeat unit in UMmPEEK, which are long-enough to entangle thereby increasing the viscosity.³⁷ This was also reflected in the apparently higher molecular mass, as recorded by the GPC due to the larger hydrodynamic volume in the case of UMmPEEK.

DLP 3D Printing of PEEK Resin Formulations. 3D printing of PEEK polymer at room temperature presents a challenge, but this challenge was addressed by utilizing a miscible (meth)acrylate PEEK polymer as the resin. Spot curing studies were conducted to estimate the curing time of the resins. Spot curing involved applying the resins onto a glass plate and exposing it to UV light from a homemade setup utilizing six UV-LED lights, (as shown in Figure S10). A single drop of resin solidified within 10 s, as confirmed by tilting the glass plate without any observable resin flow. The printing capabilities of PEEK (meth)acrylate resin formulations were assessed using the Anycubic Photon Ultra resin 3D printer (schematically represented in Figure 1). The printing parameters of the DLP 3D printer involved 30 s for the initial five layers followed by 10 s for each succeeding layer. The longer irradiation time for the initial layers is required to make the layer stick on the build plate; otherwise, the succeeding layers will collapse under its own weight. The printing of the tensile bars was performed in flat (0°) orientation because this specific orientation has been shown to exhibit better mechanical properties.^{38,39} All resins were employed to showcase their 3D printing capabilities, and it was noted that each resin produced prints with sharply defined edges. In order to achieve high-resolution 3D-printed parts (shown in Figure S11), 0.02 wt % of a fluorescent dye (2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT)) was added to the resin compositions. Dyes are frequently used in DLP 3D printing to enhance the precision of the printed item and to introduce light emission characteristics when excited by UV light. The inclusion of dye in the resin formulation modulates the penetration of light into the resin, thus controlling the curing process during 3D printing. The absence of dye in the resin may result in excessive curing in unwanted areas due to the scattering of incident light within the resin, which can limit the resolution of the 3D-printed part.^{40,41} Figure S12 shows some failed 3D-printed parts in the absence of BBOT dye.

Figure 4A displays top-view images of the intricate 3D-printed part using the UMPEEK/UMmPEEK resin formulations. Figure 4B,C exhibits sharp edges of the 3D-printed parts under UV irradiation. The uniform blue emission signifies the

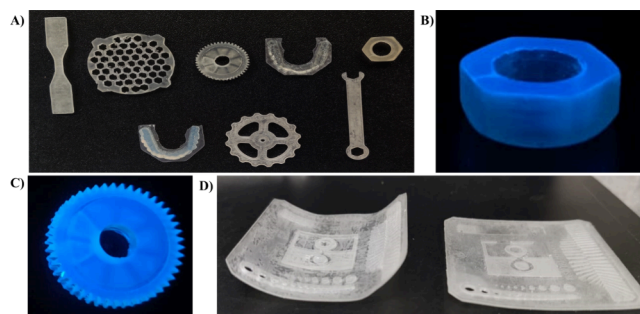


Figure 4. (A) Top view of different 3D-printed parts of UMPEEK/UMmPEEK polymers. (B,C) High-resolution 3D-printed parts of UMPEEK/UMmPEEK resin observed under UV light irradiation. (D) Left side: distorted (due to warpage) 3D print part of resin containing 10 wt % UMPEEK polymer (validation Xp2 Standard Triangle Language file); right side: flat 3D-printed part with 10 wt % UMmPEEK polymer formulation.

presence of the BBOT dye, which is evenly mixed in the resin mixture. Some issues of warpage were observed during postcure treatment for thin 3D-printed parts using UMPEEK resin formulations, which were not observed while using the UMmPEEK resin formulations. The UMPEEK acrylate 3D-printed part (resin validation Xp2 Standard Triangle Language) displayed a distorted structure after postcuring. However, it is noteworthy that this distortion was not observed when thicker 3D parts were printed, as depicted in the first three images of Figure 4. In contrast, the 3D-printed parts using the UMmPEEK resin formulation exhibited a precisely flat structure according to the resin validation Xp2 Standard Triangle Language, even after a 15 min postcuring period (Figure 4D right). It has been reported in the literature that when 3D printing thin objects there is a likelihood of plastic deformation especially in parts with elongated shapes and small thickness in the horizontal direction.⁴² The pendant pentadecyl chain present in UMmPEEK serves as an in-built “internal plasticizer” effectively reducing plastic deformation and preventing warpage in the 3D-printed thin film.⁴³

