

**DEGRADABILITY OF POLYMER COMPOSITES FROM
RENEWABLE RESOURCES**

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CERTIFICATE

This is to certify that the work incorporated in this thesis entitled “*Degradability of Polymer Composites from Renewable Resources*” submitted by Mr. Jitendra Kumar Pandey was carried out by the candidate under my supervision at the National Chemical Laboratory. Such material has been obtained from other sources has been duly acknowledged.

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(R.P.Singh)

Research guide

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
AESO	Acrylated Epoxidized Soybean Oil
CMC	Carboxymethylcellulose
CA	Cellulose Acetate
CFRP	Carbon fiber reinforced composites
CEN	Comite Europeen de Normalisation
DMSO	Dimethyl sulfoxide
DSC	Differential Scanning Calorimetry
DIN	Deutsches Institut für Normung Ev
DS	Degree of Substitution
CDA-g-PLAs	Cellulose diacetate-graft-poly(lactic acid)s
CDA	Cellulose Diacetate
DD	Degree of Deacetylation
DMA	Dynamic Mechanical Analyzer
DFC	Direct Fiber Composite
DP	Degree of Polymerization
EVSEM	Environmental Scanning Electron Microscopy
EP	Ethylene -Propylene Co-polymer
EPMA	Ethylene-Propylene-Maleic Anhydride co-polymer
EVA	Ethylene vinyl aetate copolymer
ESO	Epoxidised soybean oil
EVAc	Co-polymers of ethylene with vinyl acetate
EVAL	Ethylene- vinylalcohol co-polymer
EVAMA	EVAc modified with maleic anhydride
ESR	Electron Spin Resonance
ESCA	Electron Scanning Chemical Analysis
ELO	Epoxidized linseed oil
GPTMS	3-glycidoxypropyltrimethoxysilane
GFC	Graft Fiber Composite
GC	Gas Chromatography
GPC	Gel Permission Chromatography [Size Exclusion Chromatography]

GC- MS	Gas Chromatography – Mass Spectroscopy
HTA	Hydrogenated tallow alkyl
ISO	International Organization for Standardization
LDPE	Low Density Polyethylene
LC	Liquid Chromatography
LSC	Liquid Scintillation Counting
MC	Methyl Cellulose
MMT	Montmorillite
MAH	Maleic anhydride
MALDI-TOF	Matrix Assisted Laser Desorption Ionization Time-of-flight Mass Spectrometry
MW	Molecular Weight
MBS	Methyl Methacrylate -Butadiene-Styrene co-polymer
Na+-MMT	Sodium Montmorillite
O-PCL	Oligomeric polycaprolactone
OMMT	Organically modified montmorillite
PCL	Poly (ϵ -caprolactone)
PP-g-MA	Polypropylene grafted maleic anhydride
PS	Polystyrene
PLA	Poly lactic acid
PE	Polyethylene
PHB	Poly (hydroxybutyrate)
PHA	Polyhydroxyalkanoates
PBS	Poly (butylenes succinate)
PALF	Pineapple Leaf Fibre
PCA	Plasticized Cellulose Acetate
PS	Polystyrene
PHBV	Poly(3-hydroxybutyrate- <i>co</i> -3-hydroxyvalerate)
PVOH	Polyvinylalcohol
PVA	Polyvinylacetate
PP-MAH	Polymer functionalized with maleic anhydride.
RH	Relative Humidity
SMA	Styrene-Maleic Anhydride co-polymer
SEM	Scanning Electron Microscopy

TPS	Thermo Plastic Starch
TPP	Tripolyphosphate
TEM	Tunneling Electron Microscopy
TGA	Thermal Gravimetric Analysis
UV	Ultra violet
VATM	Vacuum Assisted Transfer Molding
WVA	Water vapor Absorption
WG	Waste Gelatin
XRD	X-Ray Diffraction
WAXD	Wide Angle X-Ray Diffraction

**ABSTRACT
ABBREVIATIONS**

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ABSTRACT

Composites of polymers from renewable resources offer an answer to maintain a sustainable development of economically and ecologically attractive technology. The innovation in the development of materials from biopolymers are the preservation of fossil-based raw materials, complete biological degradability, the reduction in volume garbage and compostability in the natural environment as well as the application possibilities of agricultural resources for the production of biomaterials are the major causes why polymeric composites from renewable resources have attracted great interest not only from academic point of view but also for industrial applications. Biodegradability is an additional benefit of renewable polymers. These polymers are not designed for high temperature and therefore their uses limited to normal ranges of biological function found in the biosphere. The present work was aimed to evaluate the degradability of different composites, obtained from renewable resources. To investigate the degradation mechanism in composites, the degradability of host polymer was evaluate under biotic and abiotic environments, where increase in biodegradation was observed after photodegradation. It was proposed that, short functionalized chains might enter into biocycle by the same mechanism as has been established for linear paraffins. The degradability of the biocomposites with cellulose, prepared by grafting method in solution and by reactive extrusion, was studied through monitoring the weight loss under composting and efficiency of fungal (*A.niger*) growth on the samples. The effect of compatibilization was also investigated in the biocomposites of poly(ϵ -caprolactone)/starch, prepared by different compatibilizing agents. The inherent biodegradability of the host polyester has been shown to increase with compatibilization within the PCL/starch compositions, with that respect, improving the dispersion of starch granules through a hydrophobic coating and reducing the interfacial tension between PCL and starch owing to the starch-surface precipitation of PCL-grafted polysaccharide (dextran) proved very efficient. It was observed that the weight loss during composting increased with the decrease in interfacial tension between filler and polymer and inherent biodegradability of host matrix does not depend very significantly on the concentration of biodegradable polymer in the host matrix, but on the compatibilization efficiency. Thermoplastic was also filled with another abundant, natural material i.e. layered silicates and their degradability was measured. The host matrix contains layered silicates was more degradable than pristine polymer. The nanocomposites were comparatively stable for

initiation process of photodegradation which may be attributed to the slow diffusion of oxygen through the matrix. In all samples, clay protects the polymer up to some extent of irradiation and this initial protection time increase with increase in dispersion extent of filler. Nanocomposites of starch were prepared via different addition sequences of plasticizer and clay by the solution method. The sequence of addition of components (starch/plasticizer/clay) had a significant effect on the nature of composite formed and accordingly properties were altered. Diffusion of plasticizer in the clay layers was easier than starch. Starch chains must penetrate through clay galleries first, followed by plasticization in order to maintain the mechanical properties. Although the enhancement of mechanical properties takes place in the clay filled composites, still the water resistance is too poor to use these composites in packaging applications at least not for liquids. A series of hydrophobicized starch were prepared and reinforced with different layered silicates. The exfoliated and intercalated composites were obtained with highly hydrophobic clay and starch having higher degree of substitution. The tendency of homogenous dispersion of clays inside matrix decrease with increase in chain length of starch ester which was attributed to the bulky structure, resulting in the slow transport around the tectoides, consequently hindrance in the migration inside the clay layers. These nanocomposites were highly hydrophobic as observed by the measurement of contact angle with water on the surface and moisture absorption at ambient humidity. The main factor affecting the moisture sensitivity seems to be degree of substitution of starch whereas, clay dispersion also have significant effect. These nanocomposites have low water absorption characteristic which make them appropriate for the applications where water absorption must be minimal. All the samples were biodegradable under composting conditions at relatively lower rate than pristine starch. The biodegradability was dependent on the degree of substitution and dispersion of filler throughout the matrix. The widening of the range of biodegradable polymeric systems is very important for future studies; therefore it is hoped that the results described in this thesis will be useful for further studies based on the use of this environmentally important scientific approach.

**CHAPTER I:
POLYMER COMPOSITES FROM RENEWABLE RESOURCES**

1.1. Introduction

Polymers have almost replaced materials such as metal, glass, wood, paper, fiber, ceramics etc. and widely applied in the fields of packaging, automobiles, building construction, biomedical, electronics, furniture, pipes and heavy industrial equipments. Polymers offer many advantages over conventional materials including lightness, resilience to corrosion and ease of processing. The commercial importance of polymers has derived intense applications in the form of composites in various fields viz. in aerospace, automotive, marine, infrastructure, military etc. [1-6]. Composite consist of two or more materials combined in such a way that the individual materials are generally not distinguishable. Polymer composites can be used in many different forms ranging from structural composites in the construction industry to the high technology composites of the aerospace and space satellite industries. The material properties of the final component are the result of a design process that considers many factors, which are characterized by the anisotropic behavior of the material and cover the micro-mechanical, elasticity, strength and stability properties. These properties are influenced by manufacturing techniques, environmental exposure and loading histories. Polymer composites from renewable resources have great advantage, particularly, as a solution to the plastic waste generated problems in the environment. One of the exciting directions for this field is the growing interface between molecular biology and polymer chemistry. This interface combines powerful control over polymer structure with the functional attributes of polymers, leading to new and useful applications for these types of biopolymers. However, overtime as, the tools of molecular biology become optimized, high volume applications will also be realized as productions costs are reduced in concert with expected increase in the cost for synthetic petroleum derived polymers. For example, plant based products including polyesters and proteins are already under study [7]. From the point of view of making novel polymers with inherent environmentally favorable properties such as renewability and degradability, a series of interesting monomers are found in the metabolism and cycles of nature. Performance during their use is a key feature of any material composites, which decide the real fate of products during use in several applications. Whatever the applications, there is often a natural concern regarding the durability /degradability of polymeric materials partly because of their useful lifetime, maintenance and replacement. The deterioration of these materials depends on the duration and the extent of interaction with surrounding circumstances where it is being used. This chapter will describe the

different composites from natural polymers, their importance and durability in the environment.

1.2. Renewable resources

Resources are often classified into renewable and non-renewable. Renewable resources are generally those resources which can restock themselves at approximately the rate at which they are extracted [8]. Non-living renewable natural resources include water, wind, tides and solar radiation - compare renewable energy. In general renewable resources are totally natural resources that is not depleted when used by human beings. Plastics, gasoline, coal and other items produced from fossil fuels are nonrenewable, because the resource is depleted, and can be used only once.

1.3. Importance of renewable resources

The benefits of naturally occurring polymers for material applications are many [9] most importantly their environmental compatibility. In addition, the use of renewable resources provides an incentive to extend nonrenewable petrochemical supplies. The agriculture industry produce sufficient supplies of some agricultural products that could be used as renewable sources for polymer feed stocks. Biodegradability is an additional benefit of renewable polymers. These polymers are not designed for high temperature and therefore their uses limited to normal ranges of biological function found in the biosphere. Composites of polymers from renewable resources offer an answer to maintain a sustainable development of economically and ecologically attractive technology. The innovation in the development of materials from biopolymers are the preservation of fossil-based raw materials, complete biological degradability, the reduction in volume garbage and compostability in the natural environment as well as the application possibilities of agricultural resources for the production of biomaterials are the major causes why polymeric composites from renewable resources have attracted great interest not only from academic point of view but also for industrial applications.

1.4. Polymers from renewable resources

A variety of naturally occurring biopolymers can be found. Some of the polymers are already used in industry, while others are only at experimental stages of investigation. A wide range of naturally occurring polymers derived from renewable resources are available for material applications (Table 1.1). Some of these such as cellulose and starch are very actively used in several products today, while many other remain underutilized. With the rapid advancement in understanding of fundamental biosynthetic pathways and

options to modulate or tailor these pathways through genetic manipulations, new opportunities for the use of polymers from renewable resources are being considered [10].

Table 1.1. Summary of biopolymers from renewable resources [10]

Polysaccharides		
Polysaccharides (plant/ algal)	polysaccharides (animals)	polysaccharides (bacterial)
Starch (amylose, amylopectin)	hyaluronic acid	chitin, chitosen
Cellulose		evan
Pectin		xanthan
Polysaccharides(fungal)	polygalactosamine	
Alginate	Pullulan	curdlan
Carrageen	Elsinan	gellan
Gums	Scleroglucan	dextan
Proteins		
Soy, zein, wheat gluten, casein, serum, albumin		collagen / Gelatin
Silks	resilin	polylysine
Adhesives	polyaminoacids	poly (γ -glutamic acid)
Elastin	polyarginyl-polyaspartic acid	
Polyesters		
Polyhydroxyalkanoates	polylactic acid	polymalic acid
Lipids / Surfactants		
Acetoglycerides, waxes, surfactants		emulsan
Speciality Polymers		
Lignin	shellac	natural rubber

1.5 .Degradation of polymeric materials

In general degradation is the process where the deterioration in the properties of the polymer takes place due to different factors like, light, heat, mechanical etc. As a consequence of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties and the article becomes brittle and the life of the material becomes limited. Thus, any polymer or its composite which is to be used in outdoor applications must be highly resistant to all the environmental conditions. The summary of degradation and stabilization can be seen in Figure 1.1

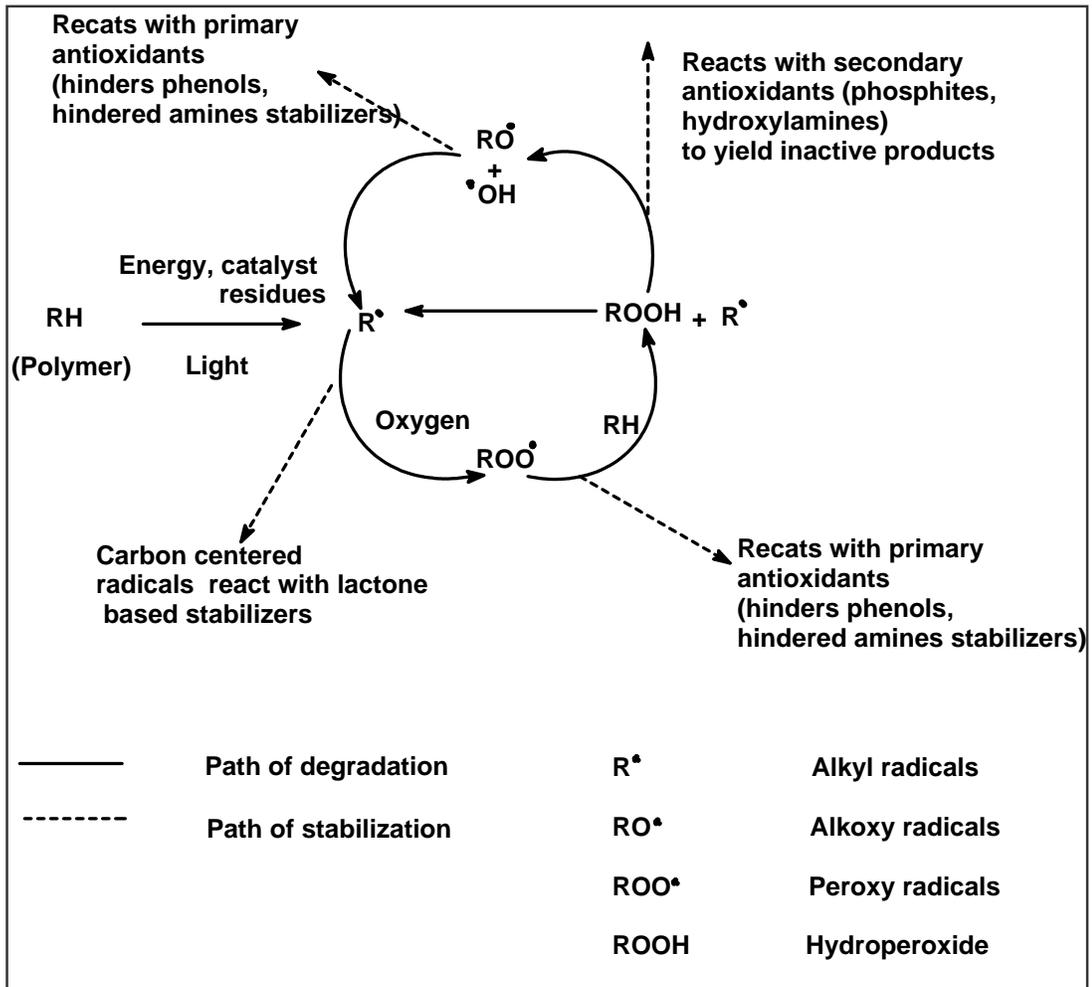


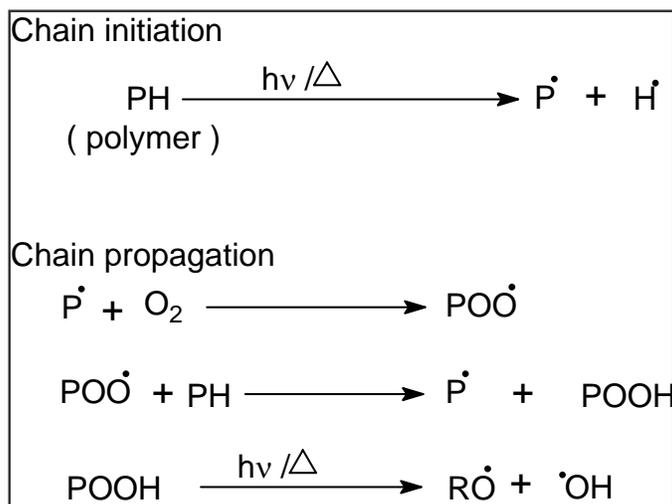
Figure 1.1. Different degradation and stabilization mechanisms.

Three main degradation processes are as follows:

1.5.1. Photodegradation

Photodegradation begins with the production of macro-radical (P^\bullet) in the amorphous regions of polymer substrate. This radical rapidly reacts with oxygen to give a

macroperoxy radical (POO^\bullet) which abstracts a hydrogen atom from the polymer backbone to produce a hydroperoxide group (POOH). The hydroperoxide group is photolytically cleaved to produce the highly reactive radicals, which continue the cycle of chain degradation in the polymer (Scheme 1.1) [11]. The cycle is terminated when two radical combine or recombine to form a non-radical product.



Scheme 1.1. General mechanisms of polymer photodegradation

1.5.2. Thermal Degradation

The fundamentals of degradation mechanisms of polymers are based on the same principles for both the thermal and photodegradation. The only exception is that photodegradation proceeds at a faster rate than thermal degradation and hydroperoxides are thermally cleaved to reactive radicals in thermal degradation.

1.5.3. Biodegradation

The definition of biodegradation is not always clear and is open to a large diversity of interpretations. Here are the definitions of some key words according to the American Society for Testing and Materials (ASTM), D20-96:

1.5.3.1. Degradable Plastic

A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and its applications in a period of time.

1.5.3.2. Biodegradable Plastic

A degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae. Biodegradability is the ability

of material to be utilized as a carbon source by microorganisms and converted safely into carbon dioxide, biomass and water. Microbial attack is started where the carbonyl group is found. A general mechanism of biodegradation in non degradable polyolefins was described by Albertsson et.al. in 1987 [12] , investigated that biodegradation can be initiated by photooxidation where carboxylic acids parts, generated through Norrish type-I and II mechanisms during oxidation process, can be consumed by microbial attack.

1.6. Miscellaneous

There are several means of polymer degradation other than thermal, photo and biodegradation. High molecular weight polymers undergoes chain scission during treatment with ultrasonic waves. X-Rays, gamma and beta rays can also cause the degradation of polymers and degradation with these high energy radiations is much more massive that degradation cause by ultraviolet light (a radiation of low energy). Polymer chains contains ester, amide and acetal functional groups in their backbone undergo degradation by the hydrolysis at a define pH. Many high molecular weight elastomers can be degraded by ozone and generates low molecular weight oligomers and /or liquid polymers those are useful in many applications. Figure 1.2 described all the possible degradation pathways of polymeric material.

1.7. Evaluation methods for degradability

The most applicable and popular measurement of degradation in thermoplastics is UV irradiation in a weather-o-meter. This practice provides a procedure for performing outdoor-accelerated-exposure testing of plastics and is applicable to a range of plastic materials including plastic films, sheets, laminates and extruded and molded products. This practice describes the test conditions that attempt to stimulate plastics exposures in desert and sub-tropical climates. Polymer samples can be irradiated in SEPAP 12/24 (from M/s Material Physico Chimique, Neuilly / Marne, France) at desirable temperature in the presence of air. The unit consists of four 400 W ‘Medium Pressure’ mercury vapor sources filtered by a Pyrex envelope supplying radiation of wavelength longer than 290 nm. These sources are located at four corners of a square chamber (~50X50cm). The inside wall of the chamber is made up of high reflection aluminum. Two fans on the wall of the chamber are monitored by a Eurotherm device and afford a regulation of the temperature of samples ($\pm 2^{\circ}$ C between 50-65 $^{\circ}$ C). Thermal degradation can be tested under inert as well as in presence of oxygen in a heating oven. The biodegradation can be studied by several means and countries have their own practice to determine the biodegradability in

polymeric materials. The ASTM and other organizations have developed the standards for testing the biodegradability in different specified conditions (Table 1.2).

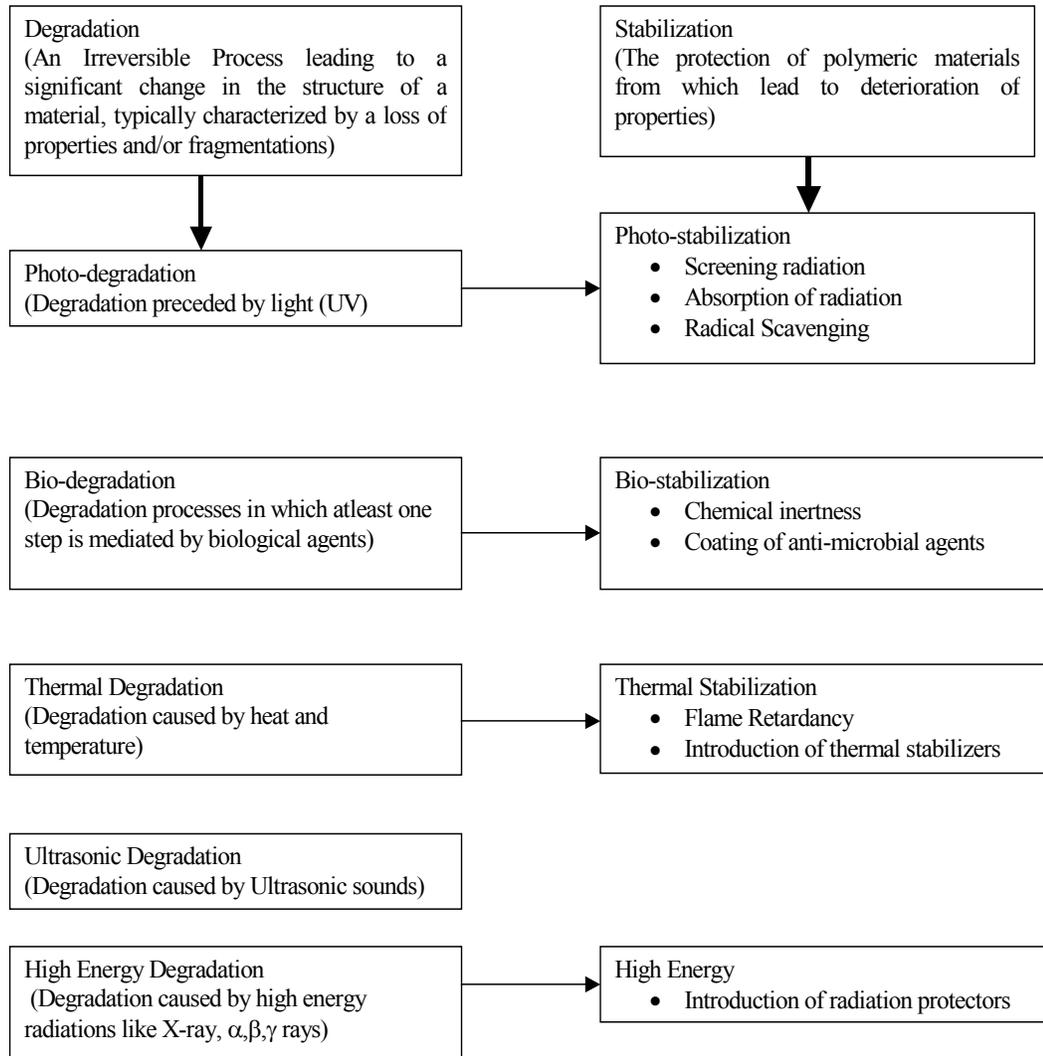


Figure 1.2. The possible degradation pathways of polymeric material

Table 1.2. ASTM test methods for determining the biodegradability

1.	ASTM D 5247	Determining the Aerobic Biodegradability of Degradable Plastics by Specific Microorganisms
2.	ASTM D 6002-96	Guide for Assessing the Compostability of Environmentally Degradable Plastics
3.	ASTM D 5338-98	Test Method for Determining Aerobic Biodegradation of Plastic materials under controlled composting conditions.
4.	ASTM D 6340-98	Test Methods for Determining Aerobic Biodegradation of Radiolabeled Plastic Materials in an Aqueous or Compost Environment.
5.	ASTM D 5209	Test Methods for Determining the Aerobic Biodegradation of Plastic Materials in the presence of Municipal Sewage Sludge
6.	ASTM D 5210	Test Methods for Determining the Anaerobic Biodegradation of Plastic Materials in the presence of Municipal Sewage Sludge
7.	ASTM D 5152	Water Extraction of Residual Solids from Degraded Plastics for Toxicity Testing.

The International Organization for Standardization (ISO) is a worldwide federation of national standards bodies (ISO member bodies). Since the working group on biodegradability of plastics was created in 1993, rapid advances have been made in this area. Table 1.3 described the methods for aerobic biodegradation those have recently advanced to Draft of International Standard (DIS) stage.

Table 1.3. ISO/DIS Methods for the evaluation of biodegradability.

ISO/DIS 14851	Evaluation of the ultimate aerobic biodegradability in an aqueous medium- method by determining the oxygen demand in a closed respirometer
ISO/DIS 14852	Evaluation of the ultimate aerobic biodegradability in an aqueous medium-method by analysis of released carbon dioxide
ISO/DIS 14855	Evaluation of the ultimate aerobic biodegradability and disintegration of plastics under controlled composting conditions- method by analysis of released carbon dioxide

These three ISO/ DIS 14851, 14852 and 14855 are recognized as useful screening tests for establishing the aerobic biodegradability or compostability of plastics. Some others test methods are DIN (German) DIN 54900-Draft for Evaluation of the compostability and CEN (European) CEN TC 261/ SC4/ WG2 for Evaluation of the compostability, biodegradability and disintegration.

Since all degradation process decreases all the properties of polymers we can use almost all analytical techniques for the evaluation of durability. The characterization of degradation can be carried out by several means those have been summarized in Figure 1.3

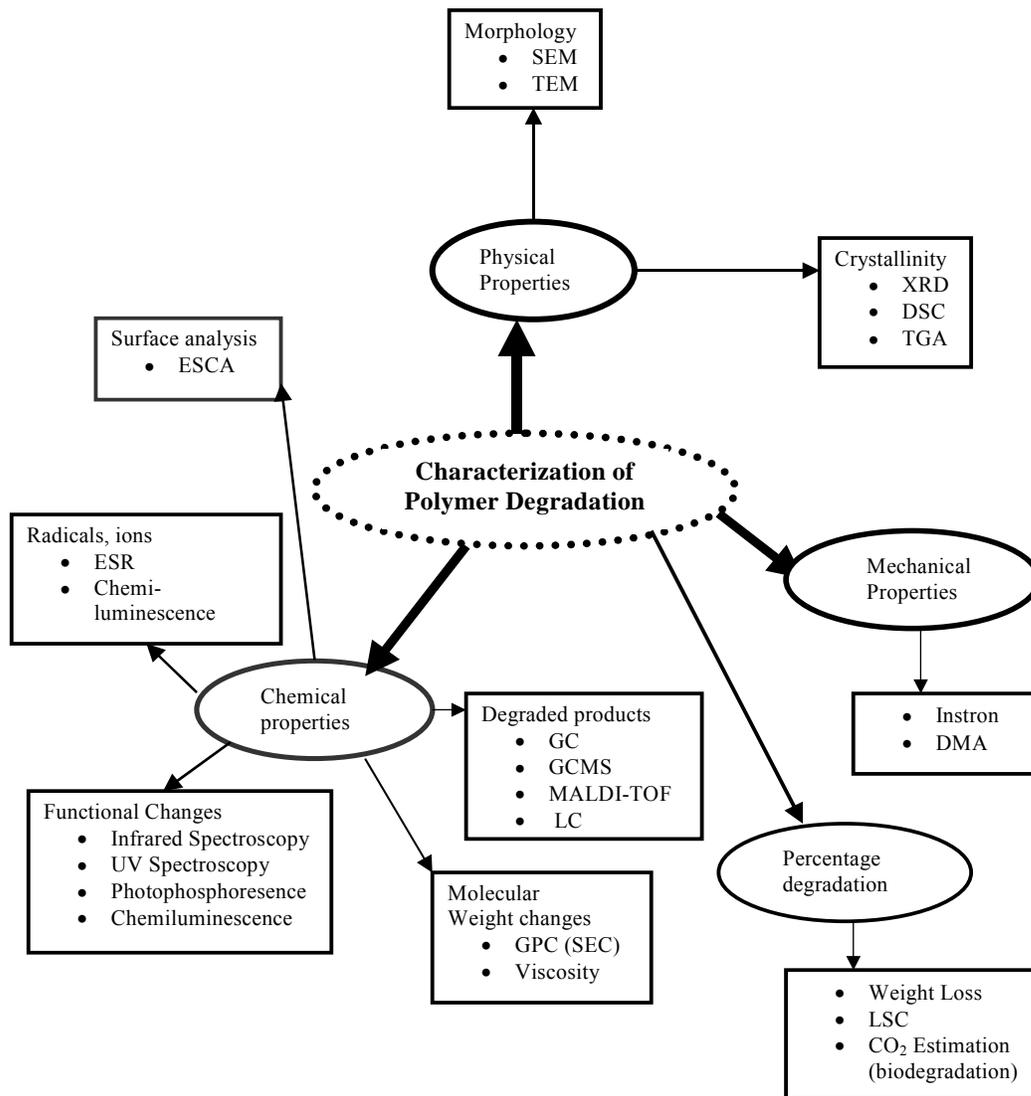


Figure 1.3. Different Evaluation methods for degradability

The study of degradation and stabilization of polymers is an extremely important area from the scientific and industrial point of view. A better understanding of the polymer degradation mechanisms will ensure the long life of the product. Enough attention has not been paid to the study of durability of biocomposites from renewable resources as compared to their preparation techniques and evaluation of material properties.

1.8. Polymer composites from renewable resources

From guitars, tennis racquets and cars to microlight aircrafts, electronic components and artificial joints, composites are finding use in diverse fields. Because of increasing environmental consciousness and demands of legislative authorities, the manufacture, use and removal of traditional composite structures, usually made of glass, carbon fibres being reinforced with epoxy, unsaturated polyester resins, polyurethanes, or phenolics, are considered critically. The present review of literature do not pretend to provide a comprehensive review of the subject of all biocomposites, their preparation, characterization and material properties including degradation due to the lack of more systematic, and broad nature of research. The efforts have been directed to address the outline of the current research in the direction of composites from renewable resources including the discussion of different preparation techniques, material properties, ecofriendly behavior and technical problems associated with them with their possible solutions. The main focus will be on the products for commodity application rather than medical and drug delivery systems.

1.8.1. Biofiber composites

Fibre-reinforced plastic composites began with cellulose fibre in phenolics in 1908, later extending to urea and melamine, and reaching commodity status in the 1940s with glass fibre in unsaturated polyesters [13]. Depending on their origin, the natural fibres may be grouped into: leaf, bast, seed and fruit origin. The best known examples are: (i) Leaf: Sisal, Pineapple Leaf Fibre (PALF), and henequen; (ii) Bast: Flax, ramie, kenaf/mesta, hemp and jute; (iii) Seed: Cotton; (iv) Fruit: Coconut husk, i. e., coir [14]. The natural fibres are lignocellulosic in nature. The main drawback of biofibres is their hydrophilic nature, which lowers the compatibility with hydrophobic polymeric matrix during composite fabrications. The other disadvantage is the relatively low processing temperature required due to the possibility of fibre degradation and/or the possibility of volatile emissions. The major constituents of biofibres (lignocelluloses) are cellulose, hemicellulose and lignin. The amount of cellulose, in lignocellulosic systems, can vary depending on the species and age of the plant. Cellulose is a hydrophilic glucan polymer

consisting of a linear chain of 1,4- β -bonded anhydroglucose units which contains alcoholic hydroxyl groups. These hydroxyl groups form hydrogen bonds inside the macromolecule itself and among other cellulose macromolecules as well as with hydroxyl groups from the atmosphere. Therefore, all of the natural fibres are hydrophilic in nature; their moisture content reaches 8–12.6% [14]. Although the chemical structure of cellulose from different natural fibres is the same, the Degree of Polymerization (DP) varies. The mechanical properties of a fibre are significantly related to DP. Bast fibres commonly show the highest DP among approximately 10,000 different natural fibres [15].

1.8.1.2. Degradability of biofibres

The lignocellulosic natural fibres are degraded biologically because organisms recognise the carbohydrate polymers, mainly hemicelluloses in the cell wall and have very specific enzyme systems capable of hydrolyzing these polymers into digestible units [16]. Biodegradation of the high molecular weight cellulose weakens the lignocellulosic cell wall because crystalline cellulose is primarily responsible for the strength of the lignocellulosics [17] and due to degradation of cellulose, the strength is lost. Photochemical degradation by ultraviolet light occurs when lignocellulosics are exposed to environment. This degradation primarily takes place in the lignin component, which is responsible for the characteristic colour changes. The surface becomes richer in cellulose content as the lignin degrades. After the lignin is degraded, the poorly bonded carbohydrate-rich fibres erode easily from the surface, which exposes new lignin to further degradative reactions. It is important to note that hemicellulose and cellulose of lignocellulosic fibres are degraded by heat much before lignin [18]. The lignin component contributes to char formation, and the charred layer helps to insulate the lignocellulosics from further thermal degradation. Biofibres change their dimensions with varying moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups which attract moisture through hydrogen bonding [19]. The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, noncrystalline cellulose (cellulose whiskers) lignin, and surface of crystalline cellulose also play major roles.

1.8.1.3. Composites from cellulose

Numerous cellulose composites have been prepared [20-23] by several methods including chemical and physical modification in cellulose as well as the host polymer matrix. Since fiber is hydrophilic in nature and generally the polymer matrix is hydrophobic, it is always

essentially required to make them compatible. Highly compatible cellulose composites have been prepared with the help of coupling agents [21,22]. Performance have been studied in many environments for example in aqueous media [24], in terrestrial environment [25], biodegradation after exposing in oxidizing, reducing, hydrogen producing bacteria in bath culture [26] and fungal degradation [27]. Self-reinforced sisal composites were prepared by molding slightly benzylated sisal fibers. The environmental degradation behavior of the materials was evaluated in this paper with reference to the effects of ageing in water, enzyme solution and soil, respectively [28]. It was found that the inherent biodegradability of plant fibers is associated with the pectin. In contrast to plant fiber/synthetic polymer composites, however, water resistance of the prepared composites is greatly increased as was characterized by the insignificant variation in the mechanical properties of the composites before and after being aged in water. With the help of cellulase and fungi, the self-reinforced sisal composites can be degraded leading to weight loss and decay of mechanical performance. In the course of cellulase induced degradation, the insusceptibility of lignin to the enzyme decelerated the rate of deterioration, while the soil burial resulted in an overall decomposition of the composites. Cellulose whiskers are structure of nanodimensions and have been successfully used for the reinforcement of matrix of natural polymers. When starch matrix was filled with cellulose whiskers a decrease in water sensitivity and increase in thermomechanical properties was observed [29]. The reinforcing effect of whiskers strongly depends on the ability of cellulose filler to form a rigid network, resulting from strong interactions by hydrogen bonds. Increasing water content induced the crystallization of amylopectin chains and the accumulation of plasticizer in the cellulose/amylopectin interfacial zone takes place. Storage modulus was decreased by two fold and the association of two relaxation processes was attributed to the glass-rubber transitions of glycerol-rich (at lower temperature) and amylopectin-rich domains (at higher temperature) where starch matrix was composed of glycerol-rich domains dispersed in an amylopectin-rich continuous phase. This plasticizer accumulation phenomenon, enhanced in moist conditions, most probably interferes with hydrogen-bonding force that is likely to hold the percolating cellulose whiskers network within the matrix. In highly moist conditions, a possible transcrystalline zone around the whiskers originates from the amylopectin chains located in the glycerol-rich domains. In addition, the coating of the cellulose whiskers by a soft plasticizer-rich interphase hinders the stress transfer at the filler/matrix interface when the material is submitted to a high strain tensile test, resulting in poor mechanical properties of

composite materials. The cellulose microfibrils were obtained from potato tuber cells and composites with starch were prepared [30]. The water sensitivity was again decrease linearly with the content of cellulose microfibrils in the matrix. The interaction between leaf wood cellulose fibers and plasticized wheat starch was studied in comparison of Low Density Polyethylene (LDPE) composites where poor interactions are well known between fiber and LDPE. There are several reports [31-36] on the reinforcement of biopolymers form biopolymers those can be referred for the further details. It has been reported that a significant change takes place in mechanical properties with respect to filler concentration of cellulose whiskers.

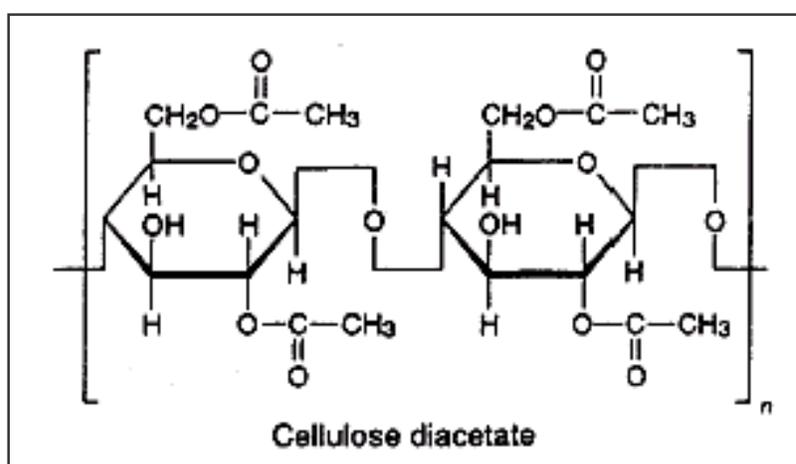


Figure 1.4. Structure of cellulose diacetate

In a broad sense, the starch and cellulose whiskers based bionanocomposites may be employed as biodegradable commodity material if we could incorporate more moisture resistance with mechanical properties. Cellulose esters, e. g. Cellulose Acetate (CA) are considered as potentially useful polymers in biodegradable applications [37-44]. CA is a modified polysaccharide synthesized by the reaction of acetic anhydride with cotton linters or wood pulp. The production of cellulose esters from recycled paper and sugar cane has also been demonstrated [44]. The structure of cellulose diacetate is represented in Figure 1.4. There has been considerable confusion regarding the biodegradability of CA. Komarek et al. [38] provided results of aerobic biodegradation of radiolabeled CA and it was found that in CA with a DS of 1.85 more than 80% of the original ^{14}C -polymeric carbon was biodegraded to $^{14}\text{CO}_2$. Gardner et al. [39] showed, based on film disintegration and on weight loss, that cellulose acetates, having DS less than ~ 2.20 , composted at 53°C and 60% moisture at rates comparable to that of PHBV. It was

generally accepted that cellulose esters with a Degree of Substitution (*DS*) less than 1.0 will degrade from the attack of microorganisms at the unsubstituted residues of the polymers, and that the ether linkages in the cellulose backbone are generally resistant to microbial attack [45, 46]. It is also reported that CA is a poor substrate for microbial attack [47]. Early evidence on the biodegradation potential of CA was reported by Cantor and Mechales [48], who demonstrated that reverse-osmosis membranes prepared from CA with *DS* = 2.5, suffers losses in semipermeability due to microbial attack. The studies on biodegradation of CA although have been given much attention in recent times; scarce attention has been paid to the biodegradation of formulated resins consisting of cellulose acetate and diluents. This should be taken into account seriously, as the melt processing temperature of the cellulose acetates exceeds that of its decomposition temperature, which implies that most cellulose acetates must be plasticized if they are to be used in thermoplastic applications [49]. Effect of plasticizer on biodegradation of CA films has been reported by Jiang and Hinrichsen [50]. In this work, biodegradation of Plasticized Cellulose Acetate (PCA) film was evaluated by monitoring the percent conversion of carbon to CO₂. A strong loss of 20% in weight occurred within the first two weeks of degradation. It was concluded that the fractions of lower molecular weight or lower substitution portion of PCA were biodegraded and removed preferentially from the film. CA of various *DS* is now being widely used as films and coatings. Commercially available CA has a *DS* between 1.7 and 3.0. CA films have a tensile strength comparable to polystyrene, which makes the polymer suitable for injection moulding [51]. CA is used to produce clear adhesive tape, tool handles, eyeglass frames, textiles and related materials. Mazzucchelli of Italy and Planet polymer of USA manufacture biodegradable plastics based on CA under the trade names, BIO CETAm and EnviroPlasticm Z respectively. BIO CETAm is targeted for the manufactures of biodegradable packaging films, retractable films, tubes, and containers for oils, powders, and other products. EnviroPlasticm Z materials are also aimed at use in products in the packaging and the industrial markets. Thus the degradable material can be obtained from cellulose or its derivatives in competitive way in comparison of traditional commodity plastics.

1.8.2. Starch composites

The degradability, preparation methods and mechanical properties of starch composites have been studied extensively [52-56]. Starch is a natural polysaccharide, which is accumulated in plant tubers, seeds, stalks and leaves in the course of their vital activity. The main sources for the commercial production of starch are potatoes, wheat, corn and

rice. The structure of starch is formed by regular stacking of the double chains of amylose and amylopectin and incorporating lipid molecules which forms complex with them. Starch comprises two polymeric components, viz., amylose and amylopectin; they are built of α -D- glucopyranose residues but differ in both structure and function. The amylose content in native starch usually varies from 20 % to 30 %, while amylopectin constitutes the greater part (70 %) of the starch molecule. At the same time, the amylose content in high-amylose starch can reach 50 % to 70 %. Amylose is a linear polymer, which consists of α -(1,4)-D- glucopyranoside residues with the average molecular mass of $\sim 10^2$ to 10^3 kg mol⁻¹. In cellular starch, the helical chains of amylose form complexes with lipids. Amylopectin contains α -(1,4)- and α -(1,6)-linked glucose residues. Extended linear chains involve α -(1,4)-bonds and a great number of shorter branchings are linked through α -(1,6)-bonds(Figure 1.5). The branchings in the starch molecule may contain, on the average, up to twenty glucose residues. Amylopectin molecules also form helices; it is noteworthy that shorter side chains form double helices. [57,58].The degree of crystallization of natural starch depend on its origin and varies from 15-45 %.

