SYNTHESIS, KINETICS AND CHARACTERIZATION OF NOVEL UNSATURATED POLYESTERS AND POLYURETHANES

submitted to the
University of Poona,
for the degree of
Ph.D

by

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under the guidance of

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FORM - A

Certified that the work incorporated in the thesis **'Synthesis, Kinetics and Characterization of Novel Unsaturated Polyesters and Polyurethanes'** submitted by Mr. U.R. Vaidya was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

VNadkarni

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Research Guide

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U.R. VAIDYA

CONTENTS

The Tables and Figures are presented at the end of respective Chapters

CHAPTER 1

SCOPE OF WORK

Polymeric materials are increasingly replacing conventional materials such as paper, cotton, wood, metal and glass in a variety of applications. Polymers are used as textile fibers, packaging films, moulded toys and household articles. Their combination of properties such as good mechanical strength, chemical inertness, water resistance and limited permeability to water and oxygen have led to the extensive use of polymers as packaging materials. However, these very properties make them non-biodegradable resulting in a solid waste disposal problem. Thus, investigations concerning the utilization/disposal of polymer waste are of considerable technological significance and social relevance.

Poly (ethylene terephthalate) is a versatile engineering thermoplastic used in volume applications like synthetic fibers, extruded films, moulded engineering components and blow moulded bottles. The worldwide consumption of PET is above 1 X 10^6 metric tonnes per year. The utilization of the PET waste has always been a subject of importance to technologists.

In the present work, the possibility of synthesizing novel unsaturated polyesters (UP) and polyester-polyols for polyurethanes (PU), from PET waste has been explored. The PET waste is first glycolysed with varying amounts of different glycols and then further processed to get UP and PU resins.

The approach allows the incorporation of the linear, terephthalic acid moiety in the polymer backbone. The direct use of pure terephthalic acid as a comonomer in polyestrification is difficult due to its high melting point and the processing difficulties arising from its sublimation during the course of the reaction.

The thesis consists of three major study elements as per details given below.

1.1. Glycolysis of PET waste :-

- Glycolysis of PET waste using varying amounts of glycols.
- Effect of the glycol type and amount on the extent of glycolysis.
- Characterization of the glycolysed PET products.

1.2. Unsaturated Polyesters :-

- Synthesis of UP resins using different glycolysed PET products.
- Study of the kinetics of polycondensation.

- Characterization of the unsaturated polyester resins.
- Determination of the mechanical and dynamic mechanical characteristics of the UP resins.

1.3. Polyurethanes :-

- Synthesis of polyester polyols from glycolysed PET waste.
- Study of the kinetics of polycondensation.
- Characterization of the polyester polyols.
- Development of formulation for polyurethane elastomers and rigid foams from the polyols.
- Determination of the mechanical and dynamic mechanical properties of the PU elastomers and foams.

In the present work, an attempt is made to generate scientific knowledge that is technologically relevant. Thus, the scope of the work illustrates the interdisciplinary nature of polymer science and technology that involves aspects of polymer chemistry, processing and mechanical testing of materials leading to specific product development.

CHAPTER 2

INTRODUCTION

Polyesters represent a commercially significant class of polymers used in a wide range of applications. The applications of polyesters may be classified into four major categories.

(i) High molecular weight aromatic polyesters for mouldings, films and fibers.

(ii) Polyesters modified with unsaturated fatty acids, commonly known as alkyds which are useful in paints and coatings.

(iii) Polyesters containing unsaturation in the backbone commonly termed unsaturated polyesters and used in fiber reinforced plastics, coatings, sheet moulding compounds and castings.

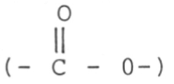
(iv) Hydroxyl terminated polyesters used as polyurethane intermediates.

Apart from the above mentioned applications polyesters are also used in many other applications like adhesives and plastisizers.

As stated earlier, the scope of the thesis includes study of novel unsaturated polyesters and polyurethanes. Therefore a brief introduction of these two classes is presented and, since in the present work these are made using

PET waste,an overview of utilization of PET waste is also given. However, before discussing these specific topics a general background of polyesters is reviewed.

2.1. POLYESTERS

Polyesters are a class of polymers containing carboxylate ester groups  $(-\overset{O}{\overset{\|}{C}}-0-)$ in the polymer backbone. By this defination they are distinguished from other ester containing polymers in which carboxylate groups form part of the pendant substituents on the polymer chain such as in cellulose acetate, poly (acrylates) and poly (vinyl esters).

Though polyesters have been known since 1863 when Lourenco synthesized poly (ethylene succinate), their first significant application was the introduction of glyceryl phthalate (glyptal) as coating and impregnating material, during World War I(1). The technological relevance of polyesters has its beginning in the researches of Kienle and Carothers in the late 1920s. Kienle's investigation of glycerol - phthalic anhydride forms the basis of alkyd resin technology. On the other hand Carothers' work on linear polyesters created a pattern of ideas that lead to the discovery of polyamide, Nylon 6,6, in 1935 and fiber and film forming polyester, poly (ethylene terephthalate) in 1941.

Today polyesters form an important class of polymers with a wide range of applications.

Polyesters are prepared by polycondensation between a bifunctinal carboxylic acid or anhydride and glycol. Some of the other common polycondensation polymers are polyamides, polyurethanes, polycarbonates, phenolics, epoxies etc. The polycondensation reaction proceeds in a stepwise manner, that is, the molecular weight increases with the extent of reaction and in order to achieve high molecular weight, the extent of reaction has to be very close to 100%(2). The reaction can be represented schematically as follows :

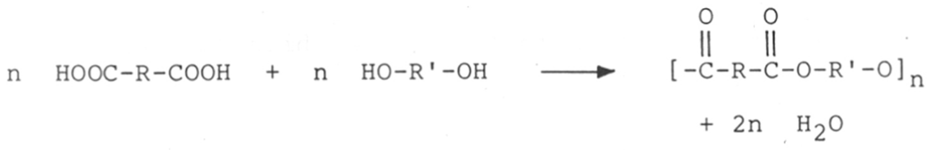
$$\begin{array}{llllll} & \text{Monomer} & + \text{ monomer} & \rightleftharpoons & \text{dimer} & + \text{ Sm} \\ & \text{Monomer} & + \text{ dimer} & \rightleftharpoons & \text{trimer} & + \text{ Sm} \\ & \text{Dimer} & + \text{ dimer} & \rightleftharpoons & \text{tetramer} & + \text{ Sm} \\ \text{or} & n \text{ mer} & + \; m \text{ mer} & \rightleftharpoons & (n + m) \text{ mer} & + \text{ Sm} \end{array}$$

Where Sm denotes small molecules. At any given time all the species of oligomers are present and any molecule can react with any other molecule.

2.1.1 Synthesis of Polyesters :-

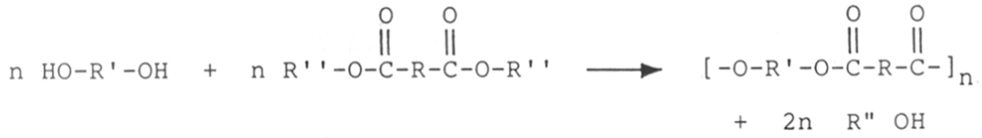
Some of the synthetic routes for preparation of polyesters are listed below :

(i) Direct esterification : involves reaction of a diacid with a dihydroxy alcohol.



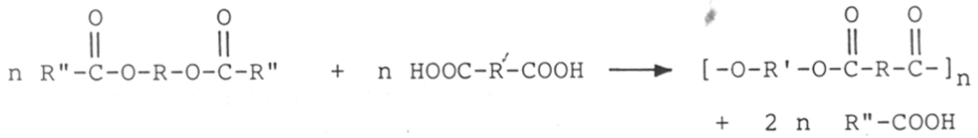
$$n\ \mathrm{HOOC{-}R{-}COOH} + n\ \mathrm{HO{-}R'{-}OH} \longrightarrow [-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-O-R'-O]_n + 2n\ H_2O$$

(ii) Alcoholysis : consists of reacting a diol with dicarboxylic acid diester.



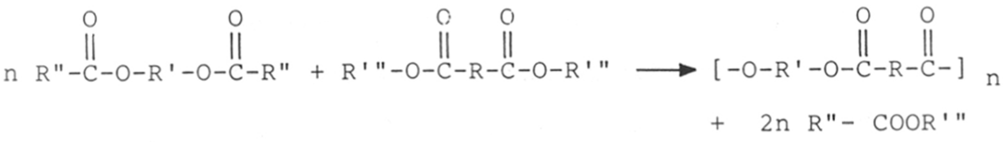
$$n\ \mathrm{HO{-}R'{-}OH} + n\ R''-O-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-O-R'' \longrightarrow [-O-R'-O-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-]_n + 2n\ R''\ OH$$

(iii) Acidolysis : by reacting dioldiester and dicarboxylic acid



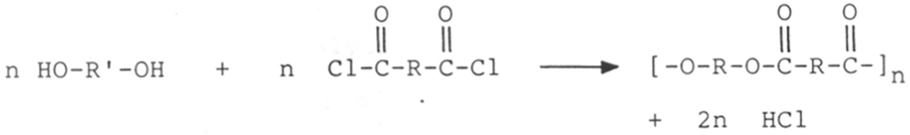
$$n\ R''-\overset{\overset{O}{\|}}{C}-O-R-O-\overset{\overset{O}{\|}}{C}-R'' + n\ \mathrm{HOOC{-}R'{-}COOH} \longrightarrow [-O-R'-O-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-]_n + 2\ n\ R''{-}COOH$$

(iv) Double ester exchange : by reacting dioldiester with dicarboxylic acid diesters



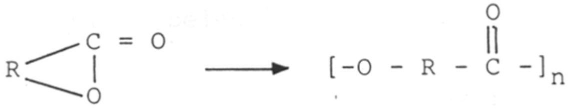
$$n\ R''-\overset{O}{\overset{\|}{C}}-O-R'-O-\overset{O}{\overset{\|}{C}}-R'' + R'''-O-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R''' \longrightarrow [-O-R'-O-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-]_n + 2n\ R''-COOR'''$$

(v) By reacting acid chloride of dicarboxylic acid with diols



$$n\ HO-R'-OH + n\ Cl-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow [-O-R-O-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-]_n + 2n\ HCl$$

(vi) By ring opening polymerization of cyclic esters



Polyesterification is an equilibrium reaction. Therefore the side product formed should be removed continuously to shift the equilibrium towards the product side.

The chemical structure of the polyester can be manipulated by proper selection of monomers. A control of molecular weight may be achieved by the use of monocarboxylic acids, which terminate the growing chain. Use of tri or polyhydroxy alcohol as a comonomer gives branched structures. Since polyestrification is a step growth reaction, it is essential to use the reactants close to their stoichiometric proportions. Any imbalance in the stoichiometry results in a lowering of the molecular weight(3,4). This phenomenon can be used as a tool to control the number average molecular weight of the polyester.

2.1.2 **Kinetics of Polyesterification** :-

The kinetic analysis of a reaction involves monitoring the rate and order of disappearance of the reactants with time. This is evaluated by analysing samples drawn at periodic intervals during the course of the reaction. The simple reaction schemes and their corresponding rate expressions are given below :

Reaction	Rate expression
$A \longrightarrow \text{product}$	$\frac{-d[A]}{dt} = k[A]$
$A + A \longrightarrow \text{product}$	$\frac{-d[A]}{dt} = k[A]^2$
$A + B \longrightarrow \text{product}$	$\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = k[A][B]$

where A and B are the reactants, and [A] and [B] are molar concentrations of the reactants. The constant k, is known as the rate constant. The generalized expression between A and B may be represented as -

$$\frac{-\,d\,[A]}{dt} = \frac{-\,d\,[B]}{dt} = k\,[A]^n\,[B]^m$$

The indices n and m signify the order of the reaction with respect to the individual reactants and the overall order of the reaction is represented as (n + m).

In polyesterification, at any given time, molecules of different degrees of polymerization are present and any two molecules can react for the growth of the polymer. It has been demonstrated that the reactivity of the functional groups is independent of the chain length(5,6). Therefore the rate of disappearance of functional groups may be taken as a measure of the reaction rate.

Polyesterification are the most extensively studied polycondensation reactions. The different rate expressions that emerge can be classified as :

- (i) Internal or self catalysed reactions
- (ii) Externally catalysed reactions
- (iii) Nonstoichiometric ratio of reactants

(i) The polyesterification reactions are catalysed by acids. In the absence of any added catalyst the diacid itself acts as a catalyst(7).

Therefore

$$\frac{-\,d\,[COOH]}{dt} = k\,[COOH]^2\,[OH] \qquad (1)$$

When stoichiometric concentration of functional groups is taken, the equation becomes

$$\frac{-\, d\,[\mathrm{COOH}]}{dt} = k\, C^3 \qquad (2)$$

Where C is the concentration of carboxyl or hydroxyl groups.

On integrating equation (2) we obtain

$$2\, k\, t = \frac{1}{C^2} - \text{constant} \qquad (3)$$

The extent of reaction, 'p' is defined as the fraction of the functional groups that have undergone reaction in a given time.

$$p = \frac{C_o - C}{C_o} \qquad (4)$$

Where C_o is the initial concentration and C is concentration at any given time

$$C = C_o\,(1 - p) \qquad (5)$$

Combining equations (3) and (5) we get

$$\frac{1}{(1 - p)^2} = 2\, C_o^{\,2}\, k\, t + \text{constant} \qquad (6)$$

Thus the reaction follows third order kinetics and a plot of $\frac{1}{(1-p)^2}$ against time would be linear.

(ii) In externally catalysed polyesterification reactions, the concentration of the added acid catalyst remains the same throughout the course of the reaction. The rate expression in this case is represented as :

$$\frac{-d\,[\mathrm{COOH}]}{dt} = k\,[\mathrm{COOH}]\,[\mathrm{OH}] \qquad (7)$$

In the form of fractional conversion, 'p', the expression is written as :

$$\frac{1}{(1-p)} = C_o\,k\,t + \text{constant} \qquad (8)$$

Thus the reaction follows second order kinetics and the plot of $\frac{1}{1-p}$ versus time would be linear.