Mechanical and Thermal Properties of 3D-Printed Parts. The 3D-printed parts were subjected to mechanical testing, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) to investigate the effect of varying the weight percentage of the UMPEEK/UMmPEEK polymer in the resin formulation. The mechanical properties were assessed by employing 3D-printed dumbbell-shaped specimens of ASTM D638 type V for each resin formulation. Tensile strength values were obtained by averaging the results from a total of five specimens. Figure 5A depicts the stress–strain plot of the 3D-printed PEEK polymer, while Table 3 provides a summary of mechanical properties, including tensile strength, Young’s modulus, and elongation at break. Analysis of the mechanical properties revealed a notable positive impact of the UMPEEK polymer compared with the reference materials.

The 3D reference resin printed parts, which are a mixture of aromatic acrylate (BPAEDMA) and cyclic (meth)acrylate (TCDDA), exhibited a tensile strength of 15 ± 2 MPa and Young’s modulus of 0.9 ± 0.01 GPa with $2 \pm 0.3\%$ elongation. The mechanical strength of the acrylate mixture reference materials depends on the chemical structure and the number of acrylate functionalities present.^{43–45} Upon increasing the UMPEEK polymer content from 5 to 10 wt % in the reference resin, the tensile strength improved from 27 ± 3 to 39 ± 2

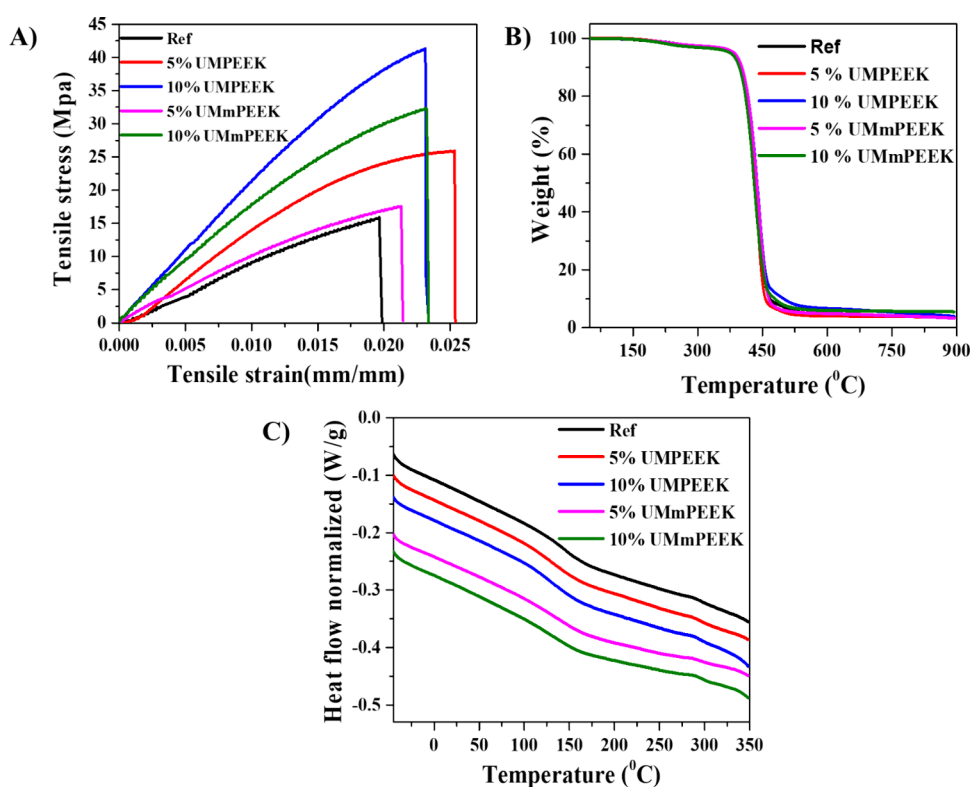


Figure 5. (A) Tensile stress–strain graph of 3D-printed parts of different resins. (B) TGA graph of all 3D-printed parts. (C) DSC graph of all 3D-printed parts.