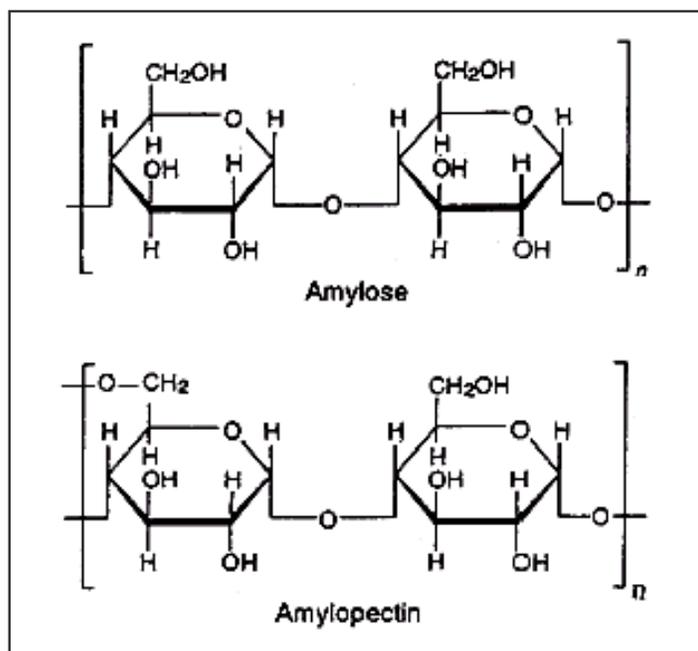


Figure 1.5. Structure of both components of starch

1.8.2.1. Composites of starch with synthetic polymers

Composites of starch with various synthetic polymers were first proposed in the 1970 - 1980's [59-63]. Most often, starch is used for the modification of PE, a film material designed for short-term use (e.g., packaging of food stuffs, agriculture and medicine, etc.). In these mixtures, starch usually plays the role of a filling agent, which ensures the biodegradation of the polymeric item after its service life is over [64]. Thermoplastic mixtures of synthetic polymers with starch are typically prepared from starch plasticised with glycerol and water. The components are mixed in an extruder at ~150 °C, which temperature ensures good gelatinization of the polysaccharide [65] and leads to the formation of two-phase mixtures the biodegradation of which begins from the surface of a starch-enriched film. Small amounts of pro-oxidants favor biodegradation by inducing oxidative decomposition of the material under natural conditions [66]. A PE- starch - vegetable oil mixture is an example of such a composition [67]. Vegetable oil plays the role of a pro-oxidant and simultaneously facilitates the mixing of the natural and synthetic polymers in the course of molding.

Mixtures of starch with an Ethylene -Propylene Co-polymer (EP), polystyrene (PS), an Ethylene-Propylene-Maleic Anhydride Co-polymer (0.8 %, EPMA) as well as with a Styrene-Maleic Anhydride Co-polymer (8 %, SMA) obtained by extrusion at 120-180 °C ,were studied at different effective mechanical moulding energies [68-71]. In these studies, the effects of the composition (40-70 % of starch) and moulding conditions on the structure and properties of starch mixtures were analysed. As in the case of starch -EPMA mixtures, [70,72] the miscibility of components improved in the presence of anhydride fragments in the synthetic polymer chain. This phenomenon was interpreted [69,70] as the chemical reaction between starch and the synthetic polymer under the influence of high temperatures and shear stress in the extruder on moulding. This reaction results in the formation of ester bonds between the carboxy groups in the co-polymer chain and the primary hydroxy groups of starch. Starch mixtures with EPMA and SMA are easy to mould, display satisfactory mechanical characteristics and are biodegradable by spores of the fungus *Penicillium funiculogum*, which is facilitated with an increase in the starch content. At low starch content, starch granules remain encapsulated within the synthetic polymer and are thus hardly accessible to microorganisms.

Co-polymers of ethylene with vinyl acetate (EVAc) or the products of saponification of acetate groups in these co-polymers are most commonly used as

components of starch mixtures. These mixtures are prepared from native corn as well as from high-amylose starch by extrusion with the Ethylene- Vinyl Alcohol Co-polymer [EVAL, 56% of $\text{CH}_2\text{CH}(\text{OH})$ units [73]. Heterogeneous mixtures of EVAL with yellow corn starch displayed a clearly defined boundary between the phases; the sizes of the domains were proportional to the extrusion time. Thomas et.al. [74] prepared phase-separated mixtures of various compositions, which contained domains (0.1-3 mm) enriched either with starch or with EVAL depending on the composition. At the starch content of 55- 60 %, the phase reversal was accompanied by drastic changes in the domain sizes.

The water resistance and mechanical properties of starch mixtures are determined by the ratio of their constituents. Absorption of moisture by films [75], prepared by blowing of mixtures of native corn starch pre-plasticised with glycerol and water and EVAL [1 : 1 (mixture A); 2 : 1 (mixture B)] varied from 2% to 11% and was greater in the films prepared from mixture B. The breaking strength of the films prepared from mixture A was one-third of that for films prepared from pure EVAL and even less for films prepared from mixture B. The use of electron irradiation (flux energy 2.5 MeV, 2500 Grays⁻¹) in the formation of thermoplastic EVAL - starch mixtures makes it possible to modify the structure and rheological properties of these compositions [76,77]. EVAL was shown to be resistant to irradiation, which causes predominantly destruction of starch macromolecules by changing their supramolecular organization and thus facilitating the mixing of starch with EVAL. The mechanical and rheological properties of irradiated mixtures differ substantially from those of the original samples. The mixtures containing high-amylose starch appeared to be the most resistant to irradiation, which can be attributed [77] to chemical reactions of the linear molecules of the amylose starch with the synthetic polymer under the influence of irradiation.

The conditions for moulding of starch mixtures with EVAL strongly influence their degradability. The favourable effect of the structural anisotropy of starch - EVAL mixtures which appears in the injection moulding on the resistance of the mixtures to the action of physiological solutions (estimated from the mass loss and changes in the mechanical properties upon ageing for 80 days) and ethylene oxide used for the sterilisation of materials in clinical practice was demonstrated by Reis et al. [78]. In-depth studies into the properties of starch mixtures with EVAc and with EVAc modified with maleic anhydride (EVAMA) were carried out by Ramkumar et al. [79-82]. Mixtures of commercial corn starch (25 % of amylose, 75 % of amylopectin) with co-polymers containing 18 % and 28

% of CH₂CHOAc units and about 0.8 % of anhydride fragments were prepared by extrusion at different temperatures, screw speeds and mixing times.

Thermooxidation resistance of mixtures of LDPE with a Methyl Methacrylate - Butadiene-Styrene Co-polymer (MBS), with EAA and plasticised starch at 190 °C was studied [83-85] by using TGA, DSC and IR spectroscopy both upon continuous heating and in the isothermal regime. It was shown that MBS and EAA accelerate, whereas starch decelerates thermooxidation of LDPE. A ternary LDPE-EAA-starch system appeared to be the most resistant to temperature, apparently due to the stabilizing effect of the co-polymer at the LDPE- starch interface.

1.8.2.2. Composites of starch with natural polymers

A great number of investigations of the past decade [86-94] were devoted to studies of starch composites with other natural polymers, such as pectins, cellulose, etc., or products of their chemical modification. The feasibility of production of biodegradable packaging films for food stuffs as well as for biomedical purposes from starch-gutta-percha mixtures was studied by Arvanitoyannis et al. [86]. Biodegradable starch mixtures with natural water-soluble polysaccharides, viz., pectins, were studied [87-89] using DMA, dilatometry, SEM and IR spectroscopy. Extrusion of corn starch mixtures with microcrystalline cellulose and Methyl Cellulose (MC) in the presence of additives, e.g., plasticisers (polyols), or without them was used to produce edible films [90]. The increase in the concentration of the cellulose component increases the rupture strength and decreases the elongation at break and the permeability of films for water vapor. Using static sorption of water vapor, it was shown [93-94] that water-soluble starch forms mixtures with MC and Carboxymethylcellulose (CMC), and this blend was degradable under sea water and other biotic conditions. Starch mixtures with ternary co-polymers based on caprolactam, dodecalactam and salts of adipic or sebacic acids with hexamethylene diamine were obtained by compression moulding [95]. The mixtures of components containing up to 30 % of starch are compatible as evidenced from the negative iodine test and the presence of a single relaxation dielectric loss peak around 50 °C. The resistance of these mixtures to water depends on the number of non-polar methylene groups between the amide bonds of the co-polymer. The biodegradation of these films in water, as in the majority of starch-containing mixtures, is facilitated with an increase in its concentration in the system.

1.8.2.3. Composites of starch after chemical modification

Another method for the preparation of starch-based materials is chemical modification of starch, which consists of polymer analogous transformations (most commonly, by esterification of the hydroxy groups) or introduction of fragments of different chemical origin into the polysaccharide macromolecule (e.g., the synthesis of the so-called graft copolymers). In this section, we shall consider the properties of the compositions containing the products of polymer-analogous conversions of starch and their mixtures with other polymers. Starch acetates differing in the degree of substitution (from 1.5 to 2.5) were obtained from high-amylose corn starch. Mechanical properties of films prepared from acetylated starch are determined by the origin of starch [96], being dependent on the content of amylose and amylopectin in the original polymer [97]. These acetate films were less hygroscopic than neat starch films. These modified starches were less biodegradable as esterification prevents the action of enzymes onto the starch by changing the nature of substrate. Carboxymethyl starch was obtained by treatment of yellow corn starch and pigweed starch (the degree of substitution = 0.1- 0.2) with chloroacetic acid [98]. Small additions of carboxymethyl starch was used for the extrusion of various food stuffs derived from semolina. It was found that modified starch improves processing of these products. Elastic edible films were prepared from hydroxypropyl starch mixed with gelatine and plasticised with polyols and water (up to 25 %) by Arvanitoyannis et al. [99]. Higher fatty acid esters of starch are promising reagents for mixing with non-polar polymers, such as PE and PP [100]. The reaction of starch with the corresponding acid chlorides in DMSO gave starch octanoates and dodecanoates with the DS of 1.8 and 2.7. The ester groups containing higher alkyl radicals improve the affinity of starch for the non-polar synthetic polymer and act as internal plasticisers. The compatibility of starch dodecanoate with PE is higher than that of starch octanoate. The starch dodecanoate-PE mixtures manifest higher thermal stabilities, greater elongation at break upon rupture and lower moisture absorption than starch octanoate-PE mixtures. However, being introduced into PE at any ratios, these substances decrease the rate of biodegradation of the mixture in comparison with starch -PE mixtures. Starches modified by the introduction of cholesterol residues [101] and mixed with high-pressure PE were used for the production of blown films. In comparison with non-modified starch, these materials are more homogenous and more stable. Biodegradation in a compost of films prepared from these mixtures occurs even faster than that of non-modified starch-PE mixtures, apparently due to the loosening of the starch structure caused by bulky cholesterol fragments.

1.8.2.4. Nanocomposites of starch

A first insight of thermoplastic starch and kaolin clay interaction was reported by Curvelo et.al. [102]. Premixture of starch, plasticizer (w/w 30 %) and clay in polyethylene bag were mixed till the formation of powder. The clay concentration was kept 0, 10, 20, 30, 40, 50 & 60 per hundred parts of thermoplastic starch. There is no discussion of XRD and TEM thus, dispersion extent of filler was not studied and very good compatibility of thermoplastic with kaolin in concentration range 10-60 phr was concluded on the basis of SEM images where no smooth area was found. The composition of 50 phr showed 135 % and 50 % increase in tensile strength and corresponding modulus relative to unfilled matrix whereas in a later study it was observed that 72 % modulus can be increased with 30 % concentration of kaolin when composites prepared by solution method [103,104]. The Tg was slightly lower than thermoplastisized starch. The observed decrease was proportional to the amount of clay in samples, during TGA analysis the residual weight was proportional to the filler content in the matrix. In the study of water absorption (at 43 & 100 % RH and $25 \pm 2^\circ\text{C}$). It was observed that presence of clay decrease this sorption which was more pronounced till 20phr after which was almost constant.

In the same direction biodegradable thermoplastic hybrids were prepared by melt intercalation method [105,106]. TPS was prepared in haake mixer (5/2/3 composition of starch /water /glycerol) after 1 hr plasticization followed by geletinization at 110°C . TPS / MMT Na⁺ hybrid have a multilayer nanostructure with alternating polymeric and inorganic silicate layers whereas, with other modified clay almost an agglomeration of large particle was found. These results were attested to the higher polymer clay compatibility in TPS / MMT Na⁺ and strong polar -polar interactions in comparison of modified clays where modifier decreases the compatibility by making the clays hydrophobic upto some extent. The increase in elongation at break was little unusual as clay led a brittle matrix but it was assumed that it may be due to the presence of stress concentration sites which lead to shear bending as this behavior was not found with other systems and their (TPS/ Closite 6A, Closite 10 A, Closite 30B.) elongation at break was even smaller in comparison of neat matrix. Same author [107], synthesized nanocomposites of TPS with natural MMT Na⁺ and Closite 30 B with 2.5, 5, & 10 % filler concentration and effect of filler concentration was studied. It was observed that TPS /MMTNa⁺ interaction became more feasible and nanocomposite formed had better tensile properties than TPS /Closite 30 B and pristine TPS. Further, the property enhancement was attributed to the greater compatibility of non-organomodified clay with starch, as both

are highly hydrophilic but this energy match varies after organic modification of clay. It was assumed that there is a possibility to control the degradation rate of the nanocomposites by varying the filler content as hydrolysis of polymer is possibly dependent on the transport of water from the surface to bulk and this transportation can be controlled by increasing or decreasing the filler content of the system. In both the reports [105,107], moisture sensitivity was not studied which is a key factor during the application of this material for packaging and it is expected that the moisture sensitivity will increase in TPS/MMTNa⁺ system as both components have the higher tendency to attract the water molecules regardless the extent of intercalation and clay concentration. Wilhelm et.al.[103] used carboxymethyl starch for reinforcement with Ca⁺⁺-Hectorite clay mineral. The nanocomposites were obtained by the solution method after dispersion of clay mineral in glycerol plasticized starch with 20% plasticizer content relative to dry weight of starch. Clay mineral was filled by 5, 10, 15, 20 & 30 % concentration in starch matrix. The effect of glycerol on the nano level construction of composites was studied. Authors concluded that increase in d-space was inversely proportional to the clay amount where the clay content was low this d-spacing was similar to that obtained only by glycerol-clay interactions. Thus, the intercalation may depend on the plasticizer / and clay content in starch/clay nanocomposite. The author did not study the complex nature of the system in detail. The TGA was carried out in temperature range of 19-900 °C and thermal stability did not increase significantly by the addition of clay. A three step reaction with maximum decomposition at 289 °C was found; first step was assigned to the water loss starting from ~30°C, second for starch/glycerol decomposition and third was for the oxidation of decomposed starch. Clay has two step process first water loss and second dehydroxylation. A significant increase in thermal stability was observed when nanocomposites of thermoplastic starch and unmodified MMT was prepared by melt intercalation method even at 5 % filler content [105]. This controversy suggested that preparation method may have an effect on the properties; here it must be worth to recall that both the systems were having different class of clays. It was proposed that intercalated fraction of plasticizer is being protected by clay and degrading at higher temperature.

1.8.2.5. Commercial biodegradable products of starch

The thermoplastic starch alone is mainly used in soluble compostable foams, such as loose-fillers, expanded trays, shape moulded parts and expanded layers, as a replacement for polystyrene. BIOTEC of Germany has conducted promising research and development along the lines of starch-based thermoplastic materials. The company's three product lines

are Bioplastm granules for injection moulding, Bioflexm film, and Biopurm foamed starch. Starch-based biopolymer thermoplastics include, in particular, TPS [108] and the group of polymer blends of thermoplastic starches with additional polymer components like aliphatic polyesters e. g. PCL and bionolle, PVA, PLA, copolymer from aliphatic diol and aliphatic as well as aromatic dicarbon acids together with especially biodegradable polyesteramides [109]. The research results on TPS bioplastics and their production processes are protected by international patents or have patents pending [110 - 113]. Under the Mater-Bi trademark, Novamont of Italy today produces four classes of biodegradable materials Z, Y, V, and A, all containing starch and differing in synthetic components. Each class is available in several grades and has been developed to meet the needs of specific applications. The current production capacity of Novamont is 8000 tons/year. Mater-Bi can be processed using conventional plastic technologies such as injection moulding, blow moulding, film blowing, foaming, thermoforming and extrusion. The physical-mechanical properties of Mater-Bi are similar to those of conventional plastics like polyethylene and polystyrene. Mater-Bi is not only recyclable but also as biodegradable as pure cellulose. The biodegradability of Mater-Bi products has been measured according to standard test methods approved by International Organizations (ISO, CEN and ASTM). The compostability of some Mater-Bi grades has been certified by the “Ok Compost” label. Mater-Bi can be used in a wide range of applications such as disposable items (plates, cutlery, cup lids etc.), packaging (wrapping film, film for dry food packaging, board lamination etc.), stationery (pens, cartridges, pencil sharpeners etc.), personal care and hygiene (sanitary napkins, soluble cotton swabs etc.) and a lot others like toys, shopping bags, mulch film etc. Various starch plastics with different trade names are now available in the market. Buna Sow Leuna of Germany has developed a line of biodegradable polymers based on esterified starch with the trade names Sconacell S, Sconacell A, and Sconacell AF. Compared to common thermoplastics, however, biodegradable products based on starch still reveal many disadvantages which are mainly attributed to the highly hydrophilic character of starch polymers. In spite of many positive results, thermoplastic starch-based materials are still at an early stage of development and the markets for such products are expected to increase in future as the properties are more improved, prices still decline, and an infrastructure for composting becomes more established.

1.8.3. Composites of PLA

PLA is linear thermoplastic polyester consist of ester linkages and produced from renewable resources [114-120]. These ester bonds are prone to both chemical and enzymatic hydrolysis. Since some properties like melt viscosity, impact factor, heat distortion temperature, gas barrier etc. are desirably not high enough for its use in various applications like PP and PE, therefore, efforts have been made toward this direction. PLA is primarily used for medical applications including sutures, drug delivery, vascular grafts, artificial skin, and orthopedic implants [121]. Synthetic biodegradable PLA, PGA, and copolymers of these, have been manufactured for biomedical applications since the 1970s. A new range of PLA biodegradable polymers is being offered by Cargill Dow Polymers [122].

1.8.3.1. Composites with natural polymers

Composites of natural polymers with PLA have been reported in literature inorder to develop a biodegradable / biocompatible products for both medical and commodity applications [123-125]. Interesting and selected examples of such type of composites are being presented here. The objectives of one study were to evaluate [123] the effects of the type of acetylated starch and the presence of PLA and ethanol on the functional properties of extruded foams, and to compare the specific mechanical energy requirements for preparing these foams. Acetylated starches prepared from potato and native (25% amylose) and high amylose (70%) corn starches were extruded with 7.5, 15% PLA and 8, 13, or 18% ethanol using a twin-screw extruder with a 160 °C barrel temperature and 180 rpm screw speed. The acetylated potato and native and high amylose corn starches had DS of 1.09, 2.05, and 2.65, respectively. Acetylated 70% amylose cornstarch agglomerates had the highest hardness whereas acetylated potato starch had the lowest. Higher DS acetylated starch had higher radial expansion ratio, compressibility, specific mechanical energy requirement, and lower bulk density than acetylated starch–PLA foams.

Cellulose diacetate-graft-poly(lactic acid)s (CDA-g-PLAs) were synthesized successfully over a wide range of composition in combination of different ways of graft polymerization [124]. A copolycondensation of lactic acid, a ring-opening copolymerization of L-lactide in DMSO and a copolymerization similar to the second, but in bulk was carried out. Each initiated at residual hydroxyl positions on Cellulose Diacetate (CDA). DSC revealed that all the copolymer products gave a single Tg, which decreased sharply from 202°C for the original CDA a value closer to Tg of PLA

homopolymer. Another paper reported [125] the grafting copolymerization of L-lactide onto hydroxyethyl cellulose or hydroxypropyl cellulose. They were obtained from Ring Opening Polymerization of lactide with hydroxypropyl cellulose or hydroxyethyl cellulose in different mole ratios at 128°C. Sn (Oct)₂ or LiCl was used as catalysts for the polymerization reactions. Both PLA- hydroxypropyl cellulose and PLA- hydroxyethyl cellulose were biodegradable polymers with a good biodegradability, lack of toxicity, and were suitable for the use as tissue engineering materials. The influence of plant fibres such as flax, jute, ramie, oil palm fibres and fibres made from regenerated cellulose on the mechanical properties of biodegradable polymers was investigated using thermoplasts like polyesters, polysaccharides and blends of thermoplastic starch [126]. The composites were produced by extrusion compounding with a co-rotating twin screw extruder. The pellets obtained were further processed into tensile test bars by injection moulding. Depending on the kind of polymer, a fibre content of 20–35% could be achieved. Generally a considerable tensile strength improvement of polyesters could not be observed. However the chemical similarity of polysaccharides and plant fibres, which consist mainly of cellulose, resulted in an increased tensile strength of the reinforced polymers.

1.8.3.2. Nanocomposites of PLA

The layered silicate PLA nanocomposites were prepared not only to increase its mechanical properties but also for enhancement of barrier properties. Many researchers [127-143] have prepared the nanocomposites of PLA and studied several properties including biodegradability in composting. The nanocomposites were prepared by melt intercalation method [128] by using O-PCL as compatibilizer. During biodegradability testing of these nanocomposites in industrial compost; an increased biodegradation was evidenced as samples were completely mineralized after 60 days. It was expected that the presence of terminal hydroxylated edge groups of the silicate layers might be one of the responsible factor for this behavior [129]. In case of 4 % filler content the silicate layers were homogeneously dispersed in the PLA matrix and these hydroxy groups start heterogeneous hydrolysis of the PLA matrix after absorbing water from compost. Since this process may take some time, the weight loss and degree of hydrolysis of PLA and PLA with 4 % filler is almost same up to one month and after that nanocomposites degraded faster and one month of composting was found a critical time for degradation rate. Lee et al. [138] prepared aliphatic unsaturated polyester, clay nanocomposites by melt intercalation. This article reported the decrease in biodegradability under composting

with intercalation and it was concluded that due to high aspect ratio and better dispersion of clay in matrix a more tortuous path formed for penetration of microorganism inside the bulk and hindered their diffusion. Moreover the decrease or increase in biodegradation in nanocomposites is under discussion and no conclusion can be made about their mechanisms on the basis of present literature. In other few attempts [141] PLA layered silicate nanocomposites were prepared by melt intercalation method in presence of a stabilizer to decrease the possibility of host matrix degradation due to heating. The degradation of PLA during processing takes place even in the presence of antioxidant, and 41.2 % decrease in number average molecular weight was observed. The adsorption of PLA for automotive parts on the minerals have been studied in order to contribute to suppressing the increase in CO₂ emissions [142]. For this application, major improvements in heat and impact resistance are needed. Thus PLA nanocomposites can be prepared successfully by melt processing but thermal stability during the preparation is a key factor which has to be solved.

1.8.3.3. Commercial degradable products from PLA

All PLA resins are manufactured using renewable agricultural resources, such as corn or sugar beets. Cargill Dow prepared a biodegradable products which applications include compostable food and lawn waste bags, yoghurt cartons, seeding mats and nonwoven mulch to prevent weed growth. DuPont's biodegradable Biomax copolyester resin, a modified form of PET, was launched in 1997. Its properties, according to DuPont, are diverse and customisable, but they are generally formulated to mimic PE or PP [122]. Because it is based on PET technology, and can be produced on commercial lines, DuPont believes that Biomax is only marginally more expensive to produce than PET itself, and significantly cheaper to produce than other biodegradable polymers.

1.8.4. Composites from Poly (hydroxy alkanates)

These are synthesized biochemically by microbial fermentation and which may be produced in the future by transgenic plants, represent natural polyesters. Bacteria are still the only real source of these polyesters; it will still require some more years of research until transgenic plants will be available for production. PHB, (commercial name Biopolm) is a biotechnologically produced polyester that constitutes a carbon reserve in a wide variety of bacteria [144] and has attracted much attention as a biodegradable thermoplastic polyester [145-147]. It can be degraded to water and carbon dioxide under environmental conditions by a variety of bacteria and has much potential for applications of environmentally degradable plastics [148]. However, it suffers from some disadvantages

compared with conventional plastics, for example, brittleness and a narrow processability window [149]. To improve these properties, various copolymers containing hydroxyalkanoate units other than 3-hydroxybutyrate have been biosynthesized [150]. PHB and the copolymer, poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), are produced by Monsanto and sold under the tradename Biopolm. PHBV polymers were first manufactured [148] by ICI in 1983 and were originally intended as biodegradable substitutes for oil-based polyolefins in films, bottles and plastic containers [151]. The actual and potential uses of PHB and PHBV for motor oil containers, film formation and paper-coating materials have been reviewed [152]. The range of possible uses of Biopolm polymers have been summarized by Amass et al. [153]. PHBVs are highly crystalline polymers with melting points and T_g similar to PP. Due to characteristics of biodegradability through non-toxic intermediates and easy processability, PHBV polymers are being developed and commercialized as ideal candidates for the substitution of non-biodegradable polymeric materials in commodity applications [154-155]. However, the prohibitive cost, the small difference between thermal degradation and melting temperature and especially the low impact resistance around the room temperature and below, due to high crystallinity and relatively high glass transition, have prevented its larger commercial applications. With the all melt-processed polymers there is the possibility of thermal degradation at temperatures in the region of the melting point (in case of PHB, melting point as calculated is 180 °C) [156]. PHB is known [157-160] to be susceptible to thermal degradation at temperature close to its melting point. This degradation occurs almost exclusively via a random chain scission mechanism involving a six-membered ring transition state [159-160]. Lehrle and Williams [161] have reported that under certain conditions random chain scission can not be responsible exclusively for the formation of the observed degradation products. In particular, it was shown that primary products are involved in a number of secondary reactions and isomerizations and, indeed, that tetramer is formed principally as a result of such secondary reactions [162]. The two monomer units i.e., 3-hydroxypentanoic acid (trivially known as 3-hydroxyvaleric acid and 3-hydroxybutyric acid of PHBV copolymer. Biopolm is also produced commercially by a fermentation process using glucose and propionic acid as carbon sources for the microorganisms. Nanocomposites of these polymers have been prepared with layered silicates by assuming that the layered silicates will improve its many material properties. The effort has been made in this direction with little explanations of the

reaction conditions and properties. Degradation of PHB [163] matrix during nanocomposites preparation was high in MMT than fluomicas. The higher degradation rate in MMT polymer was attributed to the presence of Aluminium Lewis acid sites, which catalyze the hydrolysis of the ester linkages. The enhanced barrier properties are believed to decrease the biodegradation by enhancing the path length, as the rate after 3 weeks of biotic ageing was much slower from that of neat PHB. Cellulose nano whiskers have been used to reinforce the PHB where a structural and morphological study was carried out with different load concentrations. The preparation technique of a latex of poly (β -hydroxyoctanoate) obtained from *Pseudomonas oleovorans* grown at high cell density on sodium octanoate was investigated [164] and a latex was obtained. Nanocomposite materials were also prepared from medium-chain-length poly (hydroxyalkanoate) latex [165] as semicrystalline matrix using a colloidal suspension of hydrolyzed cellulose whiskers as natural and biodegradable filler. In the both above mentioned attempt the study on degradability was not performed. The reinforcement of PHB matrixes may be carried out successfully but the real material properties preservation as in engineering thermoplastics is still an unresolved thrust area of research.

1.8.5. Composites from Natural oils

Biodegradable composites have also been developed from natural oils like epoxidized soya oil (ESO) and Epoxidized linseed oil (ELO) those have been used as monomer for production of resins. These vegetable oils have their own particular advantages e.g. they are renewable products derived from natural oils and fats are more readily biodegradable than the corresponding products made from petroleum sources. Their impact on the environment is less and the long fatty acid chains of vegetable oils impart desirable flexibility and toughness to otherwise brittle resin systems such as epoxy and polyester resins. Oil can be successfully polymerized photochemically in the presence of initiators under defined conditions [166]. Epoxy-exfoliated clay nanocomposites were prepared using [167] long- chain alkylammonium-exchanged smectite clay. The ESO composites were compared with hybrids obtained from ELO those were prepared by similar method. The biodegradability test has also been carried out on theses nanocomposites for the first time and samples were found biodegradable in initial studies [168]. Biodegradable nanocomposites were obtained by plant oil silica hybrid coatings [169] those exhibited excellent flexibility. In to a mixture of ESO and ELO and functional silane coupling reagent (3-glycidoxypropyltrimethoxysilane) GPTMS, thermally latent catalyst (a

benzylsulfonium hexafluoroantimonate derivative) was added. The Biodegradability of the ESO-GPTMS composite was evaluated by BOD measurement in an activated sludge, which reached higher than 50% after 2 months. Thus, in general it was concluded that these nanocomposites may be used as the biodegradable plastics for commodity applications.

1.8.6. Composites from Pectin

Plant cell wall pectins contain esterified polygalacturonic acid residues, the degree of esterification depending on the origin of pectin. The pectins studied, were isolated from citrus plants, sugar beet, almonds [170-172] for composites preparation. Using IR spectroscopy, it was shown [170] that the position of the band corresponding to the carboxy group of pectin changes noticeably after addition of glycerol, whereas the positions of the absorption bands characteristic of starch change to a lesser degree. The rupture strengths of glycerol-plasticised films of pectin- starch composites were studied, which changed slightly with an increase in the plasticiser content up to 45 %. Further increase in the glycerol content up to 75% sharply decreases the rupture strength and increases 10-fold the elongation at break. The increase in the starch content in the mixtures attenuates the plasticising effect of glycerol and thus makes the films more rigid [171]. The results of spectral studies suggest that plasticised films prepared from starch mixtures are highly compatible with pectin. However, phase homogeneities of the systems under study were not proved. In another report [173] the research was aimed to develop matrices for the delivery of biologically active substances for tissue regeneration. To this end, a new biodegradable matrix composed of a hydrophobic porous poly(lactide-co-glycolide), network entangled with another network of hydrophilic pectin, was fabricated in the presence of calcium chloride. The mechanical properties of the composite were found far superior to matrices containing only pectin. Pectin is also miscible with PVOH in all proportions [174]. Potential commercial uses for such films are water-soluble pouches for detergents and insecticides, pushable liners and bags, and medical delivery system devices. These films are solution-cast by air drying at an ambient temperature. For the outer packaging film, however, as for other biomaterials, there was a defect in the material properties such as tensile strength and water solubility. Citrus pectin composites have been prepared [175] and cast into films with PVOH. Elongation at break measurements revealed that pectin/PVOH films underwent a brittle to ductile transition with increasing PVOH composition. The addition of glycerol to pectin/PVOH films increased ductility significantly when films were relatively brittle. At 70°C, all compositions were soluble but

films containing pectin dissolved more rapidly than those without pectin. From the recent literature survey it was observed that pectin could be a potential polymer for the preparation of environmentally degradable composites.

1.8.7. Composites from Gelatin

Collagen constitutes as much as 30% of the total human protein and molecules exists as a triple helix, comprising of three discrete chains (three-dimensional structure), which leaves space for interchain hydrogen bonding [176]. The existing imino acids impart rigidity to the molecule and the interstitial water molecules might act as hydrogen-bond bridges, thus contributing to the stability of the helix [177]. Gelatin is obtained by the thermal denaturation or physical and chemical degradation of the collagen. Its most frequent and popular uses in the biomedical field include hard and soft capsules, microspheres, wound dressing and three dimensional tissue regeneration [178]. Tharanathan et.al. showed that gelatin produces tough films when cast together with glycerine or sorbitol [179]. Moreover, the combination of polysaccharide and protein material showed a synergism resulting in a better mechanical property [180,181]. It is believed that the presence of pectin and agar in a protein formulation could improve the moisture barrier of the resulting products [182]. The mechanical properties of gelatin based composites can be improved through various chemical treatments and graft polymerization with other synthetic polymers [183,184]. Degradability of composites films based on waste gelatin (WG) have been measured and it was studied in many environments. The results reported in this report evidenced the complete and very fast biodegradability of waste gelatin cast films. The effect of a crosslinker agent such as glutaraldehyde on both thermal properties and degradation rate was further investigated. Parallel biodegradation testing was carried out on composite films based on WG, PVA blends comprising sugar cane bagasse as filler. The films meant to be used for the preparation of self-fertilizing mulches tended to be disintegrated by soaking in water at relatively faster rate depending upon the PVA or crosslinker content. WG based films showed a higher biodegradability under soil burial conditions. Furthermore blending of WG with PVA followed by the addition of a lignocellulosic material as filler, as well as a limited amount of crosslinking, glutaraldehyde, the durability of the film could be modulated both in term of physical persistence and biodegradation rate [185]. Biodegradation of gelatin-phenol formaldehyde resin blends [186]. have been studied by soil burial testing methods . Over a period of two weeks and at an ambient temperature of 27°C the blends were found to be significantly resistant to biodegradation in the test soil

up to a composition of 7:3 gelatins to resin ratio. At higher gelatin contents, the blends suffered extensive degradation. Inorganic inclusions, presumably calcium salts that are inherently present in gelatin are believed to support bacterial growth and biodegradation of the blends. Thus gelatin gives an interesting feature about the preparation of degradable composites. This material may be applied successfully for the preparation of biodegradable material without even generating any harmful side products during degradation in any conditions.

1.8.8. Composites from Chitosan

Chitosan consists of 2-deoxy-2-amino anhydroglucose residues, is obtained by N-deacetylation of chitin, which is the second most naturally occurring biopolymer after cellulose. Since chitosan is a polysaccharide having amine groups, many papers have been published concerning utilization of chitosan as functionalized polysaccharides [187]. Apart from its biodegradable character in physiological conditions, chitosan has reactive amine side groups, which offer possibilities of modifications, graft reactions and ionic interactions. Polyester chitson hydrogels have potential use in biomedical applications like wound dressings and drug release systems, since both polyester side chains and chitosan are biocompatible and biodegradable [187]. Study on functionalized blend films such as cellulose-chitosan, PVA-chitosan have been reported [188]. Starch/chitosan blend films were prepared [189] by irradiation of compression-molded starch-based mixture in physical gel state with electron beam at room temperature. The influence of chitosan and radiation on the properties of the prepared films were investigated. The tensile strength and the flexibility of starch films were improved largely after incorporation of 20% chitosan into starch film. Furthermore, in order to produce a kind of antibacterial films, the starch/chitosan blend film was irradiated, where antibacterial activity was induced even when the content of chitosan was only 5% due to the degradation of chitosan in blend films under the action of irradiation. The tensile strength and the flexibility of starch film were improved largely after incorporating 20% chitosan into starch. The degradative activities of extracellular and cell-associated portions of rat cecal and colonic enzymes, whose activities are comparable to that in the human colon, against chitosan samples have been characterized. The effects of the Molecular Weight (MW) and Degree of Deacetylation (DD) of chitosan on its susceptibility to degradation were investigated [190]. The results show that rat bacterial enzymes had the ability to degrade chitosan with extracellular enzymes exhibiting a more profound effect than cell-associated enzymes. The reaction to bacterial enzymes degradation was dependent on both the MW and DD of the

chitosan sample. Novel chitosan gel beads have also been synthesized by coupling and chemical co-crosslinking mechanism [191]. Tripolyphosphate (TPP) and a naturally occurring crosslinking reagent, genipin, which has been used in herbal medicine, were employed, respectively, as ionic and chemical crosslinkers to prepare the chitosan-based networks of gel beads. These results reveal that the ionic/chemical co-crosslinked chitosan networks may be suitable for biomedical applications. Results of spectrophotometric and thermogravimetric [192] studies of chitosan blends with PVA, starch and hydroxypropylcellulose obtained by casting from solutions in the form of transparent films containing 0–1.0 weight fraction of chitosan have been discussed. Blends containing starch are homogeneous only in the case of low-weight fraction of starch (to 0.3). Investigations in isothermal conditions in air at temperature from 100 to 200°C confirmed appreciable improvement of chitosan thermal stability in the blends being tested. IR of the blends showed a distinct stabilization of the process of chain scission. The process of physical degradation by means of the ultrasonic action towards chitosan with mole fraction of 2-acetamido-2-deoxy- β -D-glucopyranose units has been investigated [193]. The chitosan was found highly degradable under the ultra sonic waves. The thermal degradation properties of chitosan and lactic and/or glycolic acid grafted chitosan have been studied by DSC and TGA [194], in the range of 25–500°C. Both DSC and dynamic TGA results show that the samples are thermally degraded easily after grafting the lactic and/or glycolic acid. From the isothermal TGA experiments, the initial activation energy and the activation energy at different stages was obtained. The initial activation energy of all grafted samples was much lower than that of chitosan. The FT-IR spectra of thermally degraded residues give an indication of the chitosan polysaccharide ring degradation.

1.8.9. Soy Plastics

The production, structure, composition, physicochemical properties, processing for plastics, industrial applications and biodegradable nature of soy protein biopolymer have been reviewed [195]. Protein levels as high as 55% have been observed in soybeans. Soybeans consist of discrete groups of proteins (polypeptides) that span a broad range of molecular sizes and are comprised of approximately 38% of non-polar, non-reactive amino acid residues, while 58% are polar and reactive. Modifications that take advantage of water solubility and reactivity are exploited in improving soy protein for use in plastics and other biomaterials [196-197]. Soy protein plastics of different compositions have been prepared by injection moulding [198]. Compression moulding is also used for soy

plastic processing. Less than 0.5% of the available soy protein is used for industrial products [199-200]. Soy plastics have been used for manufacturing automobile parts by Ford company [195]. Dried soy plastics display an extremely high modulus, 50% higher than that of currently used epoxy engineering plastics [201]. So with proper moisture-barrier, soy protein is a potential starting material for engineering plastics. Blending the biodegradable soy protein plastic with polyphosphate filler greatly reduced its water sensitivity, allowing new uses in moist and load-bearing environments where the unfilled plastic was not useable [202]. Development of affordable soy-based plastics, resins, and adhesives was reviewed recently [203]. The reaction product of soybean, a carbohydrate filler, a reducing agent, water and additives resulted in an improved biodegradable plastic [204] having high degree of flowability for processing by extrusion and injection moulding into solid articles with a high degree of tensile strength and moisture resistance.

1.8.10. Miscellaneous

There are several other formulations for the development of ecofriendly material from renewable resources. Interesting and recent examples shall be discussed in this section. In a report [205], butyrate kraft lignin was added to an unsaturated thermosetting resin, consisting of a mixture of acrylated epoxidized soybean oil and styrene. Composites were made by the Vacuum Assisted Transfer Molding (VATM) process with varying amounts of butyrate kraft lignin dissolved in the unsaturated resin system. Butyrate kraft lignin improved the interface adhesion between the resin and reinforcing flax fibers. SEM images illustrated a clear improvement in the adhesion of the resin to the fibers by showing the fibers fracturing together with the resin, without fiber pullout. Natural rubber was reinforced with untreated sisal and oil palm fibers [206] chopped to different fiber lengths. The effects of concentration and modification of fiber surface in sisal/ oil palm hybrid fiber reinforced rubber composites have been studied. The rubber/fiber interface was improved by the addition of a resorcinol-hexamethylene tetramine bonding system. The reinforcing property of the alkali treated fiber was compared with that of untreated fiber. The extent of fiber alignment and strength of fiber-rubber interface adhesion were analyzed from the anisotropic swelling measurements. VATM process was used [207] to make composite of plant oil-based resin [Acrylated Epoxidized Soybean Oil (AESO)] and natural fiber mats made of flax, cellulose, pulp and hemp. Recycled paper was used as a cheap resource of cellulose fiber and found to work well with AESO resin in terms of flow, impregnation and surface bonding. These low-cost natural composites were found to have mechanical strength and properties suitable for applications in housing construction

materials, furniture and automotive parts. The influence of fiber treatment on the properties of biocomposites derived from grass fiber [208] and soy based bioplastic was investigated with Environmental Scanning Electron Microscopy (EVSEM), thermal and mechanical properties measurements. Grass fibers were treated with alkali solution that reduced the inter-fibrillar region of the fiber by removing hemicellulose and lignin, which reduce the cementing force between fibrils. This led to a more homogenous dispersion of the biofiber in the matrix as well as increase in the aspect ratio of the fiber in the composite, resulting in an improvement in fiber reinforcement efficiency. The dispersion of grass fiber in matrix improved with increasing treatment time and concentration of the alkali solution. The tensile and flexural properties of alkali treated grass fiber reinforced soy based biocomposites were improved gradually with increasing alkali solution concentration and treatment time. The composites of lignin with epoxy resin have been prepared [209]. A compatibility study was carried out by optical and electron microscopy, viscosimetric determinations and thermo-optical analysis in order to establish optimum synthesis conditions of molding mass (cast resins). Lignin/epoxy composites including various fillers (lead soap, alum earth, talc, chalk, sand, trihydrate aluminium oxide, glass fibers), plasticizer (dibutylphthalate and polyester C₆) and pigments (iron-oxide and titanium dioxide) have been obtained. These composite materials can be used in the electronics industry. The degradation behavior of three commercial biodegradable plastics, PHB Sky-Green, a biodegradable aliphatic polyester made of succinic acid, adipic acid, butanediol and ethylene glycol, and Mater-Bi,[210] a composite composed of starch based biodegradable polymers, was studied in the forest soil, in the sandy soil, in the activated sludge soil, and in the farm soil at 28,37, and 60°C, respectively. Biodegradation of all three polymers was most active in the activated sludge soil. Biodegradability of PHB was highest at 37°C, while degradation of MB occurred reasonably well at 60°C. In both, the soil burial test and the modified Sturm test, the order of the biodegradation rate was PHB > SG > MB. The composites of aliphatic PCL, PHBV, PBS, and PLA with 10 wt.% untreated or acetic anhydride-treated abaca fibers were prepared [211] and their biodegradability was evaluated by the soil-burial test. In case of PCL composites, the presence of untreated abaca or AA-abaca did not pronouncedly affect the weight loss because PCL itself has a relatively high biodegradability. However, the addition of abaca fibers caused the acceleration of weight loss in case of PHBV and PBS composites. Especially, when untreated abaca was used, the PHBV and PBS composite specimens

were crumbled within 3 months. This result was a marked contrast to the fact that neat PHBV and PBS specimens retain the original shape even after 6 months.

1.9. Conclusions and future trends

Studies carried out in the past decades have demonstrated that biodegradable materials should combine high mechanical and other essential operational and technological properties (e.g., stability, low gas permeability, environmental safety, easy moulding, etc.) with biodegradability. Degradable material based on starch is the most readily available and have found wide practical applications. The properties of starch-based polymeric materials including their biodegradability depend on the compatibility of the components of composites and the structure of the systems thus prepared. However, the thermodynamic and energetic characteristics of the interaction of starch with synthetic polymers within the mixtures and the structure of such systems are still poorly known. Recent work on biocomposites reveals that in the most cases the specific mechanical properties of biocomposites are comparable to widely used glass fibre reinforced plastics. In order to be competitive, ecofriendly plastics must have the same desirable properties as obtained in conventional plastics. The most important factors to the formation of a successful biodegradable polymer industry include cost reduction as well as public and political acceptance. Existing environmental friendly polymers are mainly blended with different materials with an aim to reduce cost and to tailor the product for some specific applications. Application of biodegradable polymers in natural fibre-reinforced composites will broaden their uses. The demand for sustainable and renewable materials continues to rise. Polymeric composites from renewable resources have occupied major applications in green packaging. Although these are emerging as alternatives to existing petroleum-derived plastics; the present low level production and high costs restrict their wide spread applications. The barrier properties of such degradable polymers can be improved through nano reinforcements. The incorporation of nanoparticles in a polymer matrix reduces the permeability of penetrant molecules and thus develops high barrier composites. Nanocomposites especially biodegradable nanocomposites or nanocomposites obtained from renewable resources are an emerging new class of materials [212], total environmental/economical impacts of which need to be studied to prove the industrial and environmental potential of targeted nanocomposites for automotive applications. Biopolymers combined with suitably organically modified clays will result in environmental friendly nanocomposites.