The degree of polymerization DP is expressed as :

$$DP = \frac{1}{1-p} \qquad (9)$$

Therefore in externally catalysed polyesterification, the number average degree of polymerization increases linearly with the reaction time.

(iii) In case of polyesterifications involving nonstoichiometric amounts of the reacting groups A and B, the ratio 'r' is given by $\frac{[B]_o}{[A]_o}$ and $[B]_o$ is always greater than $[A]_o$, that is 'r' is never less than one.

The polymerization rate of such a reaction containing external catalyst can be defined as the rate of disappearance of the functional groups present in deficient amounts. (8,9)

$$\frac{-d\,[A]}{dt} = k\,[A]\,[B] \tag{10}$$

The following stoichiometry is observed,

$$[A]_o - [A] = [B]_o - [B] \tag{11}$$

The combination of equations (10) and (11) followed by integration gives

$$\frac{1}{[B]_o - [A]_o} \ln \frac{[A]_o\,[B]}{[B]_o\,[A]} = k\,t \tag{12}$$

When substituted for $r = \frac{[B]_o}{[A]_o}$ one gets

$$\ln \frac{[B]}{[A]} = \ln r + [A]_o (r-1) k t \qquad (13)$$

Therefore a plot of $\ln \frac{[B]}{[A]}$ versus time should be linear and the reaction is of second order. The degree of polymerization of such a system is given as :

$$DP = \frac{1 + r}{1 + r - 2p} \qquad (14)$$

2.2 UNSATURATED POLYESTERS

It was found in the late 1930's that polyesters containing unsaturation in their backbone, transformed into an insoluble and infusible material when exposed to heat, light and oxygen, and the rate of curing increased in presence of unsaturated vinyl monomers (10,11). These discoveries led to the first commercial application of unsaturated polyesters in coatings and mouldings. By 1942, the unsaturated polyesters found their major application area as matrix resins for glass reinforced plastics. Today, fiber reinforced plastics (FRP) is a large volume application area for unsaturated polyesters.

FRP's offer high strength to weight ratio, excellent corrosion resistance, ease of fabrication and versatility of product design in comparison with metals. Although both thermosets and thermoplastics are used as matrix materials for fiber reinforcement, the thermosets constitute the major segment. Among the thermosetting resins, unsaturated polyesters and epoxies are the most commonly used matrix materials for FRP's. The consumption of unsaturated polyester resins in USA was of the order of about 6 x 10^5 metric tons in 1987, whereas that of epoxies was only about 1.8 x 10^5 metric tons in the same year (12). Other applications of unsaturated polyesters include potting, coating, casting and lamination.

2.2.1 Synthesis of Unsaturated Polyesters :-

The unsaturated polyester (UP) resins are prepared by reacting unsaturated and saturated diacids with glycols. The resulting polyester is dissolved in an unsaturated monomer to make about 70 % resin solution.

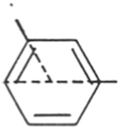
The general purpose UP resin is prepared by reacting 1 mole of maleic anhydride and 1 mole of phthalic anhydride with 2.2 moles of propylene glycol (13). About 170 ppm hydroquinone is added as an inhibitor to avoid premature crosslinking of the polyester chains during polyesterification. The reaction is carried out above 180°C in a nitrogen atmosphere. The water of reaction has to be removed continuously. The reaction is carried out till an acid value of about 30 mg KOH / g is obtained. The molecular weight of commercially used UP ranges between 1500 to 2500. The resin is cooled tc 90°C and a vinyl monomer (styrene) is added with stirring to form about 70 % solution of the resin in the monomer. The UP resins are cured using free radical initiators like peroxides(14,15).

2.2.2 Structure Property Relationship :-

The mechanical performance and chemical resistance characteristics of UP resins are generally manipulated by appropriate choice of the diols and diacids used as the building blocks of the polymer. The most commonly used unsaturated diacids are maleic anhydride and fumaric acid. In rare cases itaconic acid is used. Maleic anhydride is preferred over other acids because of its high reactivity, low melting point and lower cost. The amount of unsaturated acid moiety governs the crosslinking density, which in turn influences the brittleness and hardness of the final product. More the amount of the unsaturated moiety in the chain, harder is the product (16).

The standard saturated diacids used in UP resin synthesis include phthalic anhydride, isophthalic acid, adipic acid, succinic acid and sebacic acid. The aromatic diacids give improved rigidity, whereas the aliphatic diacids impart flexibility to the final product. Use of isophthalic acid gives better thermal and mechanical properties than phthalic anhydride, especially heat distortion temperature and chemical resistance(17). This is because of the better packing of polymer chains containing meta-meta linkages than those having ortho-ortho linkages. This effect would be even more prominent in case of linear polyester structures based on terephthalic acid having para-para linkages.

ORTHOPHTHALIC



ISOPHTHALIC

TEREPHTHALIC

However, the use of terephthalic acid is restricted because of its high melting point (> 300°C) which leads to processing difficulties such as sublimation and decomposition.

The impact strength increases with the amount of aliphatic acid. Among the aliphatic acids the impact strength increases with increasing chainlength; however, the rigidity, related to the modulus, would decrease with increasing chain length.

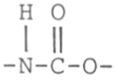
The other type of monomers for polyester synthesis are diols which include ethylene glycol, propylene glycol, neopentyl glycol etc. The ethylene glycol based polyesters exhibit less compatibility with styrene monomer whereas propylene glycol based polyesters are most compatible with the vinyl monomers and exhibit better hydrolytic stability. In order to obtain the best clarity and hydrolytic stability, neopentyl glycol is preferred. The steric hindrance provided by the pendant methyl groups in neopentyl glycol shields the ester linkages from hydrolysis(18,19). Use of bis phenol-A gives improved thermal and chemical resistance.

In summary, it is possible to tailor make UP resins to meet specific property requirement by proper selection of monomers.

2.3 POLYURETHANES

Dr.Otto Bayer's work dating back to 1937 at IG Farben Industrie, forms the basis of polyurethane chemistry(20,21). The efforts by Dr. Bayer's team to produce fibres similar to Nylon,without infringing the DuPont patent on Nylon, led to the preparation of polyurea, from hexamethylene diamine and hexamethylene diisocyanate. On the other hand the reaction of the isocyanate with glycols led to formation of polyurethanes.

During World War II, PU products were developed in Germany (Bayer) as well as in UK (ICI) and the United States (DuPont). In 1953 Bayer started offering technical know-how for continuous production of flexible foam. A somewhat similar development took place in ICI. However, Bayer's developments of polyurethane elastomers and foams provided a powerful incentive to accelerate commercial growth.

A urethane is the reaction product of an alcohol and an isocyanate. Thus, polyurethanes contain urethane linkages  $-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-$ along the chain and are prepared by reacting di or polyhydroxy alcohols with di or polyisocyanates.

$$HO-R'-OH \quad + \quad OCN-R-NCO \longrightarrow [-O-R'-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-]_n$$

The polyurethanes (PU) exhibit a wide range of properties. Their good tensile strength, abrasion resistance, and chemical resistance have made them very popular. These polymers are extensively used in flexible and rigid foams, cast elastomers, coatings, adhesives and many other applications.

The polyurethane technology consists of two major steps. The first step involves the synthesis of polyol and sometimes polyisocyanate. The monomers for synthesis are selected based on the end product requirement. The second step, which is more tricky, is formulation. The formulation includes the selection and optimization of NCO / OH ratio, catalyst system, additives, fillers etc.

2.3.1 Isocyanates :-

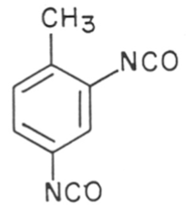
Isocyanate is the most important component of polyurethanes. Although the technology of polyurethanes is of a recent origin, the chemistry of organic isocyanates, dates back to 1849 when Wortz synthesised first aliphatic isocyanate(22). Isocyanates contain highly unsaturated - N = C = O group and therefore react readily with any compound having active hydrogen. The electronic structure of the isocyanate group can be represented as :

$$R-\overset{-}{\underset{..}{N}}-\overset{+}{C}=O \longleftrightarrow R-N=C=O \longleftrightarrow R-N=\overset{+}{C}-\overset{-}{\underset{..}{O}}$$

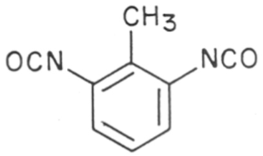
The reactivity of isocyanate group depends on the electronic environment and any factor influencing the positive charge on the carbon of isocyanate group would influence the reactivity of the isocyanate towards active hydrogen. Therefore any electron withdrawing group attached to aromatic isocyanate would increase the electropositivity on the isocyanate carbon thereby increasing its reactivity. The reverse will be the effect of electron donating group which reduces the reactivity of isocyanate. Thus, the higher reactivity of aromatic isocyanates than aliphatic isocyanates could be attributed to the increased electrophilic nature of carbon due to aromatic benzene ring.

The most commonly used isocyanates, in PU technology are listed below :

- Toluene diisocyanate (TDI)

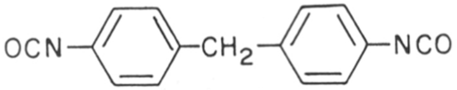


2,4 ISOMER



2,6 ISOMER

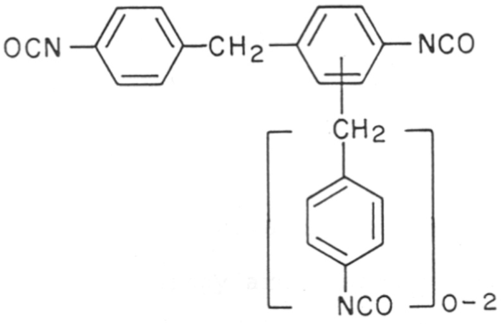
- 4,4 'diphenyl methane diisocyanate (MDI)



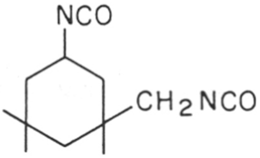
- Hexamethylene diisocyanate (HDI)

$OCN-(CH_2)_6-NCO$

- Polymeric 4,4 ' diphenyl methane diisocyanate (PMDI)



Isophoron diisocyanate (IPDI)

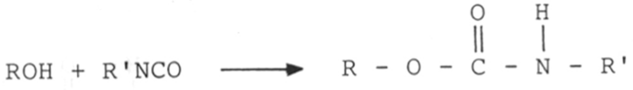


Since the two isocyanate groups of 2,4 TDI are in different electronic enviornment, the reactivities of the two differ(23). Isocyanate group at 4 position is more reactive than the one at 2 position. Similarly in IPDI the isocyanate group which is directly attached to the ring is more reactive than the other.

While the di or polyisocyanates are used extensively as reactants, they can also be converted into isocyanate terminated prepolymers for applications such as coatings, adhesives and castings. These polymers are either reacted with hydroxyl terminated compounds or with water to get final product. One can get a range of prepolymers by varying the monomers and ratio of hydroxyl to isocyanate groups. The isocyanates can be blocked using phenols or thiols which are regenerated when heated. The blocked isocyanates are used for single pack systems.

Some of the important reactions of isocyanates used in polyurethane technology are listed below :

(i) Reaction of isocyanate with alcohol



$$ROH + R'NCO \longrightarrow R - O - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - R'$$

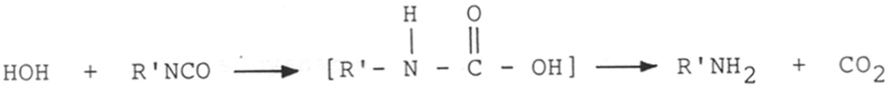
Urethane

(ii) Reaction with amine

$$RNH_2 + R'NCO \longrightarrow R - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - R'$$

Urea

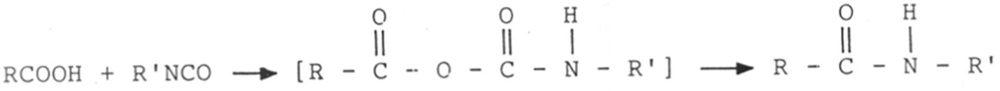
(iii) Reaction with water



$$HOH + R'NCO \longrightarrow [R' - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - OH] \longrightarrow R'NH_2 + CO_2$$

Amine

(iv) Reaction with carboxylic acid

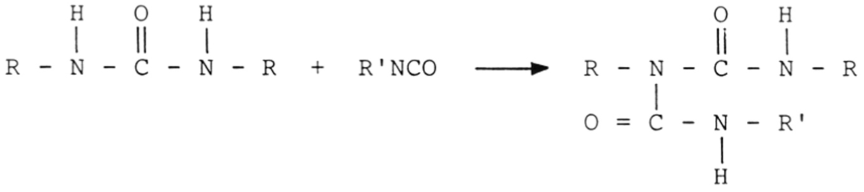


$$RCOOH + R'NCO \longrightarrow [R - \overset{O}{\overset{\|}{C}} - O - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - R'] \longrightarrow R - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - R'$$

Amide

$+ CO_2$

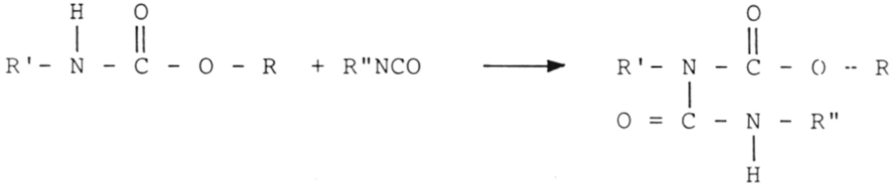
(v) Reaction with urea



$$R-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R\ +\ R'NCO \longrightarrow R-\underset{\underset{O\,=\,C\,-\,\underset{\underset{H}{|}}{N}\,-\,R'}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R$$

Biuret

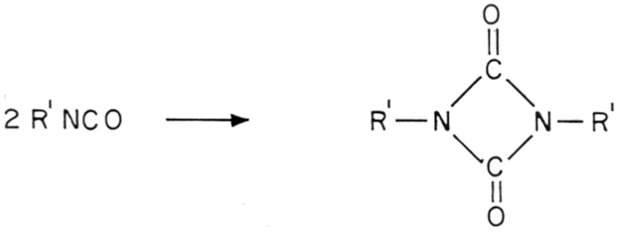
(vi) Reaction with urethanes

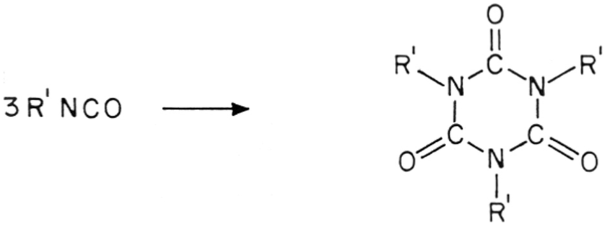


$$R'-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R\ +\ R''NCO \longrightarrow R'-\underset{\underset{O\,=\,C\,-\,\underset{\underset{H}{|}}{N}\,-\,R''}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R$$

Allophanate

(vii) Aromatic disocyanates can react with themselves to form dimer or trimer





For a given type of isocyanate the reactivity, towards active hydrogen compound depends on the electronic environment of active hydrogen containing nucleophile. Any factor increasing the nucleophilicity of reactant would increase the reactivity. Therefore electron donating groups on active hydrogen containing compound would increase its reactivity towards isocyanate whereas electron withdrawing group would decrease the reactivity(24).