Table 3. Mechanical And Thermal Properties of the 3D-Printed Parts

Resin Formulations	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (GPa)	T_g (°C)	$T_{d10\%}$ (°C)
Ref	15 ± 2	2.0 ± 0.3	0.9 ± 0.01	145	398
5% UMPEEK	27 ± 3	2.4 ± 0.1	1.6 ± 0.01	140	399
10% UMPEEK	39 ± 2	2.2 ± 0.2	2.1 ± 0.02	140	401
5% UMmPEEK	18 ± 3	2.2 ± 2.7	0.9 ± 0.01	140	402
10% UMmPEEK	25 ± 4	2.2 ± 0.3	1.7 ± 0.02	139	396

MPa, and the Young's modulus increased from 1.6 ± 0.01 to 2.1 ± 0.02 GPa while maintaining similar elongation values. Following a similar trend, the inclusion of the UMmPEEK polymer elevated the mechanical properties of the 3D-printed parts. The increase of UMmPEEK polymer from 5 to 10 wt % resulted in an increase of tensile strength from 18 ± 3 to 25 ± 4 MPa. Concurrently, the Young's modulus also improved from 0.9 ± 0.01 to 1.7 ± 0.02 GPa while maintaining a consistent elongation. Based on the mechanical properties, it could be deduced that the tensile strength and Young's modulus of the 10 wt % UMPEEK resin 3D-printed part surpassed those of the other resin-printed parts. The enhanced mechanical properties in the 10 wt % UMPEEK resin printed part were attributed to the rigid aromatic ring of the PEEK polymer. In contrast, the 10 wt % UMmPEEK resin 3D-printed part exhibited lower tensile strength and Young's modulus compared to the 10 wt % UMPEEK resin 3D-printed part. This difference was linked to the presence of the long-alkylated chain in each repeat unit of the latter, which

potentially disrupted the cross-linked network polymer, by creating space between the extended polymer chains.^{43,46} The modulus of the 10 wt % UMPEEK 3D-printed part could attain almost 60% of the tensile values of the commercial PEEK polymer.¹⁶ Despite the low incorporation of PEEK polymer in the resin formulation, its impact on enhancing the mechanical properties is noteworthy. The PEEK polymer's exceptional performance is attributed to the aromatic ring in its backbone, which imparts rigidity and strength.²⁸ The pi-pi interaction of the aromatic ring of PEEK with the aromatic unit of BPAEDMA in the reference resin acrylate is also expected to improve the strength of the printed materials.

Thermal properties of the PEEK polymer 3D-printed materials are depicted in Figure 5B,C, and the values are summarized in Table 3. In Figure 5B, it was observed that all of the 3D-printed parts showed a one-step degradation. The temperature at which a 10% loss in weight occurs, or $T_{d10\%}$, is more than 390 °C, demonstrating that all of the PEEK polymer 3D-printed parts exhibit high thermal stability. In Figure 5C, it was observed that the glass transition temperature values for all resin 3D-printed parts ranged from 140 to 145 °C. The incorporation of the modified PEEK polymers to the reference resin enhanced the tensile and mechanical properties of the 3D-printed materials, without compromising the thermal properties of the reference resin.

CONCLUSIONS

In this study, we present a remarkable achievement of DLP 3D printing of functionalized PEEK polymer at room temperature. Notably, this printed material exhibited approximately 55% of the Young's modulus found in commercial PEEK polymer. The end-capped PEEK polymers and their reaction with methacryloyloxyethyl isocyanate were successfully accom-

plished and structurally characterized. Additionally, a modified PEEK polymer featuring a long C15 alkyl chain in each repeat unit was also synthesized, which was further end-capped with a terminal methacrylate group. The resulting methacrylate PEEK polymers were incorporated into resin formulations up to 10 wt % enabling room temperature DLP 3D printing. Impressively, the printed PEEK resin parts demonstrated excellent resolution and high mechanical properties, including a tensile strength of 39 ± 2 MPa and a Young's modulus of 2.2 ± 0.2 GPa. Furthermore, the incorporation of the long C15 alkyl chain in the 3D-printed cross-linked network effectively addressed warpage issues after the post curing. Thermal analysis revealed outstanding properties, including a 10 wt % degradation temperature of 400 °C and a high glass transition temperature of 140 °C, both remarkable results for DLP 3D-printed PEEK polymer. To our knowledge, this study represents the first report of the room temperature DLP 3D printing of functionalized PEEK polymers, achieving comparable Young's modulus and exceptional thermal characteristics.