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CHAPTER II :
OBJECTIVES AND APPROACHES OF PRESENT INVESTIGATION

2.1. Objective of the Present work

Modern-day technology calls for the development of ecofriendly polymeric materials having the desirable mechanical properties [1]. The effects of environmental factors (e.g. water, atmospheric oxygen, sunlight and biological agents, such as microbes, fungi, insects, etc.) alter the service life of many articles prepared from polymeric materials [2-4]. However, the immense bulk of polymeric materials and articles made thereof put forward a problem of their further destruction or disposal after the termination of their service life. Many polymers are decomposed in the environment over a relatively long period of time; therefore, the production of biodegradable materials is as important area of research [5]. Polymers, particularly house-hold plastics and films, must be rapidly decomposed after use under the influence of chemical (atmospheric oxygen, water), physical (sunlight, heat) and biological (bacteria, fungi, yeasts, insects, etc.) environmental factors. These factors produce a synergistic effect, eventually resulting in the fragmentation of the polymer owing to the destruction of its macromolecules and their conversion into low molecular weight compounds that can be further involved in the natural circulation of substances [6]. Thus there is essential need to develop a material with good biocompatibility, desirable mechanical properties in a cost effective way. The polymeric composites from renewable resources have promising attention towards the above mentioned factors. The composites of renewable polymers have been of great interest due to their cheap availability and in a broad sense environmental degradability. The main objectives of the present work may be summarized as follows.

1. The preparation of different biocomposites of renewable resources
2. To find out the environmental durability of biocomposites and study of their mechanisms.
3. The preparation of nanocomposites from biopolymers and study their sustainability in the environment
4. To study the effect of modification of biopolymers e.g starch on the different material properties when filled with layered silicates and to study their interaction mechanisms.
5. To study the effect of compatibility on the degradation behavior in the biocomposites

2.2. Approaches

The study of photo-/bio- degradation of thermoplastics was carried out in order to understand the proper mechanism of degradation, so that correlation could be established in the form of their composites from renewable resources. The commercial plastic granule were purified to remove the additives and irradiated in the UV light. The photo degradability and biodegradability was measured. The growth of fungus, *A.niger* and weight loss during composting was monitored to study the biodegradation. Effect of UV irradiation on the durability was also investigated.

The biocomposites of thermoplastics cellulose fiber were prepared by grafting method as well as direct reactive mixing. The biocomposites were found less degradable under UV light than neat polymers. Biodegradability in compost and culture incubation enhanced after photodegradation. The effect of compatibility on the degradation of host matrix was also studied.

The layered silicates, naturally originating material, were mixed in the polymer, and their degradability was measured. It was found that these silicate filled polymers are more environmentally degradable than neat polymers.

Nanocomposites from starch, a polymer from renewable resources, were prepared with layered silicate and material properties were measured. The primary objective of this study was to find out the effect of different components on the hybrid structure. Degradability was measured in compost and all samples were readily degradable.

Starch was modified and nanocomposites were prepared by filling with organically modified layered silicates in order to obtain highly water resistance products with retained mechanical and degradable properties.

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CHAPTER III:

**DEGRADABILITY OF PE, PP AND EP COPOLYMERS UNDER
BIOTIC AND ABIOTIC ENVIRONMENTS**

3.1. Introduction

Synthetic carbon-based polymers are mostly inert towards microorganisms in the initially produced form. The long-term properties of the synthetic and natural polymers have attracted more interest during the last decade as environmental concerns have increased, due to the accumulation of solid waste, generated by the commodity plastics. Many traditional polymers such as PP, PE and PS undergo very slow biodegradation in both the stabilized and unstabilized forms [1]. It is now recognized that biodegradation can occur by two different mechanisms; namely hydro-biodegradation and oxo-biodegradation [2]. The former is much more important in the case of hydrolysable natural polymers such as cellulose, starch and polyesters whereas the latter predominates in the case of other natural polymers such as rubber and lignin. Lignin normally requires the presence of enzymes that initiate peroxidation [3]. The synthetic hydrocarbon polymers do not hydrolyse under normal environmental conditions but it was shown that, after transition metal catalyzed thermal peroxidation, they biodegrade readily in the presence of a variety of thermophilic microorganisms [4]. Although several kind of formulations filled with starch as biodegradable natural fillers [5-7], starch with pro-oxidants [8-10] have been well documented in order to achieve the biodegradability in synthetic polymers but there is no real significant discussion on short term UV irradiated biodegradability of 'additive free' PP, PE and ethylene-propylene (E-P) copolymers whereas E-P copolymers have a range of useful properties from thermoplastics to soft elastomers, depending upon the relative composition of the two monomers and manner of their entanglement. Photooxidation of these copolymers has already been well reported [11,12]. Scott et.al [13,14] have concluded that microbial action on the polymers is a secondary process and bioassimilation is related to oxygenated products. Albertsson et.al.[15,16] investigated that biodegradation can be initiated by photooxidation where carboxylic acids parts, generated through Norrish type-I and II mechanisms during oxidation process, can be consumed by microbial attack. The present investigation was intended to study the extent and effect of short-term photoirradiation on the biodegradability of PP, PE and E-P copolymers.

3.2. Experimental

3.2.1. Materials

Commercial samples of isotactic polypropylene (PP, Koylene S 30330), low density polyethylene (LDPE, Indothene 16 MA 400) were obtained from M/s Indian Petrochemicals Corp. Baroda, India and heterophasic E-P copolymers (EPF and EPQ) were obtained from M/s Himont Italia. The molar percentages of ethylene content in

copolymer samples was 7.7 and 15.1 % for EPF and EPQ respectively. These polymer pellets were purified by dissolving in refluxing xylene under nitrogen atmosphere and precipitating into methanol. The precipitated polymers were dried at 50°C in vacuum oven. These samples were assumed as additive free and designated as purified samples.

3.2.2. Preparation of films

The method of sample preparation (~100 µm thickness) has already been reported [17]. Films of polymers were prepared by compression molding in a laboratory Carver press using $175 \pm 5^\circ\text{C}$ for 2 minutes and quench cooling with cold water between two Teflon sheets.

3.2.3. UV irradiation

Films were irradiated in SEPAP 12/24 (from M/s Material Physico Chimique, Neuilly / Marne, France) at $55 \pm 5^\circ\text{C}$ in the presence of air. The unit consists of four 400 W 'Medium Pressure' mercury vapor sources filtered by a Pyrex envelope supplying radiation of wavelength longer than 290 nm. These sources are located at four corners of a square chamber (50X50 cm). The inside wall of the chamber is made up of high reflection aluminum. All samples were fixed on a rotating holder located in the center of the chamber. Two fans on the wall of the chamber are monitored by a Eurotherm device and afford a regulation of the temperature of samples ($\pm 2^\circ\text{C}$ between 50-65°C). All samples were irradiated for different time intervals. The details of the equipment are described elsewhere [18].

3.2.4. Viscosity Measurement

Decalin (decahydronaphthalene) was purified by percolation through 100-200-mesh chromatographic grade silica gel, which removes naphthalene, tetra-hydronaphthalene and oxy-compounds [19]. To inhibit oxidation, 0.1 wt % 2,6-di-ter-butyl-p-cresol was added to redistilled decalin. The intrinsic viscosity $[\eta]$ was measured by using successive dilution of only one solution (concn. = 0.2 wt %) at $135 \pm 1^\circ\text{C}$ in decaline. The error due to expansion of flask at 135 °C is negligible as preheated flask and pipette (140 °C) was used to mix the solvent in Ubbelohde viscometer. Samples were taken into viscometer and flow behavior of material was monitored.

3.2.5. Incubation in compost

The biodegradability tests were performed in a laboratory scale composter and the size of films was 5X5 cm. (5 replicates). The constitution [20] of solid waste mixture (compost) used for biodegradability testing of photooxidized and neat samples was as follow: (dry

weight): 40.8 % shredded leaves, 11.4 % cow manure/ dung, 15.8% newspaper and computer paper, 2% white bread, 7.8 % saw dust, 19.2 % food waste (dry milk, potato, carrot, banana and other vegetables) and 3.0 % urea. Total dry weight was ~5 kg. The moisture content was maintained by periodic addition of water and temperature profile of the compost during testing is shown The composting bin was covered by small fragments of green grass and moisture content was maintained by periodically spraying of water. To avoid anaerobic conditions, the bin was constantly aerated with oxygen through a hollow tube. Composting temperature varied with the temperature of the surrounding atmosphere. The temperature profile of compost is given in Figure 3.1 .

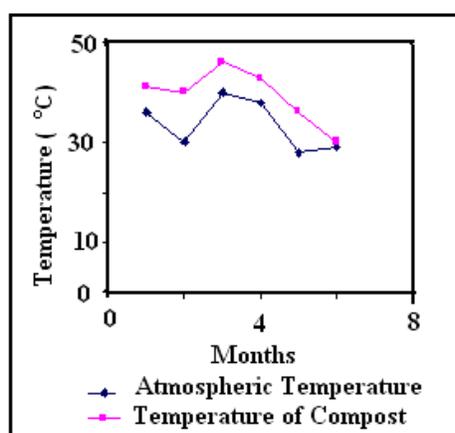


Figure 3.1 Compost temperature changes during study

3.2.6. Incubation in culture

The nutrient salt agar for *A.niger* was prepared by dissolving potassium dihydrogen phosphate (0.700 gm.), magnesium sulphate (0.700 gm.), ammonium nitrate (1.0 gm.), sodium chloride (0.005 gm.), ferrous sulphate (0.002 gm.), manganese sulphate (0.001 gm.) and agar 15.00 gm. in 1 Lit. of distilled water. After sterilizing the medium at $120 \pm 5^\circ\text{C}$ for 25 minute, pH was adjusted between 6.5-7.0 by the addition of 0.1 N solution of NaOH. For providing the solidified agar layer (depth 4-7 mm) nutrient salt was poured into sterilized petri dish. The surface of test specimen (5 X 5 cm) was inoculated by spraying the spore suspension. To avoid the contamination, petri dishes were wax sealed after incubation at $28\text{-}30^\circ\text{C}$ and 85-90 % humidity for ~6 weeks. Growth rating procedure was as follow [25]:

Table 3.1. Growth rating procedure by fungus

Growth	Rating
None	0
Less than 10 % growth	1
10-30%	2
30-60 %	3
More than 60%	4

3.2.7. FT-IR Spectroscopy

The samples were analyzed by Perkin-Elmer 16 PC FT-IR instrument and photoproducts were identified with good resolution. Irradiated samples were either analyzed immediately or were stored at 0°C until analyses were performed because of instability of oxidized polyolefins at room temperature as they can slowly oxidize during this period. The functional group generation was monitored after UV irradiation. Samples were fixed onto an aluminum holder and spectra were obtained using 10 scans summation at a resolution 4 cm⁻¹. IR rays were passing through a very small slit in the samples to minimize the scattering of light. Increase in the concentration of functional groups, generated during photodegradation by UV irradiation, was monitored by the measurement of Carbonyl and Hydroxyl Index (area under the peak).

3.2.8. Scanning Electron Microscopy (SEM)

The UV exposed films were placed in stoppered bottles containing osmium tetroxide (2 % aqueous) and allowed to stand for 48 h. The stained samples were dried under vacuum for 24 h at 50°C. These gold-coated samples were examined under electron microscope (Leica Cambridge Stereoscan 440 model) for morphological changes. Morphological changes of virgin and modified samples were briefly investigated

3.3. Results and Discussion

3.3.1. Incubation in Compost

Nature's litter is acceptable because it is biodegradable, even though it may take several years to be bioassimilated completely into the ecosystem whereas, plastics (particularly polyolefins) is normally considered as a non-biodegradable when discarded after the end of useful life in comparison of the time scale where the nature's materials assimilated into

biosystem. Most studies of the biodegradation of polymers / plastics indicates that the polymer is inert and has good microbial resistant. This feature has made it an ideal material for food packaging. Weight loss is one of the most valuable data indicating the actual biodegradation of polymeric material after composting whenever validated by parallel monitoring of the neat respirometric microbial activity bound to the carbon content of the sample under testing. The weight loss of 0, 50 and 100h irradiated, compost buried, polymer samples was measured periodically 1, 2, 3, 4, 5, and 6 months from the compost, after washing the samples with distilled water and drying in vacuum oven at 60-65°C till constant weight. Figure 3.2 (A),(B) and (C), illustrates the comparative weight loss, per surface area in g/cm^2 of irradiated and unirradiated polymer samples related to the incubation time in compost. Degradation rate (gravitational weight loss) increased rapidly with the increasing in irradiation period. Among all the samples, 100h irradiated films showed much more weight loss after five months and were unrecoverable. Sample of PP are showing comparatively high linear increase in degradation than observed for LDPE after 6 months, indicating the more susceptibility of PP to microorganisms of compost during degradation process furthermore this fact was supported by more weight loss in PP (in both forms irradiated and unirradiated) in comparison of other samples. In the case of E-P copolymers, degradation rate was increased rapidly after four-month incubation and both samples (EPF and EPQ) were not recoverable after 6 months, suggesting that initially the degradation rate was slow due to comparatively less degradable ethylene component. The 50h irradiated samples showed significant weight loss in both the copolymers but less than 100h irradiated. During the observation of unirradiated samples, weight loss of PP was higher than EPF in compost after six months. We did not study the kind of enzymes used by microorganism during the consumption of polymer samples.

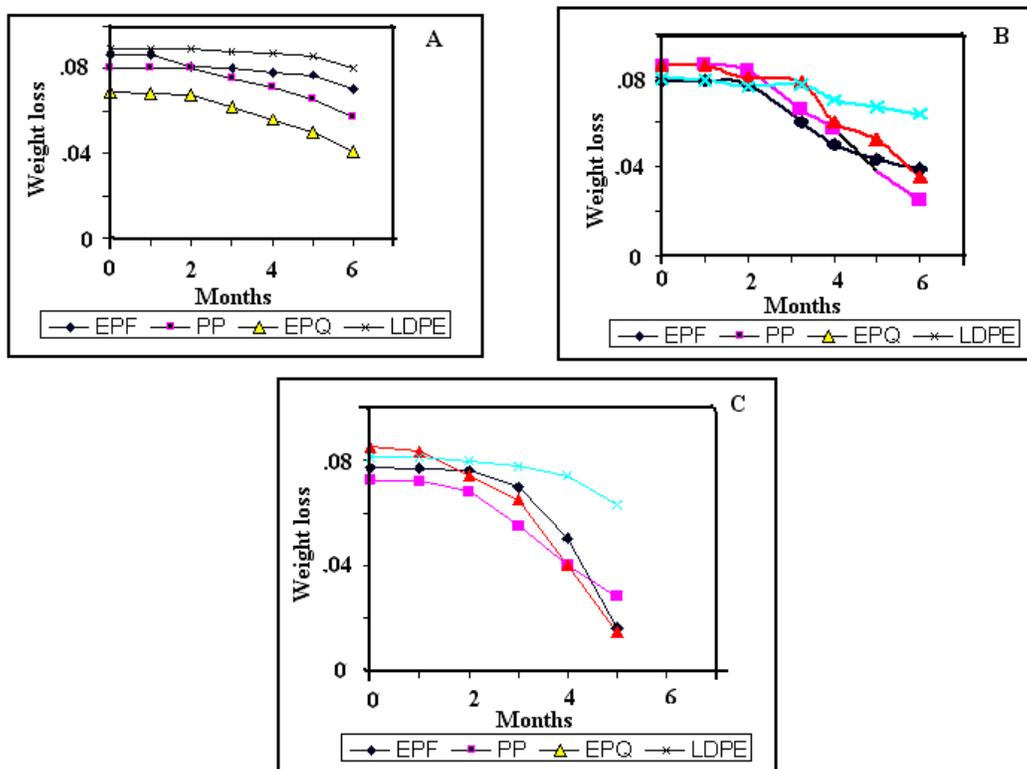


Figure 3.2. Weight loss of samples [A, without irradiation, B, 50 and C 100 h irradiation respectively]

3.3.2. Variation in viscosity

The variation in intrinsic viscosity $[\eta]$ of PP, EPF, EPQ and LDPE films after photooxidation and burial in the composting environment are tabulated in the Table 3.2. Ethylene content has an effect on molecular weight of pure PP matrix, therefore, $[\eta]$ of EPQ is higher than EPF of un-irradiated samples. The $[\eta]$ of irradiated samples was decreased as a function of irradiation time and composting whereas, negligible changes were found for unirradiated samples. A gradual decrease in $[\eta]$ was observed after one month for all the 100h irradiated samples in the composting environment with the incubation time. The presence of any appreciable cross-linking was not observed in this system as films remained completely soluble in decaline. The 50 h irradiated samples of PP and EPF showed a significant decrease in $[\eta]$ after the burial in the compost but in the case of LDPE and EPQ no such type marked decrease was observed.

Table. 3.2. Variations in the intrinsic viscosity $[\eta]$ of irradiated and incubated [M= months]

M	LDPE			PP			EPF			EPQ		
	Irradiation time (hr.)											
	0	50	100	0	50	100	0	50	100	0	50	100
0	3.41	1.98	.785	1.96	.416	.095	2.56	.634	.092	2.89	.701	.096
2	3.40	1.53	.554	1.80	.310	.065	2.40	.600	.062	2.87	.659	.076
4	3.31	.909	.402	1.51	.200	.043	2.40	.501	.041	2.86	.600	.049
6	3.10	.654	.098	1.18	.101	-	2.30	.369	-	2.80	.401	-

3.3.3. FT-IR Spectroscopy

The photodegradation can be followed by measuring the level of carbonyl and hydroxyl groups, by monitoring the area under the peak. Several type of functional groups formed during UV irradiation by Norrish type I (N I) and Norrish type II (N II) mechanisms (Figure 3.3.a). Figure 3.3 (b),(c) and (d) shows the hydroxyl and carbonyl changes and their rate of formation upon irradiation respectively. A very broad hydroxyl absorption region ($3700-3200\text{ cm}^{-1}$) with a maximum centered at 3400 cm^{-1} during photooxidation appeared. This band is due to the neighboring intramolecular hydrogen bonded hydroperoxide and alcohols. Hydrogen bonded hydroperoxide (3420 cm^{-1}) and associated alcohols (3380 cm^{-1}) were also present. The absorption in hydroxyl region is more intense in PP and EPF. The carbonyl region ($1850-1550\text{ cm}^{-1}$) is broad in PP and EPF copolymer but sharp and narrow in LDPE and EPQ. The absorption at 1712, 1722, 1740 and 1785 cm^{-1} has been assigned to carboxylic acid, ketone, ester and lactones, respectively [21-22]. The microbiological process which lead to the destruction of natural polymers such as starch, cellulose and proteins during exposure to soil is well understood. However, for the commercialised synthetic polymers, there are conflicting claims regarding their sensitivity to microbiological attack [14,15]. The useful lifetimes (normally measured by embrittlement) of films prepared from synthetic polymers when exposed to compost is of relevance to many areas. The manner and rate of degradation of a polymer are dependent on the mechanism of degradation and on the acceleration of process. It is a known fact that [27] paraffins having 10-20 carbons can be assimilated by *Mycobacterium*, *Candida*

and *Pseudomonas*. Microorganisms preferentially use n-paraffins, whereas the corresponding branched isomers remain completely inert to the biodegradation. The mechanism consists of generation of terminal carboxylic acid groups, which undergoes beta oxidation. This process removes two carbon fragments from Acetyl-CoA complex, which is formed after reaction of carboxylic acid with Co-enzyme A. Finally carbon dioxide and water releases after entering the citric acid cycle from these carboxylic acid containing short chains. Such type of functionalized chains may form in these polymers also, either by photodegradation or by microbial oxidation of terminal methyl groups during composting. This microbial oxidation in samples was confirmed as primary alcohol did not form upon treating of abiotically aged samples with NaOH [14]. The terminal carboxylic groups may also formed from the breaking of ester bonds, generate during photo degradation (Figure 3.3 (e)). Figure 3.3 (f) shows the peak of carbonyl group before and after composting of EPF copolymer and it is evident that after incubation in compost there was a decrease in the carbonyl region which must be due to the release of short chain acids in the form of degradation products during the biotic step in a similar was as in paraffins. (Figure 3.3 (g)) [15].

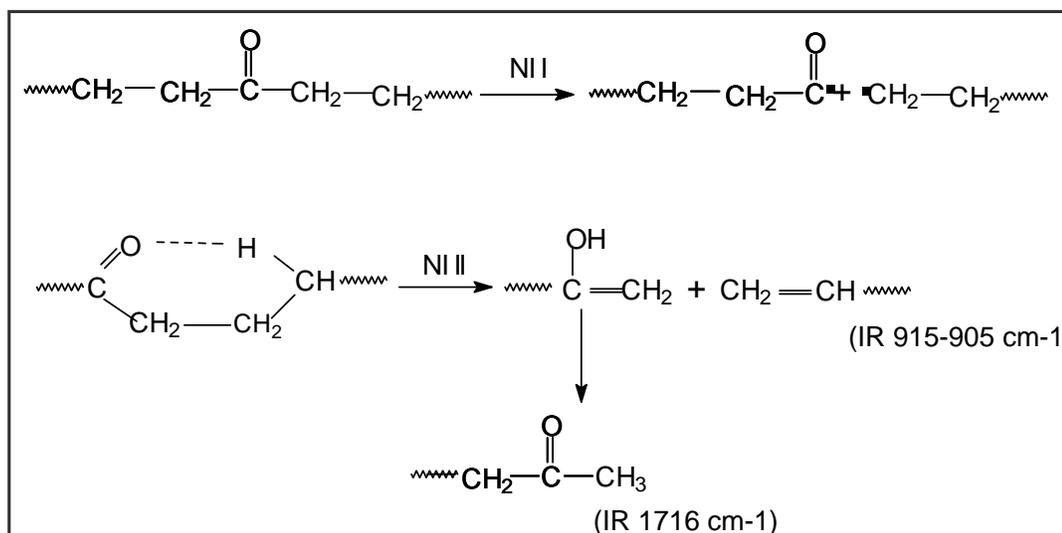


Figure 3.3.(a), Norrish type I (NI I) and Norrish type II (NI II) mechanisms of photodegradation

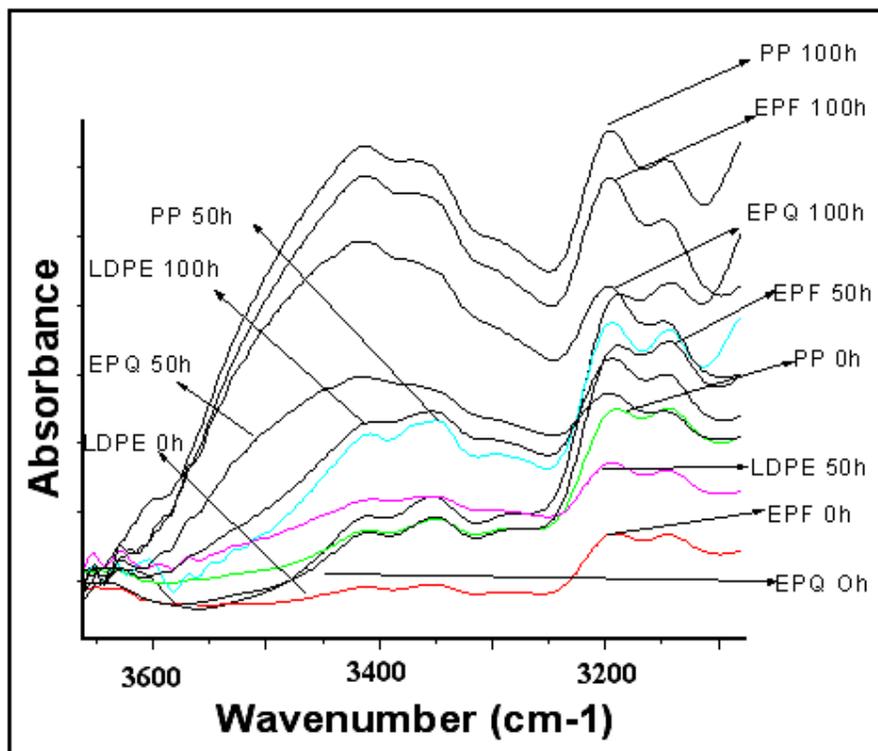


Figure 3.3 (b), Increase in hydroxyl region during UV irradiation of samples

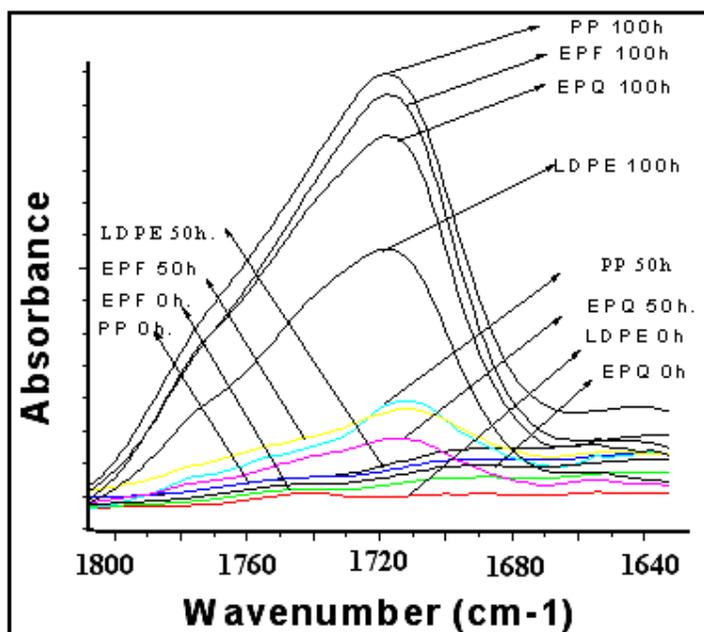


Figure 3.3. (c), Increase in carbonyl region during UV irradiation of samples

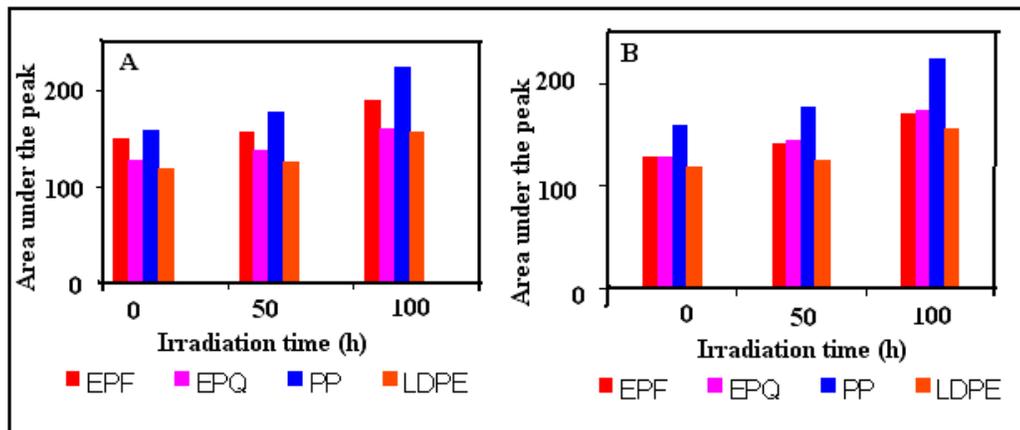


Figure 3.3. (d), Rate of formation of carbonyl (a) and hydroxyl (b) group formation

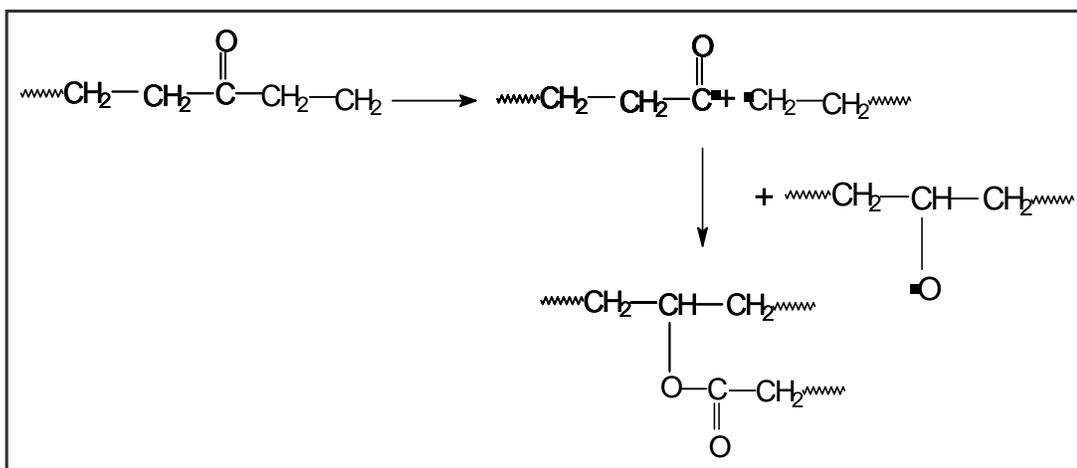


Figure 3.3 (e), Formation of ester during photodegradation

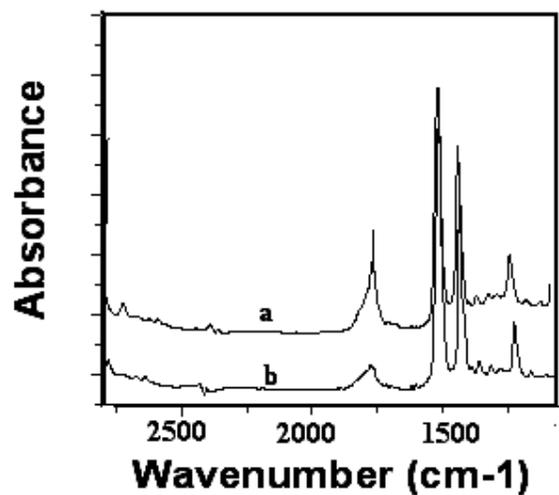
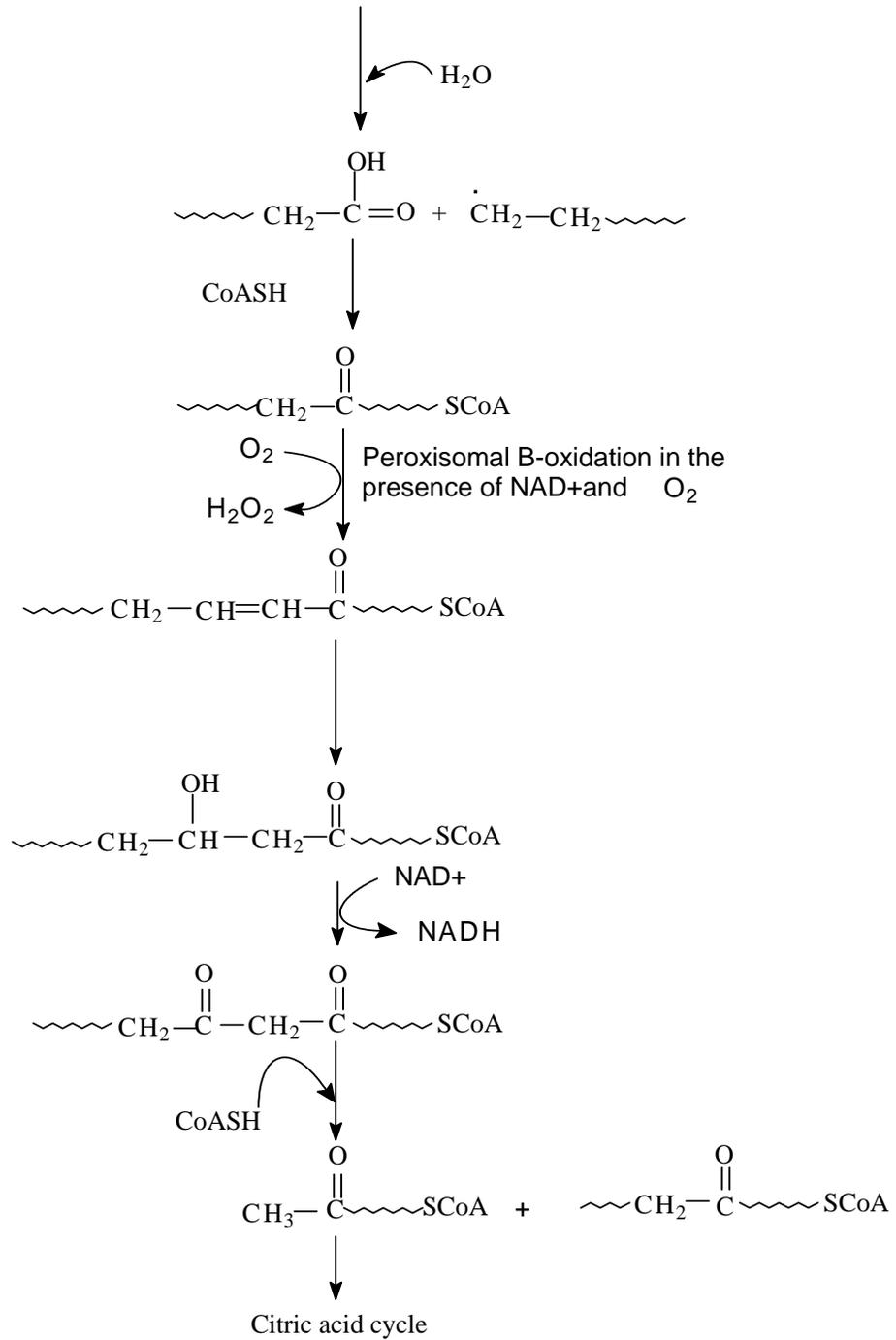


Figure 3.3. (f), UV irradiated EPF before (a) and after composting (b)

Proposed mechanism of biodegradation :

ESTER GENERATED DURING ABIOTIC DEGRADATION



CoASH == Co-enzyme

Figure 3.3 (g), Biodegradation mechanisms in polyolefin

3.3.4. Incubation in culture

Visual growth rating [26] test is valuable in assessing the performance of polymer during the use under such conditions. The samples were used as a sole carbon source for fungus e.g. *A.niger*. Table 3.3 represents the fungal colonization data (visual growth) on polymer films surface after 6 weeks of culture incubation but the initiation of fungal growth is seen by microscope within 10-15 days. The absence of any colonization in controlled petridish (petridish without film sample), clearly suggests that fungus is using polymer films as a source of survival, as there was complete absence of carbon in the nutrient agar. Among unirradiated samples, microscopic growth was observed only on PP, EPF surfaces after 6 weeks. In the case of 100h irradiated samples, the coverage of film surfaces by fungus was much more than others, and further, it may be due to the easy consumption or use of short chains as energy source by fungus, generated during the photo oxidation. The EPF films are showing high colonization than EPQ which is attributed to the more ethylene content in EPQ. Intrinsic viscosity $[\eta]$ of culture incubated samples did not change significantly for 0 and 50h irradiated samples, whereas, an increase in 100 h irradiated samples may be due to the more number of long chains remaining after elimination of low mol. wt. short chains by fungal attack.

Table 3.3. Visual growth rating of *A. niger* on polymer films [W = weeks]

W	LDPE			i-PP			EPF			EPQ		
	Irradiation time (hr.)											
	0	50	100	0	50	100	0	50	100	0	50	100
1	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0	0	0
3	0	0	0	0	1	1	0	1	1	0	0	1
4	0	0	1	1	2	2	0	1	2	0	1	2
5	0	1	2	2	2	3	1	2	2	0	1	2
6	0	1	2	2	3	4	1	2	4	0	2	3

3.3.5. Morphological aspects

Morphological changes upon UV irradiation of copolymers have been studied in our earlier work [25]. Figure 3.4 (a), (b), (c), (d), (e) and (f) are showing the scanning electron micrographs of irradiated and composted samples of PP, EPF, EPQ and LDPE respectively, it is evident from these micrographs that, there is much more surface deformation in 100h irradiated PP and EPF. Among 50h irradiated samples such type of deformation or deepness of erosion was very less which is due to the presence of less amount of oxidation products in comparison to 100h irradiated samples, generated during photoirradiation of polymer, and their more consumption by microbes, resulting in a good surface erosion in polymer films. A network of crack formation was observed with an increase in irradiation time. Formation of micro-cracks on the polymer surface is due to chain scission of polymer after UV irradiation. The cavities on surface were observed after composting of irradiated samples, suggesting that microorganisms penetrate polymer matrix during degradation process. The presence of small and large cavities on the surface may be due to the absence of uniform distribution of short branches or photodegradable products in polymer matrix, which are preferable 'foods' for microorganism.

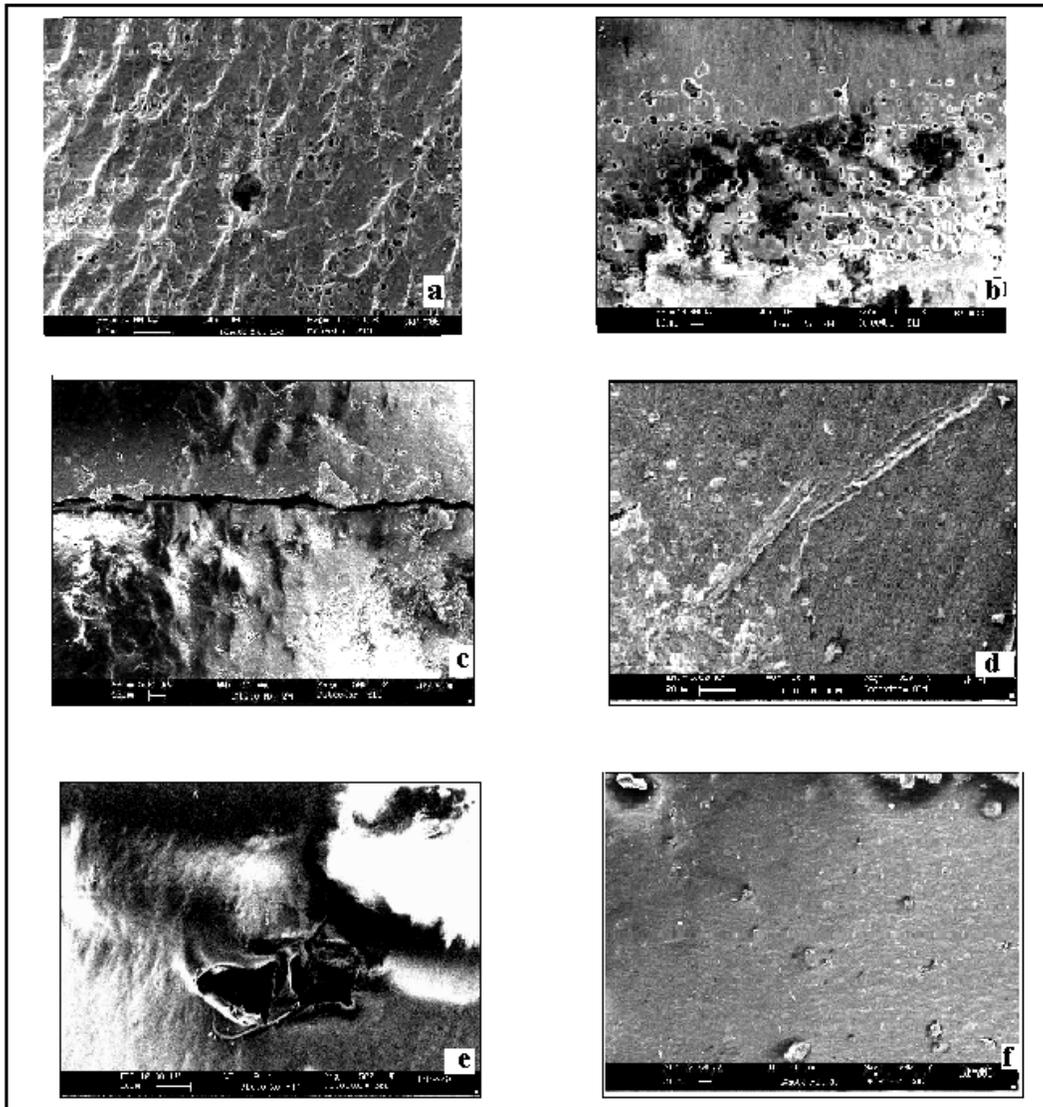


Figure 3.4. 100hr irradiated samples of EPF (a), PP (b), EPQ (c), LDPE (d) and 50 hr irradiated sample of PP (e) and EPF (f) after composting

3.4. Conclusions

The study of photo-/bio-degradation was performed under biotic and abiotic conditions and possible mechanism of degradation was studied. The hydroxyl and carbonyl groups increased rapidly from 0-100h UV irradiation. In general, a decrease in intrinsic viscosity was also observed with the irradiation and incubation time in compost. Polypropylene was more susceptible than low density polyethylene to microbial attack in neat and irradiated samples. The higher weight losses in low viscosity and longer irradiated samples, suggested that chain scission and oxidized functional groups are important biodegradable units in the biodegradation of polymers. The copolymer composition has an effect on biodegradability as EPF (7.7 % ethylene) degrades faster than EPQ (15.1% ethylene). Increasing viscosity of 100h irradiated samples after culture incubation as well as decrease in carbonyl region in FT-IR spectra after composting must be due to the elimination of those short chains, which are responsible for increases in carbonyl region after absorbing the IR light. In general, it can be concluded that photo-oxidation is a precursor of bio-assimilation [13,14] in the copolymers and it can follow the same pattern during microbial attack as has been proposed for paraffins [15,27].

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CHAPTER IV:

**DEGRADABILITY OF BIOCOMPOSITES PREPARED FROM
CELLULOSE AND PE, PP, EP COPOLYMERS**

4.1. Introduction

The need of biodegradable plastics has been increased during the past decades not only due to the increasing environmental concerns but also for its biomedical applications. The terms 'biodegradation' and 'compostability' are very common but are frequently misused. In biodegradation, the enzymes of the biosphere essentially take part at least in one step during cleavage of the chemical bonds of the material. Notably, biodegradation does not ensure that a biodegradable material will always degrade. In fact, degradation will only occur in a favorable environment, and the biodegradable material will not necessarily degrade within a short time. It is, therefore, important to couple the term biodegradable with the specification of the particular environment where the biodegradation is expected to happen, and of the time-scale of the process. Some commodity plastics can be degraded at every stage of production in both the stabilized [1] and unstabilized form [2] and also undergoes very slow biodegradation. [3,4] It is now well evident that polymer / plastics waste management through biodegradation or bio-conversion is the most suitable solution for 'Plastic Waste Management' among the other traditional methods like Incineration, Pyrolysis, Land filling etc. Several means [5-13], have been used to achieve the biodegradability / biodeteriorability /Photo-biodegradability in polymers. Scott et.al developed a wonderful photo-biodegradable film which can be successfully used to reduce the polymer waste [5-8]. Polysaccharides have been used more frequently as natural fillers for this purpose and well investigated by Griffin [9,10] and Bastioli [11], particularly in polyolefins at fairly low concentrations[12,13]. The major problem in this area seems to be incompatibility between hydrophilic polysaccharides and generally the hydrophobic nature of polymer matrix where the complex mechanism of coupling through coupling agents, morphology of interfaces, surface energy and wetting phenomenon considerations are also necessary [14,15]. Thermoplastic composite made from cellulosic materials either by change in surface tension [16], where hydrophilicity is closely related to surface energy [17], impregnation or by coupling through graft copolymerization [18-21], may be advantageously utilized for the development of biodegradable material with good physical properties and can be helpful to reduce the polymer waste and must also contribute their utility to reduce the vegetal biomass.

Several studies have been reported in the literature on the physical strength and thermal properties of fiber reinforced polymer composites where it has been established that these properties improved after reinforcement [16-21]. Few attempts have been made regarding the photo-/bio-degradation of polymer fiber composite, for example in aqueous

media [22], in terrestrial environment [23], biodegradation after exposing in oxidizing, reducing, hydrogen producing bacteria in bath culture [24] and fungal degradation [25]. There has been no real discussion / report in the literature about the effect of preparation manner as well as UV irradiation on biodegradability of polymer-agro waste composites in composting and culture environments, those could be applicable in our daily life as naturally degradable materials. In the present investigation, two composites, prepared as in earlier studies [26-28] and characterized by FT-IR, were used for the study of the performance against microbial attack in compost and culture of *A. niger* before and after UV irradiation by measuring the weight loss and fungal growth, respectively, with surface morphology changes through SEM and variation in molecular structure by infra red spectroscopy in comparison of controlled PP samples.