Thus, aliphatic amines are more reactive than aromatic amines. The reactivity of amine increases with the basicity. Secondary amines are less reactive than the primary amines(25-27). Similar trend is observed with alcohols. Primary alcohols react readily at room temperatures. Secondary alcohols react only 0.3 times fast. Tertiary alcohols are even less reactive, about 0.005 times as fast as primary alcohols(28). The reactivity of water with isocyanate is similar to that of a secondary alcohol. Carboxyl acids are somewhat less reactive than primary alcohols and water. The reactions of isocyanate with water and carboxylic acid form carbon dioxide gas and are often used in foaming reactions.

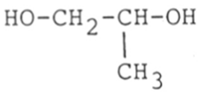
2.3.2 Polyols :-

The other major ingredient of the polyurethanes are polyols. The different types of polyols, depending on the linkages in the main chain, include polyester polyols, polyether polyols and hydroxyl terminated hydrocarbons. Polyethers are usually made from ethylene oxide or propylene oxide. These polyethers are widely used in flexible foams, paints and coatings. The polyether based polyurethanes show good hydrolytic stability and resilience(29). Hydroxyl terminated hydrocarbons mainly include hydroxyl terminated polybutadienes. These exhibit very good electrical properties and are used as potting and encapsulation resins.

Polyester polyols are used for rigid foams, elastomers, coatings, adhesives etc. Polyesters exhibit inferior hydrolytic and colour stability than polyether based polyurethanes. However, polyesters offer wide range of properties through proper selection of monomers, which have made them equally popular.

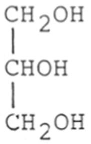
Polyesters are prepared by reacting polyhydroxy alcohols with dicarboxylic acids. The common monomers used in the synthesis of polyester polyols are summarized below :

(i) Diols

.	Ethylene glycol	$HO-(CH_2)_2-OH$
.	Propylene glycol	 $HO-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-OH$
.	Diethylene glycol	$HO-(CH_2)_2-O-(CH_2)_2OH$
.	1,4 butanediol	$HO-(CH_2)_4-OH$

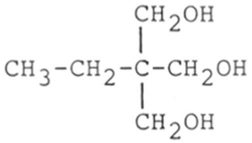
(ii) Polyhydroxy alcohols

- Glycerol



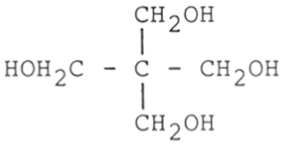
$$\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

- Trimethylol propane



$$\begin{array}{c}CH_2OH\\ |\\ CH_3-CH_2-C-CH_2OH\\ |\\ CH_2OH\end{array}$$

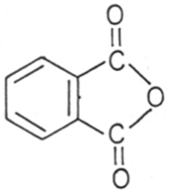
- Pentaerethritol



$$\begin{array}{c}CH_2OH\\ |\\ HOH_2C - C - CH_2OH\\ |\\ CH_2OH\end{array}$$

(iii) Dicarboxylic acids

- Adipic acid $HOOC-(CH_2)_4-COOH$
- Succinic acid $HOOC-(CH_2)_3-COOH$
- Glutaric acid $HOOC-(CH_2)_2-COOH$
- Phthalic anhydride



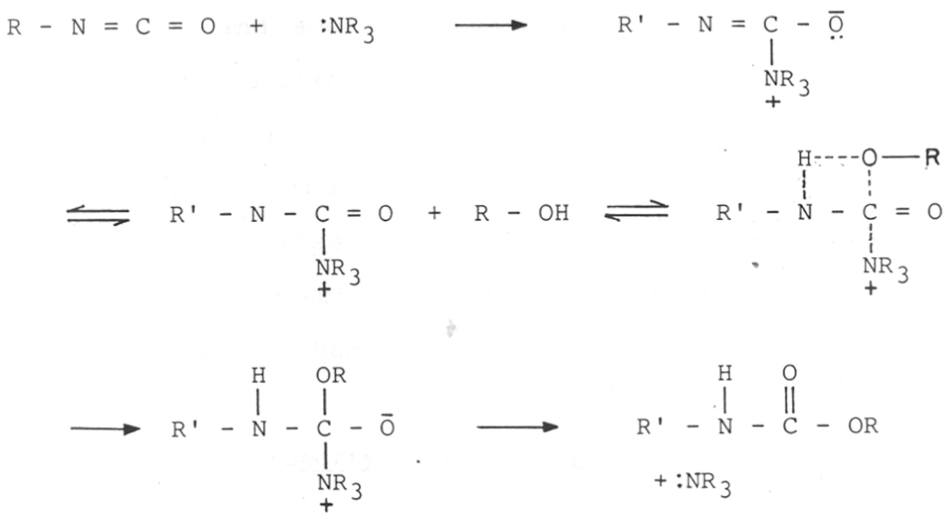
The use of terephthalic acid and isophthalic acid is restricted because of processing difficulties like lower reactivity, decomposition and sublimation.

The polyesterification is carried out above 170°C. Sometimes xylene is used to remove water of reaction azeotropically. Use of xylene improves heat dissipation and increases the rate of reaction by efficient removal of water of reaction. The reaction is carried out till a very low acid value of about 0.5 mg KOH/g is obtained. The low acid value is essential to eliminate the foaming due to carbon dioxide gas which would be generated in the reaction of isocyanate and acid.

2.3.3 Formulation Development :-

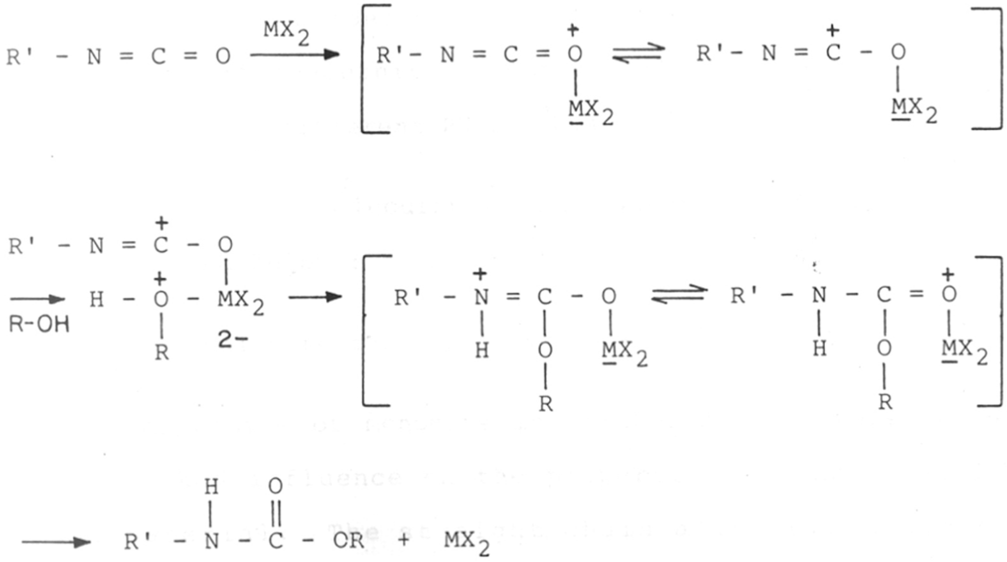
Once the polyols are synthesized, the next step is to arrive at a proper formulation with the use of catalyst to suit the processing requirements of the PU application. The rate of reaction between the polyol and the diisocyanate can be manipulated considerably with catalysts. Both acid and base catalysts have been studied. Bases are known to be better catalysts than acids. The efficiency of the base catalysts increases with basicity. Amines represent the major class of base catalysts for polyurethanes. The catalytic action of amine increases with the basicity of the amine. Tertiary amines are most commonly used amine catalysts in polyurethane chemistry.

The mechanism of amine catalysts may be represented as follows(30,31) :



The other catalysts include metal compounds like di-n-butyl tin dilaurate, stannic chloride, n-butyl tin trichloride, cobalt naphthanate etc.

The mechanism for the metal catalysed reaction can be proposed as follows(32) :



Once the type and amount of catalyst is fixed, the other optional additives like antioxidants, pigments and fillers are also incorporated in the polyol along with the catalyst. The type of catalyst and processing conditions are used to manipulate the rates of reactions of isocyanates with hydroxyl, water and acid which proceed simulataneously during synthesis of polyurethanes.

2.3.4 Structure Property Relationship :-

Because of the large number of variables associated with polyurethane technology such as the chemical structure of the polyols and diisocyanate components, their functionalities, amount and type of extenders, catalyst types and the isocyanate to hydroxyl group ratio, polyurethanes are amenable to tailor making materials, to suit desired combination of propoeties. There have been a number of investigations concerning the chemical structure-property relationships in different PU systems(33 - 41).

Some of the molecular factors governing the properties are summarized below :

(i) Chemical structure of polyol : -

The choice of monomers in synthesizing polyols has a marked influence on the properties of the final PU material. The straight chain aliphatic monomers usually impart flexibility, low glass transition temperature and higher elasticity. Incorporation of aromatic moieties in the chain which restrict the rotation of the polymer chain tend to give improved rigidity, higher melting point and higher hardness. Polyether polyols lead to more flexible products than the polyesters. Urea linkages impart more rigidity than the urethane linkages.

(ii) Molecular weight of polymer :-

The mechanical and chemical properties of the PU materials change with molecular weight upto a limiting value. Properties like melting point,tensile strength, elasticity, and Tg increase with molecular weight , whereas solubility generally decreases with molecular weight. The molecular weight is controlled by varying isocyanate to hydroxyl group ratio.

(iii) Crosslinking density :-

Generally with the increase in crosslinking, the properties like rigidity, softening point, hardness, chemical resistance etc. improve. It is controlled by the amount of the monomer having functionality more than two.

(iv) Crystallinity :-

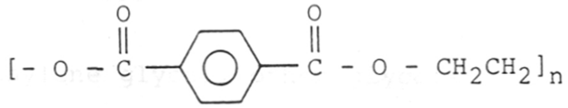
Crystallinity affects the packing of molecules, which inturn affects the properties of polymer. Higher crystallinity usually reduces solubility, flexibility and increases tensile strength, melting point and hardness.

Polyurethanes thus represent a unique class of polymers which can give a broad spectrum of properties.

2.4. UTILIZATION OF PET WASTE

As indicated earlier, PET is a versatile polymer being used in high volume applications such as synthetic fibers, films and bottles for packaging. Its world wide consumption is about 10^6 TPA(42). With such a massive consumption, the utilization of PET waste is of considerable commercial and technological significance.

PET is prepared by reacting dimethyl terephthalate or terephthalic acid with ethylene glycol. Its structure can be represented as :



PET waste can be used in moulded or extruded articles after repelletizing(43). However, during repelletization and moulding the polymer might partly degrade affecting the properties adversely. Alternatively it can be recycled with virgin monomer, bis (2-hydroxy ethyl) terephthalate (BHET)(44). The blending of high molecular waste with polymerizing monomer also affects the colour and viscosity of the melt adversely(45). Therefore it is preferred to breakdown the polymer into smallar molecules or oligomers before recycling. PET can be depolymerized into dimethyl terephthalate (DMT)(46 - 51) by alcoholysis using methanol, at high temperature (250°C) and under pressure. This regenerated DMT can be recycled with fresh DMT. However because of the high acid value of the regenerated DMT, its addition beyond about 10% of the fresh DMT leads to poor polymer and fiber properties. Therefore it is advisable to glycolyse the waste with ethylene glycol and the hydroxyl terminated oligomers be recycled with virgin BHET at the polycondensation stage of PET manufacture(52 - 63). However, in practice recycle of recovered oligomers beyond 10 - 15 % brings about undesirable change in melt viscosity and colour of the polymer(64). Therefore the large volume recycling of PET waste is still a challenging task.

Besides ethylene glycol, other glycols like diethylene glycol,propylene glycol can also be used for glycolysis of PET(65,66). The catalysts used in glycolysis include the transesterification catalysts like metal acetates(67 - 70), metal butoxides or metal oxides(71 - 73).

The reuse of these hydroxyl terminated oligomers has attracted the attention of many leading companies like Owens Corning Fiberglas, DuPont, Celanese, Hoechst (now Hoechst Celanese), Toray etc. Most of the earlier attempts to use these oligomers were directed towards the development of unsaturated polyesters(74 - 84). In recent times a lot of thrust is given on development of polyester polyols for rigid polyurethane foams, from PET waste(85 - 94)

Though considerable technological work has been done in this field, no systematic data are available in the literature concerning the kinetics and structure-property relationships in the PET waste based unsaturated polyesters and polyurethanes.