■ EXPERIMENTAL SECTION

Materials

4,4'-Difluorobenzophenone, 2,2-bis(4-hydroxyphenyl)propane, 4-fluorobenzoic acid, dibutyltin dilaurate (DBTDL), 3-pentadecylphenol, and tetrakis(triphenylphosphine)palladium were purchased from Aldrich and used as such. Bromoethanol, methacryloyloxyethyl isocyanate, tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate (TCDDA), 4-methoxyphenyl boronic acid, bisphenol A ethoxylate dimethacrylate (BPAEDMA), N-bromosuccinimide, and boron tribromide were purchased from TCI Chemicals and used without purification. The following items were bought locally: sodium sulfate (anhydrous), dichloromethane, toluene, methanol, isopropyl alcohol (IPA), potassium carbonate, diethyl amine, dimethyl sulfate, tetrahydrofuran, acetone, CHCl₃, and hydrochloric acid. For gel permeation chromatography, HPLC-grade THF was purchased from Merck Chemicals. The general methods of the characterization are similar to our previous report,⁴⁷ and the details are provided in the Supporting Information section S1.

Resin Preparation for DLP 3D Printing of Urethane Methacrylate PEEK Polymers

The PEEK resin formulations were prepared by blending different concentrations of UMPEEK and UMmPEEK polymers with tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate (TCDDA) and bisphenol A ethoxylate dimethacrylate (BPAEDMA) as reactive diluents. Initially, the polymer was placed in a 50 mL vial, followed by the addition of reactive diluents. The contents of the vial were subjected to sonication for 1 h to ensure complete miscibility of the polymer. Throughout the sonication, the water bath temperature was maintained at 30 °C. The weight percentage of the TPO photoinitiator was determined through photo-DSC experiments. The 3D-printed resin formulation excluded any organic solvents. The glass vial was completely covered in aluminum foil to protect the photoinitiator from light and to avoid prepolymerization. The resin formulations reported herein were prepared by following a similar protocol.

Curing Kinetics of Resin Formulations (Photo-DSC)

A TA Discover 250 s-generation differential scanning calorimeter fitted to an OmniCure series 2000 photo calorimetric unit was used to conduct the photo-DSC studies. A 200 W high-pressure mercury lamp with a range of 320–500 nm was used to irradiate the sample. The light from the lamp was directed through a dual-quartz light support with balanced intensity into the material's container. Sample preparation involved the precise weighing of 5 mg of resin formulation samples and placing them into the sample pan. After that, the sample pan was placed inside the DSC cell. Nitrogen gas was

continuously supplied at a rate of 50 mL/min during the measurements. The sample pans were initially maintained at isothermal temperatures (30 °C) for 2 min under nitrogen atmosphere, before being exposed to UV light. The specimen was exposed to UV light for 5 min after the electronic UV light shutter was opened. The shutter closed on its own when the irradiation period ended. The curing enthalpy was calculated by integrating the peaks in the generated data.

Measurement of Resin Viscosity

Rotational parallel plate measurements were used to evaluate the viscosity of the resin compositions; a photoinitiator was not used in this test. An Anton Paar Physica Modular Compact Rheometer (MCR) 301 was used in the experiment with a cup and bob. The photoinitiator-free resin formulation was poured carefully into a cup until it reached the predetermined mark. The bob was then rotated to provide shear during the experiment after it had been placed in the resin. The viscosity, measured in Pa·s, was determined by methodically increasing the shear rate between 1 and 1000 per second. The resin temperature was kept constant during the experiment at 30 °C.