4.2. Experimental Part

4.2.1. Material

Polymer material was the same as given in Chapter 1. Maleic anhydride (MAH) was obtained from E. Merck India, and was used after recrystallization. Benzophenone and dicumyl peroxide (DCP) were obtained from Aldrich and were used as received. All the solvents of A.R. grade were taken from S.D.Fine Chem.Pvt. Ltd., India, Coir (*Cocos nucifera*) fibers were collected from raw material by retting process, and activated by immersion in water for 15 days. After sun drying of 10 days and cutting into pieces ~2.5-3.0 mm in length, fiber were washed with distilled water and further dried in vacuum at $55 \pm 5^\circ\text{C}$ till constant weight is achieved.

4.2.2. Preparation of composites

Grafting of MAH (2.0 M) onto polymers was done in a UV reactor ($\lambda \geq 290 \text{ nm}$) for 2h in dry acetone (30 ml) taking benzophenone (0.29M) as a photosensitizer at $65 \pm 5^\circ\text{C}$. This obtained copolymer was dried under vacuum to a constant weight after soxhlet extraction in acetone for the removal of unbounded moieties. Coir fiber were immersed in the solution of graft copolymer in toluene at $80 \pm 5^\circ\text{C}$ for 5 min. keeping the concentration 5 wt.% of copolymer and soxhlet extracted, dried in the same way as mentioned above. These samples were designated as graft fiber composite (GFC). Second type of composites were prepared by direct reactive mixing of polymers, MAH (2% wt.), DCP, 0.2 % wt. and fiber (50: 50 as polymer) at $145 \pm 5^\circ\text{C}$ followed by thoroughly washing in toluene. These composites were named as direct fiber composite (DFC). Polymers used in this preparation was purified by dissolving in xylene under nitrogen atmosphere followed by

solvent extraction in methanol for removal of the additives and it was presumed that now these samples were additive free. Reference films were used as received. Both the composite samples and neat polymers were molded as films (~100 μm) by carver press.

4.2.3. Characterization and performance evaluation

FT-IR, SEM and photo-/bio-degradation was carried out as were performed in Chapter 3 [29-30]. The biodegradability was measured as % weight loss in samples after composting. The constitution of compost was (dry weight): 40.8% cow dung, 11.4% sawdust, 15.8% newspaper and computer paper, 2% white bread, 7.8% shredded leaves, 19.2% food waste (dry milk, potato, carrot, banana and other vegetables) and 3.0% urea. The temperature of the compost increased rapidly during the last days of incubation after an extra addition of the same quantity of cow dung as had initially been added. The samples were kept inside the compost at a depth of 3.5 feet. The surface of test specimen (2.5 X 2.5 cm) was inoculated by spraying the spore suspension for fungal (*A.niger*) growth. To avoid the contamination, petri dishes were wax sealed after incubation at 82-86°F and 85-90 % humidity.

4.3. Results and discussion

4.3.1. Compatibility of fiber and polymer matrix

To characterize the DFC, GFC samples and to measure the esterification extent, FT-IR spectroscopy was performed. The spectra of samples of PP are shown here, as all the spectra in this region were same for all the samples. Esters have two characteristic strong absorption bands arising from C=O and C-O stretching vibrations at shorter wavelengths due to the negative inductive effect of adjacent oxygen atoms that increase the force constant. The spectra of PP-g-MAH and PP blended MAH are shown in Figure 4.1 The absence of any observable peaks at 1360 and 1580 cm^{-1} indicates the absence of anionic form of anhydride with one carboxylic acid i.e., the maleic anhydride is present either in dicarboxylic acid dimer or cyclic form in both forms of PP-MAH samples. This was confirmed by the appearance of peaks at 1780, 1863 cm^{-1} for cyclic anhydride and 1718 cm^{-1} for carboxylic acid dimer; this peak was again confirmed by O-H stretching peak (3200-3300 cm^{-1}) because cyclic dimer has a center of symmetry. Figure 4.2 shows the spectra of both MAH bound PP after fiber treatment where a significantly detectable additional peak from 1740-1750 cm^{-1} is due to the C=O stretching of ester bond, formed between the coupling agent and fiber in the case of GFC whereas in DFC it was hardly detected which could not be used for conformation of esterification. Thus the esterification

(chemically joined cellulose moieties) were present in a greater amount in GFC compared to DFC; this fact was again supported by the high area under the peak at 1160 cm^{-1} in DFC for secondary free -OH group, supporting the presence of high amount of unreacted cellulose fiber than GFC as shown in Figure 4.3. The good extent of esterification in GFC was again confirmed by the lower water absorption (11-13%) than DFC (26%) after 35h at room temperature, and it was due to the lesser number of OH groups in GFC. The appearance of less detectable peak at 1050 cm^{-1} suggesting that primary alcoholic groups of cellulose are also participates in esterification and are likely due to the steric hindrance effect of bulky groups that prohibits the reaction. The broad spectrum near 3330 cm^{-1} (Figure 4.4) arises from -OH group in polymeric structure and since this is present at comparatively lower frequency (bathochromic effect) than the free hydroxyl group, this is due to intermolecular hydrogen bonding by the interaction between -COOH of anhydride and the -OH of fiber. In all the samples grafting efficiency of GFCs were higher than DFCs and the effect of monomer concentration on the grafting efficiency in copolymers was not observed.

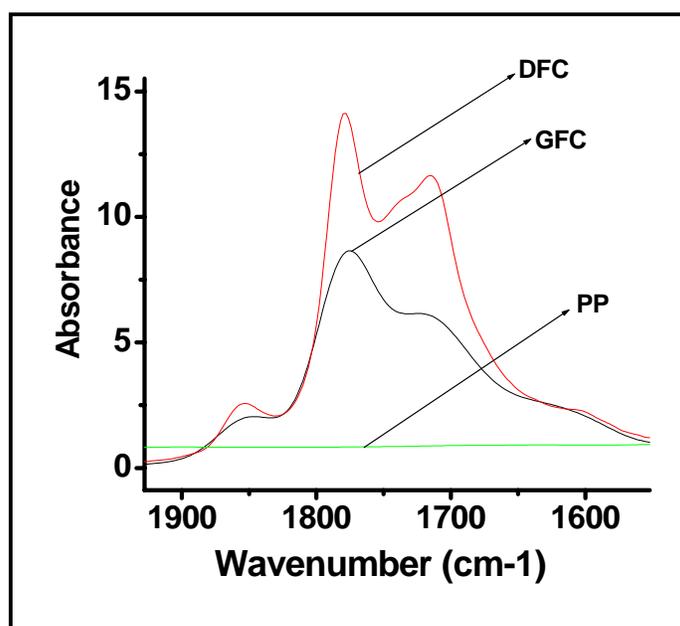


Figure 4.1. FT-IR spectra of PP after treatment with MAH

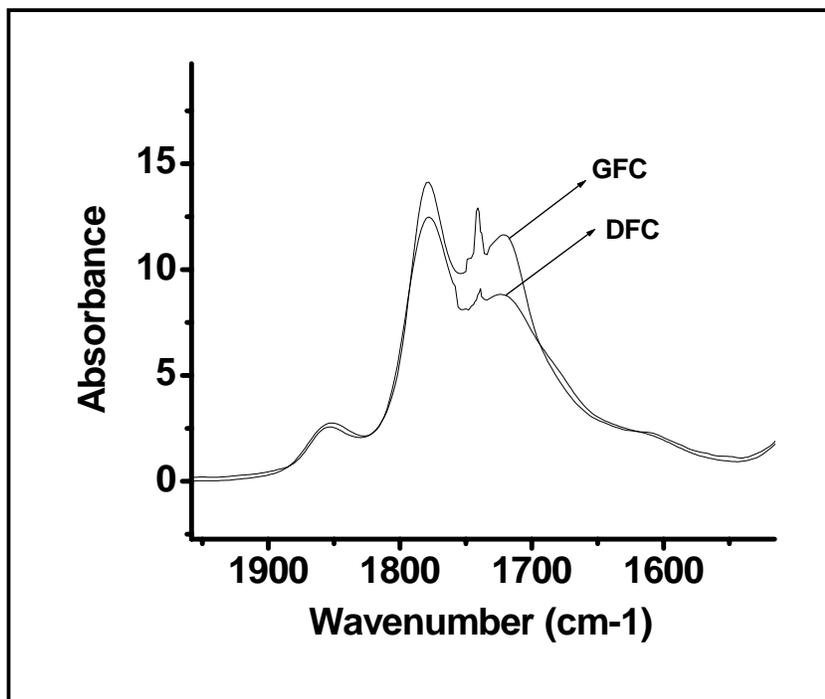


Figure 4.2. Esterification in MAH treated PP by cellulose fiber

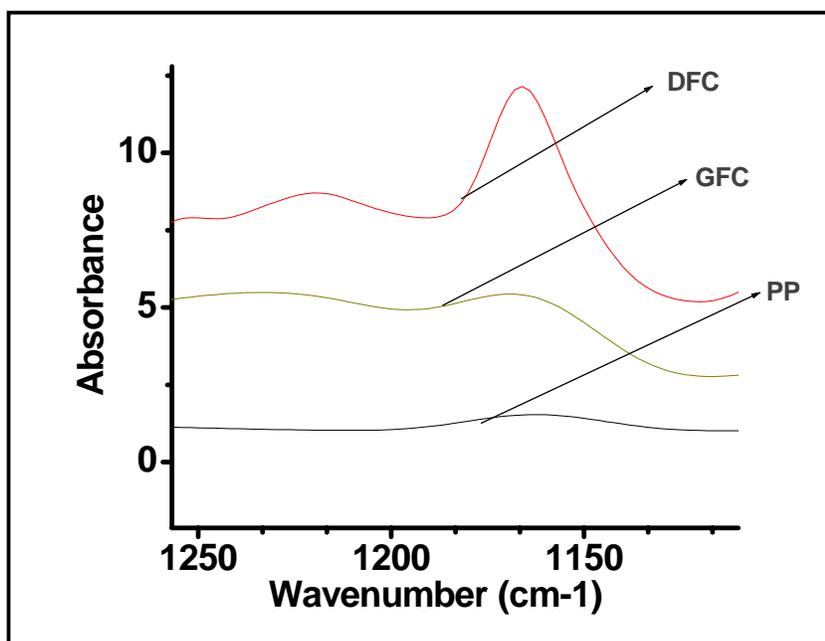


Figure 4.3. Peaks for free OH groups in the composites

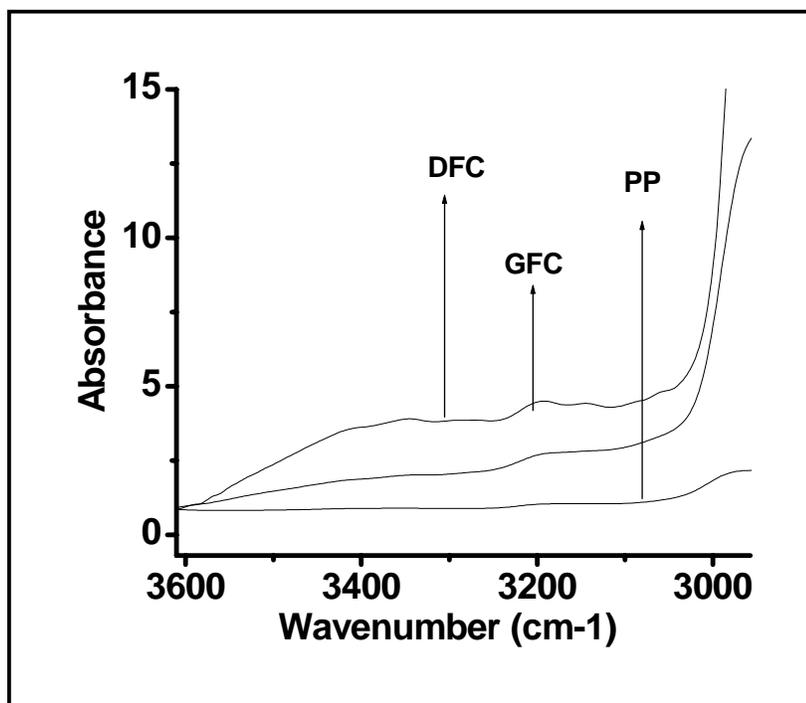


Figure 4.4. Hydroxyl bonding in the composites

4.3.2. Photodegradation

During UV irradiation, cellulosic material undergoes depolymerization or chain scission, leading to the formation of carbonyl groups and fragmentation into non-volatile or volatile products [31]. Bleek et.al. [32], found glucose (6 carbon atom) and arabinose (5 carbon atom) reducing units during the irradiation of oligosaccharides. The photoproducts generated on UV degradation of PP, PE, E-P copolymers have been extensively explained [33,34]. The absorption at 1712, 1722, 1740 and 1785 cm^{-1} for carboxylic acid, ketone, ester and lactones, respectively, are also well studied [35,36]. Monitoring of variations in hydroxyl and carbonyl regions in FT-IR is a conventional technique for measuring the photodegradation in polyolefins as the area of these regions increases during irradiation, but in the composites both groups are already present, and therefore, their appearance creates practical difficulties for the assignment of all peaks in our present system, not only for those forming in host polymer of composite during degradation but also for cellulose materials because of high overlapping of peaks to each other. The changes in hydroxyl and carbonyl region for both composites of PP are presented in Figure 4.5 (a),(b) & 4.6 (a),(b) where it is clear that carbonyl and hydroxyl regions increase in both the composites, also showed more increase for DFC in this region during irradiation which can be used as an

indication for more photodegradability. Further, it is supported by earlier crack formations in DFC and this is because of peroxide initiated photodegradation and consequently generation of keto/carbonyl species. The overall increase in these regions of composites were not as sharp as in neat polymers. The E-P copolymer containing more ethylene was less degradable than copolymer with less ethylene content. No significant difference was observed among DFC samples which were attributed to the higher and almost equal degradation under UV light due to the peroxide generated degradation during preparation. The bands around 3400 cm^{-1} in polymers during photo-oxidation indicated the generation of intramolecular hydrogen bonded hydroperoxides and alcohols. The increase in the unsaturation, as the two peaks generated at 974 & 1009 cm^{-1} for alkene and vinylene groups respectively, in the case of both composites of PP (Figure 4.7), was attributed to the abstraction of H atom corresponding to carbonyl group. This effect is more in DFCs than neat polymers suggesting the sensitization effect of CO groups of the compatibilizing agent.

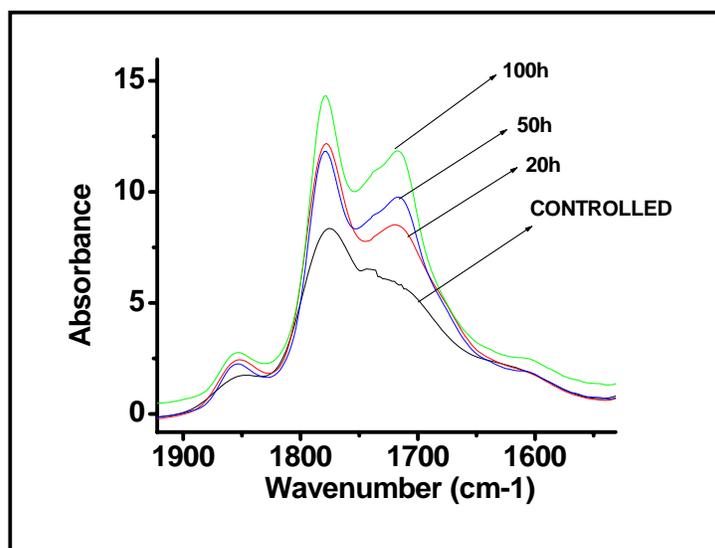


Figure 4.5. (a), Changes in carbonyl group region of DFC of PP during irradiation.

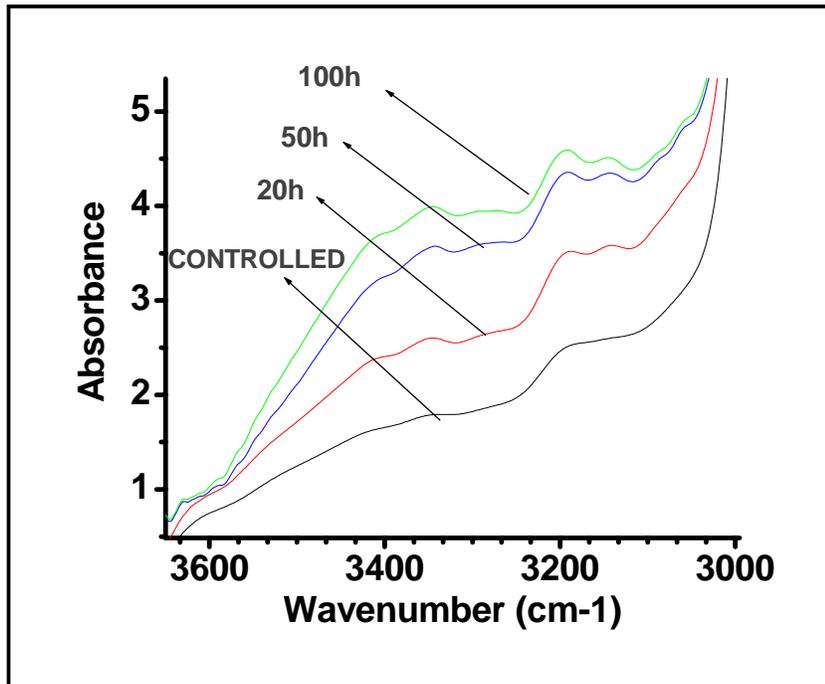


Figure 4.5. (b), Changes in hydroxyl group region of DFC of PP during irradiation

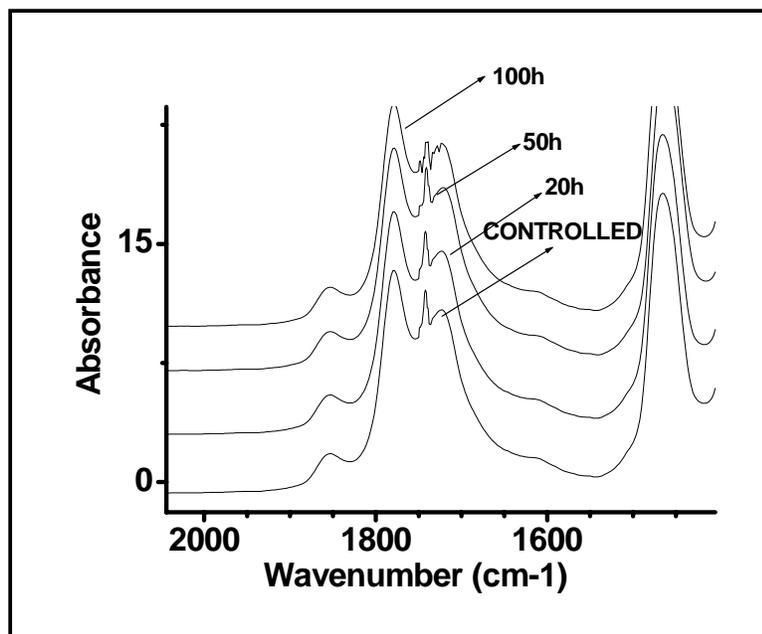


Figure 4.6. (a), Changes in carbonyl group region of GFC of PP during irradiation

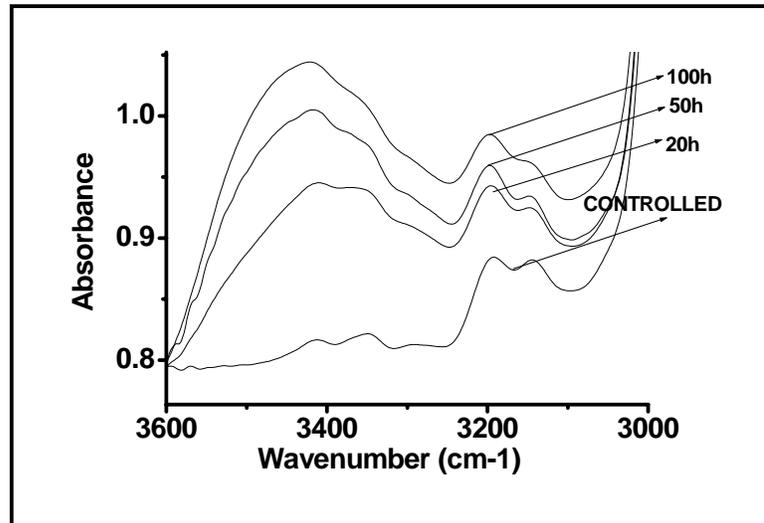


Figure 4.6. (b), Changes in hydroxyl group region of GFC of PP during irradiation

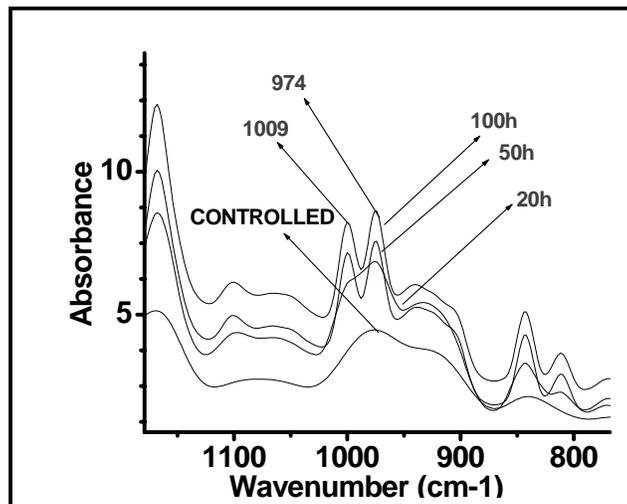


Figure 4.7. Unsaturation variations in DFC of PE composite upon irradiation

4.3.3. Biodegradation

4.3.3.1. Composting

Biodegradability was measured periodically up to 6 months in compost. It was estimated in the term of % weight loss of samples (~100 μ m thickness, 5 replicates) after washing with distilled water and drying in oven for 24h at 50°C. The effect of UV irradiation on biodegradation rate (gravitational weight loss) was also studied for this period. Results of degradation in compost among the unirradiated and irradiated samples of composites are shown in Figure 4.8-4.14. where the decrease in weight of neat polymers was less than both composites, indicating fiber degrade initially by providing hydrophilic surface for microbial adhesion. The higher weight loss of DFC than GFC after 6 months of

composting must be due to the presence of an additional 'facility' for microbial action in the form of degradation products, which have already been generating during its preparation in the presence of free radical generator peroxide. Figure 4.9, illustrates the degradation for 20h UV treated samples of PP. The significant degradation was not observed in initially exposed films, which may be attributed to the formation of initial cross linking via combination of free radicals [37] as at this stage microbes may try to penetrate into matrix of polymer after consuming the nutrients present on the surface and this fact has been eliminated for longer hour irradiation. Weight loss markedly increased for 50 and 100h UV treated samples (Figures 4.10 & 4.11).

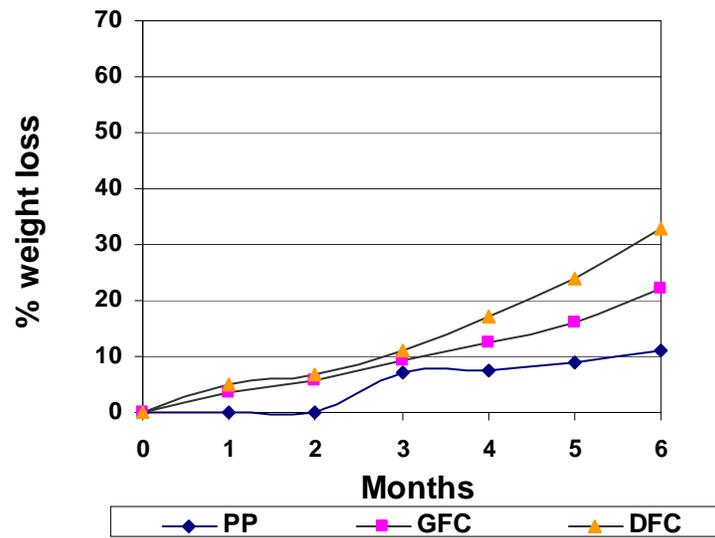


Figure 4.8. Weight loss of unirradiated samples

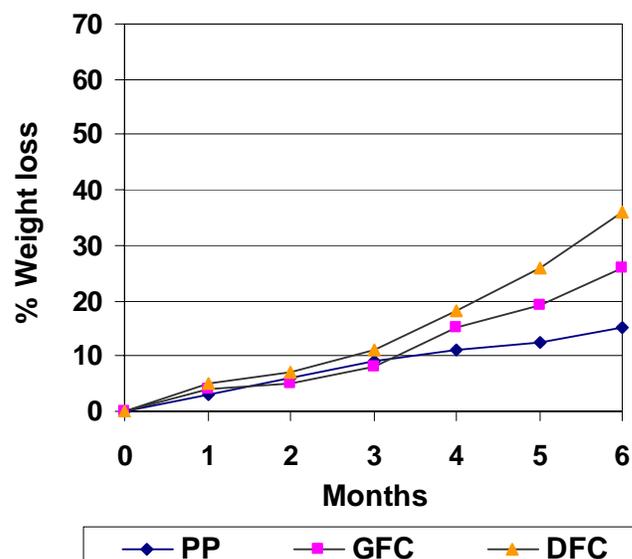


Figure 4.9. Weight loss of 20 h irradiated samples

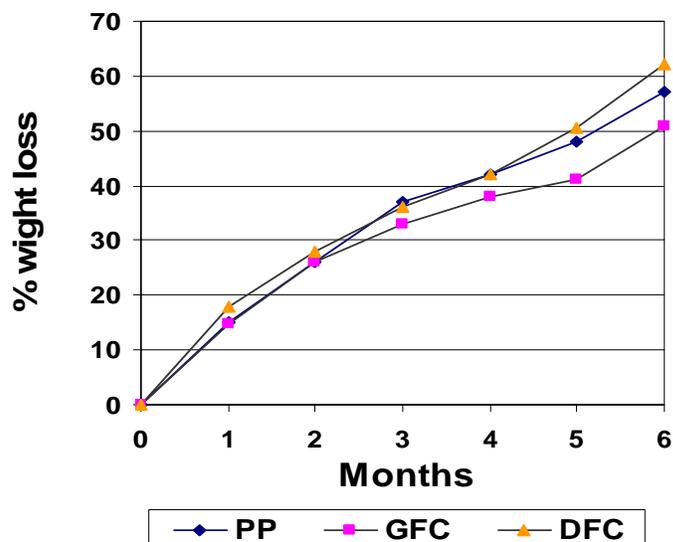


Figure 4.10. Weight loss of 50 h irradiated samples

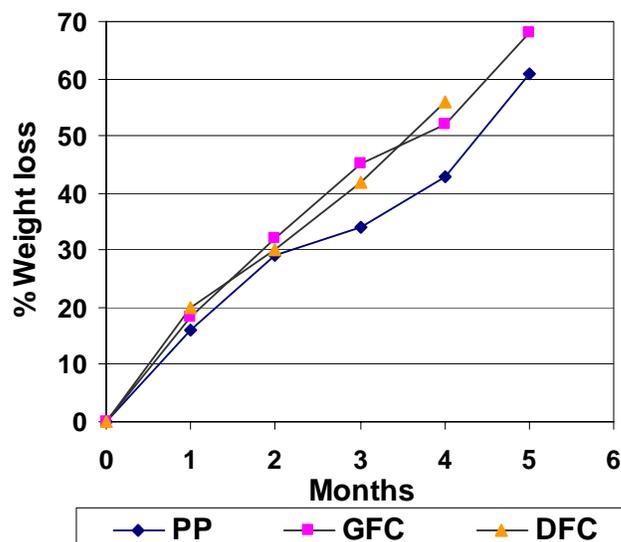


Figure 4.11. Weight loss in 100 h irradiated samples

All the 100h treated samples were unrecoverable after 5 months and DFCs samples could not be recovered after 4 month, here it should be noted that these samples had already become brittle during UV treatment. Figure 4.12-4.14 shows the biodegradation in 100 h UV irradiated and composted samples of PE and E-P copolymers. Higher weight loss of DFCs, that could not be recovered after 4 months, than GFCs can be explained as discussed earlier i.e. the higher degradation of DFCs during preparation. The samples prepared from PE showed degradation lesser than EPQ and EPF .EPF was more degradable in both the environment which indicates that the concentration of monomer can significantly alter the durability. Decreasing carbonyl / ester bond region in FT-IR spectra again strongly suggested the use of polymer as nutrients by microbes through the

well established Albertsson et. al [38-40] mechanism (Figure 4.15). Some facts are appearing necessary to take into consideration for the discussion at this stage. GFC weight loss increased around 68 % after 5 months (in case of PP) and samples could be recovered very carefully whereas DFC weight loss ~ 55 %, (in case of PP) could not recovered in the present system. The protection against brittleness in GFC must be due to the more extent of esterification i.e. more compatibilization, but since ester bond facilitate biological attack by providing a active site for Coenzyme A (Co-ASH) during hydrolysis, these samples underwent high weight loss and retained in the compost for longer time indicating that ester groups play a significant role in the biodegradation. On the other hand, weight loss of DFC (very less esterified or no esterification) was less but the samples was not recoverable due to the brittleness which was caused mainly through extreme chain scission in polymer matrix suggesting chain scission is also an important unit during biodesentegration. In all the cases photo degradation enhanced degradability in biotic environment [41, 42].

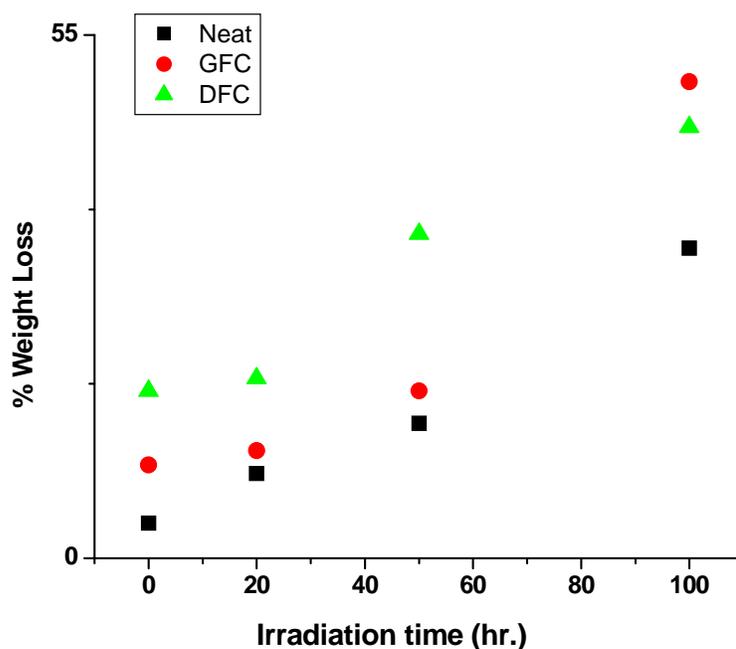


Figure 4.12. Weight loss of 100 hr UV irradiated DFC and GFC of LDPE after composting (DFC after 4 months and GFC after 5 months)

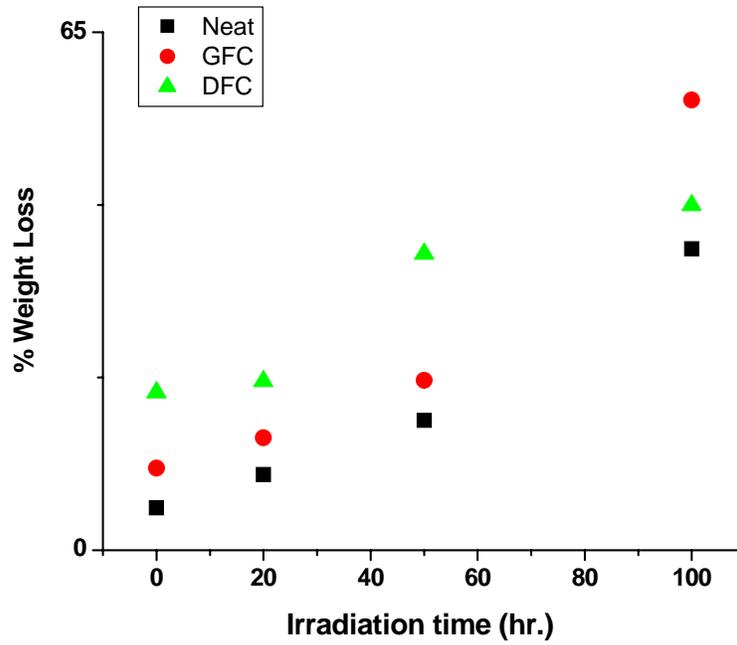


Figure 4.13. Weight loss of 100 hr UV irradiated DFC and GFC of EPQ after composting (DFC after 4 months and GFC after 5 months)

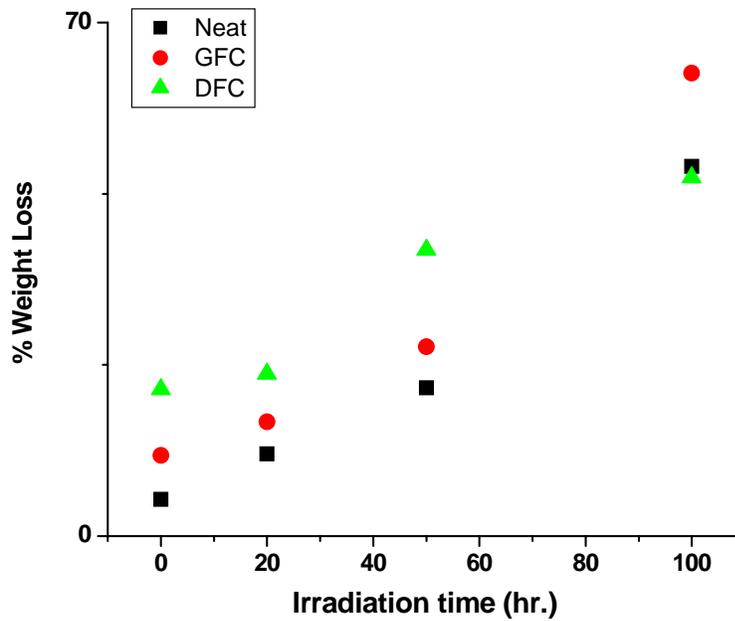
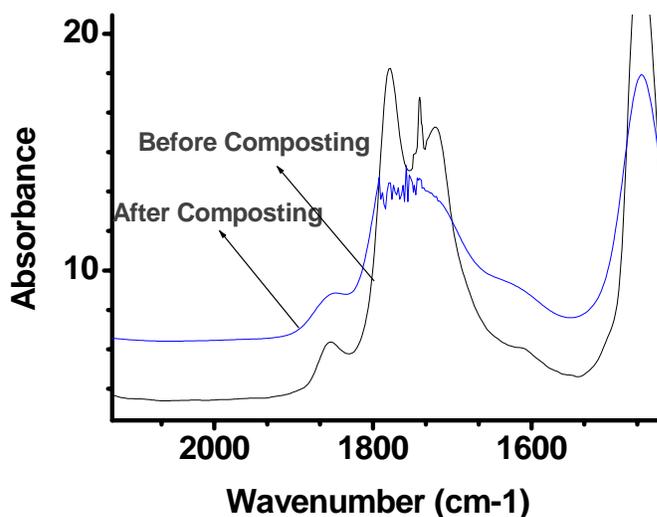


Figure 4.14. Weight loss of 100 hr UV irradiated DFC and GFC of EPF after composting (DFC after 4 months and GFC after 5 months)



4.15. IR Spectra of GFC of PP (100h, irradiated sample) after compost incubation

4.3.3.2. Culture testing

The samples were kept in the culture medium of *A.niger* as a sole carbon source for 40 days and biodegradation characteristics were compared with those in composting. Since longer time is necessary for degradation by fungus, spores were sprayed in more quantities on the surface of specimens including unirradiated samples and at a slightly increased temperature. During the incubation period, the composites were degraded gradually from the surface and characteristic morphology appeared according to SEM. Visual growth rate of irradiated and unirradiated samples are tabulated in the Table 4.1-4.4, and the growth could be seen microscopically after one week. Further the degradability rate was dependent on the irradiation time and irradiated samples were highly colonized by fungus in comparison to unirradiated samples. Fungal coverage was markedly affected by the manner of preparation of composites and copolymer composition.

Table 4.1. Visual growth rating of A.niger on PP composites

Days	PP				DFC				GFC			
	Irradiation time in hrs.											
	0	20	50	100	0	20	50	100	0	20	50	100
10	0	0	0	1	1	1	2	2	0	0	1	2
20	0	0	1	1	1	1	3	2	1	1	2	2
30	1	1	1	2	2	2	3	3	2	2	3	3
40	1	2	2	4	2	3	3	4	3	3	4	4

Table 4.2. Visual growth rating of A. niger on polymer composites of EPF

Days	EPF				DFC				GFC			
	Irradiation time in hrs.											
	0	20	50	100	0	20	50	100	0	20	50	100
10	0	0	0	0	1	1	2	2	0	0	1	2
20	0	0	1	1	1	1	2	2	1	1	1	2
30	1	1	2	2	1	2	3	3	1	2	2	3
40	1	2	2	4	2	3	3	4	3	3	4	4

Among the 50 & 100h irradiated composites, DFCs were highly colonized on surface than GFCs with in 10-15 days, which is quite obvious due the more use of DFCs as energy source by fungus i.e, easy fungal consumable products were present in more amount on the surface of specimens. In the case of GFCs samples, colonization increased gradually from 20-40 days in comparison to DFCs, where such a marked increase was not observed which must be due to the large availability of easily fungal consumable products initially and as soon as it becomes limited, fungal growth slowed down whereas in GFCs, slow ester link cleavage was in progress consequently biodegradation rate increased as a function of time. The greater degradation (visual colonization) of DFCs in the case of unirradiated samples than in GFCs as it was same during composting, indicates that the

functional groups generated during photooxidation, are initially responsible for the consumption of films by *A.niger*.

Table 4.3. Visual growth rating of *A. niger* on polymer composites of EPQ

Days	EPQ				DFC				GFC			
	Irradiation time in hrs.											
	0	20	50	100	0	20	50	100	0	20	50	100
10	0	0	0	0	1	1	1	2	0	0	0	1
20	0	0	0	1	1	1	2	2	1	1	1	2
30	0	1	1	2	1	2	2	3	1	2	2	3
40	1	1	2	3	2	2	3	4	3	3	4	4

Table 4.4. Visual growth rating of *A. niger* on polymer composites of PE

Days	PE				DFC				GFC			
	Irradiation time in hrs.											
	0	20	50	100	0	20	50	100	0	20	50	100
10	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	1	0	0	1	0	0	0	1
30	0	0	0	1	1	1	1	2	0	1	2	2
40	0	1	1	2	2	2	3	3	1	2	3	3

4.3.4. Morphological aspects

SEM is a significant and reliable tool to measure the morphological changes of degraded polymer and crucial photographs of some interesting observations of photo-, bio- and photo-biodegraded samples are highlighted in Figure 4.16-4.18. The morphological changes of UV irradiated and compost / culture incubated samples have been studied in the earlier report [30] where highly cracked network and deep eroded surface was found during the degradation of samples. The fiber coupling which may be responsible for binding the polymer matrix during degradation supported from the Figure 4.16 (a) and

4.16 (b) of 100h irradiated and culture incubated GFC on high and low magnification respectively, where it can be seen that fibers degraded much more than the other portion of composite and two type of area, one partially intact and other degraded, showed that fungus is attacking in different mode of intensity according to the substrate i.e degradation process occurring in a selective manner. From the Figure 4.16 (a), it seems that two parts of the polymer were joined together by fiber and as soon as fungus consumed this fiber, these parts start to separate and probably due to the absence of such type coupling in DFC, fragmentation takes place more rapidly and specimens could not be recovered. Cracked structures were observed in SEM micrograph of one part of GFC after last limit of compost incubation, where PP portion was cut down carefully (Figure 4.16 d). SEM micrograph of only polymer part of 100h irradiated and 4 months compost incubated DFC is shown in Figure 4.16(c) where a perfect separation of polymer surfaces is clearly visible. SEM of same sample (Figure 4.17 (e)), showed the presence of large cavity and fine fragmentation of GFC of polymer. Small vacant tracks in 100h irradiated and 40 days culture incubated sample (Figure 4.17 (f)) clearly indicated that mycelia of fungus had grown but was washed out during the washing. Figure 4.17 (g), and (h) shows the micrographs of 100h irradiated GFC and DFC of PP respectively. The formation of cavities on DFC surface is due to the removal of volatile oxidation products. Figure 4.18 (i) and (k) showed the morphological changes of degraded samples of EPF (GFC and DFC respectively) where, crack formation was lesser in GFC than DFC. In this case, highly cracked surface of DFC were observed which strongly suggest higher biodisintegration in DFC. From Figure 4.18 (j) and (l) of 50h irradiated and culture incubated GFC of EPQ, it is evident that the mycelium of fungus were grown clearly which may penetrate the film surface with time of culture incubation.

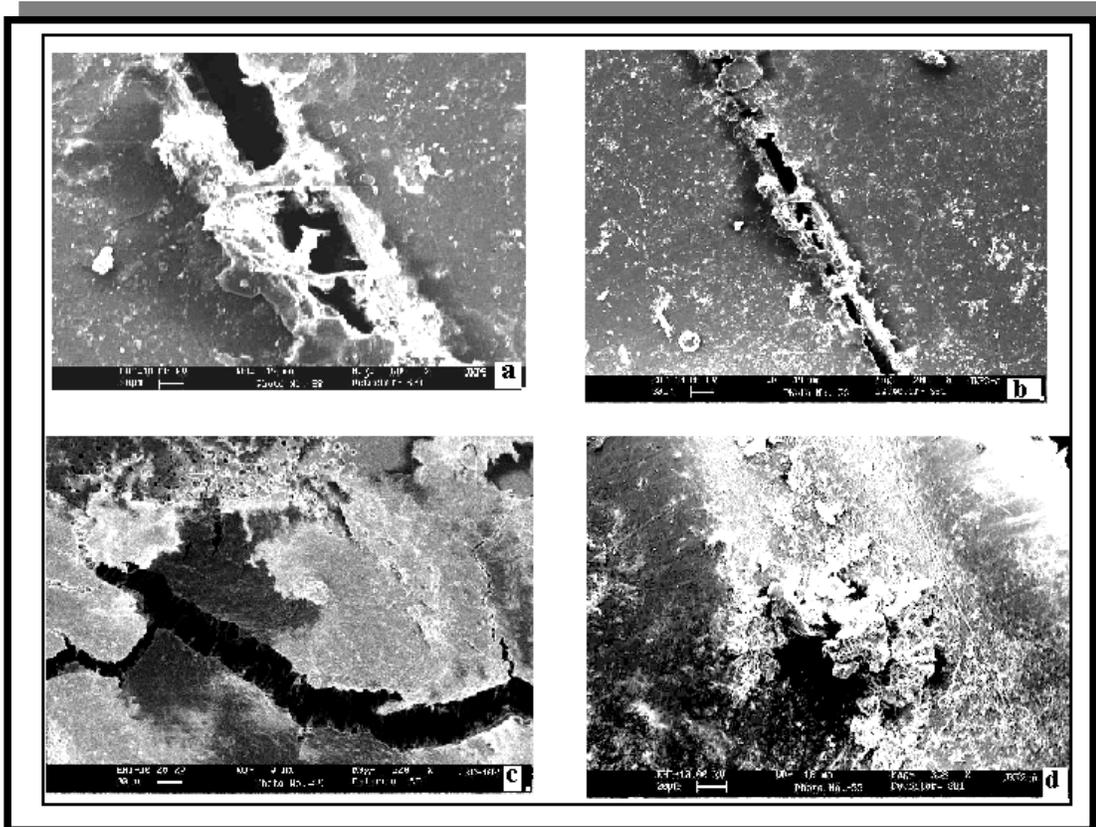


Figure 4.16. SEM micrographs of different degraded samples of a-d.