CHAPTER 3

GLYCOLYSIS OF PET WASTE

PET waste can be depolymerized by glycolysis. The earlier efforts by various workers are reported in the previous chapter. In the present work, a systematic study of depolymerization of PET waste using different types and amounts of glycols is reported.

3.1. DETAILS OF GLYCOLYSIS

3.1.1 Materials :-

(i) PET waste -

Fibre grade PET waste with a number average molecular weight ($\overline{M}n$) ranging between 18,000 to 20,000, was obtained from M/s Century Enka, Pune (India). The waste was in the form of white, opaque chunks; it was crushed to form a coarse powder.

(ii) Ethylene glycol : -

Molecular Formula	$HOCH_2CH_2OH$
Molecular Weight	62.07
Boiling range	195° - 197°C.

LR grade material was supplied by M/s S.D. Fine Chem Pvt. Ltd., Boisar (India). The purity of the material was about 99 % .

(iii) Diethylene glycol : -

Molecular Formula	$HOCH_2CH_2OCH_2CH_2OH$
Molecular Weight	106.12
Boiling range	242^{o}-$246^{o}C$

The LR grade chemical was supplied by M/s Sarabhai Chemicals, Baroda (India).

(iv) Propylene glycol (1,2-propane diol) :-

Molecular formula	$CH_3CH(OH)CH_2OH$
Molecular Weight	76.1
Boiling range	187^{o} - $189^{o}C$

The LR grade chemical was supplied by M/s IDPL, Hyderabad (India). Purity was about 99 %.

(v) Zinc acetate (dihydrate) :-

Molecular Formula	$(CH_3COO)_2$ Zn. $2H_2O$
Molecular Weight	219.49
Appearance	White, crystalline solid.

The LR grade zinc acetate was supplied by M/s High Purity Chemicals, New Delhi (India).

The chemicals were used as such, without any further purification.

3.1.2 Experimental Set-up :-

The glycolysis reactions were carried out in a 2 litre, round bottom flask with an overhead stirring assembly, a thermowell, a gas bubbler and a reflux condenser. A 2 litre heating mantle was used for heating. The schematic of the glass reactor is shown in Figure-1.

3.1.3 Experimental Procedure :-

The PET waste was glycolysed with ethylene glycol (EG), propylene glycol (PG) and diethylene glycol (DEG). The amounts of the ingredients taken for the glycolysis reactions are summarized in Table - 1.

The total charge of reactants for each reaction was 1200 g. 0.5% w/w zinc acetate, based on the weight of PET, was used as catalyst. The reactions were carried out under reflux conditions in nitrogen atmosphere, for 8 hours.

3.2 CHARACTERIZATION OF GLYCOLYSED PET

3.2.1 Determination of Free Glycol :-

A weighed quantity of the glycolysed product was extracted with water and filtered. The filtrate containing water, free glycol and some water soluble oligomers, was concentrated by evaporation of water and then chilled to precipitate out the water soluble oligomer. This was filtered again. The second filtrate, thus obtained, contained water and free glycol. The residues remaining after first and second filtration were dried to remove water and weighed together. The difference between the original and final weight represents the amount of free glycol removed by water extraction.

The amounts of free glycol found in the glycolysed products are reported in Table - 2.

3.2.2 Hydroxyl Value Determination :-

The hydroxyl value denotes the number of milligram of potassium hydroxide needed to neutralize the acetic acid which combines with one gram of the sample. This is a measure of the free hydroxyl groups in the sample. The glycolysed products were characterized for the hydroxyl value, which is required for fixing the stoichiometric proportions of reactants in polyesterification for a fixed hydroxyl to carboxyl ratio. The hydroxyl values of the glycolysed products after removal of free glycol, were also determined to investigate the extent of depolymerisation.

In the conventional method, the sample is refluxed with pyridine/ acetic anhydride mixture for determining its hydroxyl value. This procedure is quite time consuming.

Therefore, the rapid method (catalysed) (95) was used for the analysis. This method reduces the analysis time and also avoids heating of the sample. The method is illustrated below.

The acetylation mixture is prepared first. In a 250 mL volumetric flask, 1.2 g of 72 % perchloric acid is taken, followed by 150 mL of dry, distilled ethyl acetate. 8 mL of distilled acetic anhydride is then added dropwise by burette, while cooling the solution with ice. The mixture is cooled to 5°C. 42 mL of acetic anhydride is then carefully added. The mixture is allowed to stand for 30 minutes at room temperature. The total volume is then made up to 250 mL with ethyl acetate.

In order to determine the hydroxyl value, a weighed quantity of the resin sample is dissolved in 5 mL of ethyl acetate to which 5 mL of the acetylation mixture is added by pipette. The reaction is carried out for 20 minutes at ambient temperature. 2 mL water is then added followed by 10 mL of pyridine/ water (3 : 1) mixture. The free acetic acid is then titrated against about 0.5 N standard alcoholic potassium hydroxide solution. Similarly a blank experiment without sample is also run simultaneously.

The hydroxyl value is computed by using the following formula:

$$\text{Hydroxyl value} = \frac{56.1 \times N \times (V_1 - V_2)}{W}$$

where N = Normality of KOH solution

V_1 = Volume of KOH solution required to neutralize the blank

V_2 = Volume of KOH solution required to neutralize the sample.

W = Weight of the sample.

The hydroxyl values of the glycolysed PET products determined per procedure given above, are reported in Table-2.

3.2.3 <u>Thin Layer Chromatography (TLC)</u> :-

The analysis of PET oligomers, extracted from high molecular weight polymer, by TLC is reported(96 - 99). The TLC analysis of glycolysed PET was carried out in order to qualitatively check the presence of oligomers in the glycolysed products. The samples were dissolved in phenol / tetrachloroethane solvent system(97,99) Silica gel was used as the stationary phase and chloroform/ethanol solvent system was used as the mobile phase.(97,99). The TLC plate was activated at 100°C before running the analysis.

3.2.4 High Performance Liquid Chromatography (HPLC) :-

The separation of PET oligomers, extracted from chips and films using GPC[(100 - 102)] and HPLC[(103)] has been reported.

In the present work the glycolysed PET products were separated by preparative HPLC. The equipment used was, a 'Jobin Yvon Miniprep L.C. (France)'. The solvent system was selected on the basis of TLC studies. The best possible separation was observed in chloroform + 5% butanol system for EG based products, chloroform + 8 % butanol for PG based products and chloroform + 5% ethanol for DEG based products. The EG based glycolysed products could be well separated but PG and DEG based products could not be effectively separated because of a large number of identical species. The samples were injected as 15 % solution in tetrachloro ethane/phenol solvent system. The injection volume was about 2 ml. The column pressure was about 14 bars and solvent pressure about 10 bars. The detector was a refractive index (RI) detector. The equipment was an old model and did not have the flowmeter for measuring elution rate. Therefore the flow rate had to be adjusted manually. The approximate rate was about 2-8 ml/min. Since the flow rate was not identical for each analysis, the retention times were not quoted for comparison. The fractions were collected separately and evaporated to get quantitative information. The fractions so collected were analysed by NMR. The samples were dissolved in DMSO-d_6 for NMR analysis.

3.2.5 **Number average molecular weight ($\bar{M}n$)** :-

(i) End group analysis :-

Since the molecules of the glycolysed products are bifunctional and hydroxyl terminated, the molecular weights can be calculated by using the formula :

$$\bar{M}n = \frac{56.1 \times 1000 \times 2}{\text{hydroxyl value}}$$

(ii) Vapor pressure osmometry (VPO) :-

The instrument used for the determination of $\bar{M}n$, was a "Knauer Vapor Pressure Osmometer". In the VPO apparatus, two matched thermistors are suspended in a thermostated chamber. Six syringes are so fixed that 1st syringe reaches one thermister and other five reach the second without opening the chamber. The chamber is previously saturated with the solvent vapor. The difference in the resistance of the thermistors is balanced by placing drops of equal size of the pure solvent on the thermistors. Once the thermistors are matched, one drop of pure solvent is put on one thermistor and a drop of same size of the solution is put on the other thermistor. Since the vapor pressure of the solvent in the solution is less than that of the pure solvent, condensation takes place on the solution drop. It thus becomes, both, diluted and heated by the latent heat of vaporization of the solvent. The temperature of the solution drop increases, until the vapor pressure of the solvent in it, at the new higher temperature, reaches that of the pure solvent at the original temperature. The difference in the temperature of the two droplets is sensed by the thermistors and is indicated as the difference in the resistance of the two thermistors. Since lowering of vapor pressure is a colligative property, its value depends on the number of molecules of solute in the solution.

The variation of the colligative property of polymer solution with concentration can be represented as follows(104)

$$\frac{\Delta R}{KC} = \frac{1}{\overline{M}n} \quad 1 + \tau_2 C + g \tau_2^2 C^2 \qquad (15)$$

where ΔR = difference in the resistance of the two thermistors.

K = calibration constant dependent on temperature and nature of the solvent.

τ_2 = second virial coefficient.

g = polymer - solvent interaction function.

The last term is insignificant at low concentrations and can be neglected.

Therefore,

$$\frac{\Delta R}{C} = \frac{K}{\overline{M}n} + \frac{K\ \tau_2}{\overline{M}n} C \qquad (16)$$

The value of $\overline{M}n$ can thus be calculated from the intercept of the linear plot of $\frac{\Delta R}{C}$ versus C.

In the present work, .ethyl acetate was used as solvent. The calibration constant was determined by using five different dilute concentrations of benzil (MW = 210) in ethyl acetate, ranging between 0.0005 to 0.01 mole. The chamber was maintained at 50°C.

The molecular weight of each sample was determined by using five dilute solutions ranging between 2 to 6 g /lit. The sample solutions were filtered to remove the suspended particles comprising of pigment (TiO_2), dust, and very small amount of high molecular weight PET. The values of the molecular weight are reported in Table - 2.

It is known that the glycolysis reaction is first order with respect to the glycol$^{(105)}$. Thus the extent of glycolysis depends on the amount of glycol. Table - 3 shows the physical constants of diesters of terephthalic acid with ethylene glycol, propylene glycol and diethylene glycol.

Referring to the data in Table - 2 it is seen that the hydroxyl value of glycolysed product, after removal of free glycol, increases with increasing amount of glycol for all the three types of glycols. Similarly the molecular weight of the glycolysed product decreases with increasing glycol amount. Both these observations indicate that the extent of depolymerization is dependent on the amount of glycol. The extent of depolymerization was found to be maximum for the EG glycolysed product, UVWE - 3. The hydroxyl value of UVWE -3, after removal of free glycol is 440 and it is comparable to the theoretical hydroxyl value of 442 for BHET (Table -3). However, the hydroxyl values of UVWP - 3 and UVWD - 3 are lower than the theoretical hydroxyl values of the corresponding diesters with propylene glycol and diethylene glycol. This suggests that the extent of depolymerization is lower in the case of PG and DEG relative to EG at the same weight ratio of the diol to PET waste.

Table - 4 shows the effect of the molar quantity of EG on the extent of glycolysis. Since the three glycols have different molecular weights, at any fixed weight ratio of the glycol to PET waste the molar quantity of PG and DEG in the glycolysis mixture is less than that of EG. Therefore, the extent of depolymerization in PG and DEG glycolysed PET products is less than that of the EG based products at any given weight ratio. It is seen from Table - 2 that though the extent of glycolysis depends on the amount of glycol, very small quantity of the diol is actually consumed in the reaction for breaking down the PET polymer chains.

The TLC analysis also indicated that the extent of depolymerization is lower for PG and DEG. Figure - 2 shows the TLC of UVWE-1, UVWP-1 and UVWD-1. The TLC of EG based products manifested one prominent spot along with a couple of faint spots. The dark spot could be assigned to BHET. The TLC of PG based products showed about four dark spots with considerable tailing. The TLC of DEG based product exhibited more than four dark spots with extensive tailing, indicating even broader molecular weight distribution.

It is also found from the TLC analysis that for any given type of the glycol, the molecular weight distribution becomes narrower with increasing amount of glycol. The observed lower extent of depolymerization of PG based systems may also be due to the secondary hydroxyl group on PG, which is known to be less reactive than the primary one.

The structures of probable oligomers arising from the glycolysis of PET with EG,PG and DEG are indicated below :

(i) EG Glycolysis :-

EG - TPA - EG

EG - TPA - EG - TPA - EG

and similar higher oligomers.

(ii) PG Glycolysis :-

EG - TPA - PG

PG - TPA - PG

EG - TPA - EG

and similar higher oligomers.

(iii) DEG Glycolysis :-

EG - TPA - DEG

DEG - TPA - DEG

EG - TPA - EG

and similar higher oligomers.

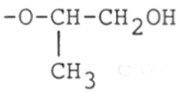
The observations made in TLC analysis are well supported by the HPLC analysis. Figures - 3,4 and 5 show the chromatograms of EG,PG and DEG glycolysed PET respectively. Table-5 shows the weight percentages of different factions. The fractions are numbered in the reverse order as they are eluted out, because the highest oligomer comes out first and the smallest comes out the last. It is seen from the Table that the amounts of higher oligomers decrease with the increasing amount of glycol in the glycolysis. The distributions of PG and DEG based products are very wide. The structures determined by NMR analysis show that the oligomers from EG glycolysed PET are well separated. Figures - 6,7,8 and 9 give the NMR spectra of 1st, 2nd,3rd and 4th fraction.

The 5th fraction, comprising of the highest molecular weight oligomer, was not soluble in DMSO d_6. The integration of the spectra confirm the following structures :

1st fraction - EG - TA - EG [BHET]
2nd fraction - EG (TA - EG)$_2$
3rd fraction - EG (TA - EG)$_3$
4th fraction - EG (TA - EG)$_4$

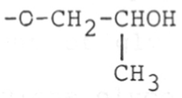
However, the spectra of each fraction of PG based system showed the presence of more than one species. The separation could not be achieved because of very close resemblance in the structure of the species. The probability of the mixture of species in any fraction of PG based product is greatly increased because of assymetric nature of propylene glycol. A sample spectra of 4th fraction of the glycolysed UVWP-1 (Figure-10) shows three doublets in the region 1 to 1.5 δ ppm indicating the presence of 3 types of methyl groups which can be represented as :

(i)



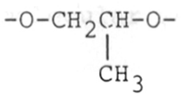
$-O-\underset{CH_3}{CH}-CH_2OH$

(ii)



$-O-CH_2-\underset{CH_3}{CHOH}$

(iii)



$-O-CH_2\underset{CH_3}{CH}-O-$

Thus, the possible number of structures increase with the molecular weight of the oligomer. The increased number of fractions with increase in the amount of PG indicates that the extent of glycol exchange with EG increases which gives rise to more types of species.