DLP 3D Printing of Urethane Methacrylate PEEK Polymer Resins

An AnyCubic Photon Ultra resin 3D printer was used for the DLP 3D printing of the resin compositions without organic solvents. The resin bed of the DLP printer had dimensions of 102.4 × 57.6 × 165 mm³ and a 405 nm LED light source. An UNO Genetic laser power meter was used for recording the LED light source's intensity of 10 mW cm⁻². The printing process was started by carefully adding resin to the resin bed until it reached a predetermined level. The printing of the resin formulation was performed at room temperature. The dimension of each printed layer was 100 μm, and the exposure time for the first five layers was set at 30 s. Each succeeding layer was exposed for 10 s. The printed object was subjected to postprocessing treatment after washing with IPA in a resin washer for 3 min followed by postcure for 15 min under UV light in a 360° rotating curing platform fitted with 12 UV lights of wavelength 405 nm covered with plastic cage.

Mechanical Test of 3D-Printed Part

The tensile strength of the 3D-printed part was examined using the Instron series 33R4204 model of the Universal Testing Machine, which has a 1 KN capacity load cell. The tensile test involved 3D printing ASTM D638 type V specimens with dimensions measuring 63.5 mm in length, 9.53 mm in width, and 3.2 mm in thickness. To ensure accuracy, a total of five 3D-printed tensile specimens were tested, and the resulting average value was recorded as the final result. Each specimen in the experiment had a gauge length of 10 mm, and the stretching rate was 5 mm/min at room temperature. Mechanical properties such as toughness, elongation, Young's modulus, and tensile strength were determined.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaenm.4c00275>.

Synthesis of 3-pentadecyl 4,4'-biphenol, 2-hydroxyethyl 4-fluorobenzoate, polyether ether ketone (PEEK) polymer, modified polyether ether ketone (mPEEK) polymer, urethane methacrylate PEEK and mPEEK, SEC plot, photo-DSC plot, spot curing, high-resolution 3D-printed part (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Asha S. K. — Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune 411008, India;
Academy of Scientific and Innovative Research, Ghaziabad

201002 Uttar Pradesh, India; orcid.org/0000-0002-3999-4810; Email: sk.asha@ncl.res.in

Authors

Shibam Pal – Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune 411008, India; Academy of Scientific and Innovative Research, Ghaziabad 201002 Uttar Pradesh, India

Yogesh Gaikwad – Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Pune 411008, India; Academy of Scientific and Innovative Research, Ghaziabad 201002 Uttar Pradesh, India

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsaenm.4c00275>

Author Contributions

Shibam Pal: Conceptualization, Synthesis and Characterization, Investigation, Validation, writing the first draft. **Yogesh Gaikwad:** Synthesis. **Asha Syamakumari:** Conceptualization, Formal analysis, Investigation, Writing—original draft, Writing—review and editing, Resources, Supervision.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been financially supported by the Center of Excellence (CoE) (F.No. 25014/2/2015-PC-II (FTS: 14428)) supported by the Ministry of Chemical and Fertilizers, Department of Chemicals and Petrochemicals, and Science & Engineering Research Board (SERB), Government of India, Project (CRG/2021/008626). Shibam Pal thanks CSIR for the senior research fellowship (SRF).