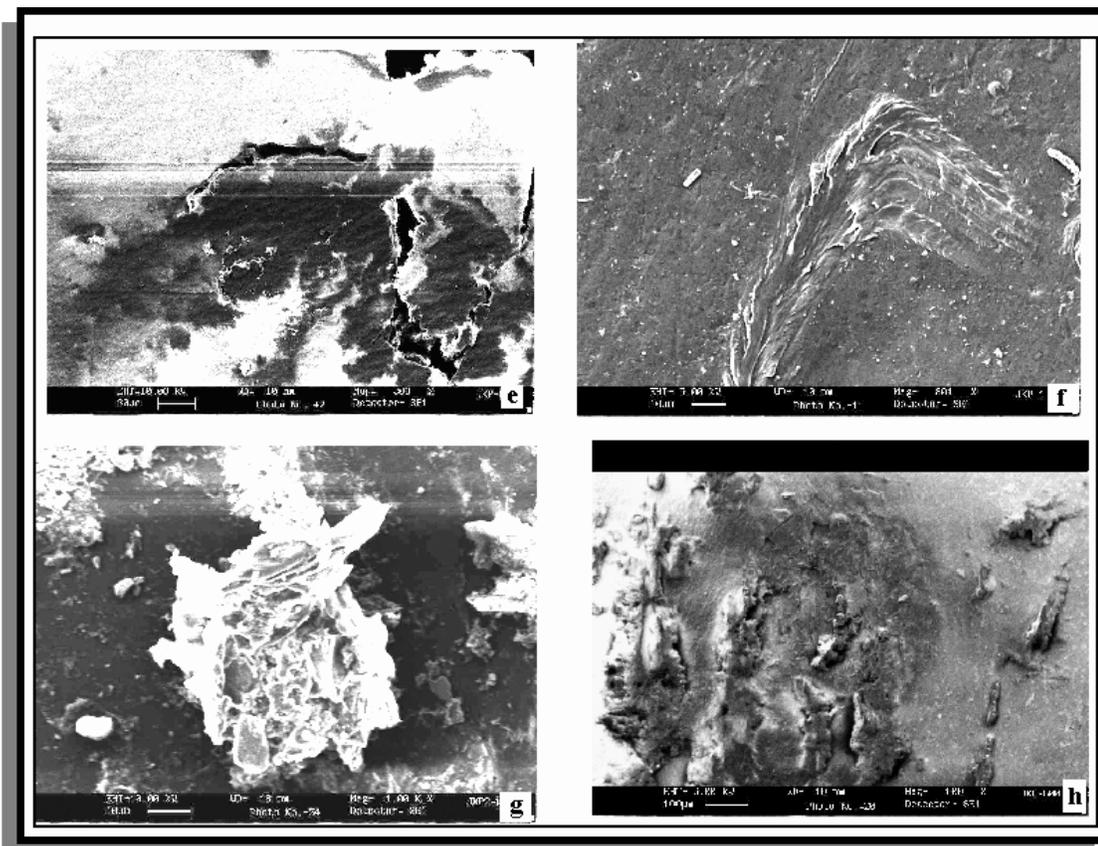


Figure 4.17. SEM micrographs of different degraded samples of e-h.

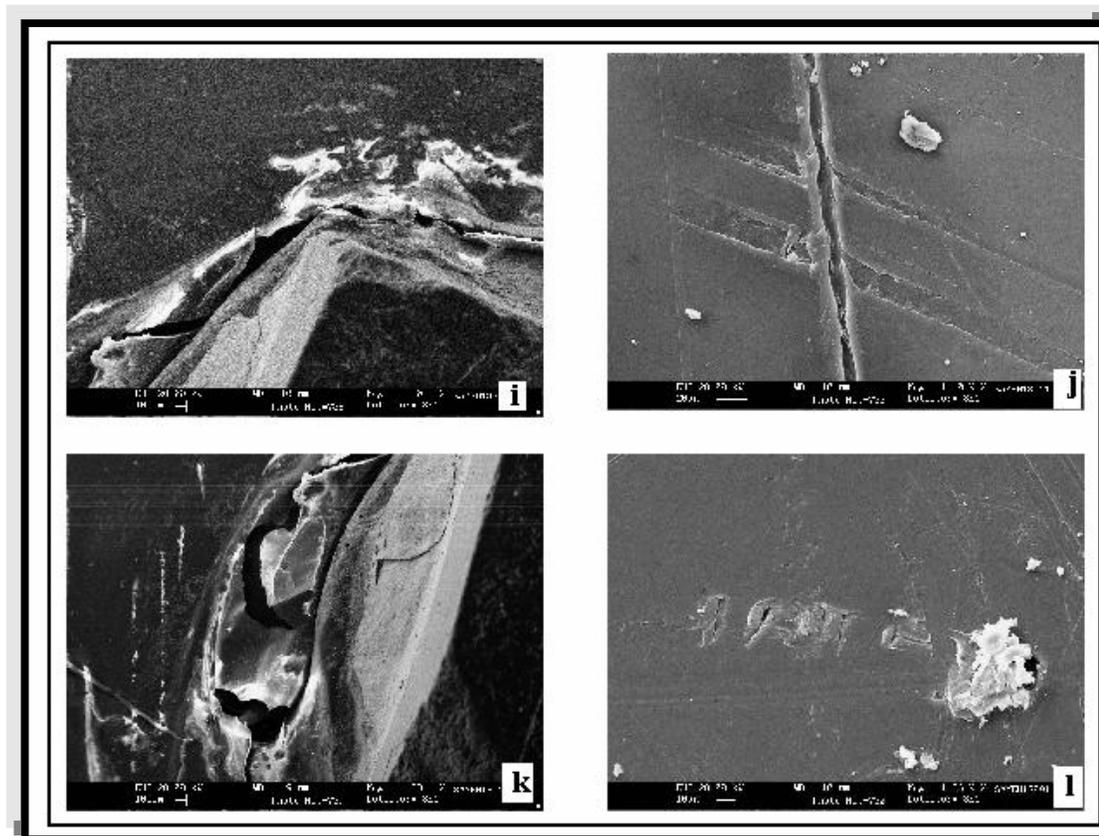


Figure 4.18. SEM micrographs of different degraded samples of i-l.

Thus from over all study of degradability of cellulose fiber and thermoplastic composites indicated that compatibilization played a dominant and key role during actual biodegradability in agro waste polymer composites. Further, the investigations on the effect of compatibilization on degradability were extended by studying the degradability of biocomposites prepared from starch and PCL. These blends and composites were prepared by our collaborators from, UMH, Belgium [43,44] and studies on the degradability in both the above mentioned environments were performed. The aim of this study was to evaluate the practical applications of these composite materials as well as to study the effect of various compatibilizing techniques on inherent biodegradability of PCL. Four types of composites were prepared from PCL and starch. The material used in the composite preparation was commercial grade PCL (CAPA 650) and supplied by M/s Solvay S.A. Belgium and granular corn starch, high amylose corn starch (HACS) and waxy maize corn starch (MCS) with amylose/amylopectine weight ratios of 30/70, 70/30, 0/100, respectively, obtained from , M/s Bioplastics Inc. USA.

The biodegradability was determined by measuring the weight loss of composted samples over 250 days (three replicates) after thorough washing with water and drying under vacuum until constant weight. All composite materials were molded between two Teflon sheets into thin films (~100 μm , 5×5 cm) at 55±5 °C by applying 160 kg/cm² pressure for 20 s using a preheated carver press. Samples were extracted by boiling chloroform. This solution was filtered, and the soluble part was collected after evaporation. The soluble part was considered as PCL, not consumed by microbes in composting. The intrinsic viscosity [η] of the solute in chloroform was determined at room temperature starting from a concentration of 0.1 wt.% by successive dilution. The thickness of the samples was measured as an average over 10 values. The percentage weight loss was calculated by: $100 \times (\text{Initial weight of component} - \text{Final weight of component}) / \text{Initial weight of component}$.

A. PCL–granular starch blends

PCL–starch compositions were prepared by mechanical kneading on a two-roll mill at 130 °C for 15 min. in different weight ratios. The time-dependent weight loss is shown in Table A.1 for PCL–granular starch compositions with starch content lower than or equal to 50 wt.% ($M_{\text{nPCL}}=49,000$ and $M_w/M_n=1.4$). Higher content of starch is responsible for the formation of very brittle materials that are highly difficult to melt process. It emerges from these data that PCL undergoes a slow degradation compared to the blends with starch (Table A.1, entry 1). Increasing starch content in the blends favors the degradation rate as evidenced by an enhancement of weight loss as a function of time (Table A.1, entries 2–6). In contrast, the percentage of weight extracted from composted samples is mostly independent of the initial PCL–starch composition. Therefore, considering that only PCL can be solubilized in boiling chloroform, it confirms that granular starch is rapidly degraded, while the host matrix is almost left unaffected in composting. The negligible change in PCL [η] from 1.20 to 1.18 dL/g up to 120 days of incubation is another proof of the chemical inertia of the polyester under the investigated composting conditions. For longer composting time (250 days), [η] decreases down to 0.85 dL/g which can reflect a higher accessibility of PCL chains due to starch consumption. In agreement with the latter assumption, a higher hydrolytic degradation occurs due to higher chain mobility at 35–40 °C together with an activation of thermophilic microbes [45].

Replacing granular corn starch by HACS and waxy MCS significantly reduces the degradation rate, at least up to 120 composting days (Table A.1, entries 5, 7 and 8). In

contrast, the weight loss after 250 days reaches a very similar value whatever the nature of the starch granules. Similarly, the fungal growth is slightly slower for the PCL–starch blends made of HACS and MCS until the 8th week, but reaches the same level of growth after 15 weeks (Table A.2). Consequently, neither the amylose/amylopectin weight ratio, nor variations in the mean average diameter of starch, are key parameters that determine the degradation kinetics and the fungal growth. **Figure A.1** shows a scanning electron micrograph of a (60:40) PCL–HACS blend after 250 composting days. Many holes are observed randomly dispersed all along the surface, indicating the selective consumption of starch granules, leaving behind intact polymer matrix.

Table A.1. Weight loss of PCL/starch blends during composting

Entry	Composition(PCL / Starch)	Weight Loss (%)			(% Weight loss of extracted fractions after 250 days composting)	
		90 days	120 days	250 days	PCL	Starch
1	100/0	0.86	1.11	45.62	-	-
2	90/10	1.63	2.20	56.58	51.94	98.35
3	80/20	1.85	2.30	61.48	52.36	97.96
4	70/30	2.80	3.50	66.13	52.49	97.97
5	60/40	11.10	11.30	70.50	52.88	96.93
6	50/50	11.71	13.36	75.84	53.77	97.98
7	60/40 HCS	2.82	5.65	72.04	54.98	97.63
8	60/40 MCS	3.21	6.31	72.94	55.65	98.89

Table A.2. Fungal growth onto the surface of PCL/starch blends

Entry	Composition (PCL/starch)	Fungal growth efficiency					
		1 st week	3 rd week	5 th week	8 th week	12 th week	15 th week
1	100/0	0	1	1	2	2	3
2	90/10	0	1	2	3	3	3
3	80/20	0	1	2	3	3	4
4	70/30	1	1	2	3	3	4
5	60/40	1	2	3	3	3	4
6	50/50	1	2	3	3	4	4
7	60/40 HACS	1	2	3	3	3	4
8	60/40 MCS	1	2	3	3	4	4

B. Hydrophobic coating of starch granules and melt blending with PCL

The hydrophobic coating of granular corn starch was performed by reacting the hydroxyl groups available at the starch surface with *n*-butylisocyanate in bulk without any solvent under microwave treatment at 400 W for 5 min in the absence of any catalyst [43]. These surface-treated starch granules are coined 'C₄ starch'. Another hydrophobic coating was achieved by reacting the surface by hydroxyl function with octadecyltrichlorosilane ('C₁₈ starch'). Corn starch granules were suspended in THF, previously dried by refluxing over sodium–benzophenone radical-anion for 48 h and freshly distilled. Triethylamine (dried over BaO for 48 h and distilled) was added as a catalyst, and the reaction mixture was stirred at 50 °C for 1 week. Coated starch granules were recovered by filtration, washed with water and dried under reduced pressure until constant weight. FTIR spectroscopy was used to demonstrate the high grafting efficiency as determined from the decrease of the absorbance corresponding to hydroxyl functions at 3330 cm⁻¹. After chemical modification, the coated starch particles were melt blended with PCL so as to reach final PCL–starch compositions of 70/30 for C₄ starch and 60/40 for C₁₈ starch.

The mechanical properties of granular corn starch-filled PCL compositions are improved by compatibilization [43]. Three strategies were investigated, including the hydrophobic coating of starch granules, the surface-localized addition of PCL-grafted dextran amphiphilic copolymers, and the use of PCL-grafted granular starch. The mechanical property changes were clearly related to parameters such as filler dispersion, interfacial tension, interfacial adhesion and reinforcement by PCL crystallization. **Table B.1** shows the effect of the compatibilization by a hydrophobic coating of starch granules on the biodegradation of the composite materials. Both of the hydrophobic coatings (C₄ starch and C₁₈ starch) enhanced the degradation rate in composting. However, starch granules coated with a butyl shell showed the highest degradation. Indeed, the weight loss is significantly increased for the PCL–C₄ starch composition, and the amount of PCL that can be extracted was decreased. These observations are fully confirmed by the time evolution of the sample thickness and the PCL [η] (**Figure B.1** and **Figure B.2**). There is a very similar relation between both sample thickness decrease and weight loss in function of biodegradation time, while [η] changes are clearly more pronounced for the PCL–C₄ starch blend. The slight increase in PCL [η] during the first 60 days can be explained by the selective diffusion of the shorter PCL chains out of the matrix and their eventual consumption by microbes in a similar way to what is observed during the hydrolytic

degradation of polyester implants in aqueous media [46]. SEM does not show a clear difference between the degradation surfaces of PCL–C₄ starch and PCL–C₁₈ starch (Figure B.3 and B.4). However, the significant increase in PCL weight loss in PCL–C₄ starch compared to a 70:30 PCL–starch blend confirms that compatibilization and/or homogeneity of the two separated phases are in favor of the degradation of the host polymer.

Table B.1. Effect of the starch granules surface coating on the weight loss of PCL/starch blends during composting

Entry	Composition (PCL / starch)	Weight Loss (%)			(% Weight loss of extracted fractions after 250 days composting	
		90 days	120 days	250 days	PCL	Starch
1	70/30	2.80	3.50	67.23	52.49	97.97
2	70/30C ₄ starch	4.19	5.63	77.26	67.98	98.95
3	60/40	11.10	11.30	70.50	52.88	96.93
4	60/40C ₁₈ starch	12.87	14.16	75.11	60.13	97.59

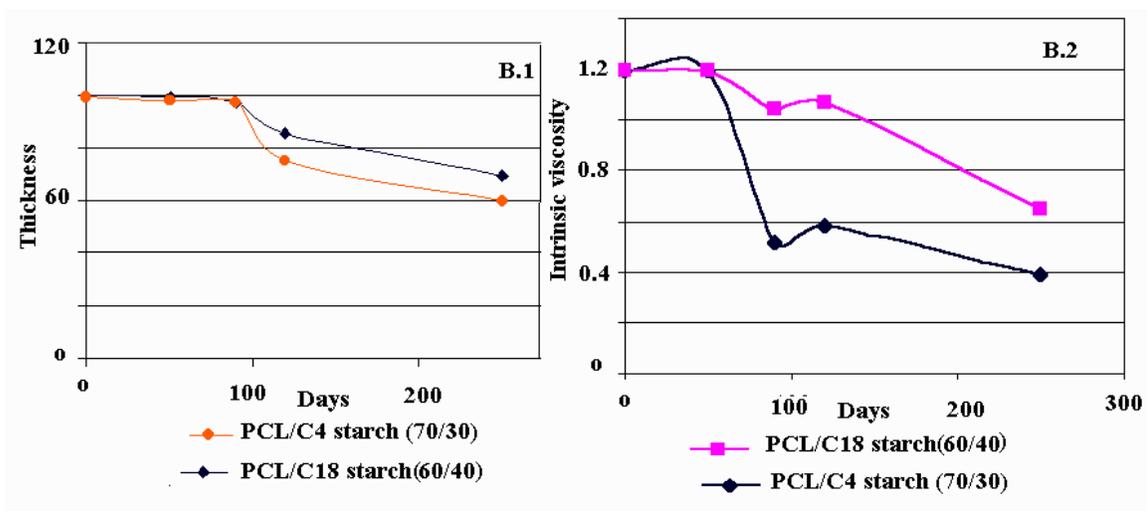


Figure B.1. and B.2. Change in Intrinsic viscosity and Thickness during degradation

C. Synthesis of PCL-grafted dextran copolymers and use as compatibilizer in PCL–granular starch blends

The three-step synthesis and characterization of PCL-grafted dextran copolymers (PGD) have been reported [44]. Typically, dextran T10 (from Pharmacia Biotech; $M_n=6600$) was first partially silylated at 50 °C in DMSO–THF solution with 1,1,1,3,3,3-

hexamethyldisilazane as the silylating agent. The material was recovered by precipitation in heptane, followed by filtration and drying. In a second step, the polymerization of ϵ -caprolactone (CL) was initiated in toluene solution at 60 °C from the hydroxyl groups remaining free along the partially silylated dextran after activation with triethylaluminum. The PCL-grafted silylated dextran copolymer was then recovered by precipitation in heptane, followed by filtration and drying. In a final step, deactivation of aluminum alkoxide growing sites and deprotection of silylated dextran hydroxyl groups were carried out by dissolution in THF and addition of dil aq HCl. The in situ precipitated PGD was recovered by filtration and drying. In this study, two PGD copolymers were used with the following molecular characteristics: PGD1 with $F_{\text{PCL}}=0.60$, $\text{DP}=8$ and $\text{Ng}=10$, and PGD2 with $F_{\text{PCL}}=0.89$, $\text{DP}=20$ and $\text{Ng}=21$ (where F_{PCL} is the weight fraction in grafted PCL, Ng is the number of polyester grafts per dextran chain and DP is the average degree of polymerization of PCL grafts). It is worth noting that PGD copolymers were precipitated at the surface of starch granules before melt blending with PCL at 130 °C. Precipitation of the copolymers onto cornstarch granules was carried out by dissolving PGD 1 or 2 copolymers into a toluene suspension of granular starch and then dropwise adding a poor solvent for the graft copolymers, i.e., heptane. **Table C.1** illustrates the degradation rate of the (60:40) PCL–starch blends added with 5 wt.% of PGD1 and PGD2, respectively. The location of PCL-grafted dextran at the interface between granular starch and PCL tends to decelerate the degradation for the initial period of composting as attested by the time dependence of sample weight loss. This is confirmed by a slow thickness decrease compared to that of a non-compatibilized 60:40 PCL–starch blend. Such behavior is in contrast with the significant increase of weight loss when the temperature as well as composting time is increased. The weight loss of extracted PCL is also drastically increased when comparing entries 1 and 3 (**Table C.1**) with the time. These data clearly indicate that the difference in biodegradability must be due to the variation in weight fraction of PCL. **Figure C.1** shows the PCL intrinsic viscosity change as a function of time. Compared to non modified PCL–starch blends, the addition of 5 wt.% PCL-grafted dextran favors the degradation of the polyester chains. Remarkably, an increase in $[\eta]$ of PCL is observed between 60 and 90 composting days, followed by a sharp drop occurring as the time of composting increases. The viscosity increase can be explained by the diffusion of shorter polyester chains and their eventual assimilation by microbes as already proposed for blends involving surface-coated starch granules. **Figure C.2-4** show the SEM of (60:40) PCL–starch blends with and without compatibilization by PGD1 and PGD2.

Based on the relative homogeneity and erosion of the surface, compatibilized compositions appear rougher and more degraded, particularly the sample prepared from PGD2. The fact that the surface of native PCL–starch blend is smoother may reflect a preferential consumption of starch granules to the detriment of the host matrix. The PCL weight fraction also affects the fungal colonization on the surface of these samples.

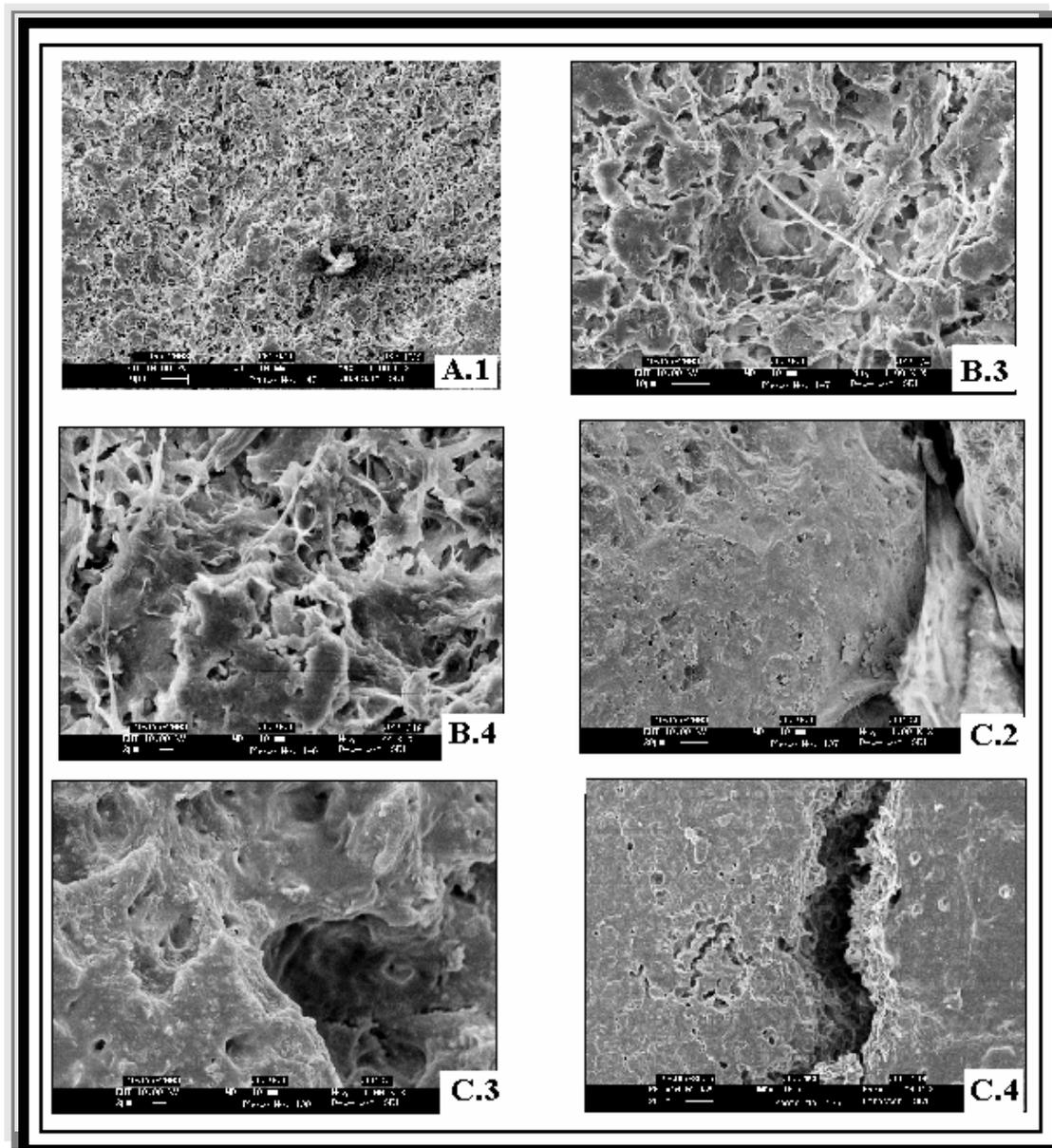


Figure A.1, B.2, B.3 and C.2, C.3, C.4 showed surface morphology of different degraded samples of PCL-Starch composites

Table C.1. Weight loss of the PCL/starch blends, comptabilized with PCL-grafted dextran onto the granular starch surface during composting

Entry	Composition (PCL / starch blend)	Weight Loss (%)			(% Weight loss of extracted fractions after 250 days composting	
		90 days	120 days	250 days	PCL	Starch
1	60/40	11.10	11.30	70.50	52.88	96.93
2	60/40+PGD1	2.61	3.19	74.43	58.93	97.68
3	60/40+PGD2	9.06	11.19	76.59	63.03	96.93

Table C.2 shows the slower surface coverage by fungus when PGD2 is substituted for PGD1. As a conclusion, dextran-grafted PCL copolymers enhance the degradation of the polyester matrix, particularly when PCL is the major component. In contrast, a high PCL weight fraction in the copolymer first disfavors the adhesion of fungus.

Table C.2. Fungal growth onto the surface of PCL/starch blends comptabilized with PCL-grafted dextran onto the granular starch surface

Entry	Composition (PCL/starch)	Fungal growth efficiency					
		1 st week	3 rd week	5 th week	8 th week	12 th week	15 th week
1	60/40	1	2	3	3	3	3
2	60/40+PGD1	1	1	2	3	3	4
3	60/40+PGD2	0	1	1	2	3	4

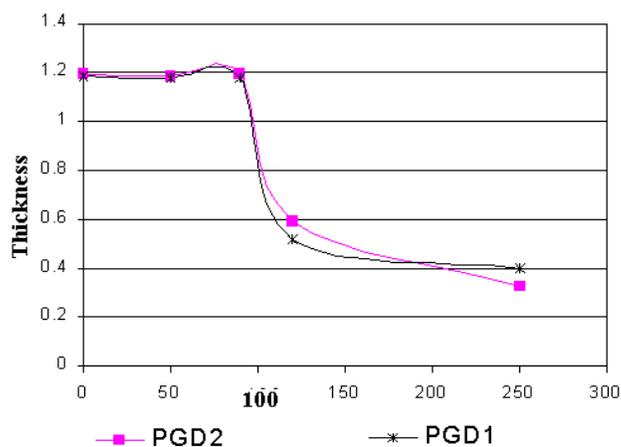


Figure C.1. Time dependence of the PCL intrinsic viscosity of the PCL/starch samples in composting. Effect of the precipitation of PCL-grafted dextran: PGD1 and PGD2

D. In situ PCL grafting onto starch granules and melt blending with PCL.

The PCL-grafted starch particles (PGS) were obtained by in situ ring-opening polymerization of CL in the presence of granular starch [47,48]. Typically, dried cornstarch granules and CL (50/50 by weight) were introduced in a round-bottom flask previously purged with nitrogen, added with 1 wt.% triethylaluminum and heated up to 90 °C for 10 min. The polymerization was terminated by fast cooling at room temperature. Weight fraction in grafted PCL chains (F_{PCL}) was determined by gravimetry after selective extraction in toluene of the non-grafted PCL chains. F_{PCL} was 4% for a monomer conversion of 86% (PGS1). PGS2 was obtained by an alternative procedure in which starch and triethylaluminum were first reacted in toluene suspension at rt for 2 h, then the toluene was removed out by filtration under inert and dried atmosphere, followed by the addition of CL, allowing the polymerization to proceed. The surface-treated starch granules were recovered as aforementioned leading to a F_{PCL} equal to 24% for a monomer conversion of 96% (PGS2). PGS2 has been used without any extraction except for an aliquot that enables one to determine the number-average molecular weight of free/non grafted PCL chains ($M_n=60,000$). In the next step, PGS1 and PGS2 have been melt blended with the PCL matrix in order to reach a final PCL–starch composition of 60/40.

Table D.1 and **Table D.2.** show the time dependence of weight loss and fungus growth of 60:40 PCL–starch compositions obtained by melt blending PCL with PGS granules. The composition added with PGS1 degrades faster than the one with PGS2 for longer composting. Similarly, fungal growth is easier with PGS1, although the presence of PGS slows down microbes adhesion onto the surface. Once microbes have been adsorbed, their penetration into the structure is rapid and they consume both starch and PCL. The morphological aspects of composted PGS1 and PGS2 containing compositions are shown in **Figure D.1 and 2**, respectively. The cracked surface of PGS1 could be clearly seen even at lower magnification, and this sample was more biodegraded than PGS2. This fact was fully confirmed by the higher decrease in thickness with PGS1. It was observed that the $[\eta]$ decreases sigmoidally for the composition added with PGS1, while the dependence of PCL–starch surface-treated with PGS2 is very similar to previous observations (hydrophobic coating and PCL-grafted dextran as compatibilizer). All these observations tend to demonstrate that the covalent grafting of PCL chains onto starch may play the role of a barrier reducing starch availability and delaying bioassimilation of both starch and PCL when the weight fraction in PCL reaches 24% and/or the PCL segments are able to crystallize. In contrast, when granular starch is poorly grafted by PCL (PGS1), the good

dispersion, interfacial properties and adhesion, as well as the amorphous state of short grafted PCL segments are responsible for an increase in the degradation rate of both starch and PCL.

Table D.1 Weight loss of PCL/starch blends compatibilized with in situ grafted PCL onto starch granules, during composting

Entry	Composition (PCL / starch blend)	Weight Loss (%)			(%) Weight loss of extracted fractions after 250 days composting	
		90 days	120 days	250 days	PCL	Starch
1	60/40	11.10	11.30	70.50	52.88	96.93
2	60/40/PGS1	18.96	21.76	80.50	69.56	96.39
3	60/40/PGS2	4.78	7.06	78.06	64.56	98.31

Table D.2 Effect of starch-surface grafting by PCL chains on the fungal growth at the surface of samples

Entry	Composition (PCL/starch)	Fungal growth efficiency					
		1 st week	3 rd week	5 th week	8 th week	12 th week	15 th week
1	60/40	1	2	3	3	3	4
2	60/40/PGS1	0	1	3	3	4	4
3	60/40/PGS2	0	1	2	2	4	4

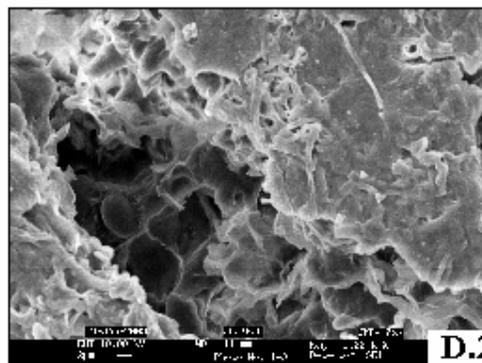
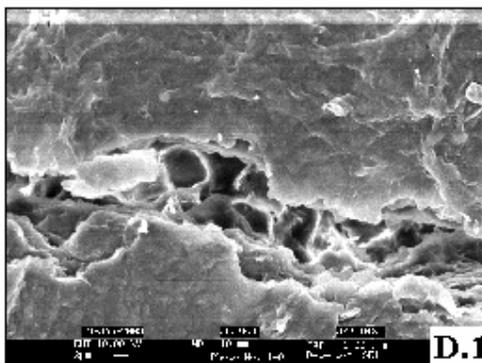


Figure D.1 and D.2 showed surface morphology of different degraded samples

4.4. Conclusions

Photodegradation study shows that composites prepared from direct mixing method were more photodegradable than commercial polymers and composite prepared by grafting method. Biodegradability was increased with the increasing time of UV treatment. There was a significant effect of method of preparation of samples on the durability. In compost incubation, weight loss of unirradiated samples for directly prepared composites was more than composite prepared by grafting method. It must be because of additional degradation which has already been taken place during preparation through peroxide initiated photo-oxidation, consequently there was generation of more active sites for microbial attack by providing functional groups. In culture incubation, irradiated graft composites were showing uniform coverage of surface by fungus. Composition of E-P copolymer significantly influence the degradation behavior of composites and degradation decrease with increase in ethylene content. From the overall observation of the study, in general it was concluded that thermoplastic-agro waste composites may play a key role as an ecofriendly material. The study on the effect of compatibilization on the inherent biodegradability of host matrix in composites was extended by investigating the biodegradability of the PCL-starch composites, which has been shown to increase with compatibilization. In that respect, improving the dispersion of starch granules through a hydrophobic coating, and reducing the interfacial tension between PCL and starch owing to the starch-surface precipitation of PCL-grafted polysaccharide (dextran) proved to be very efficient. Grafting of PCL onto starch granules may suffer from an increase of PCL crystallinity in the direct vicinity of the starch surface, which reduces the accessibility to microbes. It depends on the grafting efficiency and the weight fraction of grafted PCL chains. In other words, a balance might have to be found between the improvement of adhesion required for mechanical purposes and an acceptable degradation rate.

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CHAPTER V:

**DEGRADABILITY OF POLYMER COMPOSITES PREPARED FROM
LAYERED SILICATE**

5.1. Introduction

Polymer composites can be used in many different forms ranging from structural composites in the construction industry to the high technology composites for the aerospace industries [1]. It is well established that the stress transfer from polymer matrix to filler decide the fate of a composite in terms of its different properties. The material properties of polymer composites are strongly dependent on the degree of intimate contact between the phases. In recent years it has been found that polymer filled with layered silicates often exhibit remarkable improvement of mechanical, thermal and physicochemical properties when compared with pure polymer even at very low filler concentration due to the nanolevel interactions with polymer matrix [2]. These layered silicates have attracted great attention because of their cheap, easy availability and renewable nature and high aspect ratio which gives greater possibility of energy transfer from one phase to another. To ensure the best product, either a surfactant/modifier in clay is adequate to offer sufficient excess enthalpy for the promotion of complete and homogenous dispersion of mineral filler in polymer or functionality in the host matrix is usually required [3,4]. The nanocomposites of polyolefins e.g. polyethylene (PE) and polypropylene (PP) with enhanced material properties have been prepared [5,6] in order to improve their competitiveness for engineering applications. Performance during use is the key feature of any such type of material/ composites [7], which decide the real fate of products during use in outdoor applications. The degradability of polymer nanocomposites have been reviewed recently [8]. PP nanocomposite were found to be more degradable than pure PP under UV irradiation [9] however, the cause of this behaviour was not explained in detail. Similarly, nanocomposites of PE were found less durable in comparison to pristine PE under UV exposure and the acceleration of photodegradation was attributed to the clay and modifier [10]. In the present chapter study on the oxo-/bio-durability of PE nanocomposites under accelerated weathering followed by biodegradation in composting was carried out. A further objective was to study the effect of layered silicate on the bioassimilation mechanisms. FT-IR spectroscopy was used to monitor the functional groups during accelerated weathering and composting. Biodegradability was measured by the variation in gravitational weight while samples were kept in a composting environment. Morphological changes and the extent of filler dispersion were evaluated by SEM and WAXD respectively.

5.2. Experimental

5.2.1. Materials

Clay, Cloisite 20A (CL20) (2θ was 3.64° , d-spacing 24.2 \AA), modified with dimethyl dehydrogenated tallow ammonium ion ($2 \text{ CH}_3 \text{ N}^+ \text{ HT}$, where HT is Hydrogenated Tallow ($\sim 65\%$ C18; $\sim 30\%$ C16; $\sim 5\%$ C14) anion: chloride) contain 36 % modifier (measured by Perkin Elmer TGA-7 instrument at the flow rate of $10^\circ\text{C} / \text{minute}$) was from Southern Clay Products, Inc. Low density polyethylene (PE) Indothene 16 MA 400) was kindly supplied by M/s Indian Petrochemicals Corp. Baroda, India. Maleic anhydride (MA) (E. Merck, India) was recrystallized from chloroform before use.

5.2.2. Preparation of nanocomposites and characterization

PE nanocomposites were prepared by melt compounding at $140 \pm 2^\circ\text{C}$ using Brabender mixer having chamber size of 50 cm^3 with screw speed of 60 rpm for 20 minutes, after maleation by direct mixing of maleic anhydride and peroxide. These samples were molded into thin films ($\sim 100 \mu\text{m}$, $5 \times 5 \text{ cm}$) at $140 \pm 2^\circ\text{C}$ by applying 150 kg/cm^2 pressure for 30 seconds between two Teflon sheets using a preheated Carver press. Films were quenched cooled for 2 min. The LM (PE after functionalization with MA) was melt blended with LP (neat PE) and different compositions were made having constant filler concentration of 5 % (w/w). The WAXD pattern of samples was obtained by a Rigaku (Japan) diffractometer with Cu- $K\alpha$ radiation at 50 kV between the scan range of 2θ from 2-10 degree by the scan rate of $1^\circ / \text{minute}$. The d-spacing was calculated by Bragg's equation where the λ was 0.154 nm. The grafting efficiency [11] of MA was evaluated by elemental analysis and FT-IR spectroscopy after drying for 24 hrs at 110°C under vacuum. For SEM, all UV exposed films were placed in stoppered bottles containing osmium tetroxide (2 % aqueous) and allowed to stand for 48 h. followed by washing with water and dry ethanol. These stained samples were dried under vacuum for 24 h at 50°C and coated with gold to examine under electron microscope (Leica Cambridge Stereoscan 440 model) for morphological changes. FT-IR (Fourier Transform infrared 16 PC Spectrometer) was used to characterize the photo-oxidation in the polymer films and interest was mainly focused on the changes in hydroxyl ($3700\text{-}3100 \text{ cm}^{-1}$) and carbonyl region ($1600\text{-}1800 \text{ cm}^{-1}$).

5.2.3. Durability evaluation

Photo-irradiation of the films was carried out in an accelerated weathering chamber (SEPAP 12/24 (M/s Materiel Physico Chimique, Neuilly/Marne, France) at 60 °C. The chamber consists of (4 x 400W) medium pressure mercury vapor lamps supplying radiation longer than 290 nm. The details of the equipment are described elsewhere [12]. Composting studies (5 X 5 cm films, 5 replicates) were carried out as previously reported [13-15] and disclosed in Chapter3. Temperature was dependent on the climatic conditions and temperature inside the compost chamber was always higher than surroundings, which increased rapidly during last days of incubation after extra addition of microbe nutrients. The samples were kept inside the compost at ~ 1meter depth. The biodegradability was determined by measuring the weight loss (%) of composted samples after thorough washing and drying under vacuum until constant weight was obtained.

Table 5.1. Different composition of composites where, +, +++, represents the exfoliated, +, +, + ordered exfoliated or highly intercalated, ++ intercalated and + microcomposites structures

LM (Maleated polymer)	LP (Neat polymer)	DE (Dispersion Extent)	Sample name	Series
100	0	++++	a	A
90	10	++++	b	
80	20	++++	c	
70	30	+++	d	B
60	40	+++	e	
50	50	++	f	C
40	60	++	g	
30	70	+	h	D
20	80	+	i	
10	90	+	j	
0	100	+	k	

5.3. Results and discussion

5.3.1. Structure of composites

The chemical modification of PE is essentially required to improve the phase adhesion of with clay. The bands at 1720, 1640, 1784, & 1791 cm^{-1} were attributed to the carbonyl group reacted with moisture from anhydride, vinylic groups generated due to chain scission during processing, MA oligomer and MA single unit respectively. The peaks at 1360 and 1580 cm^{-1} indicate absence of the anionic form of anhydride with one carboxylic acid i.e., MA is present either as a dicarboxylic acid dimer or in the cyclic form. This was confirmed by the appearance of peaks at 1780, 1863 cm^{-1} for cyclic anhydride and 1718 cm^{-1} for carboxylic acid dimer. The disappearance of the characteristic absorption band for out of plane deformation of -CH at 722 cm^{-1} may be due to the sublimation and cyclization of unreacted maleic anhydride. Figure 5.1. shows spectra of different composition of LM and LP where the absorbance in carbonyl regions decreases with the increase in LP. The nature of composites with the Dispersion Extent (DE) is shown in Table 5.1 with schematic representation in Figure 5.2 (a). It was possible to classify [16] all candidates by the inspection of WAXD pattern in order to understand the effect of clay dispersion on photodegradation and biodegradation. The 'A' series represents nanoscaled dispersion (++++), 'B' represents an exfoliated structure with preserved periodicity (+++), 'C' indicates intermediate of intercalated and microcomposites (++) & 'D' were for microcomposites (+). Absence of any basal reflection peak in 'a', 'b' and 'c' (Figure 5.2 (b)) confirm the nanoscaled dispersion of clay inside the polymer matrix and the lack of any ordered structure of filler which is well known for exfoliated structure whereas, a significant shifting of characteristic peak of clay in 'd' and 'e' (Figure 5.2 (c)) imply the presence of a ordered exfoliated structure or very highly intercalated system which may corresponds to the alternation of few polymer chains and filler, similarly, XRD signals collected for 'g' was in the form of a intense shape with shifting of clay native peak revealed the presence of silicates in the periodic manner but highly distributed through out the matrix. Figure 5.2 (d)) represents the XRD pattern of sample 'f' and absence of any shifting was observed but the intensity of peak was decrease which may be attributed for neither intercalation nor microcomposites and this was considered as boundary line for nanodispersion and microcomposites. Rest all the samples were typically microcomposites as there was no change in peak of clay for these candidates. As soon as we decrease the functionalization extent by adding the LP in LM the agglomeration of CL20 start and tendency toward formation of microcomposites increased. The specimens, having similar

WAXD pattern were kept in same series whereas, the DE in one series may not be absolutely same due to the difference in polarities. The remaining samples were typically microcomposites as there was no change in the WAXD peak of CL20. Thus nanocomposites could be obtained upto a certain functionality where the surface energy matching was sufficient enough to allow penetration of polymer chains through the silicate layers.

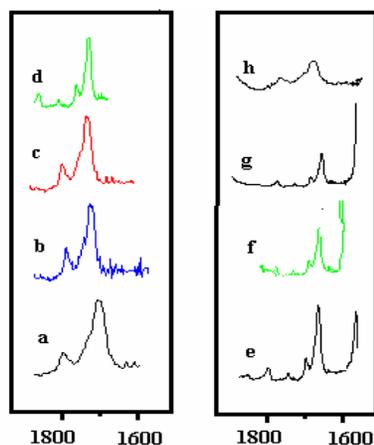


Figure 5.1. Variation in functional groups after maleation of polymer at 140°C for 10 minute with 60 rpm

5.3.2. Photodegradability of composites

5.3.2.1. Photodegradation products

A good understanding of oxidative degradation reactions under UV light may predict the active life of a synthetic polymer and its composites. FT-IR spectral changes during photooxidative degradation were monitored and interest was mainly focused on carbonyl ($1600-1800\text{ cm}^{-1}$) and hydroxyl group ($3600-3200\text{ cm}^{-1}$) variation upon 50, 100, and 150 hrs. irradiation as these are the main region of spectral changes during photodegradation of polyolefins [17]. The spectra sequel of Figure 5.3 & 5.4 depicted the carbonyl region of 90/10 LM/LP composition (+++++) and neat film respectively. Photodegradation products were same in pristine polymer and composites as evidenced by FT-IR. In general, both groups (hydroxyl, carbonyl) underwent an increase with irradiation time in a traditional way where, a very broad hydroxyl absorption region ($3700-3200\text{ cm}^{-1}$) with a maximum centered at 3400 cm^{-1} during photooxidation appeared due to the neighboring intramolecular hydrogen bonded hydroperoxide and alcohols. Hydrogen bonded hydroperoxide (3420 cm^{-1}) and associated alcohols (3380 cm^{-1}) were also present. The

absorption at 1712, 1722, 1740 and 1785 cm^{-1} have been assigned to carboxylic acid, ketone, ester and lactones, respectively. The peaks at 1641 cm^{-1} , with 910 cm^{-1} for trans vinylene and 989 cm^{-1} for vinylidene confirm the chain scission of host matrix [18-20]. Thus from over all degradation pattern the mechanisms of photodegradation of PE nanocomposites was similar to neat polymer, the only difference was found is that the higher degradation in clay filled composites.