Similarly the DEG based systems also exhibited a large number of oligomeric species which could not be isolated and identified effectively. The NMR spectra of 4th fraction of UVWD-1 is shown in Figure-11. The singlet at 4.7 δ indicates the incorporation of DEG in the chain. Similarly the multiplicity in the aromatic signals near 8 δ indicate the presence of aromatic rings with different chemical environment, arising from various combinations of EG and DEG with terephthalic acid.

It would be desirable to separate the mixed species after derivatization of glycolysed PET followed by identification by NMR using shift reagents and by mass spectroscopy in order to get a better idea of the molecular structure distribution.

Thus it is concluded that the extent of depolymerization of PET by glycolysis depends on the amount of glycol. The extent of glycolysis was found to be higher in glycolysis by ethylene glycol as compared to the glycolysis by PG and DEG. The molecular weight distribution was observed to be the broadest in the case of DEG glycolysed PET products. This may be due to the presence of a number of oligomeric species arising because of the lower extent of depolymerization.

TABLE - 1

Conditions of Glycolysis of PET Waste

Sr. No.	Glycolysis reaction	Type of glycol	Reflux temp. °C	PET waste		Glycol		
				wt.g	weight %	wt.g	weight %	moles
1.	UVWE - 1	EG	200	750	62.5	450	37.5	7.26
2.	UVWE - 2	EG	200	600	50.0	600	50.0	9.68
3.	UVWE - 3	EG	200	450	37:5	750	62.5	12.10
4.	UVWP - 1	PG	200	750	62.5	450	37.5	5.92
5.	UVWP - 2	PG	200	600	50.0	600	50.0	7.89
6.	UVWP - 3	PG	200	450	37.5	750	62.5	9.86
7.	UVWD - 1	DEG	230	750	62.5	450	37.5	4.24
8.	UVWD - 2	DEG	230	600	50.0	600	50.0	5.66
9.	UVWD - 3	DEG	230	450	37.5	750	62.5	7.07

TABLE - 2

Characterization Data on Glycolysed PET Products

Sr. No.	Glycolysed PET code	Weight % of glycol used in glycolysis	Weight % of free glycol after glycolysis	Before removal of free glycol		After removal of free glygol		
				Hydroxyl value mg KOH/g	Mn (end group)	Hydroxyl value mg KOH/g	$\overline{\mathrm{Mn}}$ (end group)	$\overline{\mathrm{Mn}}$ (VPO)
EG based								
1.	VVWE - 1	37.5	32	610	184	374	300	320
2.	UVWE - 2	50.0	45	870	129	402	279	290
3.	UVWE - 3	62.5	58	1070	105	440	255	272
PG based								
4.	UVWP - 1	37.5	35	516	217	240	467	480
5.	UVWP - 2	50.0	47	717	156	295	380	399
6.	UVWP - 3	62.5	60	933	120	326	344	276
DEG based								
7.	UVWD - 1	37.5	33	385	291	190	590	684
8.	UVWD - 2	50.0	46	520	216	210	534	640
9.	UVWD - 3	62.5	56	650	172	215	522	610

TABLE - 3

Physical Constants of Diesters of EG, PG and DEG with Terephthalic Acid

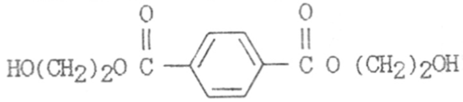
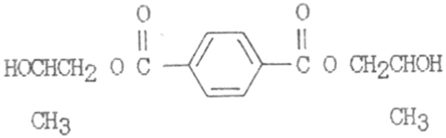
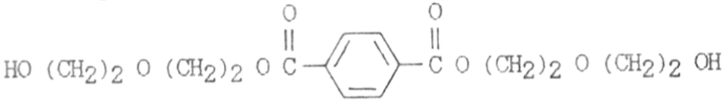
Sr. No.	Type of glycol	Diester with terephthalic acid	Molecular weight	Hydroxyl value mg KOH/g	M.P. °C
1.	EG	bis (2-hydroxy ethyl) terephthalate [BHET] 	254	442	109
2.	PG	bis (2-hydroxy propyl) terephthalate [BHPT] 	282	398	131
3.	DEG	bis [2-(2-hydroxy ethoxy) ether] terephthalate 	358	313	35

TABLE - 4

Effect of Molar Quantity of EG on the Extent of Depolymrization

Sr. No.	Glycolysed PET code	Weight % of EG in glycolysis reaction	Moles of EG for 100 g of PET	* Extent of depolymerization
1.	UVWE - 1	37.5	0.97	0. 161
2.	UVWE - 2	50.0	1.61	0.9095
3.	UVWE - 3	62.5	2.69	0.9955

$$* \text{ Extent of depolymerization} = \frac{\text{Hydroxyl value of glycolysed PET after removal of free glycol}}{\text{Hydroxyl value of BHET monomer}}$$

TABLE - 5

Weight Percent of Oligomers by HPLC Analysis

Sr. No.	Glycolysed PET code	Type of Glycol	Percent of glycol in glycolysis	Weight Percent of Fractions						
				1	2	3	4	5	6	7
1.	UVWE-1	EG	37.5	53.1	27.0	13.9	5.0	1.0	-	-
2.	UVWE-2	EG	50.0	67.4	27.8	4.8	-	-	-	-
3.	UVWE-3	EG	62.5	85.5	13.7	0.8	-	-	-	-
4.	UVWP-1	PG	37.5	32.9	24.9	14.2	17.7	10.3	-	-
5.	UVWP-2	PG	50.0	6.4	28.6	34.5	4.1	6.3	15.2	4.9
6.	UVWP-3	PG	62.5	5.1	25.2	51.4	2.9	12.1	3.3	-
7.	UVWD-1	DEG	37.5	14.5	34.8	31.9	18.8	-	-	-
8.	UVWD-2	DEG	50.0	38.3	26.3	13.6	13.4	6.8	1.6	-
9.	UVWD-3	DEG	62.5	39.6	30.5	21.4	8.5	-	-	-