REFERENCES

- (1) Mondschein, R. J.; Kanitkar, A.; Williams, C. B.; Verbridge, S. S.; Long, T. E. Polymer Structure-Property Requirements for Stereolithographic 3D Printing of Soft Tissue Engineering Scaffolds. *Biomaterials* **2017**, *140*, 170–188.
- (2) Kutlehria, S.; D'Souza, A.; Bleier, B. S.; Amiji, M. M. Role of 3D Printing in the Development of Biodegradable Implants for Central Nervous System Drug Delivery. *Mol. Pharmaceutics* **2022**, *19*, 4411–4427.
- (3) Ligon, S. C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem. Rev.* **2017**, *117*, 10212–10290.
- (4) Vasamsetty, P.; Pss, T.; Kukkala, D.; Singamshetty, M.; Gajula, S. 3D Printing in Dentistry - Exploring the New Horizons. *Mater. Today Proc.* **2020**, *26*, 838–841.
- (5) Boyraz, P.; Runge, G.; Raatz, A. An Overview of Novel Actuators for Soft Robotics. *Actuators* **2018**, *7*, 48.
- (6) Arantes, I. V. S.; Crapnell, R. D.; Whittingham, M. J.; Sigley, E.; Paixão, T. R. L. C.; Banks, C. E. Additive Manufacturing of a Portable Electrochemical Sensor with a Recycled Conductive Filament for the Detection of Atropine in Spiked Drink Samples. *ACS Appl. Eng. Mater.* **2023**, *1*, 2397–2406.
- (7) El Magri, A.; El Mabrouk, K.; Vaudreuil, S.; Chibane, H.; Touhami, M. E. Optimization of Printing Parameters for Improvement of Mechanical and Thermal Performances of 3D Printed Poly(ether Ether Ketone) Parts. *J. Appl. Polym. Sci.* **2020**, *137*, 49087.
- (8) Zhuo, P.; Li, S.; Ashcroft, I. A.; Jones, A. I. Material Extrusion Additive Manufacturing of Continuous Fibre Reinforced Polymer Matrix Composites: A Review and Outlook. *Compos. Part B Eng.* **2021**, *224*, No. 109143.
- (9) Wu, T.; Jiang, P.; Zhang, X.; Guo, Y.; Ji, Z.; Jia, X.; Wang, X.; Zhou, F.; Liu, W. Additively Manufacturing High-Performance Bismaleimide Architectures with Ultraviolet-Assisted Direct Ink Writing. *Mater. Des.* **2019**, *180*, No. 107947.
- (10) Borrello, J.; Nasser, P.; Iatridis, J. C.; Costa, K. D. 3D Printing a Mechanically-Tunable Acrylate Resin on a Commercial DLP-SLA Printer. *Addit. Manuf.* **2018**, *23*, 374–380.
- (11) Wang, Y.; Li, X.; Chen, Y.; Zhang, C. Strain Rate Dependent Mechanical Properties of 3D Printed Polymer Materials Using the DLP Technique. *Addit. Manuf.* **2021**, *47*, No. 102368.
- (12) Amini, A.; Guijt, R. M.; Themelis, T.; De Vos, J.; Eeltink, S. Recent Developments in Digital Light Processing 3D-Printing Techniques for Microfluidic Analytical Devices. *J. Chromatogr. A* **2023**, *1692*, No. 463842.
- (13) Quan, H.; Zhang, T.; Xu, H.; Luo, S.; Nie, J.; Zhu, X. Photo-Curing 3D Printing Technique and Its Challenges. *Bioact. Mater.* **2020**, *5*, 110–115.
- (14) Stansbury, J. W.; Idacavage, M. J. 3D Printing with Polymers: Challenges among Expanding Options and Opportunities. *Dent. Mater.* **2016**, *32*, 54–64.