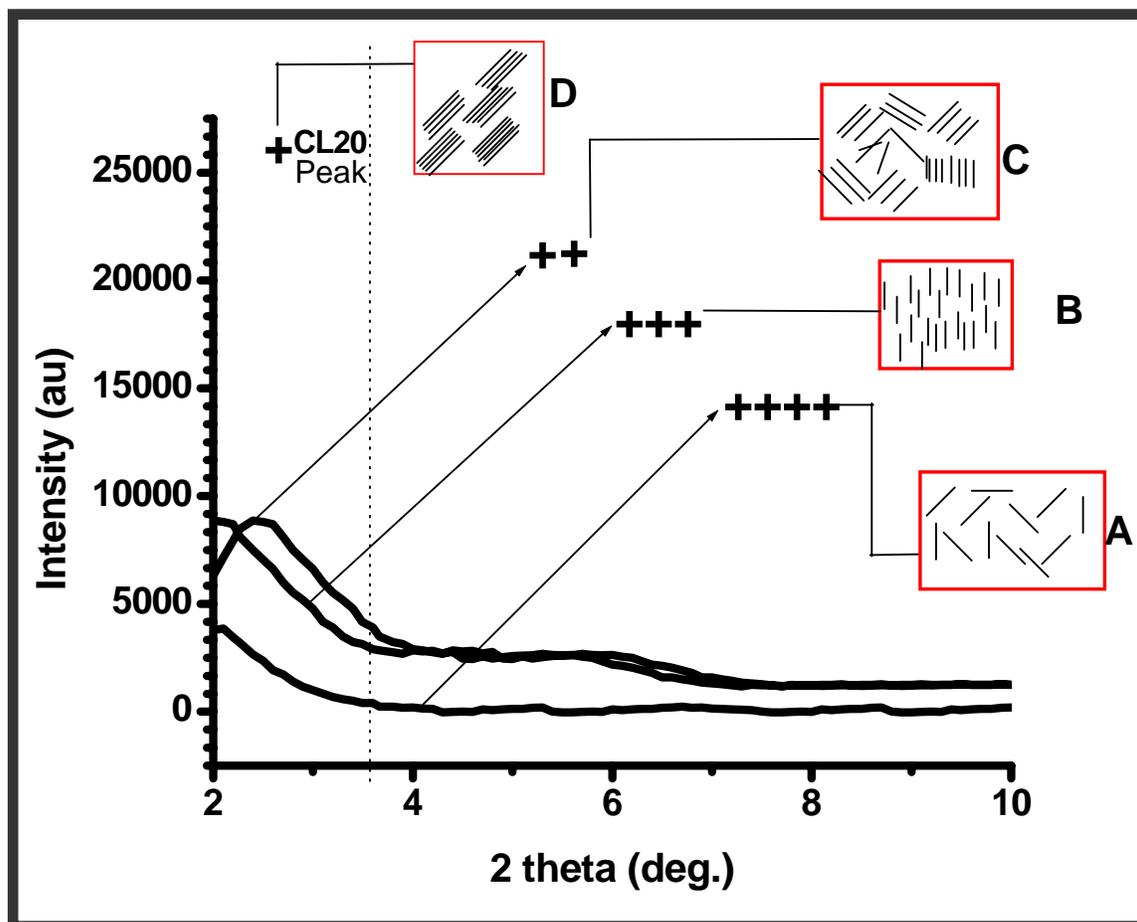


Figure 5.2 (a), Schematic representation of the filler Dispersion Extent into the matrix of host polymer in different series of samples

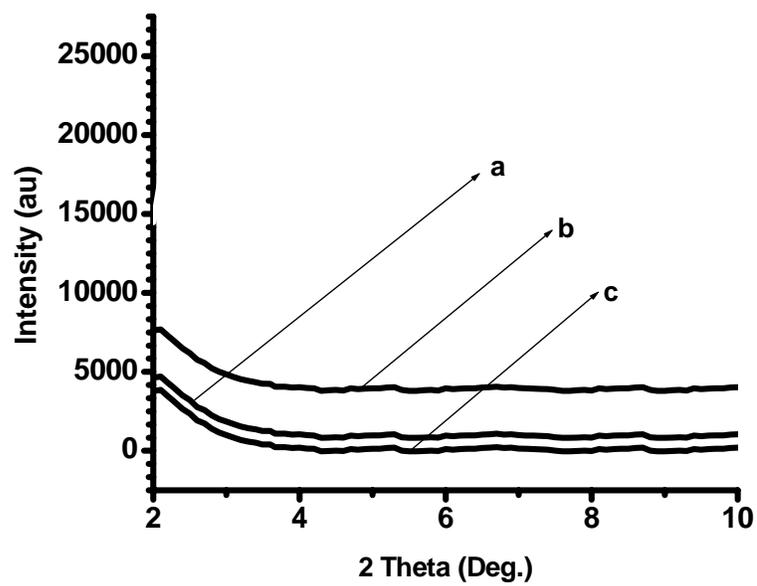


Figure 5.2. (b), The XRD pattern of a, b and c

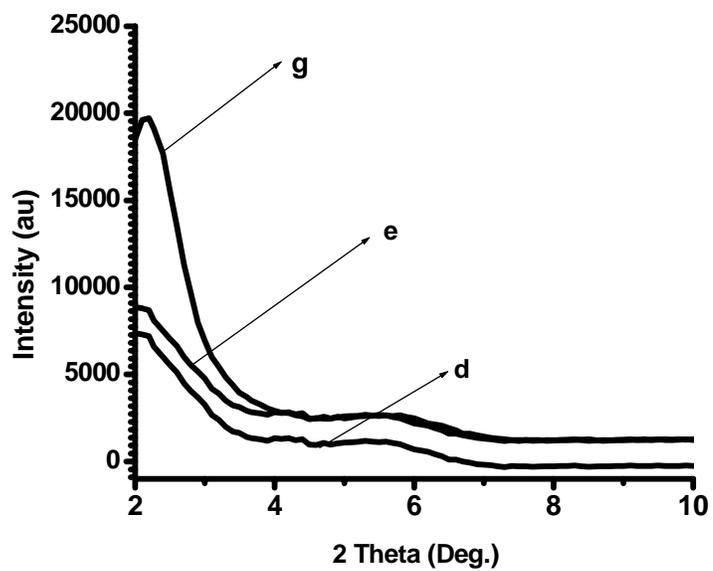


Figure 5.2. (c), The XRD pattern of d, e and g

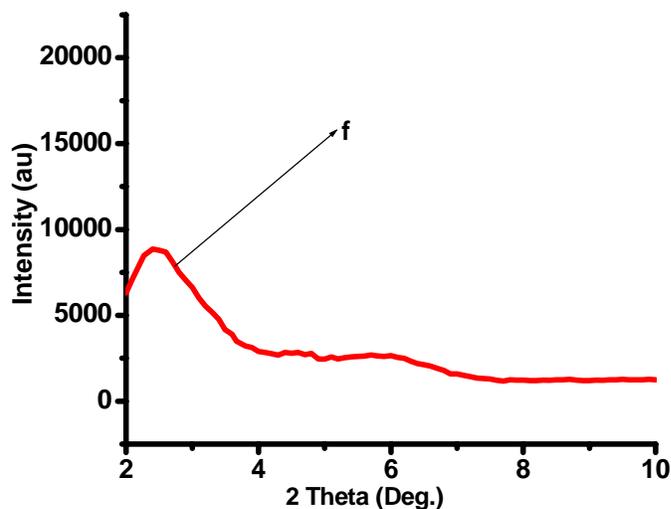


Figure 5.2. (d), The XRD pattern of f

5.3.2.2. Effect of DE and LM content on photodegradation

After 50 hrs. irradiation, degradation increased with LM concentration in composites regardless the DE of CL20. This may be either due to the sensitization effect of MA functional groups or the generation of free radicals during mixing of peroxide for MA grafting, those may further propagate the degradation in comparison of neat films. This tentative conclusion was confirmed by studying the behavior of 'A' series where degradation increased (< neat PE) with LM content after 50 hrs. as DE was almost same. Here, it may be concluded that the exfoliation, intercalation and microcomposites nature is a recessive factor in comparison of maleation extent to decide the fate of polymer at 60°C under UV light in presence of air under longer UV treatment and samples shows more stability as soon as we move toward microcomposites. All composites were highly degradable and reached to the brittle point earlier than neat film after 150 hrs of irradiation. MA functionalized polymer (without clay) was more degradable than the one filled with CL20. This indicates that the presence of clay, in any form (microcomposites or nanocomposites), inside the matrix may protect the degradation under UV light up to some extent and nanoscaled dispersion of clay increases the induction period of samples and degradation initiate with delay. Thus DE of filler affects the induction period whereas, LM concentration affects over all fate of composites for 150 hrs UV exposure.

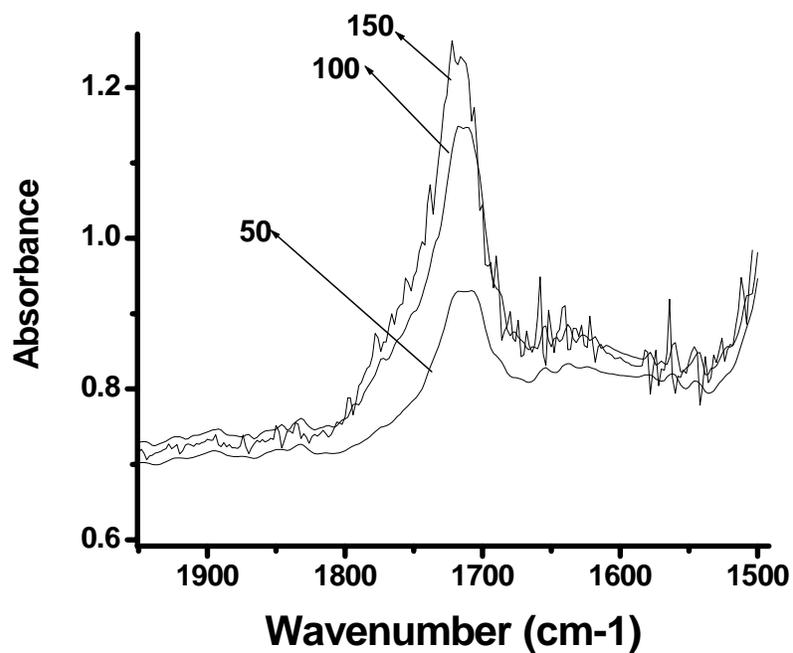


Figure 5.3. Increase in carbonyl region upon photoirradiation for 'b' (90/10, LM/LP) composites

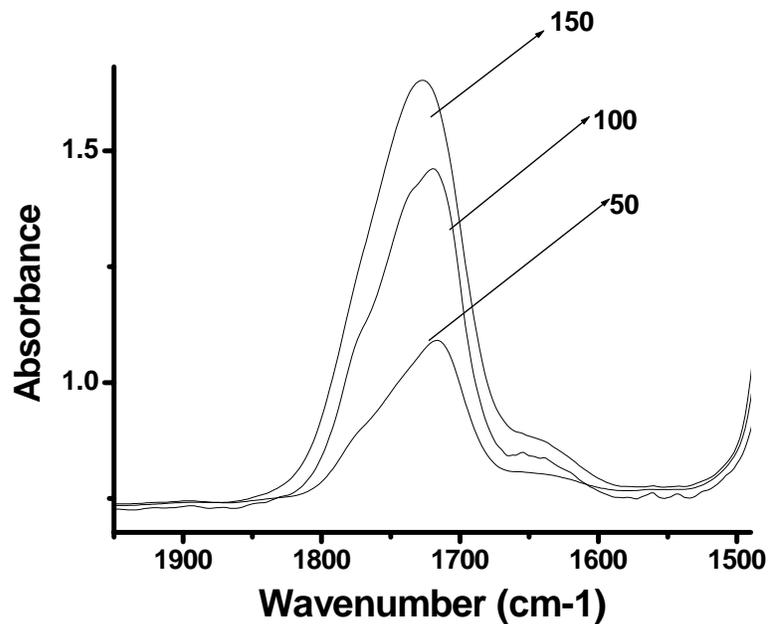


Figure 5.4. Increase in carbonyl region upon photoirradiation in presence of air for neat polymer samples

The SEM of 'b' showed a highly cracked surface in comparison of microcomposites 'i' after 150 hrs irradiation at lower and higher magnifications (Figure 5.5a1, 5.5a2 & 5.5c). The surface erosion decrease as soon as LP concentration increase as can be seen from SEM of 'c' (Figure 5.5 b). In previous attempts [9,10] such kind of behavior (higher stability of nanocomposites for initial UV irradiation) of polyolefin nanocomposites during oxidative degradation could not be observed and the effect of dispersion state (either nanocomposites or microcomposites) on degradation was not appeared conclusive. The most probable argument for this behavior must be the slow oxygen diffusion through matrix due to the increased diffusion path in presence of clay. The nature of matrix decide the oxygen diffusion and the degree of packing of chains decrease the number and size distribution of preexisting voids or holes, since chains are sandwiched between the clay surface ,restricting the mobility. The formation of low molecular weight photoproducts is more likely to occur in the case of polymers that have short branched reactive groups and further enhanced the degradability o polymer matrix [25].

The stability was evident from surface morphology also after careful observation of SEM of sample 'j', a microcomposite, where slight cracked surface was found and there were no change on the surface of 'b' after 50 hrs. irradiation. (Figure 5.6a & 5.6b). It is worth to recall that sample 'j' contain less amount of LM (which is highly sensitive to UV light) even it underwent more degradation than nanocomposites 'b' (having more LM concentration) after 50 hrs. Thus initially, barrier effect of nanoclay prevent the degradation and overcome the LM induced photodegradation. This fact was eliminated for longer UV irradiation of samples and degradability increase with LM concentration. The sudden increase in degradability or decrease in stability after 50 hrs exposure to UV light for exfoliated and intercalated samples may be explained as follows: i) The chance of intramolecular propagation increases, as neither chains nor oxygen can move freely throughout the matrix as in the neat films or phase separated composites. This restricted motion may generate in chain carbonyl group via case formation (the hydroperoxide group may abstract labile atom i.e. tertiary bonded hydrogen at carbon atom generating an intermediate bi radicals which subsequently gives a carbonyl group), which is further helpful to propagate the degradation ii) Another cause may be the nature of termination reactions during degradation those can again generate the free radicals. Nanocomposites must follow the II c path preferably in comparison of II a and II b (Figure 5.7) because oxygen pressure inside the matrix should be higher than the micro and neat samples as oxygen can not come out so easily from matrix. Further it was supported by the presence

of oxides in 'A' series exfoliated nanocomposites (II d & II e), which probably generates in oxygen rich environments and possibly, when peroxy radicals would be present at neighboring position.

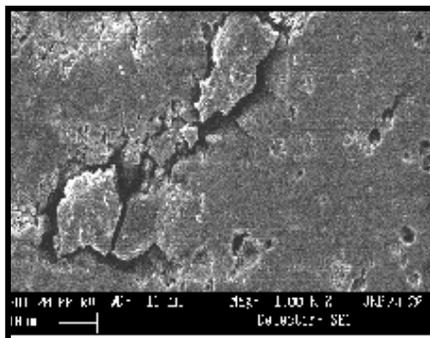


Figure 5.5a1, 150 hrs. irradiated nanocomposite of series 'A' (samples 'b'90 /10, LM/LP)

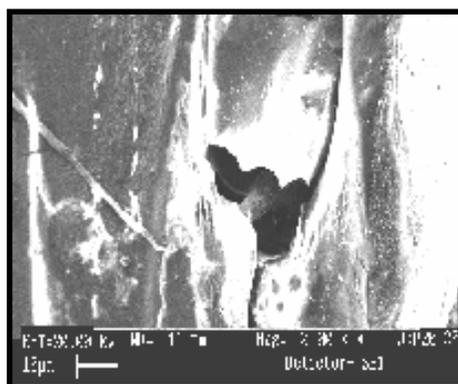


Figure 5.5 a2, 150 hrs irradiated nanocomposite of series 'A' (samples 'b'90 /10, LM/LP) at higher magnification

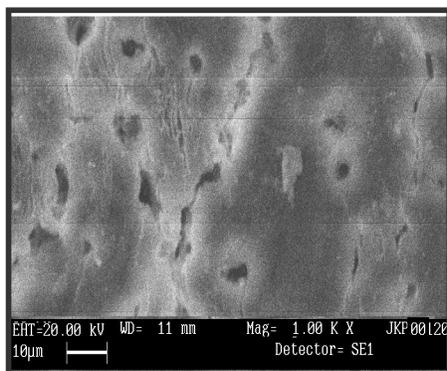


Figure 5.5 b, 150 hrs irradiated nanocomposite of series 'A' (samples 'c', 80 /20, LM/LP)

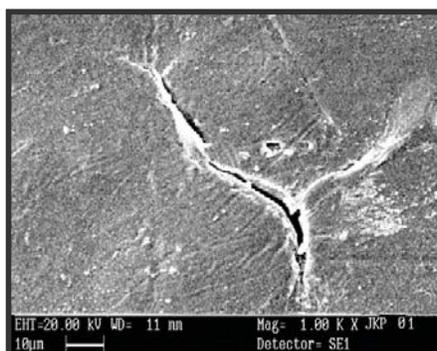


Figure 5.5c, 150 hrs irradiated microcomposite of series 'D' (sample 'i', 20 /80, LM/LP)

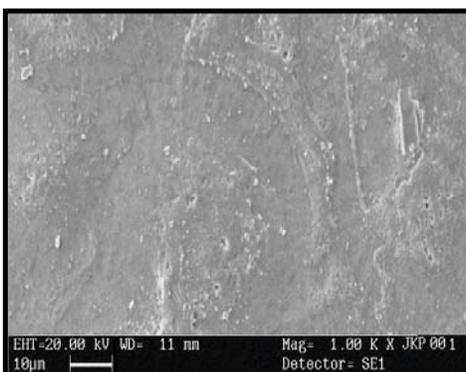


Figure 5.6a, 50 hrs irradiated nanocomposite of series A (sample 'b' 90 /10, LM/LP)

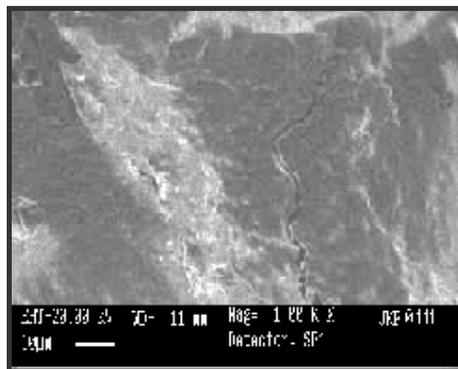


Figure 5.6b, 50 hrs irradiated microcomposite of series 'D' (sample 'j' 10 /90, LM/LP)

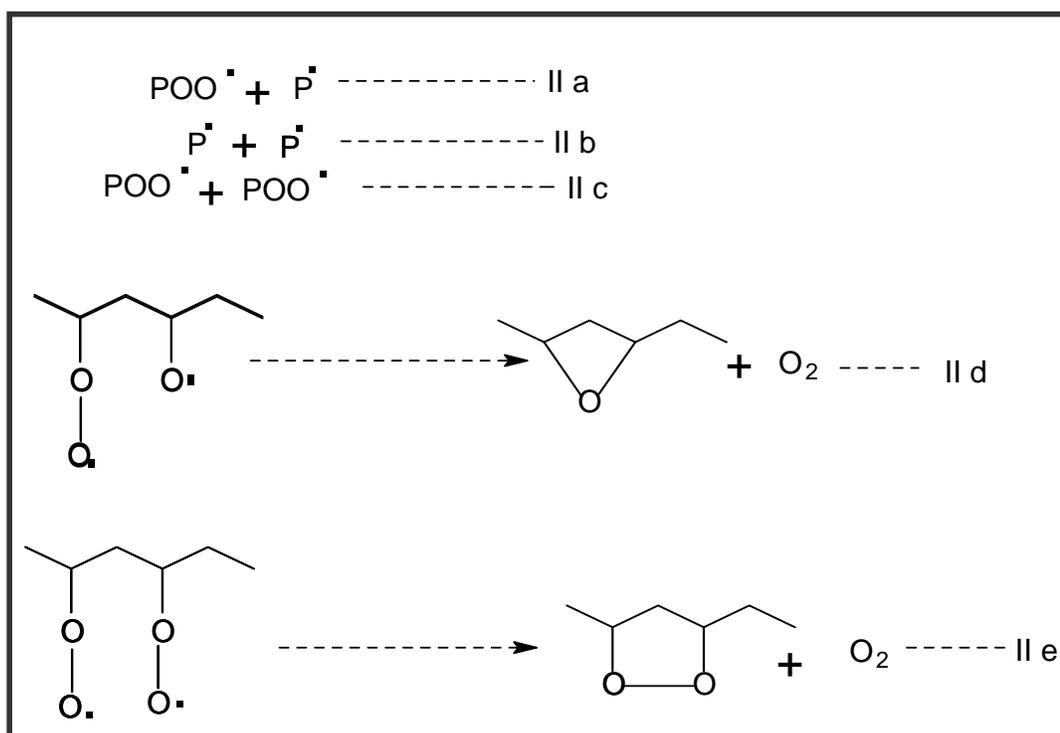


Figure 5.7. Different termination reactions (II a to II c) and formation of different species resulting from combinations of peroxy radicals (II d & II e)

5.3.2.3. Effect of modifier on photodegradation

To study the effect of modifier on the photostability, the sample of 'j', 'k' and composites of LP / Closite Na⁺, (without organic modifier, $2\theta = 7.78$, d spacing 11.7 Å) were compared during UV irradiation. These all were typical microcomposites in nature as evidenced by WAXD. Here it must be noted that the homogenous dispersion

of CL20 in specimen containing LM ('j'), must be more feasible in comparison to other samples due to polarity matching with filler. Higher degradation of 'j' in comparison of all can be attributed to the sensitization of LM, as modifier was same as in 'k'. Further, probability of uniform dispersion in 'j' was higher. The higher degradation in this sample indicate that DE can not over come from the sensitized degradation by LM in the polymer for longer hrs irradiation .No differences in the durability of 'k' and LP/ Closite Na+ composites was detected which is the indication of ineffectiveness of the modifier during photodegradation. The role of surfactant is open for speculation at this stage and one can not neglect the effect of modifier on degradation mechanisms due to the possible reactions with any of photodegradation product and more study is required to reach up to a final conclusion [9,10].

5.3.3. Biodegradability of composites

Samples before and after UV irradiation were kept in compost for 3 months. The variation in weight of samples is tabulated in Table 5.2. Specimens (5 replicates) were kept in vacuum at room temperature just after irradiation to reduce any kind of post degradation process before putting in compost. All the unirradiated samples were stable in compost for initial 3 months except pure LM (1.2 % weight loss) which was attributed to initial degradation during processing resulting the generation of microbes 'loving' photoproducts whereas, the same films containing nanofiller was stable in compost . In the case of 50 hrs. irradiated samples, only microcomposites exhibited weight loss after 2 months. All the 100 hrs. irradiated samples underwent weight loss from first month. The 150 hrs irradiated samples of 'A', 'B' & 'C' series could not be recovered after 3 months whereas, it was possible to recover samples of class 'D'. These all results confirm that photodegradation enhances biodegradation [21-24], because of the microbes active sites, generated after oxo-degradation and allow them to consume the material. The initial stability of nanocomposites in compost may be explained in the following ways ;

1. The ammonium ion has anti-microbial activity and can inhibit the microbial consumption of the material. This fact was confirmed as amongst unirradiated composite samples, only LM underwent weight loss.
2. The increase in compostability with photodegradation was either due to generation of microbes loving photoproducts or the consumption of

ammonium ion during photodegradation. Ammonium ion may be consumed during UV exposure and weight loss increase monotonically with LM content. Further the weight loss was due to the leaching of some photo products/ clay, as there was no residue left after 45 hrs stirring of samples in water at room temperature.

Table 5.2. Composting study of all samples for 3 months [M= Months]

M	Samples (according to LM concentration in compositions from 100 to 0 as illustrated in Table 1.										
	% Weight Loss										
	50 hrs. Irradiated										
	a	b	c	d	e	f	g	h	i	j	k
1	0	0	0	0	0	0	0	2.7	2.5	2.2	0
2	0	0	0	0	0	0	0	3.3	2.7	2.4	0
3	0	0	0	0	0	3.2	3.5	3.9	3.0	2.6	1.2
	100 hrs. Irradiated										
	a	b	c	d	e	f	g	h	i	j	k
1	3.8	3.7	3.7	3.6	3.3	3.0	2.8	3.0	2.9	2.6	2.0
2	6.0	5.8	5.6	5.3	5.0	4.5	4.4	3.9	3.6	3.3	3.0
3	-	-	-	-	-	7.6	6.0	4.5	4.1	3.8	3.5
	150 hrs. Irradiated										
	a	b	c	d	e	f	g	h	i	j	k
1	9.6	9.3	9.1	8.2	7.8	7.0	6.5	5.8	5.3	5.0	4.0
2	15.5	13.7	10	9.6	9.1	8.9	8.6	8.0	7.5	6.8	6.1
3	-	-	-	-	-	-	-	9.0	8.8	7.8	7.3

It is well established [13, 21], that after photodegradation polyolefins consumed by citric acid cycle where functionalized samples may follow the β -oxidation process during microbial degradation which may lead to the decrease in carbonyl group. As soon as incubation time increases the microorganisms consumed the low molecular weight

photoproducts, those are in more amount in the nanocomposites than other samples. A clear decrease in carbonyl region was observed when compared to unirradiated and 150 hrs. irradiated samples after two months composting particularly in 'b' & 'd'. (Figure 5.8). The surface of 'b' was highly eroded as revealed by SEM (Figure 5.9a) where clear pattern of cracking can be seen. The surface of 'h', a microcomposites, (Figure 5.9b) shows two distinct region, one having voids and other intact, suggesting the selective consumption of samples by microbes. The presence of cavities on the surface after composting of irradiated samples, suggesting that microorganisms penetrate the surface during degradation process. The heterogeneous and eroded surface must be due to the absence of uniform distribution of photodegraded products, which are preferable sites for microbial consumption.

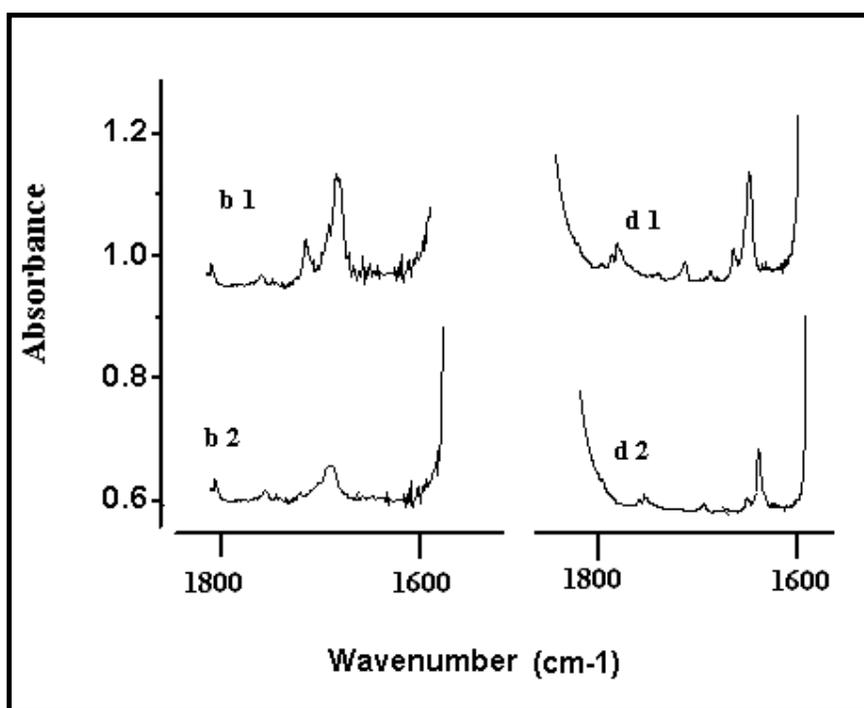


Figure 5.8. Changes in carbonyl region after 2 months composting of 150 hrs irradiated 'b' and 'd' (90/10 and 70/30 LM/LP compositions). 1 and 2 represents changes before and after composting respectively

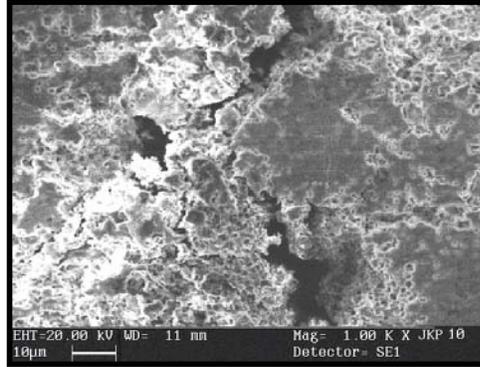


Figure 5.9a. 150 hrs. irradiated nanocomposites of series 'A' (sample 'b' 90 /10, LM/LP)after composting

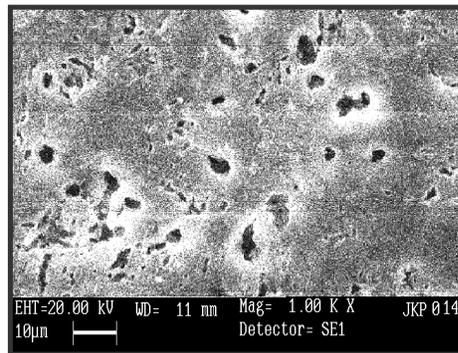


Figure 5.9b. 150 hrs irradiated microcomposite of series D, (sample 'h', 30 /70, LM/LP) after 3 months composting

5.4. Conclusions

The durability evaluation of nanocomposites was performed under accelerated UV weathering and composting conditions. Nanocomposites were highly degradable than neat polymer and microcomposites for 150 hrs irradiation under oxygen at 60°C due to the degradation during processing and maleic anhydride functionalization. The nanocomposites were comparatively stable for initiation process of photodegradation which may be attributed to the slow diffusion of oxygen through the matrix. In all samples, clay protects the polymer up to some extent of irradiation and this initial protection time increase with increase in dispersion extent of filler. The biodegradability also follow same pattern except for initial days when samples were stable in composting but as soon as photodegradation time increase the samples of nanocomposites exhibited increase in weight loss. From the FT-IR spectroscopy, it is evident that the low density polyethylene followed Albertsson et al [21], mechanism during biodegradation even after filling with clay. The effect of clay modifier on the stability of nanocomposites under UV irradiation was not observed in the present system, whereas to reach some final conclusion more study may be required. In general it can be concluded that the maleated functionalized low density polyethylene nanocomposites are not durable against biotic as well accelerated UV environment. Thus, we may get highly improved material properties by nanocomposites but durability in outdoor application is a challenge and it would be the best way to develop nanocomposites by modification in clay rather than functionalization of thermoplastics to increase the outdoor durability. These nanocomposites must be advantageous from disposal point of view and may not have waste problem due to their higher degradability than pristine polymer.

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**CHAPTER VI:
DEGRADABILITY OF BIOCOMPOSITES PREPARED FROM STARCH AND
LAYERED SILICATES**

6.1. Introduction

In order to develop an environmentally friendly material, many efforts have been made as the solution of plastic waste generated problems in the environment, particularly by one time use disposable commodity materials [1-4]. Polyolefins, the most recognized family of synthetic polymers for packaging materials, contribute significantly in the generation of waste whereas, these polymers can be bio-assimilated after generation of functional groups by different pretreatments [5-7]. Most of the research attention is focused on the replacement of petro-based commodity plastics by biodegradable material in a cost effective manner with competitive mechanical properties. The mixing of biopolymers in the matrix of these thermoplastics [2,3, 8-11] have been recognized as a relevant way to get rid of plastic waste but this blending leads to a phase separation and reduction in mechanical properties due to the lack of compatibility between hydrophilic biopolymer and generally hydrophobic thermoplastic. Therefore, in the resulting product, consumption of natural biomaterial by microbes takes place, leaving behind fragmented thermoplastic matrix. In the family of the polymers of renewable resources, starch has been considered as the most promising material for this purpose as it exists abundantly and may form a cost effective end product [12-14]. Compatibility of starch can be improved by the modification of hydroxyl group and may be used at fairly high amount in the composites to obtain the tailored material [15-17].

The blends of starch with anhydride-containing copolymers (up to 70 wt% starch in the whole composition) [18-19] have been reported. MaterBi® from Novamont is claimed a commercially available and compostable product made of compatibilized aliphatic PCL/starch blends and is being used for preparation of films and sheets [20]. By destroying the crystalline structure of starch under pressure and heat with plasticizers (e.g., water, glycerol and other polyols), it is possible to convert it into thermoplastic starch (TPS, where starch content is as high as 95%), which could be processed alone or with a particular synthetic polymer [16,21-23] but the moisture sensitivity limits its applications for many purposes. Although water resistance can be improved by adding poly(ethylene-co-vinyl alcohols) [24] or by cross linking [25-26] still it has not come to real practical use as traditional plastics. An increased biodegradability of starch-PCL blends was found with the compatibilization and it was displayed that the compatibilization not only increased mechanical properties but also the accessibility of comparatively less active matrix against microbes [27]. In all starch based systems, the mobility of polymer chains determine the generation of chain to chain interactions and entanglement, processing

parameters and composition and are believed to influence the mechanical properties but, the direct relation in the structure and properties of resulting products are very complex and little known. Moreover, the total goal in the area of starch thermoplastic composites is to enhance processibility, compatibility and water resistance in a very cost effective manner as these factors decide the fate of starch based product in the form of a substitute for petro based materials. Recently a new class of hybrid material of polymers and layered silicates has emerged and well known for reinforcing the several material properties due to the high aspect ratio and easy phase to phase energy transfer, even at very low filler concentration, if uniformly and completely dispersed in the host matrix [28-30]. A tremendous improvement in mechanical and barrier properties was observed when starch matrix was filled with layered silicates and well ordered nanocomposites were obtained by melt intercalation method [31,32] with plasticized starch. During synthesis of nanocomposites, polymer chains from bulk try to penetrate inside silicate layers and depending on penetration extent, intercalated or exfoliated structure is formed. If polymer chains are not able to penetrate effectively microcomposites formation takes place. There are a number of parameters which decide this degree of diffusion viz. modification of clay, polar-polar interactions, molecular weight of polymer, packing density inside the gallery and concentration of filler [33]. The preparation of nanocomposites is still a trial and error effort, ranging broadly from a lower filler concentration to higher by varying the different parameters like mentioned above and optimization of parameters is usually done by examination of several formulations . In the present study, it was found out that except all these deciding parameters of composite structure, the sequence of mixing can also affect the nature of resulting product, whether it will be a nano level distribution or micro level, at least in starch clay nanocomposites prepared by solution method. Since both components (starch & plasticizer) of composite (starch/ clay /plasticizer) must show the tendency toward accommodation inside the gallery space of filler, due to the presence of polar –polar interactions with clay, the study of interactions may insure the preparation of tailored nanocomposites of starch. In the present investigation, the behavior of starch / plasticizer (glycerol) with clays was studied to determine the cause of intercalation and hence to understand the process taking place. Mechanical properties, thermogravimetric analysis, moisture sensitivity of the composites were studied. XRD results were used to evaluate the interaction extent between filler and starch /glycerol and different structural presentations were made on the basis of these results.

6.2. Experimental

6.2.1. Material

Native corn starch, with 15 % moisture content and glycerol was obtained from S.D. Fine-Chem. Pvt. Ltd. (India). Clay, sodium montmorillonite (Cloisite Na +) was from Southern Clay Products, Inc. USA, having Cation Exchange Capacity (CEC) 90 meq/100 gm.

6.2.2. Preparation of nanocomposites

The clay was dispersed in water at 35 ± 5 °C for 48 hrs. till the formation of colloid like hazy suspension. Weight of clay and starch was taken after drying at 110 °C. Plasticizer concentration was 20 % (w/w) of dry starch and clay concentration was constant at 5 % (w/w) in all the compositions. The starch/ clay / glycerol (75 /5/20) were mixed by the following ways: i) Starch was gelatinized with water followed by plasticization and then clay slurry was added. This mixture was heated for 30 minute at boiling point and obtained composite samples were designated as STN1, ii). The clay slurry was mixed with starch in water and heated at boiling point for 30 minutes with constant high stirring, followed by the addition of plasticizer. These samples were named as STN2, iii) starch, clay slurry and glycerol were mixed together and heated for 30 minute at boiling point, these specimens were known as STN3 and iv) glycerol was mixed with clay slurry and stirred for 5 hrs. at room temperature followed by addition of starch. This mixture was heated at boiling temperature for 30 minutes and samples were designated as STN4. The glycerol-clay (ST-GLC) mixture was also prepared under the same condition to study the migration efficiency of plasticizer into clay layers. Commonly, after completion of all procedures, solution was poured in petridishes and dried in vacuum oven at 50-60 °C. The films of ~150-200 μm thickness were obtained and samples were equilibrated at 25 ± 2 °C for two weeks at 43 % relative humidity (RH) according to the ASTM E 104.

6.2.3. Characterization and measurements

6.2.3.1.WAXD

The WAXD pattern of samples was obtained by a Rigaku (Japan) diffractometer with Cu-K α radiation at 50 kV between the scan range of 2θ from 2-10 degree by the scan rate of 1° /minute. The d-spacing was calculated by Bragg's equation where the λ was 0.154 nm.

6.2.3.2. Thermogravimetric Analysis (TGA)

TGA was performed under nitrogen flow at heating rate of 10 °C/min in the temperature range of 25 -500°C by the Perkin Elmer TGA-7 instrument after maintaining the samples for 2 weeks at 25 ± 2 °C.

6.2.3.3. Mechanical Properties

These all samples were molded at $150 \pm 5^\circ \text{C}$ for 40 seconds in between Teflon sheets at 5000 pound pressure followed by quench cooling for 2 minutes. Mechanical properties of five samples for each composition, were determined using an Instron universal machine at 27°C with cross head speed of 1.5 mm /min, after conditioning for 3 weeks at 67 % RH. The data for the samples those failed close to the grip was excluded.

6.2.3. 4. Water Uptake (WU)

The specimens were cut in the shape of rectangular strips with dimension of 10 mm X 10 mm X 1 mm. It was supposed that films were thin enough so that molecular diffusion was considered to be one dimensional. The samples were dried till the constant weight under an vacuum oven to remove the moisture before water absorption testing by gravimetric methods and this weight was taken as initial weight (W_i). The samples were conditioned at 98 % RH for 50 hrs. and increase in weight was taken as final weight (W_f). The water content or water uptake percentage was measured by using following formula $[W_f - W_i] / [W_i] \times 100$. This type of water sensitivity measurements are better than classical technique of immersion in water as starch is very sensitive to liquids water which may partially be dissolved after exposure. Conditioned samples were removed gently and weighed using a four-digit balance. The samples were dried till the constant weight under an oven to remove the moisture before

6.2.3.5 . FT-IR and Biodegradability in compost.

FT-IR (Fourier Transform infrared 16 PC Spectrometer) was used to characterize the composite samples, interest was focused mainly on the changes in CH_2 stretching and bending bands. SEM was done after complete drying of the samples after composting as was given in Chapter 3 and 4. The samples were exposed to compost for different time intervals. The nature of compost was same as has been described in the Chapter 1. Additional feeding was done by mixing 100gm bread in the composting bin. Variation in sample weight was use to determine the biodegradation. In fact, all samples showed a weight increase in the starch-based systems due to water absorption after immersing in the compost. The weight loss is defined as the difference between the water absorption in pure water and in compost at the same exposure time. In the second case percentage of water absorption is always lower than in pure water.

6.3. Results and discussion

6.3.1. Structure of nanocomposites

The dispersion extent of silicate layers has typically been elucidated by XRD, which allow a direct evidence of polymer chain confinement into the silicate gallery. The XRD pattern of all samples is shown in Figure 6.1. which suggest the presence of ordered structure in all the composites as complete diminishing of characteristic peak of clay (Cloisite Na⁺, $2\theta = 7.54^\circ$, d-spacing = 1.17 nm) was not found. The presence of narrow peaks except STN2, is an evidence of the higher stacking order in clay layers and confirming the finite diffusion of polymer chains with repeat distance of few nanometers between chains and layers. The highest increase in d-spacing for STN2 specimens ($2\theta = 3.30^\circ$, d-spacing = 2.68 nm) and lowest for STN1 ($2\theta = 6.37^\circ$, d-spacing = 1.38 nm) was observed whereas, STN3 shows a significant shift of theta towards lower direction with an intermediate gallery height ($2\theta = 4.58^\circ$, d-spacing = 1.93 nm). From the observations, it was apparent that there must be some interactions, which decides the chain diffusion into gallery of clay, as all components had the same concentration in composites. After plasticization, starch chains could not be diffused inside clay gallery and this must be due to the electrostatic attraction between the functional groups of starch and glycerol resulting in the formation of a big mass by developing hydrogen bonding bridges, affecting the global mobility of polymer (Figure 6.2). Another cause is the decrease in polar-polar attraction between the hydrophilic clay and starch as in this case starch is also attracted by the plasticizer. In other words a counter balance of driving forces (polar-polar attraction of clay is partially balance by electrostatic hydrogen bonding between starch and plasticizer) takes place, which consequently decrease the attractive forces between clay and starch. This argument was become more explanatory by obtaining the XRD pattern of clay and starch mixture where an increase in d-space was higher than STN1 (for ST-GLC, $2\theta = 5.43^\circ$, d-spacing = 1.62 nm and for STN1, $2\theta = 6.37^\circ$, d-spacing = 1.38 nm), and this fact gave the credit to conclude that plasticizer also face the difficulties in moving towards the gallery due to the electrostatic H-bonding with starch and could not intercalate as freely as in the absence of starch. Further, when the composites were prepared without earlier plasticization (STN2), the characteristic peak was highly diminished giving the indication of high extent of intercalation i.e. the extensive diffusion of polymer chains inside galleries of clay, which results in high dispersion of filler throughout the matrix. These results confirm the presence of attraction forces in all the systems, which are decisive factors for the effectiveness of dispersion in the overall polymer matrix. The gallery height was not increased in the case of STN2 after plasticization, suggesting that plasticizer can be accommodated among starch chains which may not lead to any further

increase in gallery height. In the case of STN3, increase in d-spacing was less than STN2 but significantly higher than for STN1 and little higher than glycerol-clay mixture which may be attributed to the diffusion of starch chains inside the filler. Here, if we suppose that, complete diffusion of plasticizer had taken place in this sample, and then also the increase in gallery height is more than in ST-GLC, which confirmed the migration of starch chains. Since complete diffusion of plasticizer is not possible due to presence of interactions between plasticizer and starch, it was concluded that both the components have moved towards gallery faster than STN1 and slower than in STN2 in the STN3 samples. In a previous study [31,32] the non escaping of small molecules in thermoplastic starch –clay nanocomposites, prepared by melt intercalation method, inside gallery was argued by the absence of significant increase in gallery height. Thus, there is a clear effect of preparation method on the starch migration inside clay galleries, which increase when solution method is applied. In the present system a clear migration of plasticizer inside unmodified clay layers was observed. Moreover, the possibility of better dispersion of clay in the starch matrix decreases if glycerol and starch will allow together for the diffusion inside the layers of silicates.

When another set of the composites (STN4) were prepared by the mixing of starch in the mixture of clay and glycerol , which had already been stirred at room temperature for 5 hrs. , followed by heating the whole solution at boiling point for 30 minutes, a XRD pattern showing greater gallery height than ST-GLC and STN1 but less than STN2 & STN3 was found (STN4 , $2\theta = 4.96^\circ$, d-spacing = 1.78nm). These results were surprising because glycerol was supposed to increase the gallery height and act as surfactant, which would have been facilitated the penetration of starch chains. Further, in this composition starch diffusion should be more as starch chains have two attractions one; with clay and otherone with plasticizer, inside the clay. The explanation for this behavior may be as follows;

1. There was enough amount of plasticizer outside the clay stacks after a optimum migration inside the layers as only glycerol can not cause the individualization of silicates layers. The un-migrated plasticizer can form hydrogen bond bridges with the starch molecules resulting in slow diffusion as in STN1. Further, the un-plasticized starch chains may require an additional force to replace the plasticizer on the surface of filler. Thus, the number of contact decrease by starch on the clay surface.