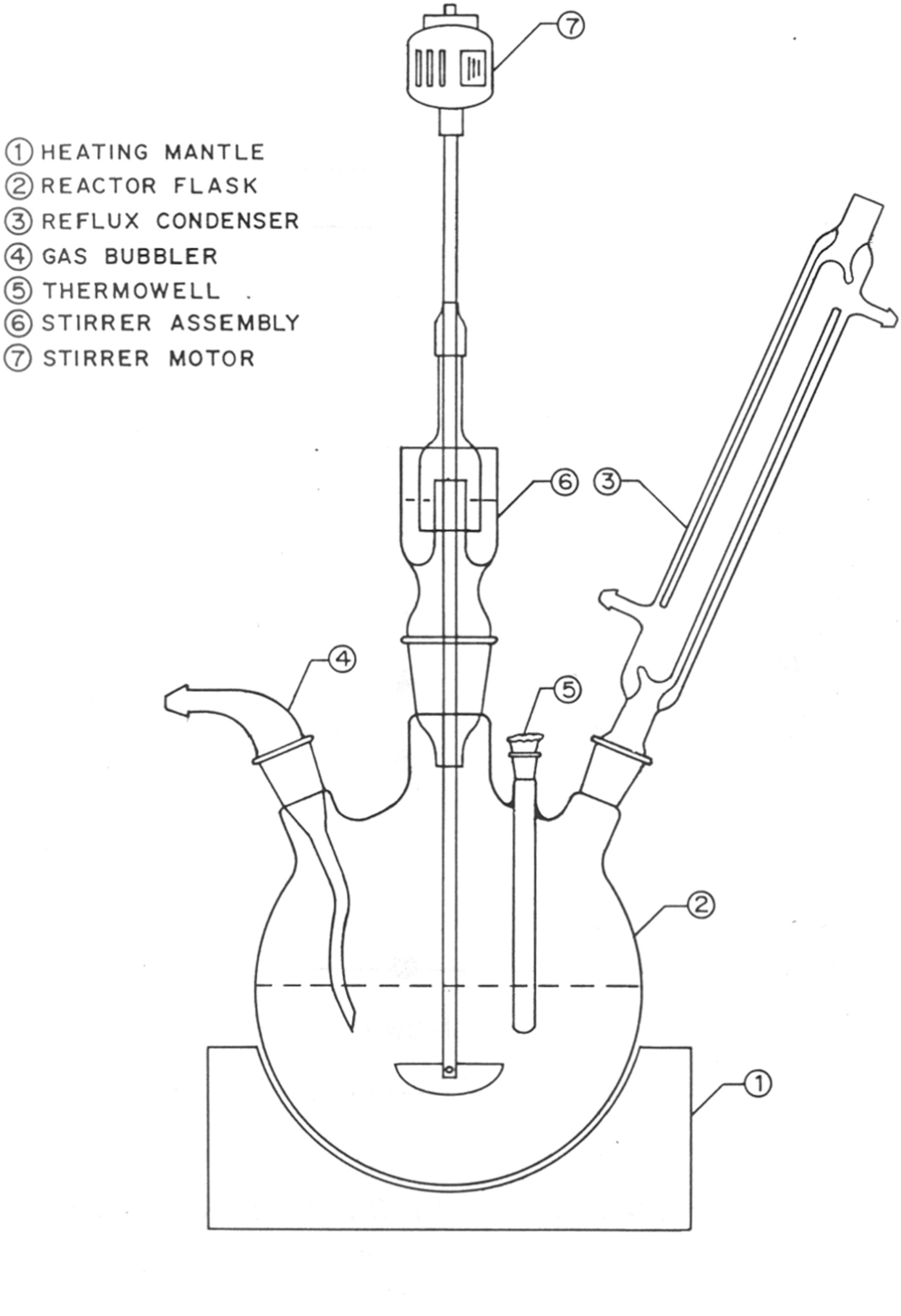


FIGURE.1: LABORATORY REACTOR ASSEMBLY FOR GLYCOLYSIS

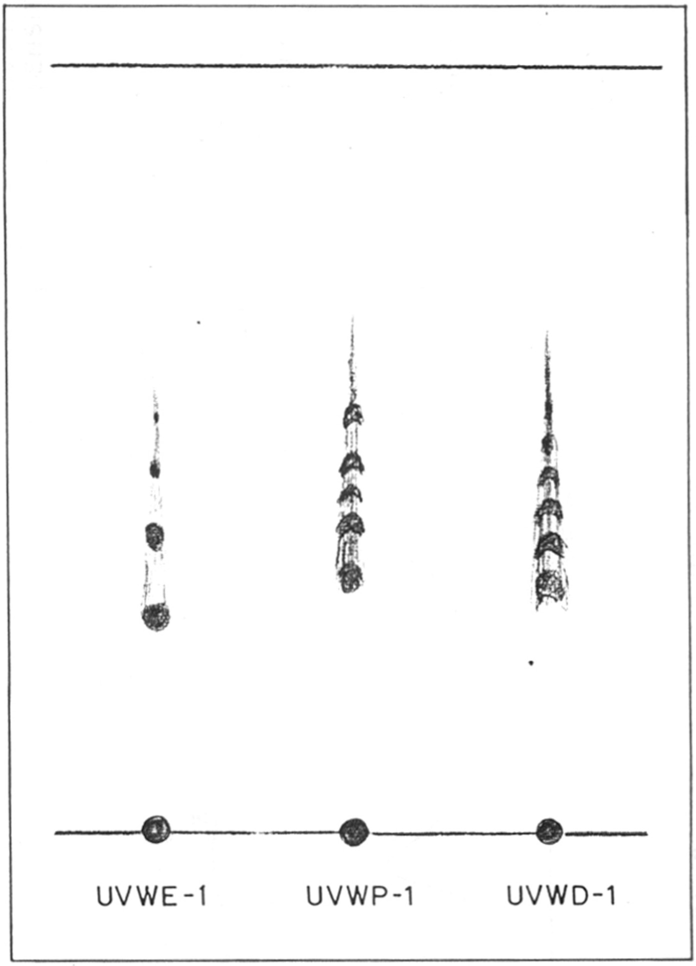


FIGURE 2: TLC OF GLYCOLYSED PET WASTE

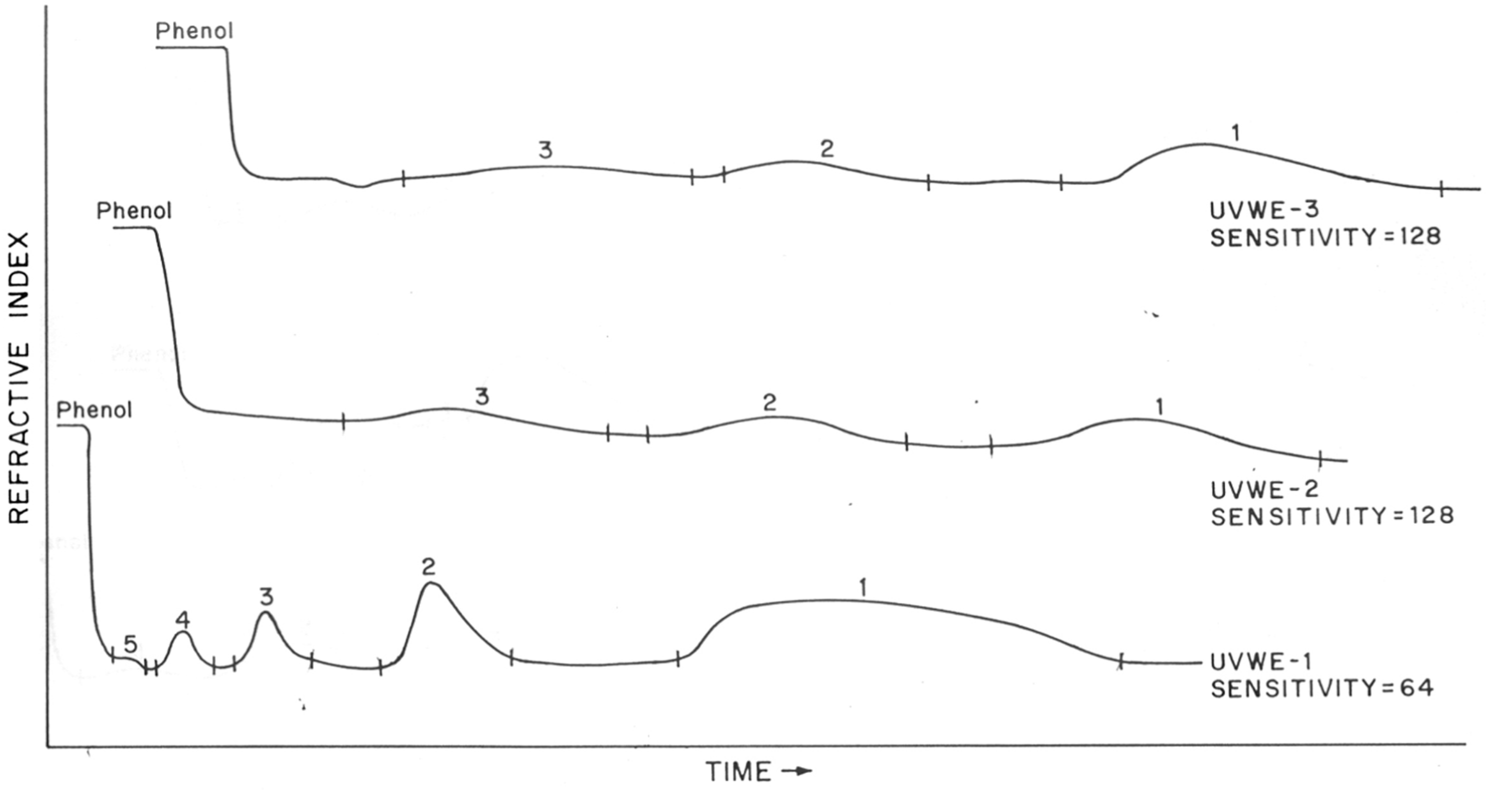


FIGURE 3: HPLC GRAPHS OF EG GLYCOLYSED PET

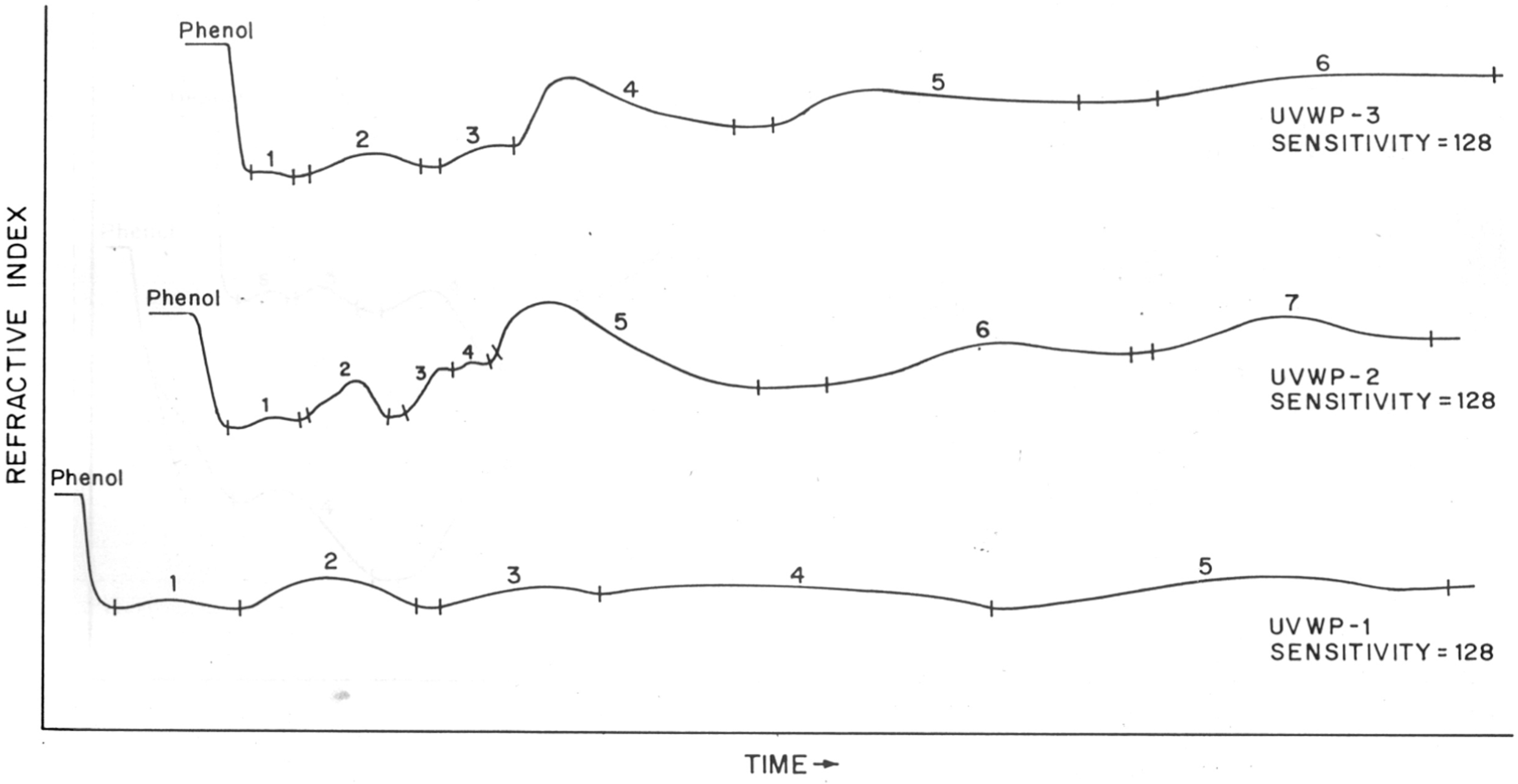


FIGURE 4: HPLC GRAPHS OF PG GLYCOLYSED PET

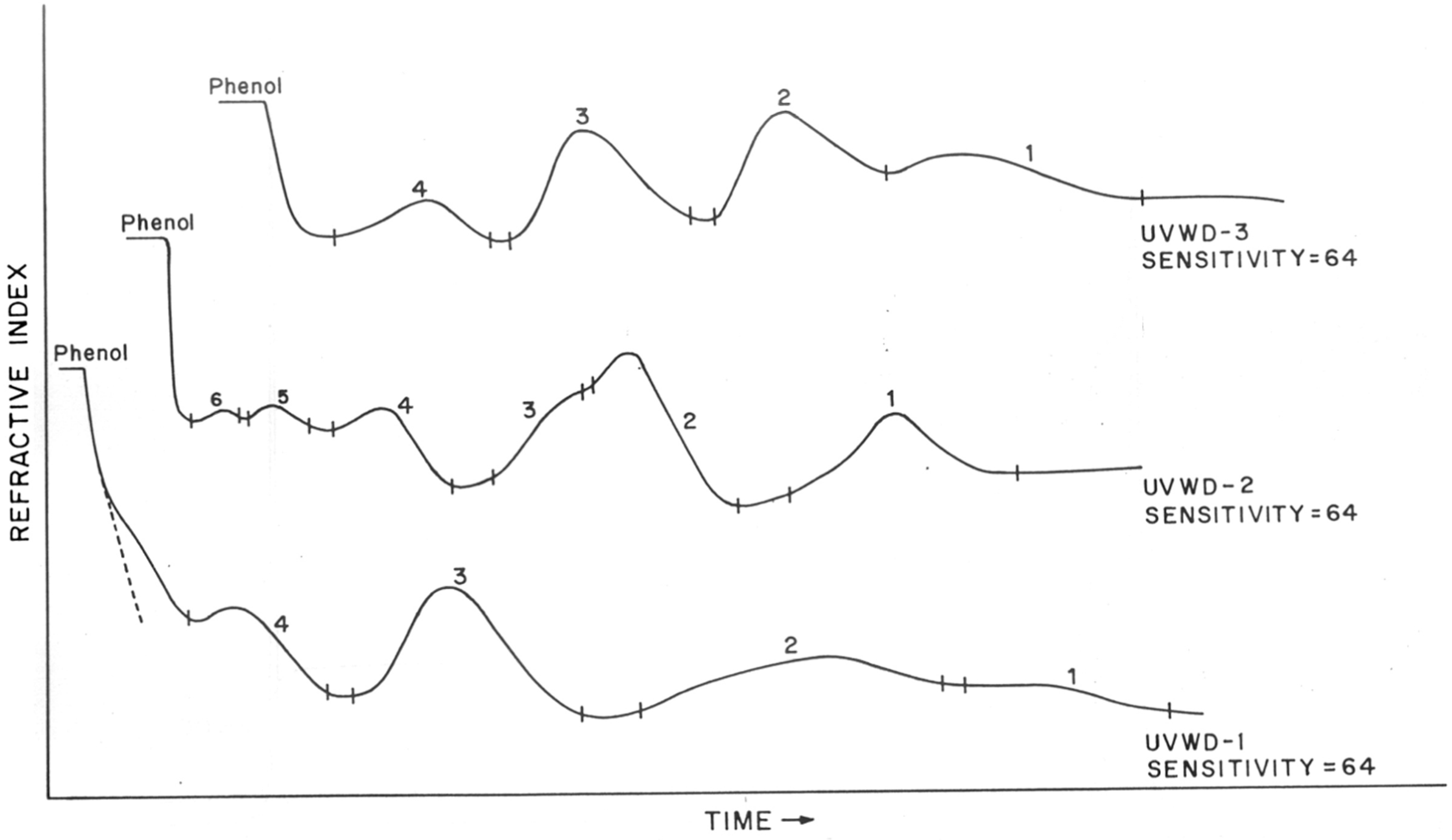


FIGURE 5: HPLC GRAPHS OF DEG GLYCOLYSED PET

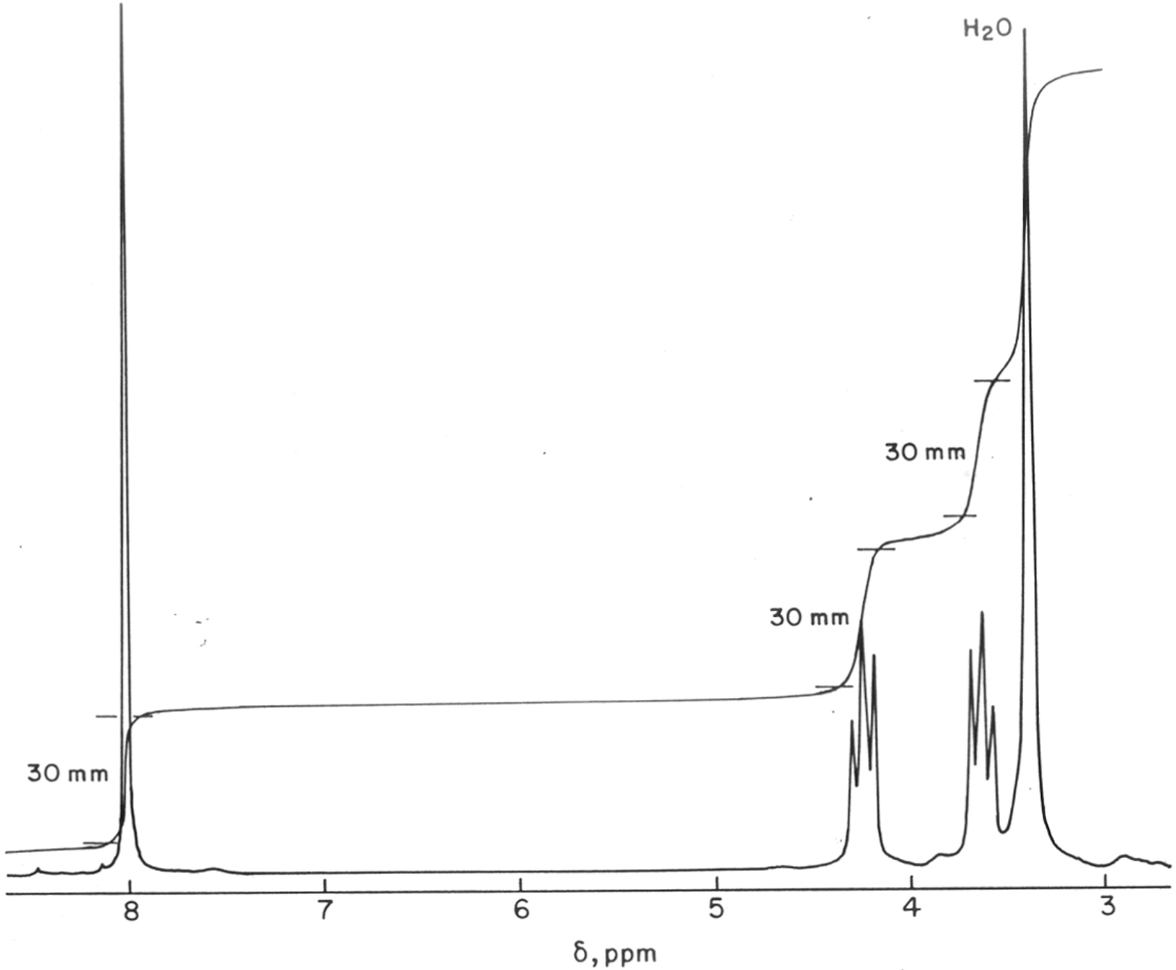


FIGURE 6: NMR SPECTRA OF 1st FRACTION OF EG GLYCOLYSED PET

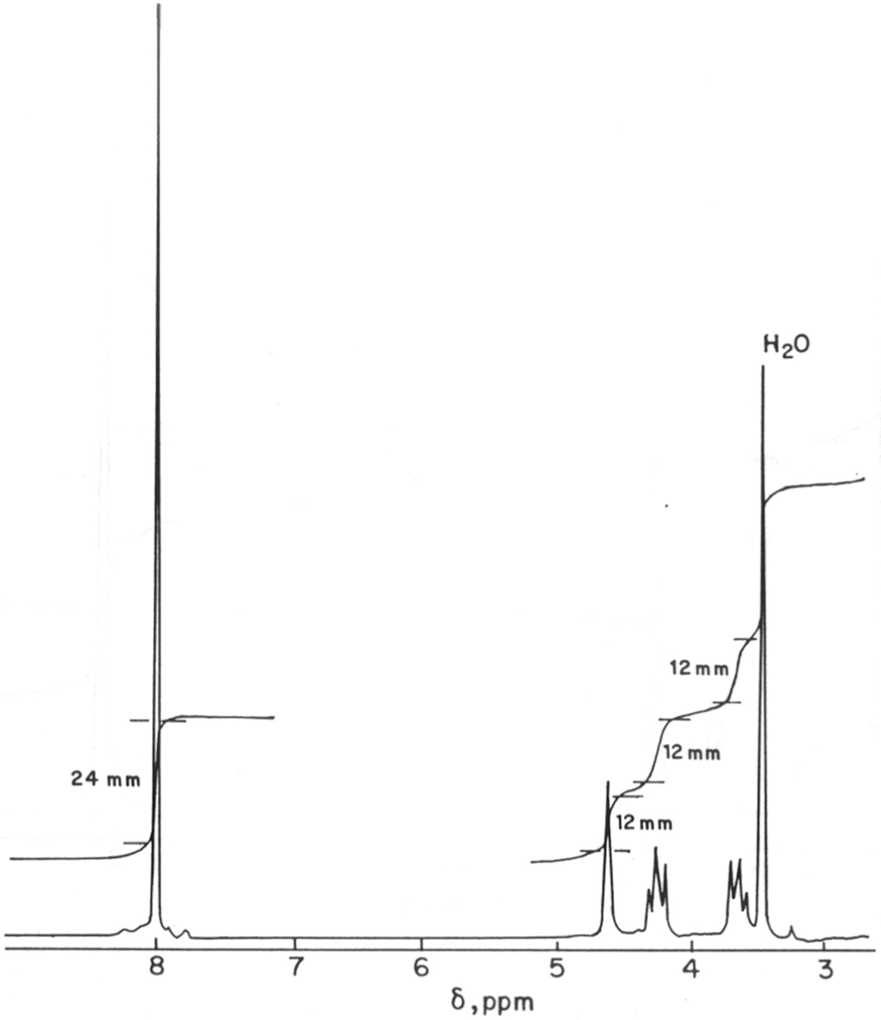


FIGURE 7: NMR SPECTRA OF 2nd FRACTION OF EG GLYCOLYSED PET

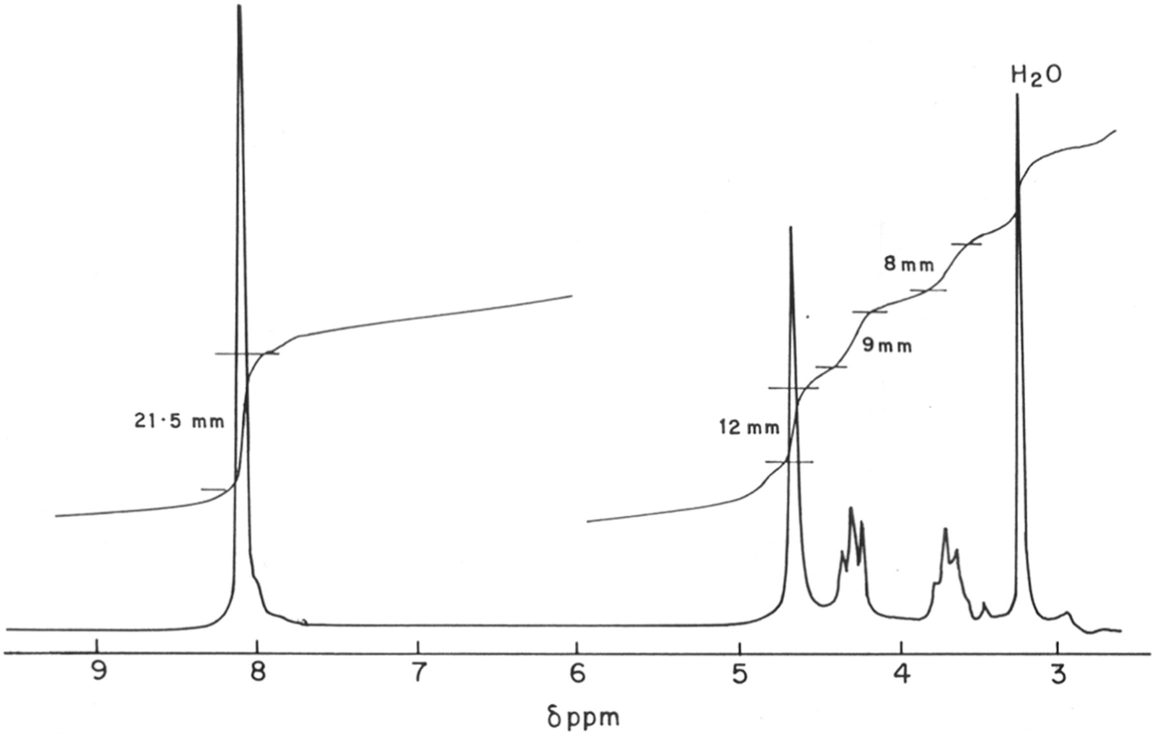


FIGURE 8: NMR SPECTRA OF 3rd FRACTION OF EG GLYCOLYSED PET

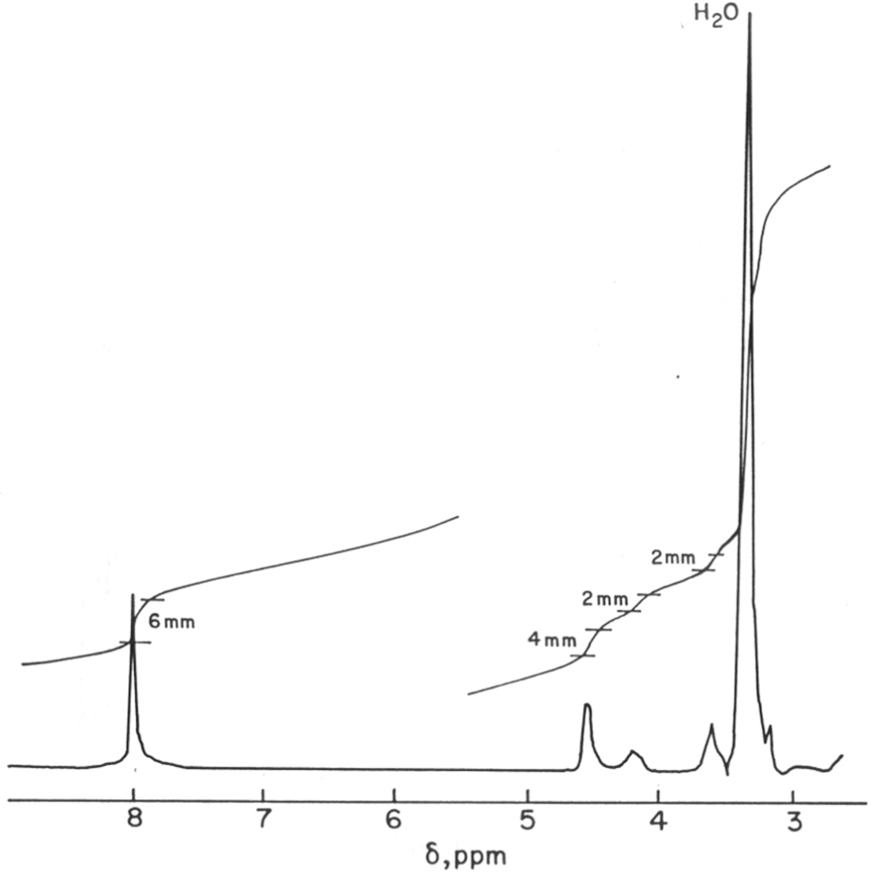


FIGURE 9: NMR SPECTRA OF 4th FRACTION OF EG GLYCOLYSED PET

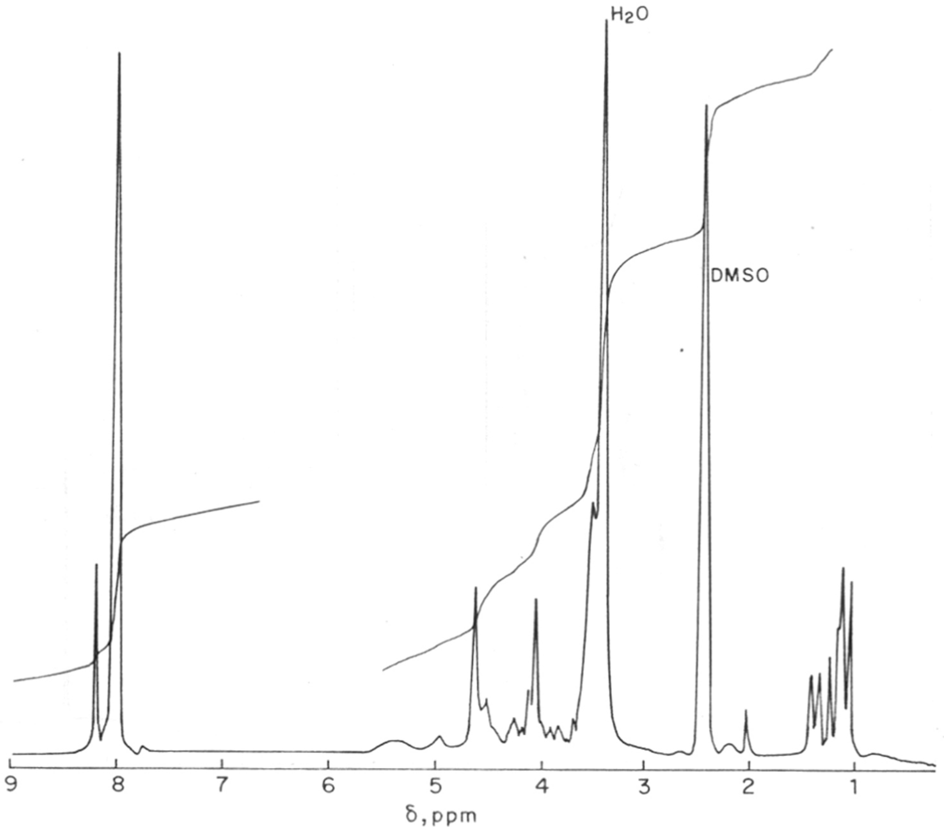