- (15) Das, A.; Chatham, C. A.; Fallon, J. J.; Zawaski, C. E.; Gilmer, E. L.; Williams, C. B.; Bortner, M. J. Current Understanding and Challenges in High Temperature Additive Manufacturing of Engineering Thermoplastic Polymers. *Addit. Manuf.* **2020**, *34*, No. 101218.
- (16) Rae, P. J.; Brown, E. N.; Orler, E. B. The Mechanical Properties of Poly(ether-Ether-Ketone) (PEEK) with Emphasis on the Large Compressive Strain Response. *Polymer* **2007**, *48*, 598–615.
- (17) Myles, A.; Griffith, A.; Riyad, M. F.; Jiao, Y.; Mahmoudi, M.; Minary-Jolandan, M. 3D-Printed Ceramics with Aligned Micro-Platelets. *ACS Appl. Eng. Mater.* **2023**, *1*, 1892–1902.
- (18) Lin, L.; Schlarb, A. K. Effect of the Varied Load Conditions on the Tribological Performance and the Thermal Characteristics of PEEK-Based Hybrid Composites. *Tribol. Int.* **2016**, *101*, 218–225.
- (19) Roskies, M.; Jordan, J. O.; Fang, D.; Abdallah, M.-N.; Hier, M. P.; Mlynarek, A.; Tamimi, F.; Tran, S. D. Improving PEEK Bioactivity for Craniofacial Reconstruction Using a 3D Printed Scaffold Embedded with Mesenchymal Stem Cells. *J. Biomater. Appl.* **2016**, *31*, 132–139.
- (20) Wang, Y.; Müller, W.-D.; Rumjahn, A.; Schwitala, A. Parameters Influencing the Outcome of Additive Manufacturing of Tiny Medical Devices Based on PEEK. *Materials* **2020**, *13*, 466.
- (21) Boydston, A. J.; Cui, J.; Lee, C.-U.; Lynde, B. E.; Schilling, C. A. 100th Anniversary of Macromolecular Science Viewpoint: Integrating Chemistry and Engineering to Enable Additive Manufacturing with High-Performance Polymers. *ACS Macro Lett.* **2020**, *9*, 1119–1129.
- (22) Tan, K. H.; Chua, C. K.; Leong, K. F.; Cheah, C. M.; Cheang, P.; Abu Bakar, M. S.; Cha, S. W. Scaffold Development Using Selective Laser Sintering of Polyetheretherketone-hydroxyapatite Biocomposite Blends. *Biomaterials* **2003**, *24*, 3115–3123.
- (23) Pohle, D.; Ponader, S.; Rechtenwald, T.; Schmidt, M.; Schlegel, K. A.; Münstedt, H.; Neukam, F. W.; Nkenke, E.; von Wilmsowky, C. Processing of Three-Dimensional Sintered Polyetheretherketone Composites and Testing of Osteoblast Proliferation in Vitro. *Macromol. Symp.* **2007**, *253*, 65–70.
- (24) Vaezi, M.; Yang, S. Extrusion-Based Additive Manufacturing of PEEK for Biomedical Applications. *Virtual Phys. Prototyp.* **2015**, *10*, 123–135.
- (25) Deng, L.; Deng, Y.; Xie, K. AgNPs-Decorated 3D Printed PEEK Implant for Infection Control and Bone Repair. *Colloids Surfaces B Biointerfaces* **2017**, *160*, 483–492.
- (26) Rinaldi, M.; Ghidini, T.; Cecchini, F.; Brandao, A.; Nanni, F. Additive Layer Manufacturing of Poly (Ether Ether Ketone) via FDM. *Compos. Part B Eng.* **2018**, *145*, 162–172.
- (27) Hu, B.; Duan, X.; Xing, Z.; Xu, Z.; Du, C.; Zhou, H.; Chen, R.; Shan, B. Improved Design of Fused Deposition Modeling Equipment for 3D Printing of High-Performance PEEK Parts. *Mech. Mater.* **2019**, *137*, No. 103139.