2. The tetrahedral sites in the layers, containing Si^{+4} (a Lewis acid site), might be helping in intercalation of oxygen containing functional groups (O-H-) in starch. In the case of STN 2, these sites were engaged with OH of glycerol and unavailable during penetration of starch chains as the diffusion start after surrounding the filler particles. Again the concentration of glycerol inside the gallery may increase the packing density, which will disfavor the penetration of polymer chains.
3. Another the most probable explanation may be that, as soon as starch chains start interacting with glycerol present in the gallery, a close packing starts, which may generate a solid like structure after a definite penetration of starch chains. At this stage diffusion of other chains becomes difficult resulting a micro- composite.

The migration of plasticizer inside clay galleries was studied by FT-IR spectroscopy, which gives more realistic information about the different interactions at molecular level. IR bands between $2800\text{-}3000\text{ cm}^{-1}$ are related to the stretching of CH_2 and bands around 2920 and 2850 cm^{-1} , generates due to the asymmetric and symmetric stretching of methylene respectively. Peaks at $1472\text{-}1466\text{ cm}^{-1}$ arises due to the scissoring vibrations of CH_2 . These scissoring bands shows variations with inter chain interactions, packing arrangement and ordering of methylene chains [34]. Figure 6.3. showed FT-IR spectra of glycerol, obtained at room temperature, with different components. The shifting of band from 2925 to 2920 cm^{-1} after clay mixing suggest an increase in packing density thus the surface area per guest (starch) chains decreased. There was no change in this band for STN4 specimen, which was attributed to the close packing in the silicate layers. The increase in packing density or decrease in chain motion of glycerol after mixing with clay was further confirmed from the rising of CH_2 bending at 1472 cm^{-1} . Thus the migration of glycerol into silicate layers increases in the absence of starch which increase the packing density increase, which inhibit the further penetration of starch chains resulting in conventional type of composites.

6.3.2. Effect of filler dispersion on the material properties

6.3.2.1. Mechanical properties

The results, obtained by measurement of mechanical properties of the composites are tabulated in Table 6.1. The modulus of composites increased significantly for all candidates as compared with unfilled matrix irrespective of the preparation fashion. The highest enhancement in STN2 and lowest in STN1 suggests that the stiffness increase with

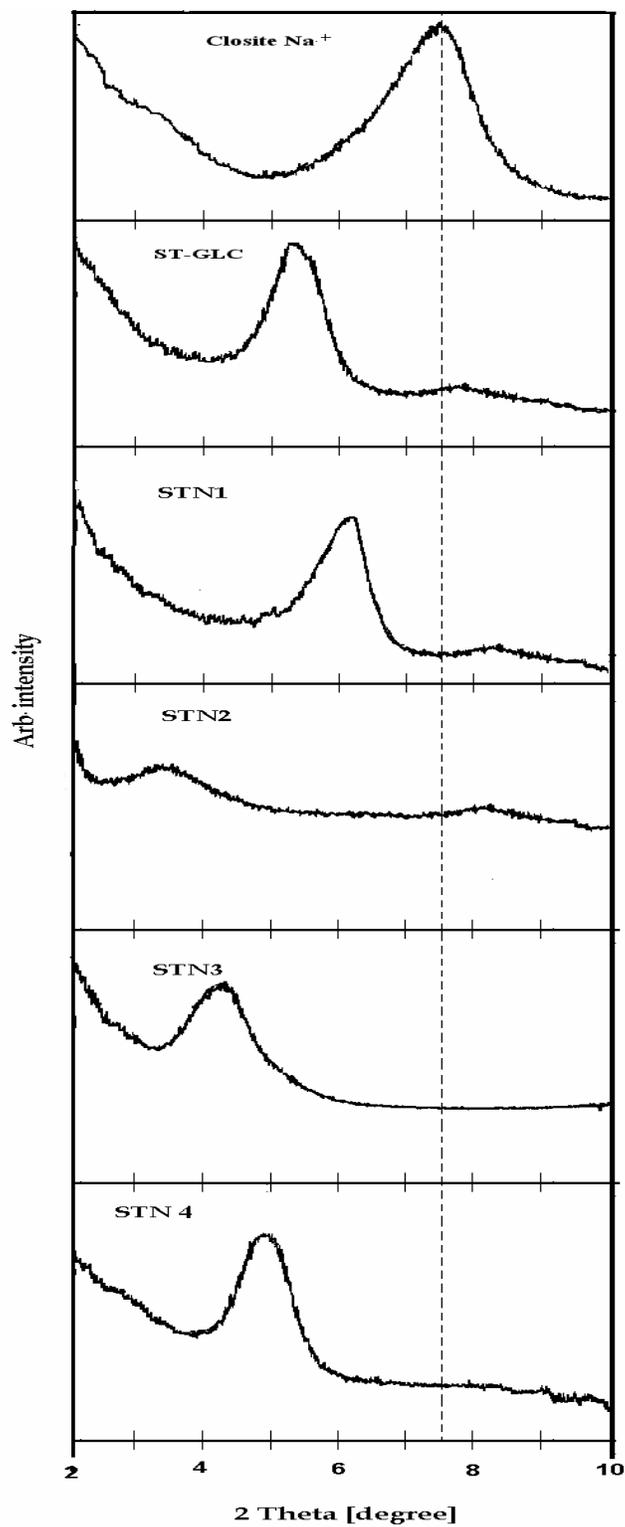


Figure 6. 1. The XRD pattern of all composites and neat Cloisite Na+ including glycerol –clay composition

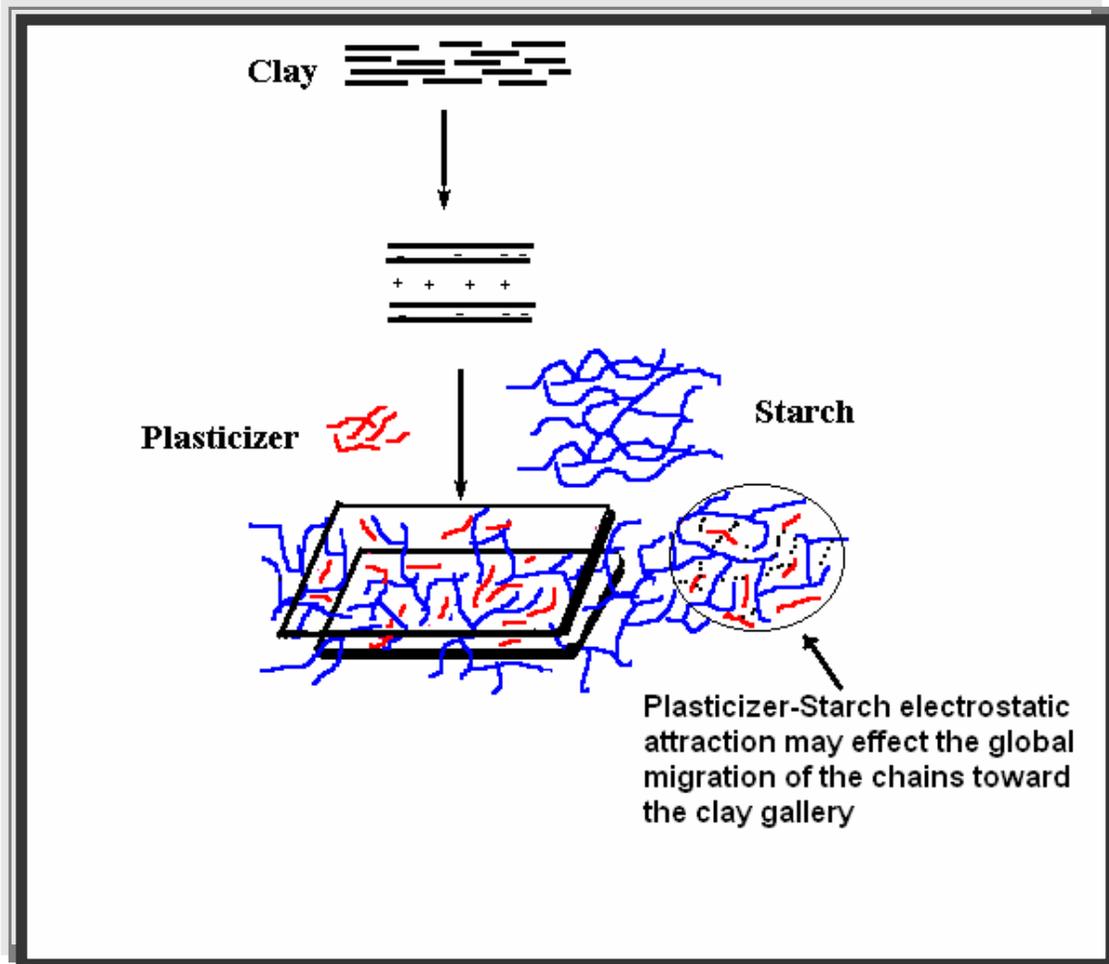


Figure 6.2. Representation of interactions between plasticizer and starch during migration towards clay galleries

the gallery height of silicate layers in the matrix. Such kind of improvements are well known in intercalated /exfoliated nanocomposites for other polymers also and are attributed to the higher reinforcing effect of layered fillers [28,29]. A significant increase in of STN2 as compared with other samples indicates that the extent of plasticization is sufficient enough which allow the segmental mobility of starch chains. Thus when glycerol was mixed after starch diffusion inside the clay gallery, it can migrate throughout the system owing to its smaller size and retaining the plasticizer efficiency. In the case of STN1, a significant reduction in strain is attributed to the presence of large stacks of filler inside the matrix consisting agglomerates of layered silicates those are surrounded by polymer chains. STN3 showed intermediate results but strain was less than unfilled starch

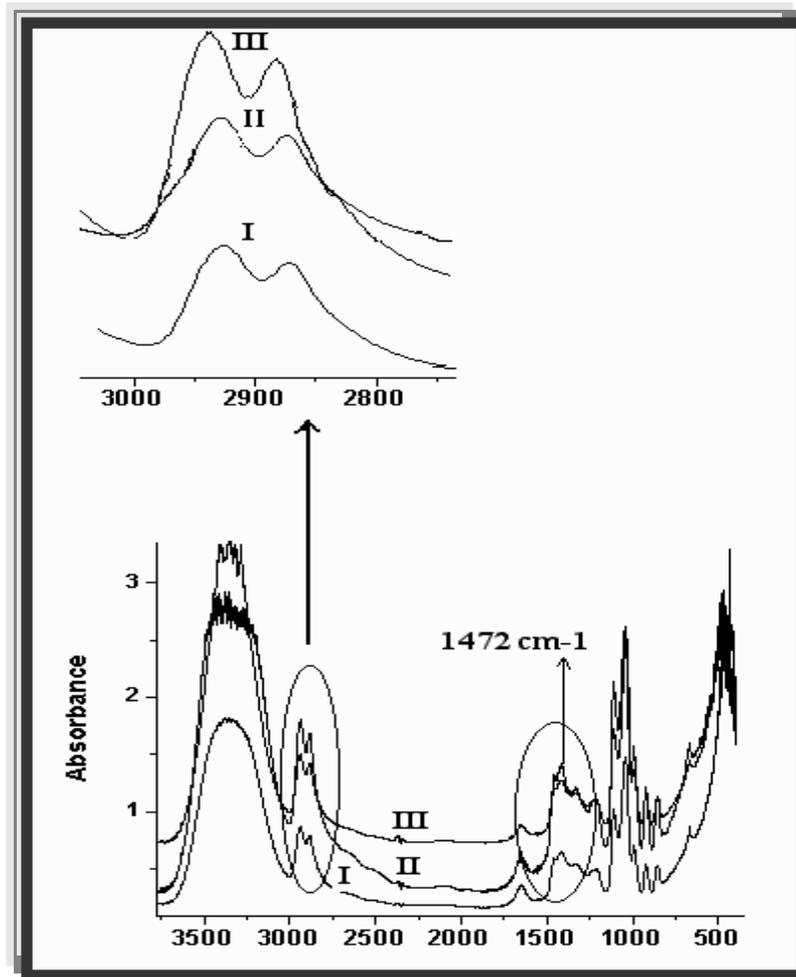


Figure 6. 3. FT-IR spectra of glycerol clay mixture (I), STN4 (II) and glycerol (III) which confirm the decrease in plasticization efficiency. The specimen of STN4 exhibited the results close to STN3 but are not significantly different which gives the information that most of the glycerol resides inside the gallery space and is not available for electrostatic bonding with starch leading a restricted motion of chains

Table 6.1. Mechanical properties of different composites

Sample	Young's Modulus [MPa]	Maximum strain [%]
Plasticized starch	790	10
STN1	820	6
STN2	825	12
STN3	824	9
STN4	821	7

6.3.2.2. Moisture resistance

Moisture sensitivity of starch-based material is a key challenge towards the substitution of traditional plastics for commodity, most precisely, for packaging applications. The water uptake during the exposure at RH 98 % was evaluated for 50 hrs. (Figure 6.4). The increased permeability of starch films after plasticization has been reported against water, gas and solute [35]. The plasticized starch films showed the highest moisture sensitivity in comparison of other samples. Plasticization increased the hydrophilicity of the starch matrix as around 1.5 times, which is attributed to the increase in chain mobility at room temperature by breaking the attraction forces in host matrix and consequently increase in concentration of exposed moisture prone hydroxyl groups facilitating diffusion of water molecules throughout the polymer matrix. After mixing with clay, an overall decrease in hydrophilicity, regardless the clay concentration in the systems, must be attested to the presence of barriers in the form of torturous path of clay, which generate difficulties in diffusion through the matrix. The STN1 specimens absorbed less moisture than plasticized starch, which was due to the increased pathway generated by clay dispersion.

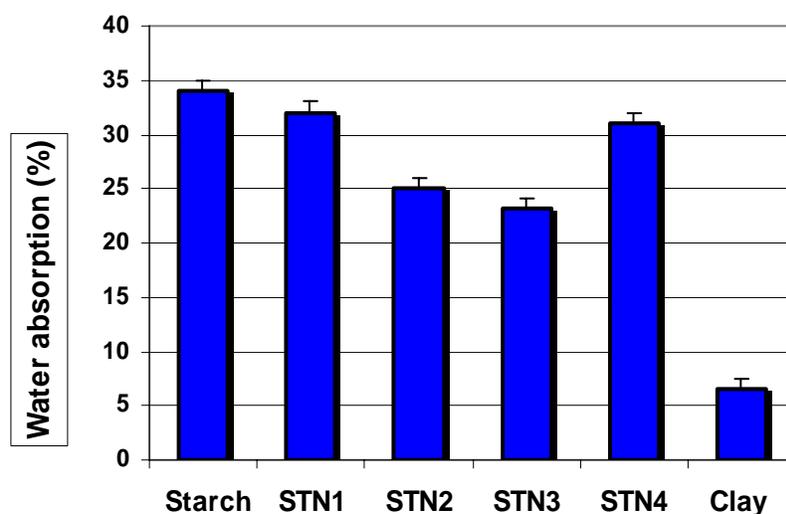


Figure 6.4. Water absorption at 98 % RH and $25 \pm 2^\circ\text{C}$ for 50 hrs.

The concomitant increase in water resistance in case of STN2 must be attributed to the excellent dispersion of fillers which could resulting a higher engagement of OH groups with layers, making them less available for moisture. Secondly, the number of barriers also increased in this composition. Since the plasticizer was added after clay

dispersion in the matrix therefore, the plasticizer also moved towards gallery i.e. there were two attraction forces working together to pull the plasticizer inside the gallery, clay – plasticizer and plasticizer- starch attractions. This conclusion was strongly supported by increase in elongation at break of this system. The resistance shown by STN3 against moisture was comparatively higher than STN2. Thus, water sensitivity can be altered more effectively by dispersion extent of clay than the presence of moisture sensitive groups, as the concentration of these functional groups present in STN3 was higher than STN2. Water absorption by STN4 is higher and almost equal to STN1. Thus, for higher water resistance clay must have an optimum ordered structure that could develop an effective and sufficiently enough diffusion paths.

6.3.2.3. Thermal properties

In general, thermal stability of polymers increases after filling with inorganic fillers [28]. The results of TGA are depicted in Figure 6.5. A three-step process was clearly observed in the composites. All specimens showed highest weight loss at 296 °C. The I, II and III step were attributed to the water loss, starch plus glycerol decomposition and final decomposition of remaining starch during oxidation. The percentage mass loss was decreased in second step and increased in third for all composites suggesting that the decomposition temperature of glycerol and starch has shifted to higher temperature i.e thermal stability increased for starch and glycerol after clay filling and this must be because of protection of starch and glycerol by silicate layers. Furthermore, STN2 presented the highest thermal stability in comparison of all specimens, which is attributed to the higher dispersion of filler in the matrix. The concentration of exposed hydroxyl groups was least in the STN2, as has been discussed earlier, which may be another cause of thermal stability. Significant difference was not found in the thermal stability of STN1, STN3 & STN4 but it was better than unfilled plasticized-starch matrix. The decrease in plasticization extent after removal of water is expected, at least at those segments of polymer where glycerol could not reach effectively as it was not perfectly homogenized in these systems (STN1, STN3 & STN4), and since water content was more in STN 1, this effect (decrease in plasticization efficiency) was obviously more pronounced. As soon as water evaporates, the starch chains may tend to reorganize and low degree of ordering tend to convert into higher degree. The over all phenomenon may result in the re-association of starch chains after formation of entanglement or juncture points and again the chances of helical structure formation increases. This reorganizing may decrease the thermal decomposition temperature of the matrix. Thus, there may be three factors deciding the

fate of clay filled starch against thermal treatment, i) exposure of hydroxyl groups ii) clay dispersion extent in the host matrix and iii) reassociation of starch chains. The factors can be written in the following order of effectiveness of samples during thermal treatment:

Clay dispersion > Hydroxyl groups exposure > Reassociation of matrix chains.

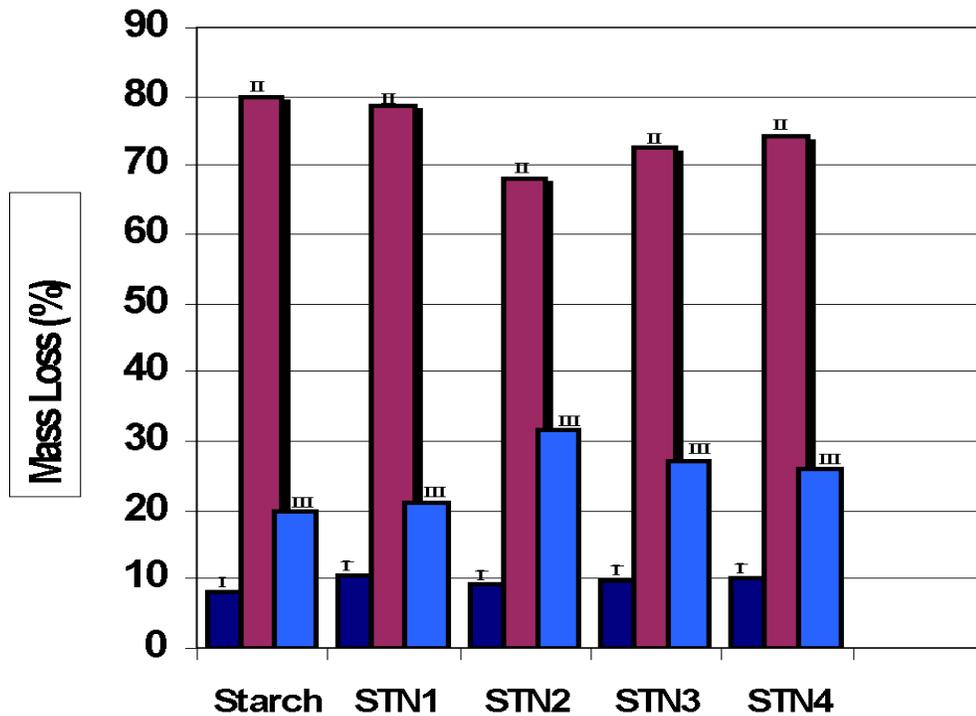


Figure 6.5. Mass loss (%) during thermogravimetric analysis of samples at the rate of 10°C /min. [I step corresponds to the weight loss of water, II step is the weight loss relative to total mass of samples, III step is the weight loss relative to mass of plasticizer and starch in the samples]

All three are present effectively in the STN2 whereas, poorly in STN1 and as intermediate in STN3 and STN4. Finally, all results of this study tend to demonstrate the effect of preparation methods and sequence of addition of components, on the composite nature. The possible ways of interaction by which the four types of composites were obtained are illustrated in Figure 6.6. Starch and glycerol migrate into clay galleries as both have polar-polar attraction with clay. Glycerol is preferred over starch in this competition owing to its smaller size. The rate of diffusion of both starch and glycerol inside the layers decrease when mixed together because of mutual attraction forces, which formed a mass like structure resulting in slow transport around the tectoides and

consequently delay in migration inside the silicate layers (Figure 6.2). If already plasticized starch is mixed with clay, a microcomposite formed and whatever the increase in gallery height observed is due to the migration of some glycerol inside the layers. The best nanocomposites were formed when first starch–clay was mixed followed by plasticization. In this case, starch chains involve only in one dominant polar-polar attraction with clay and confinement occurs without interference. At this moment, the plasticizer molecules have double attraction towards gallery space; first with clay and second due to electrostatic hydrogen bonding formation with starch chains. Since the plasticizer is small in size, it can be accommodated in gaps of starch chains between the silicate layers. This process leads to an efficient plasticization of starch matrix retaining the elongation of resulting product. The increase in modulus was not very significant in the composites which may be a indication of insufficient concentration of filler as at the high concentration [36] modulus can increase by many fold but it is not necessary that the silicate layers are individualized at nano level. The composites can not be immersed in water due to extreme moisture sensitivity. All the composites were water resistant at least till 50 hrs. and this fact (high water resistance) may be easily eliminated for prolonged exposure because clay will swell and gallery space will increase with time which may result in complete leaching of components .

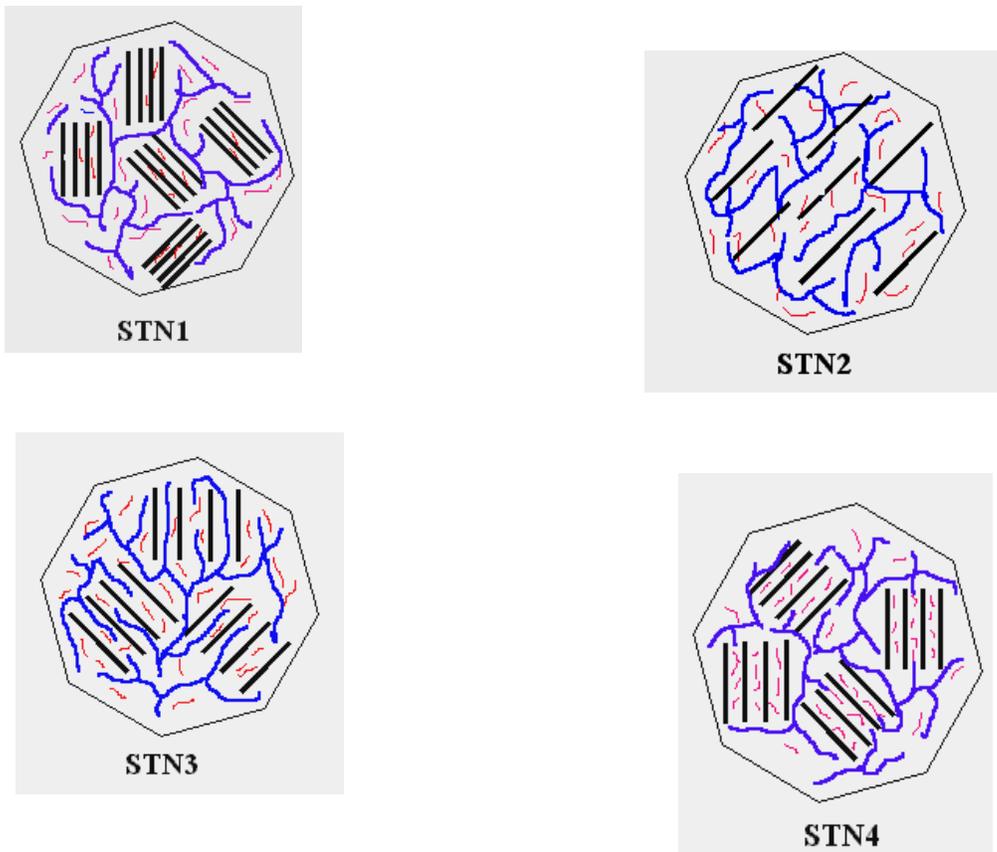


Figure 6.6. Different structure of composites. Composite formed by the mixing of filler into plasticized starch (STN1), composite structure formed by the mixing of filler into starch followed by plasticization (STN2), composite structure formed by the together mixing of all components (clay/starch/plasticizer) (STN3) and composite structure formed when starch was mixed into slurry of plasticizer and clay (STN4). The thick bold rods indicate the silicate layers whereas; red and blue color represents the plasticizer and starch respectively

6.4. Degradability of composites

Biodegradability was measured in compost and percentage weight loss is shown in Figure 6.7. Samples could not be recovered after 3rd week of composting. The exfoliated composites showed slow degradability in the beginning of the experiments, which became almost equal to other samples after last limit of composting. It must be due to the high diffusion path generated by layered silicates and the diffusion of microbial chemicals

those are responsible for the degradation slowed down. It has been found that layered structure of clay blocks the transmission of moisture through the starch matrix. This dramatic lowering in water vapor diffusion was attributed to the presence of dispersed clays those increase the path of diffusion [31]. As soon as time of composting increase this factor may be excluded due to the swelling of clay, which further enhance the microbial action for biodegradation. Similar conclusion was drawn by Lee et al. [37] in case of unsaturated polyester, clay nanocomposites, prepared by melt intercalation, that the decrease in biodegradability under composting with intercalation must be due to high aspect ratio and better dispersion of clay in matrix which generate a more tortuous path for penetration of microorganism inside the bulk and hindered their diffusion.

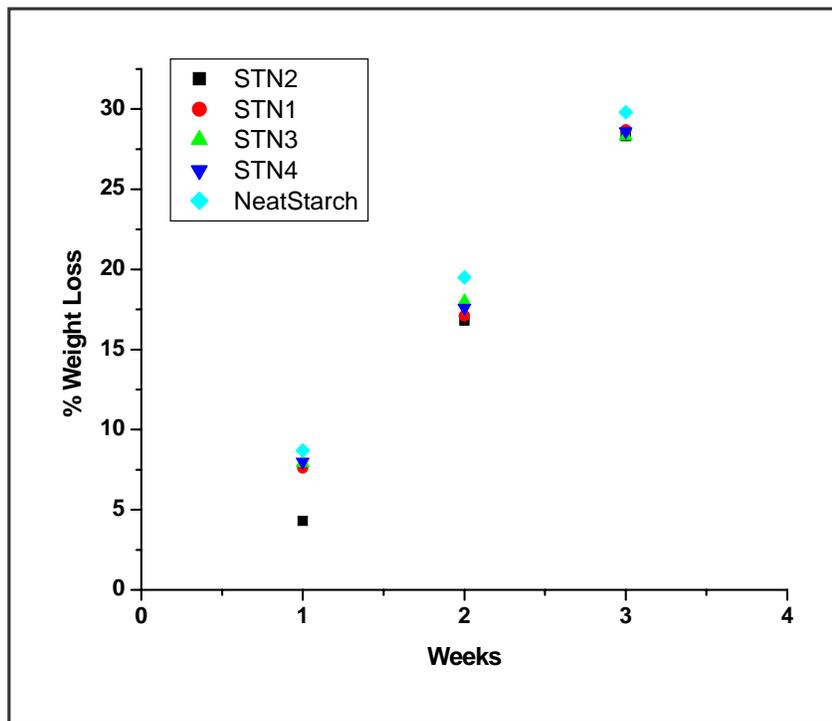


Figure 6.7. Compostability of composites

6.5. Conclusions

An improvement in material properties of all the composites could be achieved by better dispersion of clay. Better dispersion can be achieved by first mixing of starch and filler followed by plasticization. Thus, the interplanar distance of clay strongly depends on the sequence of mixing. Although the enhancement of mechanical properties takes place in the clay filled composites, still the water resistance is too poor to use these composites in packaging applications at least for liquids. From moisture sensitivity point of view, well ordered intercalated structure are also helpful to increase the moisture sensitivity in comparison of the structure consisting of individual nanometer dispersion of layered silicate in starch matrix. Diffusion of plasticizer inside the clay is easier than starch. Starch chains must penetrate through clay galleries first, followed by plasticization in order to maintain the plasticization efficiency. The biodegradability was affected initially by dispersion of clay layers but reached equal after last limit of composting. The material properties of layered silicate–starch composites may not change very significantly by a small decrease or increase in gallery height of filler. The composites obtained, are very far from becoming a substitute for traditional commodity plastics like polyethylene and polypropylene mainly because of their extreme moisture sensitivity.

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CHAPTER VII:
**DEGRADABILITY OF BIOCOMPOSITES PREPARED FROM MODIFIED STARCH
AND LAYERED SILICATES**

7.1. Introduction

Biopolymers of renewable resources have been considered as most promising natural material for the development of ecofriendly green products to reduce the plastic waste generated problems. There are many sources of biodegradable plastics from synthetic polymers (Polyesters, Polyhydroxyalkanoates etc) to natural polymers (starch, gelatin, chitosan etc) [1-3] and among them starch based thermoplastics has been considered more important to replace the petroleum based polymers [4]. When starch is converted to plastic material it offers a strong alternative for synthetic polymers from standpoints of conserving our petroleum resources and providing biodegradable end products [5]. On one hand, products of starch suffers changes in dimensional stability which leads to decrease in many useful properties due to high moisture sensitivity whereas on the other hand abundant supply, low cost, renewability, biodegradability and the ease of chemical modification make starch an extremely attractive material for modern technologies [6]. Starch can be used in several different form in order to generate different ecofriendly products [5,7].

Starch modification is another attractive way to produce thermoplastic materials and is a well known procedure [8,9]. One negative point in all those efforts was the molecular weight reduction of starch during modification, due to the high susceptibility of starch to solvents and acid chlorides or anhydrides used for the acylation. Lately, there is a renewed interest in the preparation of modified starches with acetate [10], hydroxypropyl [11] and fatty-acid ester (C4–C6) groups [12]. The main aim is to produce a fully biodegradable thermoplastic material, which will have the appropriate properties (especially mechanical), for replacing, whenever possible, the non-biodegradable plastics. The acetylated starch would have several advantages as a structural fiber or film forming polymer compared to native starch. The acetylation is a well known reaction and relatively easy derivative to synthesize. Native starch acetate is considerably more hydrophobic than starch and have been shown to have better tensile properties retention in aqueous environment [10-12]. Another advantage is that starch acetate has better solubility in comparison to native starch and could be easily cast from simple solvents.

Organic–inorganic hybrid have attracted great interest since they exhibit unexpected hybrid properties synergistically derived from the two components and melt intercalation into layered silicate has been proven to be an excellent technique to prepare polymer–layered silicate hybrid [13,14,15]. These layered silicate filled polymers exhibited excellent mechanical properties even at very low filler concentration. The

present chapter described the material properties of different modified starches when filled with natural and organically modified layered silicates. The two strategies were combined together and solution blending of clays was followed by melt intercalation with starch. The study was aimed to prepare the hydrophobic starch nanocomposites of different compositions. The biodegradability was also studied in composting environment.

7.2. Experimental

7.2.1. Material

Native corn starch, with 15 % moisture content and glycerol triacetate (plasticizer) was obtained from S.D. Fine Chem. Pvt.Ltd. (India). Clay, sodium montmorillonite (Na+MMT) having Cation Exchange Capacity (CEC) 90 meq/100 gm, Closite 6A (6A), Closite 30B (30B) and Closite 10A (10 A) were from Southern Clay Products, Inc. USA. The surface hydrophobicity of these clays were in the following order 6A>> 10A > 30B > Na+MMT whereas the initial gallery heights are shown in **Table 7.1**. Acetic anhydride, pyridine, lithium chloride, butyryl chloride and *N,N*-Dimethylacetamide (DMAC) were AR grade from Aldrich Chemical Company and used as received.

Table 7.1. Different type of clays

Clay	Ammonium cation	XRD peak position (2θ) degree	Basal spacing (001) nm
Closite 6A	(CH ₃) ₂ (HT) ₂ N ⁺	2.49	3.57
Closite 30B	(CH ₃)(T)(CH ₂ CH ₂ OH) ₂ N ⁺	4.73	1.88
Closite 10A	(CH ₃) ₂ (HT)(CH ₂ C ₆ H ₅)N ⁺	4.51	2.00
Na+MMT	None	7.85	1.17

[T= tallow (~ 65 % C18, ~30 % C16, =5% C14), HT= hydrogenated tallow, anion = chloride].

7.2.2. Preparation of starch derivatives

The starch was destructed by dissolution in DMSO, followed by the precipitation from ethanol. Such a treatment allows the disintegration of the organized packing of the chains to obtain more isolated macromolecules with an increased accessibility of reactive groups. Starch acetate (SA) of three different degree of substitution (DS) 0.8, 2.1 and 2.7 (SA1, SA2 and SA3 respectively) were prepared after little modification in the processes reported in the literature in order to get the desirable DS [18,19]. DS was measured traditionally by titration method [16, 17].

7.2.2.1. Preparation of starch acetate

50 g of over night dried starch was added to 1L of pyridine and heated to 95°C for 2 hrs under nitrogen atmosphere. Then 165 ml of acetic anhydride was added dropwise, the temperature was lowered to 75 °C and reaction continued for 22 hrs. The suspended and dissolved polymer was coagulated with 1 liter of isopropanol with stirring. The white fibreller mass, separated from the solution was filtered off and collected. This filtrate was washed thoroughly with ethanol. The product (63.7 gm.) was dried under vacuum at 40 °C temperature.

7.2.2.2 .Preparation of butyryl derivative

A mixture of water (1L) and starch (60 gm., 0.37 mol) was heated to 80 °C, with stirring and the mixture was maintained at that temperature for 1 hrs. DMAC (500 ml) was added and the temperature was readjusted to 80 °C. A mixture of DMAC and water (250 ml) was removed by distillation under reduced pressure at 85 °C whilst, at the same time aliquots of DMAC (250ml) were added to maintain a minimum of 500 ml reaction volume. This process was repeated until the mixture was deemed anhydrous by obtaining the DMAC distillate of constant boiling temperature. LiCl (3gm, 0.07 mol) was added with stirring. After 10 minute, the reaction temperature was adjusted at 80°C for 30 minute. According to the modification to be made, appropriate quantities of pyridine and acyl chloride were added. The lithium chloride, DMAC and starch are believed to form a ternary complex, as is the case for cellulose [20]. The original pattern of inter- and intra-molecular hydrogen bonds within and between the cellulose chains can be changed in solution in lithium chloride and *N,N*-dimethylacetamide. At the same time, the hydrogen bond acceptor properties of DMAC are expected to enhance the nucleophilicity of the exposed hydroxyl groups to attack by various electrophilic reagents. The inclusion of pyridine acts not only as a nucleophilic acylation catalyst, but also as a base. During the reaction, hydrochloric acid is formed as a by-product, which reacts with excess pyridine to form its pyridinium salt; this salt is easily separated from the reaction product by dissolution in 70% v/v aqueous MeOH, the solvent mixture used to precipitate the desired product. The mixture (after addition of pyridine and acyl chloride) was poured into vigorously stirred aqueous MeOH (70% v/v) (1500 ml) whereupon the product precipitated. It was washed with further aqueous methanol (2×1500 ml) and dried at 50°C. The crude product was re-dissolved in hot toluene (3000 ml) and then precipitated by addition of acetone (2×1000 ml). The product was filtered and dried overnight at 50°C before weighing. All these starches were soluble in toluene, pyridine and tetrahydrofuran. The dried samples

were stored in a vacuum desiccator over P₂O₅ for further analysis. **Table 7.2** explained the properties of butyryl modified starch.

Table 7.2. Calculated DS-values based on elemental analyses, and yields of modified starches

Reagent	Sample name	Starch reagent molar ratio	C %	H %	DS	Yield (%)
Butyryl chloride	BC1	1:3:0	57.6	7.5	2.79	98
	BC2	1:1:5	54.0	7.1	1.52	98

7.2.3. Preparation of Composites

The OMMTs (organo modified clays) were dispersed in toluene for 24 hrs at 50 ± 5° C and were poured in the R.B containing desirable weight of dried modified starches. This mixture was heated at 75± 5° C for 10 hrs. under nitrogen atmosphere. Starch acetate-clay was mixed with glycerol triacetate with overhead stirrer after removal of solvent followed by drying. This total mixture (starch/clay/ plasticizer) was blended in Microcompounder (a small scale twin screw compounder from DSM) at 100 rpm and 145° ± 5°C for 5 minutes. Plasticizer content was constant, 20 % w/w and filler concentration was varied to 5 & 7 % (w/w) on the basis of dry starch. The internal plasticization provided by the bulky side groups has a profound effect on their ability to form films, compared to pure starch. The film formation properties of the neat samples were depending mainly on the DS and not on the length of the side group. The esters with high DS can form flexible films more easily.

7.2.4. Contact angle

The water contact angles were measured on a Goniometer, Rame-Hart NRL, (Model 100-00 230), USA using freshly prepared deionized water, filtered through membrane filter. The drop volume was 2 mL. The static contact angles of the water on the substrate surface were determined by ‘sissile drop’ method, measured within 30 sec of placing the drop at room temperature (27 ± 3 °C). The reported values are an average of minimum 10 values, measured at different places on the sample.

7.2.5. Transmission Electronic Microscopy (TEM)

TEM was obtained using an acceleration voltage of 200 kV. The samples were ultramicrotomed with a diamond knife at the room temperature to give 70-nm-thick section.

7.2.6. FT-IR, Water Uptake (WU) and degradability testing were performed in the same conditions as has been described in the Chapter 6. Samples were removed periodically and cleaned carefully with cotton cloth followed by drying in vacuum before measuring the weight on a four digit balance. The samples were conditioned for 4 weeks as in Chapter 6 before testing.

7.3. Results and Discussion

7.3.1. Characterization

The FT-IR of unmodified starch is shown in the Figure 7.1 and comparison with modified starches were made. In the native starch spectrum, the characteristic broad peak in the region of 958-1190 cm^{-1} is attributed to the CO bend stretching. Another strong peak due to hydrogen bond stretching appears at 3000-3600 cm^{-1} . The intensity of this peak decreases with increase in DS. The higher the DS greater the decrease in band intensity. Strong bands in the FT-IR spectra of modified starch of SA1, SA2 and SA3 showed the absorption around 3200-3600 cm^{-1} which is known for O-H-vibrations of hydroxyl groups of starch, which decrease with increase in DS. Absorption at 1110 cm^{-1} (-C-O-C-) also increases significantly with DS. These variation in spectra confirmed that reaction went on smoothly and hydroxyl group substitution takes place. Figure 7.2 shows the FT-IR spectra of butyrylated starch of higher DS-values near to 3. The spectroscopic profiles contain an intense band at 1746 cm^{-1} and 2800 -2930 cm^{-1} corresponding to ester carbonyl and methyl/ methylene groups respectively. The both peaks increase with the DS of hydroxyl group.

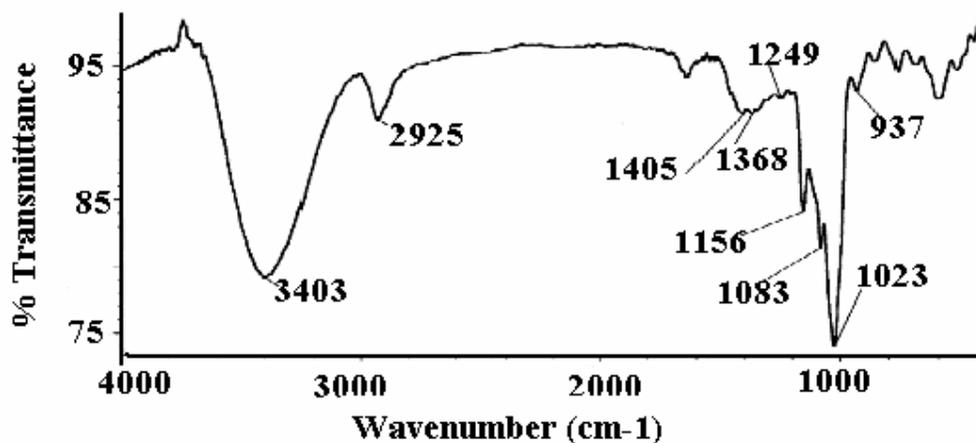


Figure 7.1. FT-IR spectrum of unmodified starch

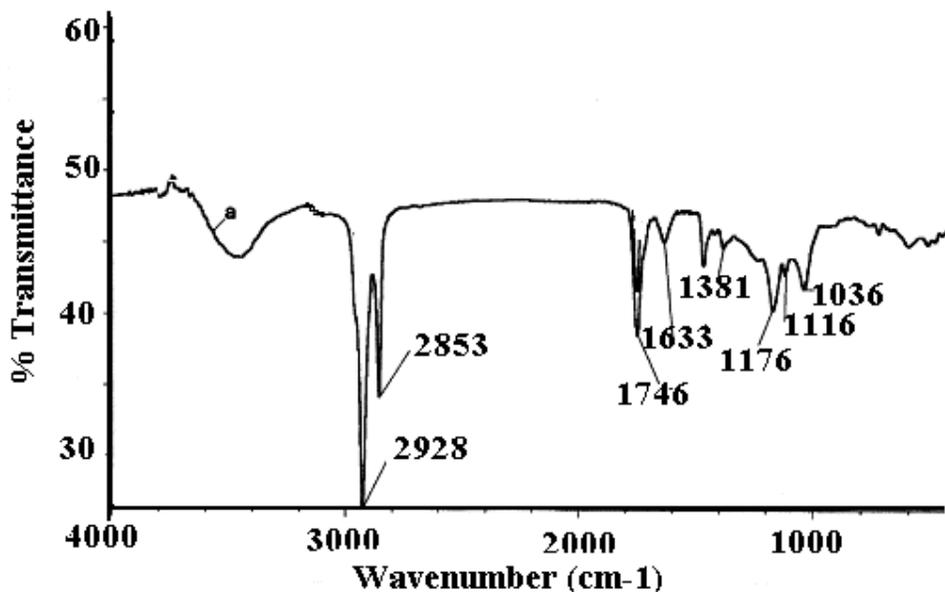


Figure 7.2. FT-IR spectra of butyrylated starch

The structure of nanocomposites in the nanometer range has typically been elucidated using WAXD and TEM. WAXD allows a direct evidence of the intercalation of the polymer chain into clay galleries. On the other hand TEM offers a qualitative understanding of internal structure through direct visualization. The variation in d-spacing have been tabulated in Table 7.3 a, b and c.