FIGURE 10: NMR SPECTRA OF 4th FRACTION OF PG GLYCOLYSED PET-UVWP-1

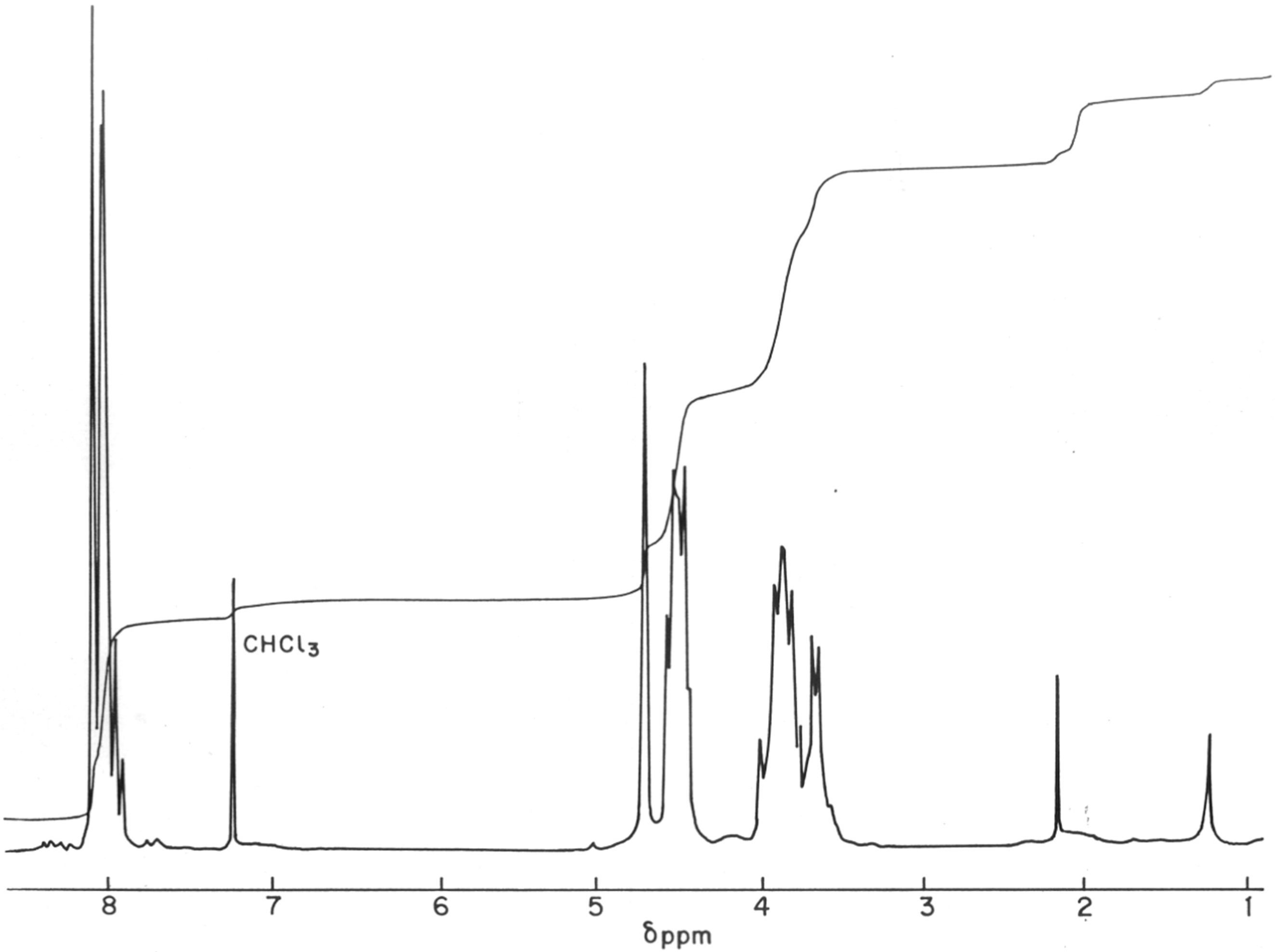


FIGURE 11: NMR SPECTRA OF 4th FRACTION OF DEG GLYCOLYSED PET-UVWD-1

CHAPTER 4

UNSATURATED POLYESTERS

As stated earlier, unsaturated polyesters (UP) are prepared by reacting unsaturated and saturated diacids with diols. The conventional general purpose UP resin is prepared by reacting maleic and phthalic anhydride with propylene glycol. Certain characteristics of UP resins, namely, the heat distortion temperature, chemical resistance, and hardness are improved by using isophthalic acid in place of phthalic anhydride. The thermomechanical properties may be improved further with the use of terephthalic acid (TPA) because of the para-para linkage. However, the direct use of TPA is restricted due to the processing difficulties resulting from its high melting point and sublimation during polyesterification.