- (28) Lee, C.-U.; Vandenbrande, J.; Goetz, A. E.; Ganter, M. A.; Storti, D. W.; Boydston, A. J. Room Temperature Extrusion 3D Printing of Polyether Ether Ketone Using a Stimuli-Responsive Binder. *Addit. Manuf.* **2019**, *28*, 430–438.
- (29) Hegde, M.; Meenakshisundaram, V.; Chartrain, N.; Sekhar, S.; Tafti, D.; Williams, C. B.; Long, T. E. 3D Printing All-Aromatic Polyimides Using Mask-Projection Stereolithography: Processing the Nonprocessable. *Adv. Mater.* **2017**, *29*, No. 1701240.
- (30) Tawade, B. V.; Shaligram, S. V.; Valsange, N. G.; Kharul, U. K.; Wadgaonkar, P. P. Synthesis and Properties of Poly(arylene Ether)s Based on 3-Pentadecyl 4,4'-biphenol. *Polym. Int.* **2016**, *65*, 567–576.
- (31) Rekha, N.; Asha, S. K. Solvent-Induced Self-Assembly in Cardanol-Based Urethane Methacrylate Comb Polymers. *J. Polym. Sci. Part A Polym. Chem.* **2009**, *47*, 2996–3009.
- (32) Sadavarte, N. V.; Halhalli, M. R.; Avadhani, C. V.; Wadgaonkar, P. P. Synthesis and Characterization of New Polyimides Containing Pendent Pentadecyl Chains. *Eur. Polym. J.* **2009**, *45*, 582–589.
- (33) Honkhambe, P. N.; Pasale, S. K.; Bhairamadgi, N. S.; Kumbhar, K. P.; Salunkhe, M. M.; Wadgaonkar, P. P. Poly(ether Ether Ketone)s and Poly(ether Ether Ketone)s Containing Cardo Decahydronaphthalene Groups: Synthesis and Characterization. *J. Appl. Polym. Sci.* **2011**, *122*, 1607–1613.
- (34) Schmaljohann, D.; Häußler, L.; Pötschke, P.; Voit, B. I.; Loontjens, T. J. A. Modification with Alkyl Chains and the Influence on Thermal and Mechanical Properties of Aromatic Hyperbranched Polyesters. *Macromol. Chem. Phys.* **2000**, *201*, 49–57.
- (35) Castell, P.; Wouters, M.; Fischer, H.; De With, G. Kinetic Studies of a UV-Curable Powder Coating Using Photo-DSC, Real-Time FTIR and Rheology. *J. Coatings Technol. Res.* **2007**, *4*, 411–423.
- (36) Kuhnt, T.; Morgan, F. L. C.; Baker, M. B.; Moroni, L. An Efficient and Easily Adjustable Heating Stage for Digital Light Processing Set-Ups. *Addit. Manuf.* **2021**, *46*, No. 102102.
- (37) Ge, T.; Tang, K.; Yu, Y.; Tan, X. Preparation and Properties of the 3-pentadecylphenol In Situ Modified Foamable Phenolic Resin. *Polymers* **2018**, *10*, 1124.
- (38) Hanon, M. M.; Alshammas, Y.; Zsidai, L. Effect of Print Orientation and Bronze Existence on Tribological and Mechanical Properties of 3D-Printed bronze/PLA Composite. *Int. J. Adv. Manuf. Technol.* **2020**, *108*, 553–570.
- (39) Farkas, A. Z.; Galatanu, S. V.; Nagib, R. The Influence of Printing Layer Thickness and Orientation on the Mechanical Properties of DLP 3D-Printed Dental Resin. *Polymers* **2023**, *15*, 1113.
- (40) Gastaldi, M.; Cardano, F.; Zanetti, M.; Viscardi, G.; Barolo, C.; Bordiga, S.; Magdassi, S.; Fin, A.; Roppolo, I. Functional Dyes in Polymeric 3D Printing: Applications and Perspectives. *ACS Mater. Lett.* **2021**, *3*, 1–17.
- (41) Wang, F.; Chong, Y.; Wang, F. K.; He, C. Photopolymer resins for luminescent three-dimensional printing. *J. Appl. Polym. Sci.* **2017**, *134*, 44988.
- (42) Mukhtarkhanov, M.; Shehab, E.; Ali, M. H. Experimental Study on Warpage Phenomenon of Wax Parts Manufactured by Fused Filament Fabrication. *Polymers* **2024**, *16*, 208.
- (43) More, A. S.; Pasale, S. K.; Honkhambe, P. N.; Wadgaonkar, P. P. Synthesis and characterization of organo-soluble poly(ether ether ketone)s and poly(ether ether ketone)s containing pendant pentadecyl chains. *J. Appl. Polym. Sci.* **2011**, *121*, 3689–3695.
- (44) Spiegel, C. A.; Hackner, M.; Bothe, V. P.; Spatz, J. P.; Blasco, E. 4D Printing of Shape Memory Polymers: From Macro to Micro. *Adv. Funct. Mater.* **2022**, *32*, No. 2110580.
- (45) Choi, Y.; Yoon, J.; Kim, J.; Lee, C.; Oh, J.; Cho, N. Development of Bisphenol-A-Glycidyl-Methacrylate- and Trimethylolpropane-Triacrylate-Based Stereolithography 3D Printing Materials. *Polymers* **2022**, *14*, 5198.
- (46) More, A. S.; Pasale, S. K.; Wadgaonkar, P. P. Synthesis and Characterization of Polyamides Containing Pendant Pentadecyl Chains. *Eur. Polym. J.* **2010**, *46*, 557–567.
- (47) Pal, S.; Asha, S. K. Thiol-Ene-Based Degradable 3D Printed Network from Bio Resource Derived Monomers Ethyl-Lactate and Isosorbide. *Eur. Polym. J.* **2024**, *205*, No. 112761.