Table 7.3. d-spacing in the composites (-, showed no change in characteristic peak)**Table 7.3 a ,composites of SA1**

Sample	SA1							
Filler	Na+MMT,		6A		30B		10A	
Concentration of filler (5% w/w)	5	7	5	7	5	7	5	7
Gallery space (nm)	Exfo.	1.88	-	-	2.01	-	2.30	-
2 θ value (degree)	-	4.7	-	-	4.39	-	3.84	-

Table 7.3 b, composites of SA2

Sample	SA2							
Filler	Na+MMT,		6A		30B		10A	
Concentration of filler (5% w/w)	5	7	5	7	5	7	5	7
Gallery space (nm)	1.64	-	3.67	-	3.48	2.20	2.69	-
2 θ value (degree)	5.39	-	2.40	-	2.53	4.01	3.84	-

Table 7.3 c, composites of SA3

Sample	SA3							
Filler	Na+MMT,		6A		30B		10A	
Concentration of filler (5% w/w)	5	7	5	7	5	7	5	7
Gallery space (nm)	-	-	Exfo.	Exfo.	2.34	-	3.00	2.12
2 θ value (degree)	-	-	-	-	3.78	-	2.94	4.16

In the composites of SA 1 with Cloisite 6A at 5 & 7 % and with Cloisite 30 B and Cloisite 10 A at 7 % filler, the original peaks remaining in the resulting products, revealed that no confinement of starch chains occurred in these composites. This may be due to the increasing tendency of agglomeration with the concentration and decrease in polar-polar interactions. Thus microcomposites were formed where clay remains in the form of agglomerate as can be seen from TEM (Figure 7.3 a and 7.3 b for Cloisite 6 A and Cloisite 10A respectively at 7 % filler content in SA1).

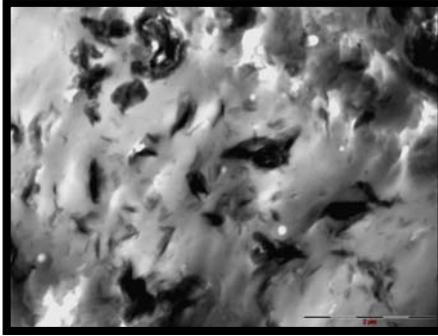


Figure 7.3 a, SA1 with Cloisite 6A at 7 % filler loading

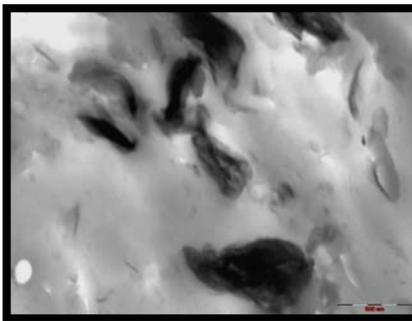


Figure 7.3 b, SA1 with Cloisite 10 A at 7 % filler loading

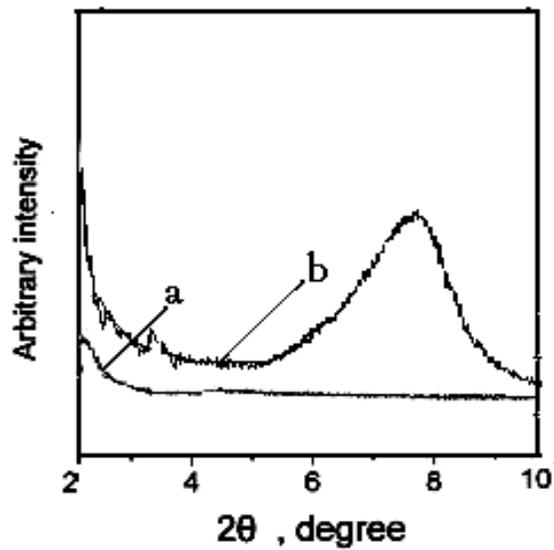


Figure 7.3 c, XRD pattern of SA1 filled with 5 % Na+MMT (a) and characteristic peak of neat clay (b)

The sample of SA1 with Cloisite 30 B at 5 % filler loading exhibited slight shifting toward lower theta angle, suggesting the individualization of few clay platelets inside the host polymer matrix but the shape of peak and shifting did not changed significantly which gave the credit to conclude that from SA1 neither intercalated nor exfoliated composites were formed at any concentration of OMMTs filler. When SA1 was mixed with Na+MMT an exfoliated structure was generated (Figure 7.3 c) must be due to the polarity matching between hydrophilic Na+MMT and SA1 (having DS of .8). The XRD pattern of SA2 (Figure 7.4 a) showed almost intercalated composites with Cloisite 30 B at 5 % filler loading where a very significant shifting was observed. The little increase in gallery height with Cloisite 10A at 5 % filler concentration was also observed with the same intensity of peak indicating the separation of few silicate layers inside the matrix in these samples. Figure 7.4b and 7.4c showed the TEM of SA2 filled with Cloisite 10 A and Na+MMT at 5 % filler concentration respectively where the individualization of silicate layers could be observed and the formation of a structure in between microcomposite and intercalated nanocomposites was assumed.

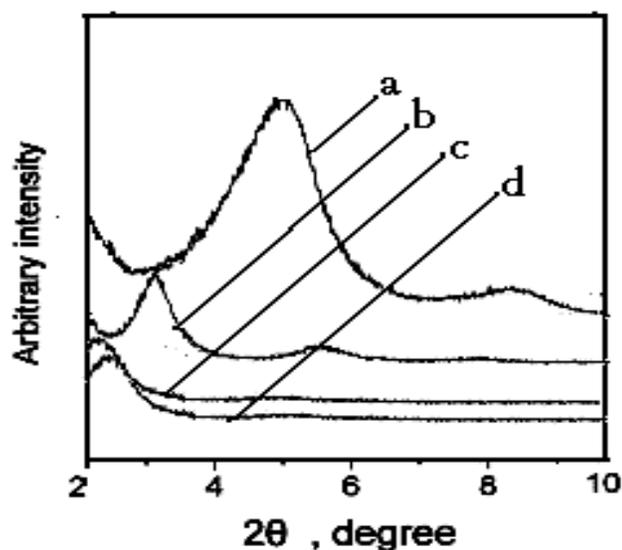


Figure 7.4 a, XRD pattern of SA2. [a) filled with 5 % Na+MMT, b) filled with 5 % 10A, c), filled with 5 % Cloisite 6A and d) filled with 5 % 30 B]

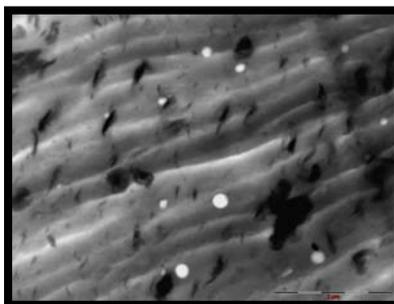


Figure 7.4 b, SA2 filled with Cloisite 10 A at 5 % concentration

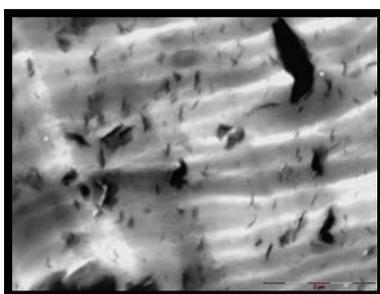


Figure 7.4 c, SA2 filled with Na⁺MMT at 5 % concentration

XRD signals collected for SA3 (Figure 7.5 a), a highly hydrophobic starch, showed that characteristic peak was totally absent in the Cloisite 6 A -SA3 composition at 5 & 7 % filler concentration which confirmed the formation of exfoliated composites and this observation of XRD was strongly supported by the TEM images (Figure 7.5b and 7.5c). where individualization of different layers could be found. The dark lines are the silicate layers in TEM. Each layer of filler is disordered and dispersed homogenously in the matrix. It is consistent with the absence of (001) plane in XRD pattern. XRD data obtained for the Cloisite 10 A-SA3 at 5 % concentration was in the form of intense peak, with very significant shifting of native peak toward lower theta angle indicated the presence of silicate layers in the periodic manner but highly distributed throughout the matrix or it may be considered as very ordered clay structure in exfoliated manner. Similarly highly distributed clay layers might be present in the Cloisite 30 B -SA3 at 5 % with preserved periodicity as peaks remain intense with significant shifting.

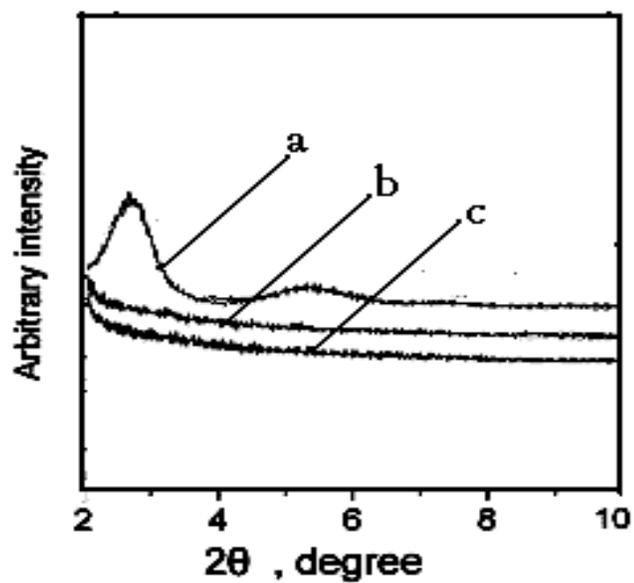


Figure 7.5. a, Exfoliated samples of SA3 at 5% and 7 % (b and c respectively) filler concentration of Cloisite 6A. 'a' showed XRD peak of SA3 filled with Cloisite 10 A at 5 %

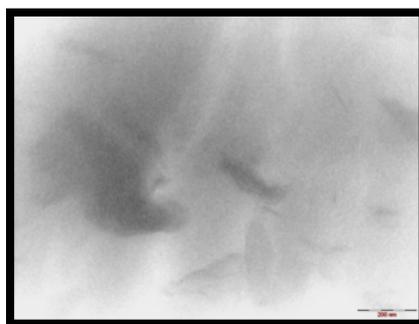


Figure 7.5. b, TEM of samples of SA3 5% filler concentration of Cloisite 6A

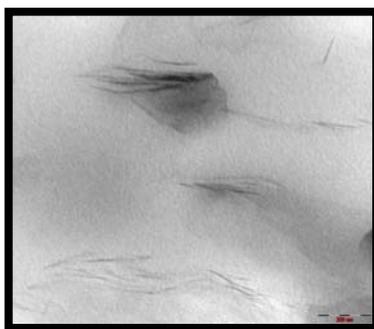


Figure 7.5 c, TEM of samples of SA3 at 7 % filler concentration of Cloisite 6A

Thus from all the composites, three true nanocomposites were obtained first by SA 1 with Na⁺ MMT and secondly SA3 with Cloisite 6A at 5 & 7 % filler loading . Rest of the samples were either intercalated nanocomposites with reserved periodicity or typical microcomposites. It may be argued here that any component (starch, plasticizer, water if remaining) may escape from the starch matrix and cause the swelling of clay which can exhibit an increase in d-spacing of silicates. Since, there was no increase in the d-spacing of neat plasticized starch at all with Cloisite 6 A and 30B, it was concluded that chances of escaping of other components were negligible. In order for the polymer to fully wet and intercalate the clay or the organo clay tactoids, it is imperative that the surface polarities of the polymer and clay be matched. Polar type interactions are also critical for the formation of intercalated or exfoliated nanocomposites through melt blending.

7.3.2. Thermal properties

TGA analysis was carried out under nitrogen atmosphere and according to TGA curves (Figure 7.6 & 7.7) the decomposition temperature was elevated with an increase in the DS. Neat starch showed decomposition at 293 °C whereas starch with DS of 2.7 decompose at 343 °C. Morita [21] considered decomposition of starch due to intermolecular and intramolecular dehydration reactions. Thus it is conceivable that substitution of hydroxyl groups resulted in the improvement of thermal stability.

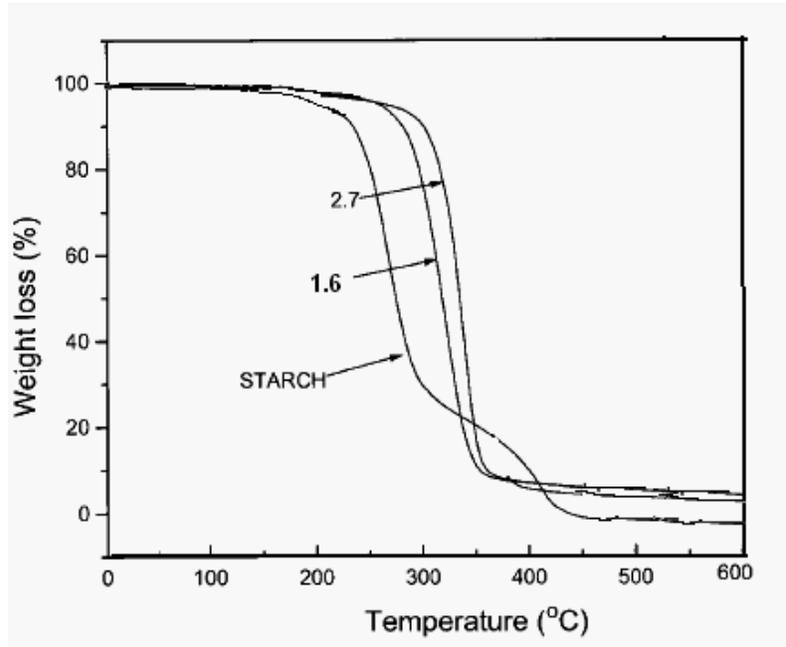


Figure 7.6 . TGA curves of neat starch and starch acetate

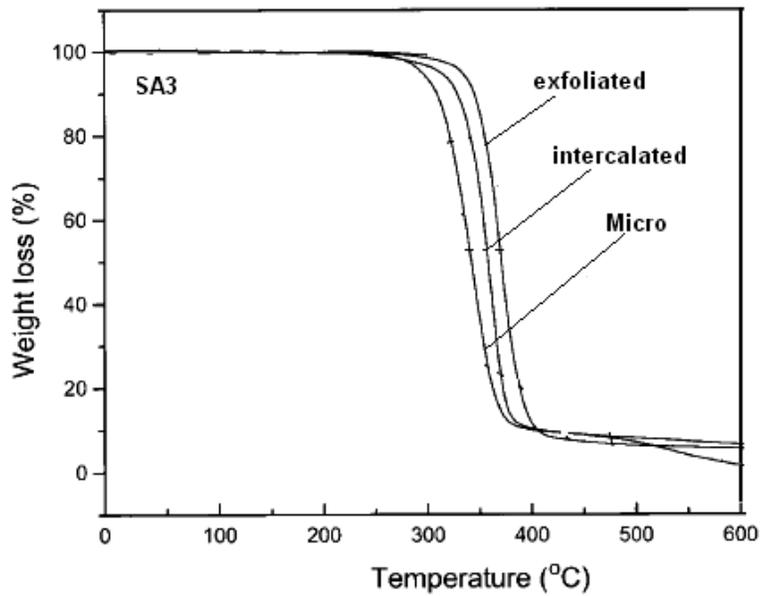


Figure 7.7. TGA curves of SA3 filled with layered silicates

TGA curves of clay filled starches of intercalated and exfoliated samples are shown in Figure 7.7. 50 % weight loss of SA3-Closite 6A at 5 % loading took place at 366 °C (23°C higher than SA3), intercalated composites with Closite 10 A showed at 354 °C and microcomposites at 345 °C. These results indicated that thermal stability increases after filling with clay and it is much better when clay is homogeneously dispersed. It is worth to recall that all OMMTs and starch showed initial weight loss at around 100 °C must be due to the evaporation of moisture. Thermal stability of SA1 and SA 2 was also increased significantly by filling with layered silicates. All micro composites and intercalated composites showed significant increase in the thermal stability at all filler concentrations. It must be noted that the unmodified starch contain ~2 wt percentage moisture even after over night drying in vacuum. This is because natural starch is very hydrophilic and can absorb upto 15 % of its weight of moisture under normal room conditions and considerably more when relative humidity approaches 100 %. The greater thermal stability of modified starch compared to neat starch is due to the low content of hydroxyl groups. Thus the over all TGA results suggested that the temperature of thermal decomposition increase in case of exfoliated composites. This thermal behavior was caused by insertion of polymer chains inside the clay galleries. This beneficial effect can also be explained on the basis of increase in the diffusion path of oxygen and volatile products throughout the composite material.

7.3.3. Water uptake

The moisture sensitivity of starch based system is a serious challenge to the researchers and many efforts are being made in this direction [3, 18]. In the sorption measurement mass of sorbed penetrant was measured as a function of time. The water uptake during exposure to 98 % RH of the various compositions are shown in Table 7.4 after 4 days exposure. It was found that each component absorbed water during the experiment. The diffusivity of water in starch based system is generally influenced by the microstructure of material such as porosity that can develop during drying and also by water affinity of the components. The addition of plasticizer generally increase the gas, water and solute permeability of the films. These swelling data presented in the Table 7.4 are the mean of several trials and the reliability of measurement was very good. It was found that by filling the clay in starch matrix, water of absorption decrease for almost every composition regardless of the nature of clay dispersion. This must be due to the barrier in the way of moisture in the form of clay layers. SA 1 was found less hydrophilic than neat starch. This

result strongly suggest that hydrophobic modification of starch is more important factor that clay dispersion as SA2 showed more water resistance than SA1 with Na+MMT at both filling concentrations must be due to the high hydrophilic nature of Na+MMT and since it was microcomposites the water uptake was significantly higher. Here, as can be seen that SA3, filled with Na+MMT, a microcomposites, showed no change in water absorption, confirmed that clay dispersion affects the water sensitivity of the composites.

Table 7.4. Water Uptake (%) of different samples at 98 %RH

SA1, [38]							
Na+MMT		6A		30B		10A	
Filler concentration							
5	7	5	7	5	7	5	7
35	37	37	36	34	35	33	34
SA2, [27]							
21	27	19	22	23	25	22	24
SA3, [18]							
17	18	7	9	13	14	12	14

Exfoliated composites of SA3 showed tremendous water resistance and only 7% water was absorbed. Rest all the composition of SA3 with all type of clays exhibited higher water resistance amongst all compositions. Thus in general water resistance can be improved by hydrophobization of the constituted components in the system. When there is competition between hydrophobic modification and clay dispersion, hydrophobic modification played decisive role whereas, when water resistance decided only by clay dispersion than disordered clay layers showed more water resistance than microcomposites.

7.3.4. Contact angle

The contact angle increases with increasing carbon chain length and DS (Table 7.5) as expected, because of the hydrophobic character of the side chains. The carbon chains conformation and remaining helicoidal structure of starch in the starch esters prevent the formation of hydrogen bonds between free OH groups of starch esters and molecules of water, resulting in higher hydrophobicity. The contact angle technique was used in order to quantitatively characterize the affinity of water of the samples. Table 7.5 presents the results of contact angle measurement for all the components. These results indicate that

modified starch become more hydrophobic as the number of carbon atom increased. It was observed from the results that surface of exfoliated composites were more hydrophilic with Na+MMT but water absorption was less, which confirm that mobility of water inside matrix, decide the fate of sample during exposure of water instead of surface characteristics. When surface was hydrophobic as well as clay was dispersed in highly disordered way the water resistance can be increased tremendously as in case of SA3. Another observation could be drawn from these results about the possibility of formation of intercalated or exfoliated nanocomposites as we know that compatibility and optimum interactions between polymer matrix, organically modified silicate layers are crucial factors for the dispersion of filler inside matrix. Although contact angles of all the composites were not significantly affected with the dispersion of clay still the measurement could give the information about surface hydrophobicity of the samples.

Table 7.5. Contact angle (degree) of different compositions [values in [] showed the water absorption by neat samples]

SA1 [76]							
Na+MMT		6A		30B		10A	
Filler concentration							
5	7	5	7	5	7	5	7
70	72	78	76	77	76	78	78
SA2 [85]							
81	84	90	88	86	85	88	87
SA3 [94]							
91	92	95	94	95	93	95	94

It is clearly seen that as soon as surface energy increased samples showed more affinity with less hydrophobic layered silicates and similarly when surface energy is decreases starch chains showed more affinity with less hydrophilic silicates as exfoliated composites were formed with SA3-Closite 6A system. Thus the most prominent feature of highly substituted acetate was its higher hydrophobicity in the form of nanocomposites which was comparable with synthetic polymers like polymethyl methacrylate (PMMA), which has contact angle of 85⁰ thus these samples may be considered as hydrophobic nanocomposites of starch. .

7.3.5. The nanocomposites of butyryl modified starches

After studying the different interaction possibilities with starches of different DS, it was possible to tailor the composite of different substituted starches with layered silicates. e.g if contact angle of starch is very high than it must have chance to form intercalated composites with hydrophobic clays like Cloisite 6A or 30 B. On the basis of similar assumption the nanocomposites of butyryl modified starches were synthesized successfully. The samples, BC1 and BC2 were filled with most hydrophobic clay i.e Cloisite 6 A at 5 % filler concentration under the same experimental conditions as mentioned above. The 5 % filler concentration was selected as it was found most effective in all the systems when filled with starch acetates. Table 7.6 and 7.7 represents the d spacing, the decomposition temperature at which it decompose 50 % and contact angle with water uptake results respectively. A beneficial effect of the increasing chain length on the thermal stability was observed. A previous study has shown [22] that water is the main product of decomposition during thermal degradation of starch, which formed by the intramolecular or intermolecular condensation of starch hydroxyl. Thus the higher degree of substitution has a positive effect on the thermal stability of modified starch.

Table 7.6. Composites of butyryl starches

Sample name	d-spacing (nm)	Contact angle (degree)	
		Neat sample	Composites
BC1	3.67	94	94
BC2	Exfoliated	92	93

Table 7.7. Thermal stability and water uptake by composites of BC1 and BC2

Sample	Thermal stability at which 50 % loss occurs (°C)		Water Uptake at 98 % RH	
	Neat sample	Composites	Neat sample	Composites
BC1	350	361	11	12
BC2	340	358	16	11

The composites with lower DS exhibited exfoliated structure as evidenced by XRD and TEM (Figure 7.8 & 7.9), in comparison to composites with higher DS. In addition to small stacks of intercalated layered silicates, exfoliated sheets were also observed, consistently

with the formation of intercalated and exfoliated structure as have been observed in other systems also [25]. In order for the polymer to fully wet and intercalate the clay or the organo clay tactoids, it is imperative that the surface polarities of the polymer and clay should be matched. Polar type interactions are also critical for the formation of intercalated or exfoliated nanocomposites through melt blending. In most of the work dealing with polymer layered silicates nanocomposites organoclays showed better dispersion in a polymer matrix than unmodified natural clays because of the hydrophobicity of the polymer. Thus BC1 must form intercalated or exfoliated composites which was not observed in the present study. This behavior must be due to one of the following regions. 1) for the formation of nanocomposites of layered silicates there should be an optimum interlayer distance between a disordered monolayer and solid like paraffinic arrangement of aliphatic chains of modifier. If the packing density is high, aliphatic chains may try to form a solid like arrangement, disfavor the confinement of polymer chains. Thus as soon as chain length increase, the tendency toward the formation of nanocomposites decrease even with highly hydrophobic clay. This fact was confirmed by the formation of intercalated composites of BC1 with Cloisite 10 A where increase in d-spacing was more than composites formed between BC1 and Cloisite 6A. 2).

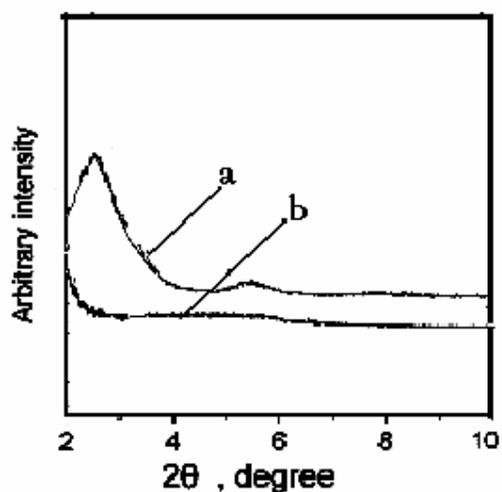


Figure 7.8. XRD of BC2 with 5 % filler concentration , ‘a’ for BC1 and ‘b’ for BC2.

There may be some conformational changes of glucose rings, which may have hindered the penetration of chains through gallery. 3) Higher chain length may decrease the global mobility of polymer toward gallery resulting in microcomposites. The contact angle did not change significantly by filling with clay in case of BC1 than in BC2 indicated a

decrease in the affinity toward water, which must be due to increased hydrophobicity as well as the presence of barrier in the form of clay. The thermal degradation temperature increase by filling with clay and it was more for BC1 than BC2. Both sample showed greater water resistance by filling with Closite 6 A. Again the main factor affecting the water uptake seems to be DS as BC1 exhibited more resistance than BC2. The side chains may also have some effect on the water uptake of the composites as in BCs it was higher than SAs, this fact can be attributed to the presence of more hindrance for making hydrogen bonds with water

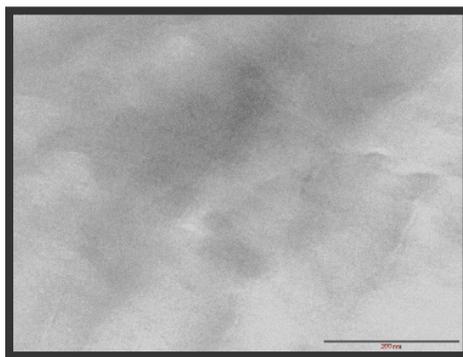


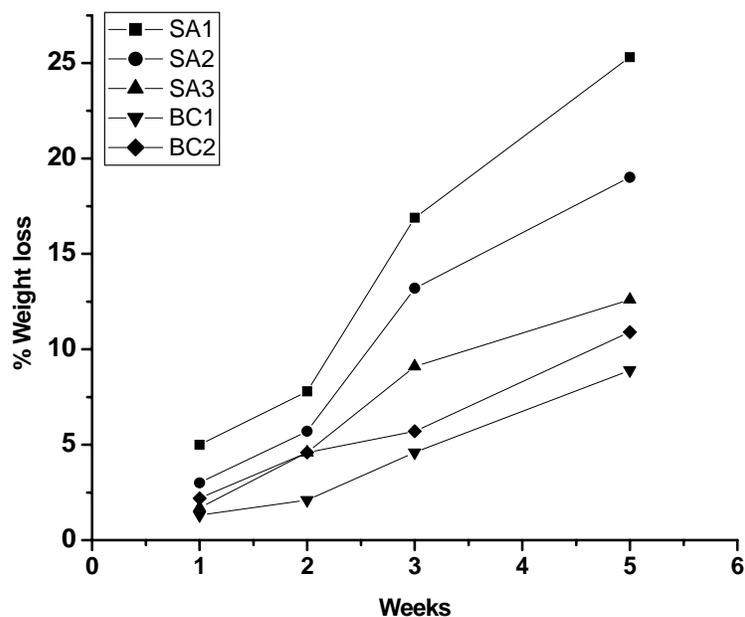
Figure 7.9 TEM of BC2 with 5 % filler concentration

7.3.6. Biodegradability

Biodegradability is a very critical issue concerning any material from renewable resources and the production of new material without biodegradability would be of little value. The results of biodegradation, measured by weight loss of neat samples and composites after composting are shown in the Figure 7.10-7.12. The biodegradability of modified starches was lower than neat films as neat samples underwent higher weight loss during the study. The samples having low DS were more degradable than samples of higher DS (Figure 7.10). It may be due to introduction of more number of groups those may inhibit the enzymatic action of microbes, which are responsible for the biodegradation of starch. If length of side chains increase then degradation rate decrease as BC1 underwent slower degradation than BC2. The results were in accordance with the contact angle data and the degradation rate decrease with increase in the hydrophobicity. Similar observations were made when starch acetate of different acyl contents were subjected to enzymatic hydrolysis [23]. Bacteria consuming starch used enzymes such as α,β -amylases, those act by the complex formation in an active site close to the ether bond between two α -D-

glucopyranose groups lead to its breaking [24]. Since most of these bonds are shielded in the starch ester groups the above complexes are more difficult to form. It must be noted however, that many microorganisms also produce enzymes called esterase, which are able to break ester linkages. Thus the actual biodegradation process may involve all the above mentioned processes and enzymes together. The biodegradability of samples after filling with clays in SA3 is shown in Figure 7.11. It must be noted here that, SA3 was highly hydrophobic and exhibited all kind of composites viz, micro, intercalated and exfoliated composites with 5 % Na+MMT, 5 % 30B and 5% 6A respectively, which made it possible to study the effect of clay dispersion on the composting of samples. It was seen that exfoliated composites exhibited slow compostability in comparison of microcomposites whereas, microcomposites were less degradable than neat SA3.

Figure 7.10 Degradation of neat samples



These results indicated that clay may protect the degradability of samples in any form of dispersion and lowest degradability of exfoliated structure indicating that higher diffusion path may decrease the migration of enzymes resulting the slow weight loss. Thus, exfoliated structure exhibited lower degradation than microcomposites and good dispersion of clay inhibit the degradation of material. To study the effect of clay modifier on the degradability, specimens of SA1 were taken with 7 % filler concentration with all the OMMTs and Na+MMT (Figure 7.12). Here, it was considered that all are microcomposites having same dispersion of clay and will give the effect of modifier on the degradability under composting conditions.

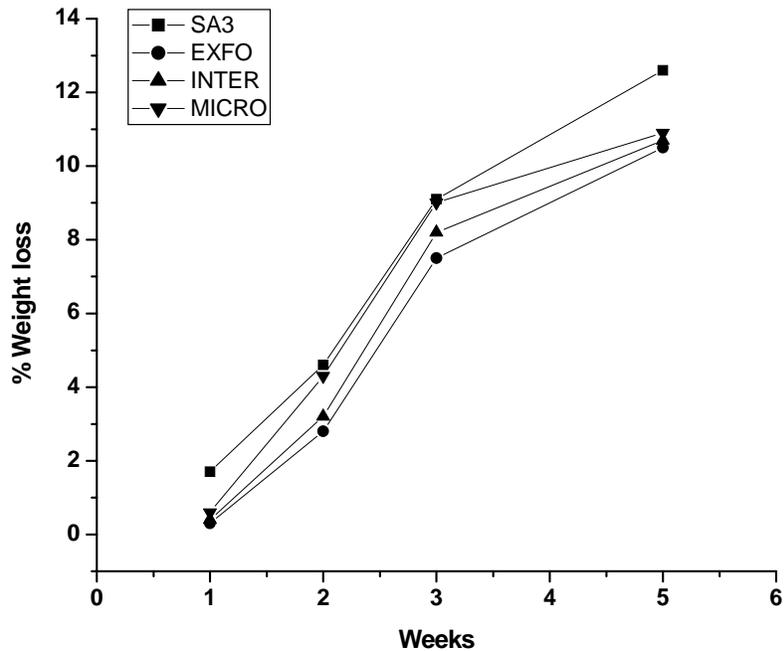


Figure 7.11. SA3, degradation of samples of different dispersion

All the samples exhibited lower degradability in comparison to neat samples regardless of the nature of clay till 5th week. Thus the presence of clay decrease the degradability of composites. The results of last week composting indicated that all samples underwent almost similar weight loss. The samples filled with Na⁺MMT, neat clay without modifier, showed weight loss near to the neat samples whereas, samples containing modifier were underwent less weight loss. This may be due to the antimicrobial effect of cation and since these were microcomposites, cation may be leached out with time and cause the increase in degradation. Compostability test carried out for the BC1 and BC2 showed that degradation decrease with increase in DS and filling with clays (Figure 7.13). From the overall study of degradation it was clear that increase in DS and clay dispersion decrease the degradability in compost.

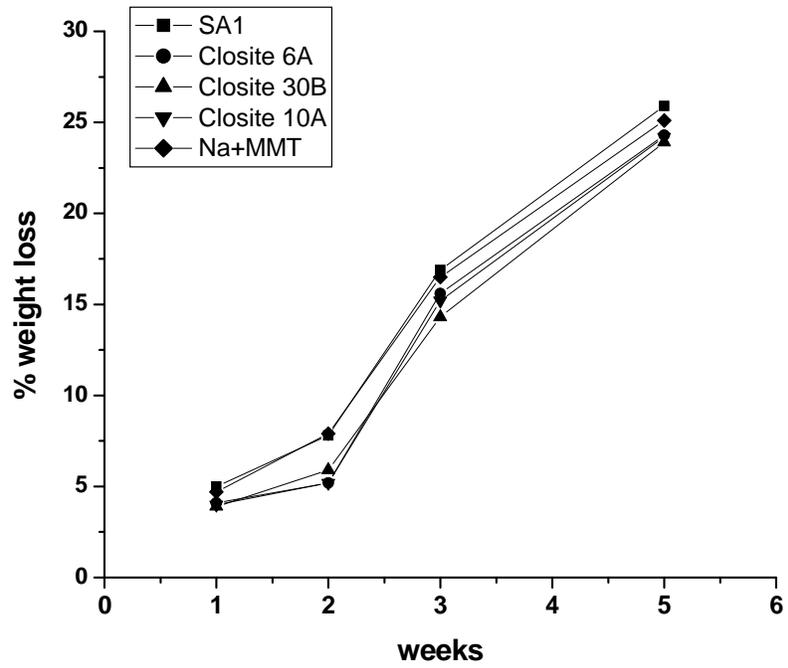


Figure 7.12. SA1 samples showing the effect of modifier

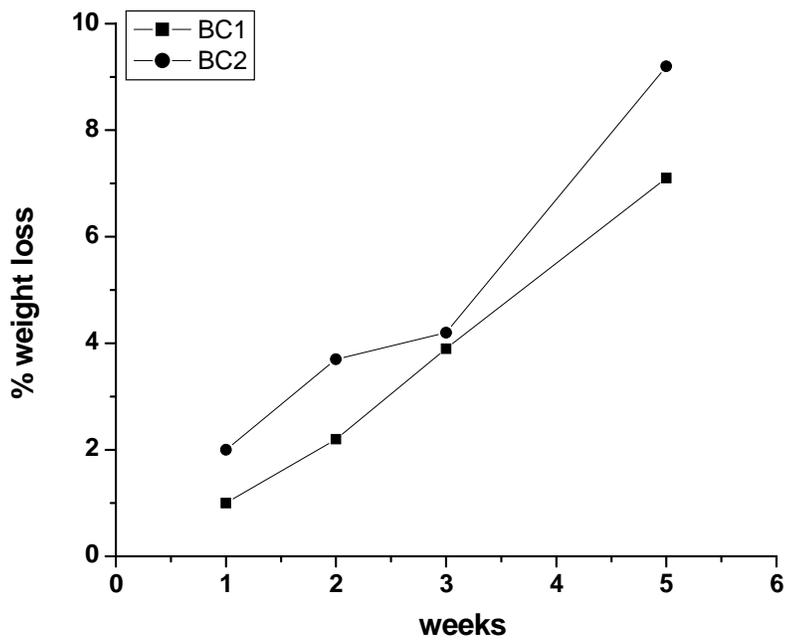


Figure 7.13. Weight loss in B1 and BC2 after filling with Cloisite 6A at 5 % concentration.

7.4 . Conclusions

The starch was modified with different degree of substitution, chain length and were filled with different type of layered silicates. The compositions were prepared by solution method followed by melt mixing and gave well intercalated / exfoliate nanocomposites. The nanocomposites could be formed only after matching of surface energies of layered silicate as well as polymer. The hydrophobicity was increased after substitution of hydroxyl group as well as by filling with modified layered silicates. All composites exhibited higher thermal stability during measurements. The prepared composites are biodegradable in natural composting environments and their rate depends upon the degree of substitution as well as dispersion of clay. Initially the degradation rate was slow which may be either due to long diffusion path in the form of clay layers or due to antimicrobial activity of clay modifier or both. The biodegradability of these materials, however appeared to be rather low compared to the pure starch, especially for those, having higher degree of substitution with intercalated/ exfoliated structures after filling with organo-modified clays.

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**CHAPTER VIII:
SUMMARY AND CONCLUSION**

8.1. Summary and conclusions

Degradability of different polymeric systems was studied under biotic and abiotic environments. Functional groups, e.g., carbonyl and hydroxyl increases rapidly with increase the time of UV irradiation. Biodegradability was increased after photodegradation due to the generation of short chain functional groups, which may undergo biocycle and ultimately convert into carbon dioxide and water. In case of ethylene propylene copolymers, sample containing lower amount of ethylene monomer were found to be more degradable than samples having greater amount of ethylene content. The biocomposites of these thermoplastics with cellulose were prepared by two methods viz. grafting and direct reactive mixing of fiber. There was a significant effect of the method of preparation on the degradability and composites prepared by direct reactive mixing were found more degradable. It was proposed that, compatibility increase the biodegradation of host matrix. These studies were extended, by investigating the biodegradability of polyester-starch composites. Improving the dispersion of starch granules through a hydrophobic coating, and reducing the interfacial tension between PCL and starch owing to the starch-surface precipitation of PCL-grafted polysaccharide proved to be very efficient for degradability of host matrix. Thermoplastic was also filled with another abundant, natural material i.e. layered silicates and their degradability was measured. It was concluded that although, highly improved material properties can be obtained by the nanocomposites, still durability in outdoor application is a challenge and it would be the best way to develop nanocomposites by modification in clay rather than functionalization of thermoplastics to increase the outdoor durability. These nanocomposites must be advantageous from disposal point of view and may not have waste problem due to their higher degradability than pristine polymer. Renewable polymer, starch was filled with natural and organomodified clays with and without modification and an enhancement in material properties was observed. By increasing the hydrophobicity it was possible to increase the moisture resistance of these nanocomposites. The prepared composites are biodegradable in natural composting environments and their rate depends upon the degree of substitution as well as dispersion of clay. Initially the degradation rate was slow which may be either due to long diffusion path in the form of clay layers or due to antimicrobial activity of clay modifier or both. The biodegradability of these materials however appeared to be rather low compared to the pure starch, especially for those, having higher degree of substitution with intercalated/ exfoliated structures after filling with organo-modified clays.

8.2. Future Prospective

New environmental regulations, societal concerns, and growing environmental awareness have triggered the search for new products and processes those are compatible with the environment. Composites from renewable resources are now moving into the mainstream and the composites that are biodegradable or based on renewable “feedstock” may soon be competing with commodity plastics. Biodegradable nanocomposites are the wave of the future and considered as the materials of next generation. Presently there are two appropriate methods to achieve this objective to reinforce the polymer by silicate layers; the processing of inorganic fillers with melt polymer and in-situ polymerization of monomers. For the development of biodegradable nanocomposite it is essential to minimize the thermal degradation of main polymer matrix during processing. Although the nanocomposites of starch have been developed successfully with desirable mechanical properties, the moisture sensitivity of these composites is very poor and can not be used for packaging particularly for liquids. The widening of the range of biodegradable polymeric systems is very important for future studies; therefore it is hoped that the results described in this thesis will be useful for further studies based on the use of this environmentally important scientific approach. True environmentally degradable nanocomposites would exhibit much improved strength and stiffness with little sacrifice of toughness, having reduced gas/water vapor permeability, lower coefficient of expansion and improved heat deflection temperature.

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10. Green Nanocomposites form Renewable Resources : Effect of plasticizer on the structure and material properties of clay filled starch , **Jitendra K.Pandey** and R.P.Singh , *Starch/Starke* (In press, 2004)
11. An overview on the degradability of nanocomposites, **Jitendra K.Pandey**, P.A.Kumar, K.R.Reddy and R.P.Singh , *Polymer Degradation and Stability* (In press, 2004)
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13. Degradability of biocompositse prepared from agro-waste and E-P copolymers under abiotic and biotic environments, **Jitendra K.Pandey**, A.P.Kumar , R.P.Singh, *Journal of Environmental Polymer Degradation* (submitted, 2004)
14. Green Nanocomposites of Starch (Under preparation)

SYNOPSIS

The thesis entitled '*Degradability of Polymer Composites from Renewable Resources*' is divided into 8 chapters.

There is growing interest in developing bio-based products and innovative process technologies that can reduce the dependence on fossil fuel and move to a sustainable materials. Biodegradable bio-based composites and nanocomposites are the next generation of materials for the future. Renewable resource-based biodegradable polymers including cellulosic plastic (plastic made from wood), corn-derived plastics and polyhydroxyalkanoates (plastics made from bacterial sources) are some of the potential biopolymers which in combination with clay reinforcement, can produce nanocomposites for a variety of applications.

Composites of polymers from renewable resources are of great importance and are economically compatible [1-5]. The commercial importance of polymers has been deriving intense applications from the composites in various fields, such as aerospace, automotive, marine, infrastructure, military etc. [6-7]. Performance during use is a key feature of any material/ composites, which decide the real fate of products during use in outdoor applications. Whatever the applications, there is often a natural concern regarding the durability of polymeric materials partly because of their relative newness and their useful life time, maintenance and replacement. The deterioration of these materials depends on how long and to what extent; it interacts with its surroundings.

Few attempts are made to estimate the durability of polymer fiber composite, for example in aqueous media [8], in terrestrial environment [9]. There has been no published report in the literature on the effect of preparation method as well as UV irradiation on biodegradability in the additive free polymer-agro waste composites in composting and culture environments. The material properties of polymer composites are strongly dependent on the degree of intimate contact between the phases [10,11]. In recent years it has been found that layered silicates filled polymer composites often exhibit remarkable improvement of mechanical, thermal and physicochemical properties when compared with pure polymer even at very low filler concentration due to the nano level interactions with polymer matrix [12-14]. These layered silicates have attracted great attention to the researcher because of their cheap, easy availability and high aspect ratio, which gives greater possibility of energy transfer from one phase to another. Nanocomposites of this category are expected to possess improved strength and stiffness with little sacrifice of toughness reduced gas/water vapor permeability, lower coefficient of thermal expansion and an increased heat deflection temperature opening an opportunity for the use of new,

high performance, light weight green nanocomposite materials to replace conventional petroleum based composites.

The investigation on the durability of such kind of composites those prepared by different methods, have been studied in details in the present thesis. The effect of preparation method, filler concentration and other compatibilizers on the durability have also been studied.

Objectives

The main objectives of the present study are:

1. The preparation of different composites of PP, PE, and E-P Copolymers from renewable resources e.g. starch, cellulose with different concentrations.
2. To modify the biopolymers as well as thermoplastics in order to enhance the compatibility between both the matrix.
3. To study the durability of composites under artificial UV irradiation and biotic conditions.
4. The use of biopolymers as modifiers for filler to increase the dispersion in the matrix and to study the effect of modifiers on the durability of these composites.
5. To study the effect of compatibility on the durability of composites and to investigate their mechanisms.

Chapter I

This is introduction chapter and will be giving the details of definitions, preparation and technical requirements for the preparation of composites. This chapter meticulously delivers a comprehensive literature incorporating the significant work done by prominent scientist in this area. The existing and emerging applications of this work are also presented.

Chapter II

The objectives and application of the present study are explained in the present chapter.

Chapter III

This chapter includes the degradability of neat thermoplastics in different environments and elucidation of degradation mechanisms. The study of degradation in neat polymer was carried out and correlated with the degradation behavior of composites.

Chapter IV

The agro waste (coir fiber) was used to prepare the biocomposites of PP. The PP was modified and composites were prepared by two different manner. The study of degradability was carried out in both the environments and it was found that

biocomposites were less stable than the neat polymers. Preparation methods have significant effect on the degradability and highly compatible composites were highly stable. The effect of copolymer composition (ethylene / propylene) on the degradability was also studied.

Chapter V

This chapter describes the degradability of nanocomposites of these thermoplastics with layered silicates. The durability was measured under biotic and abiotic conditions. It was found that nanocomposites are more degradable than neat polymers. There must be modification in filler not in the host matrix to enhance the performance of these nanocomposites.

Chapter VI

The composites of starch and clay were prepared with different clay (filler) concentrations. The performance evaluation was carried out under natural conditions. Thermal degradation, water absorption and mechanical properties were also studied in detail.

Chapter VII

Chemical modification of the starch was done and products of different degree of substitution were prepared. This chemically modified biopolymer was filled with modified and unmodified layered silicates. The durability of these composites was measured under biotic conditions.

Chapter VIII

This chapter summarizes the results and describes the salient conclusions of this study. Additional thoughts for further research are also expressed.

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