The use of glycolysed PET in UP resins would enable one to synthesize resins with the terephthalic moiety in the polymer backbone, eliminating the processing difficulties associated with the use of pure TPA. Secondly the waste is converted into a value added product.

It was seen in the priliminary experiments that the glycolysed product based on EG, when reacted with maleic anhydride, gave resins which were not compatible with styrene monomer. Therefore, further efforts were focused on the development of UP resins from glycolysed products based on PG.

4.1 PREPARATION OF UP RESINS

4.1.1 Materials :-

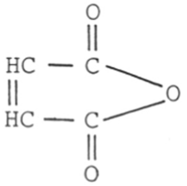
(i) Glycolysed PET waste (Refer to section 3.1) :-

(a) UVWP - 1 with hydroxyl value of 516

(b) UVWP - 2 with hydroxyl value of 717

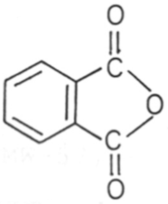
(c) UVWP - 3 with hydroxyl value of 933

(ii) Maleic anhydride :-

Molecular Formula	
Molecular Weight	98
Melting Point	54 - 56°C

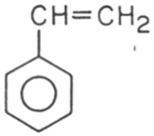
The chemical was supplied by M/s High Purity Chemicals, New Delhi (India). The purity was above 99 % .

(iii) Phthalic anhydride :-

Molucular Formula	
Molecular Weight	148.12
Melting Point	132 - 134°C

The chemical was LR grade with purity above 99 % . It was supplied by M/s. Loba Chemie, Bombay (India).

(iv) Styrene monomer :-

Molecular Formula	
Molecular Weight.	104.15
Boiling Point	145 - 146°C

The momomer was supplied by S D Fine Chem Pvt. Ltd., Boisar (India). Purity was about 99 % . The monomer was inhibited with about 15-20 ppm tertiary butylcatachol. All the chemicals were used as such without further purification.

4.1.2 **Synthesis of Unsaturated Polyesters** :-

The glycolysed products were polyesterfied with maleic anhydride at a fixed value of the hydroxyl to carboxyl ratio of 1.1. The amount of the glycolysed PET product required for the reaction was computed based on its hydroxyl value without glycol separation.

Thus, three UP reins, coded UVMW-57, - 58, and - 59 were prepared by reacting 1193.9 g of UVWP - 1 with 489.9 g of maleic anhydride, 1109.4 g of UVWP - 2 with 681.7 g of maleic anhydride and 1012.6 g of UVWP - 3 with 750.3 g of maleic anhydride. A general purpose resin was prepared by reacting 396.2 g maleic anhydride and 592.4 g of phthalic anhydride with 669.6 g of propylene glycol for comparison of kinetics.

The polyesterification reactions were carried out in a 3 litre round bottom reactor having a distillation condenser, a thermowell, a gas bubbler and stirring assembly. The reactants were heated from room temperature to 180°C in nitrogen atmosphere in about 90 minutes. Then the temperature was held at 180°C for about 3 hours and finally raised to 200°C and maintained until the acid value reached about 32 mg of KOH/g. The water of reaction was removed throughout the course of reaction. The amount of water of condensation and the acid value were monitored during the reaction. At the end of the reaction about 170 ppm (0.425 g) hydroquinone was added to the liquid resin.

The acid values were determined by titrating a weighed quantity of the resin, dissolved in acetone, with about 0.2 N standard alcoholic KOH solution. Phenolphthalein was used as indicator.

$$\text{Acid Value} = \frac{56.1 \times \text{Normality of KOH} \times \text{mL of KOH}}{\text{Weight of resin}}$$

Small quantities of the resins were removed and preserved for further characterization, at the end of the reaction.

The viscous resin was then cooled to 100°C. Styrene monomer was carefully added to form about 70 % solution of the resin in styrene. Nitrogen flow and stirring was continued till the resin reached room temperature to avoid any premature thermal polymerization. The resins were further diluted with styrene to get 4-5 different concentrations ranging between 70 % to 60 % w/w resin.

4.2 RESIN CHARACTERIZATION.

4.2.1 End Group Analysis :-

(i) Carboxyl group analysis :-

The carboxyl groups are determined in the form of acid value. The acid value is defined in terms of milligrams of potassium hydroxide required to neutralize one gram of the sample. The method for determination of acid value is already described in section 4.1.2. The acid values of the resins, before mixing styrene, are reported in Table - 6.

(ii) Hydroxyl value determination :-

The method for determining hydroxyl value is described in section 3.2.2. The hydroxyl values were determined, before addition of styrene monomer; the values are reported in Table - 6.

Referring to Table - 6, it may be noted that although the carboxyl values of the resins are comparable, a gradual decrease in hydroxyl value is observed in the PET waste based resins. UVMW-57 has the highest and UVMW-59 has the lowest hydroxyl value. The hydroxyl value of the GP resin is comparable to the PET waste based resins.

4.2.2 **Molecular Weight Determiantion** :-

(i) By end group analysis :-

The number average molecular weight of the linear polyesters can be determined by end group analysis using the following relationship :

$$\overline{M}n = \frac{56.1 \times 1000 \times 2}{\text{Hydroxyl value + Acid value}}$$

The results are shown in Table - 6.

(ii) By vapor pressure osmometry :-

The method is discussed in section 3.2.5. The measurements were carried out on the resins before addition of styrene monomer. The results are reported in Table - 6.

Although the values determined by the two methods are in agreement for UVMW-57 and - 59, a slight variation is observed in the case of UVMW-58 and GP reins. This deviation may be due to a wide molecular weight distribution (refer chapter-3). However, vapor pressure osmometry is a more sophisticated and reliable method for interpretation. The molecular weights of the PET waste based resins are comparable to that of the GP resin. The diols with lower molecular weights are more reactive. When polyesterification is carried out using diols of different molecular weights, at a fixed OH to COOH ratio, and the reaction is stopped at a perticular acid value, the system with lower molecular weight glycol is bound to undergo a greater extent of reaction. Therefore the molecular weights are likely to be higher, unless the difference in the molecular weights of the diols is too large. Similar trend is observed in PET based resins. The end group analysis shows an increase in the molecular weight with a decrease in the molecular weight of the diol used for polyesterification. However, the VPO results indicate that the molecular weight of UVMW-58 is greater than that of UVMW-59. This could be attributed to the wider molecular weight distribution of polyesters arising from different reactivities and MWD of the diols used for the synthesis.

4.2.3 Viscosity Measurements :-

Commonly, FRPs are made by hand layup procedure wherein the resin should have viscosity low enough to enable brushing, whereas for hot moulding and dough moulding, a higher viscosity is preferred. Thus, viscosity is one of the most important characteristics from processing point of view. The resins, therefore, were characterized for their viscosity behavior at different amounts of styrene monomer.

The measurements were carried out using a Brookfield viscometer. The instrument has a spindle attached to a spring. The spindle rotates in the liquid sample. The resistance offered by the liquid to the rotation of the spindle is indicated by a pointer, on a 0 to 100 scale. The spindle size and the speed of rotation (rpm) can be changed to get the reading in the range of the scale. The reading , when multiplied with an appropriate factor, for the perticular spindle at a fixed rpm gives the resin viscosity in centipoise. The factor can be found from a factor finder chart supplied with the instrument.

Since the viscosity varies exponentially with temperature, all the measurements were conducted in a constant temperature bath, at 31°C.

Figure - 12 shows the variation in the viscosity with percentage of styrene for all the four UP resins. The viscosity is found to be highly dependent on the amount of styrene. The viscosity also depends on the molecular weight of the polyester. It is observed that the PET waste based resins exhibit higher viscosities than the ortho phthalic acid based GP resin. The trend in the viscosity variation of PET waste based resins is consistant with the trend of molecular weights determined by VPO. Table - 7 shows the amounts of the different chemical moieties present in the UP resins. UVMW-57 has a composition comparable to that of the GP resin. The main difference is in the nature of the aromatic diacid. The former has terephthalic acid giving linear para-para linkages, whereas the later has orthophthalic acid in the back bone adversely affecting chain linearity. It is observed from Figure - 12 that the viscosity of UVMW - 57 is slightly higher than that of the GP resin. This may be due to better packing of polyester chains with p-p linkages in the PET waste based resin. However, the viscosities of UVMW -57 and GP resin may be considered comparable from processibility viewpoint.

4.2.4 Gelation Behavior :-

A gel is formed as a result of partial crosslinking of the polymer inhibiting its flow. This phenomenon governs the proccessibility of the resin, since the processing time has to be shorter than the gelation time.

Unsaturated polyesters are normally cured by free radical polymerization, using peroxide initiators such as methyl ethyl ketone peroxide (MEKP), benzoyl peroxide (BPO) and cumene hydroperoxide (CHPO),at high temperatures (> 70^{o}C). The reaction can be initiated at room temperature using promoters or accelerators along with the peroxide initiator. The commonly used promoters include amines like dimethyl aniline, diethyl aniline and metal salts like cobalt naphthanate, cobalt octoate etc. The curing reaction is an exothermic reaction. The exotherm temperature is a measure of the reactivity of the resin at a given concentration of the initiator and promoter. Faster the reaction, greater is the extent of exotherm. A higher exotherm during the curing process may lead to greater shrinkage and stress concentration points in the moulded finished product. Hence, it is important to control the exotherm and the gelation behavior of the resin.

In the present work, MEKP was used as the initiator with cobalt naphthanate as the promoter for investigating the gelation and exotherm behavior of the UP resins. The amount of the initiator used was 1.5 % w/w and that of the accelerator was 0.5 % w/w based on the resin. The investigations were carried out with 50 g resin in well-insulated glass beakers.

The gelation time was determined using a 'Tecam gelation timer' supplied by M/s Techne, UK. The instrument comprises of a timer and a spindle. The spindle moves up and down. The spindle is dipped in the liquid resin after initiating the crosslinking reaction. Once the instrument is switched on, the spindle starts moving up and down in the resin and simultaneously the timer starts. When the resin gels, the spindle stops moving and so does the timer. The time indicated on the timer is recorded as the gelation time.

Figure - 13 shows the effect of styrene percentage on the gel times of the polyesters. The gel times for the PET waste based resins are found to be considerably shorter than the GP resin, indicating that the PET based resins are more reactive. The amount of styrene monomer does not have a significant effect on the gelation time over the range of styrene percentage studied. Among the PET based resins, the trend is consistant with the viscosity and molecular weight values determined by VPO. Greater the molecular weight shorter is the gel time.

During the investigation of gelation time, the temperature of the reaction mixture was monitored by a thermometer. The maximum temperature attained by the resin during the curing reaction was noted as peak exotherm. Figure-14 shows the effect of styrene percentage on the peak exotherm. The extent of exotherm would depend on the amount of unsaturation in the polymer chain. Table - 7 shows the weight percentage of the maleic acid moiety, which is the measure of unsaturation, present in each resin. It is seen in Figure - 14 that the exotherm increases with amount of maleic acid moiety in the polymer backbone. The peak exotherm increases with the amount of styrene. Usually the styrene percentage is fixed at about 35 % to get optimum property performance. The effect of styrene percentage on the peak exotherm is less prominent in case of the GP resin, as compared to the PET waste based resins.

The gel times of the resins, based on PET waste are very low as compared to the GP resin. These short gelation times would make processing of the resin very difficult particularly in contact moulding operations. Therefore, it is essential to prolong the gelation time. The geltime can be altered by varying the amount of the initiator and accelarator. UVMW-57, which is comparable to the GP resin in its flow characteristics and composition, was used to investigate further the effect of the intiator and accelerator amounts on the gelation behavior. Table - 8 summarizes data showing the effect of the amount of initiator and accelerator on the gelation time and peak exotherm. It is seen that the gel time can be altered over a wide range from 11 to 100 minutes by merely changing the initiator/accelerator amounts. Similarly the peak exotherm temperature can also be controlled. It is therefore concluded that the use of other initiator and accelerator systems may also allow manipulation of the gelation behavior of the resins to suit processing requirements.

Thus the PET based resins may be used successfully in place of GP resins without facing any processing difficulty.

4.3 KINETICS OF POLYESTERIFICATION

The details regarding kinetics of the polyesterification reaction, which is a condensation polymerization are already discussed in the second chapter of the thesis.

The kinetic investigations are normally conducted under isothermal conditions. However, when the polymerization is carried out on a commercial scale, the reactants are mixed and then gradually heated to a temperature (175°C) lower than the boiling point of the glycol. The temperature is then held there for sometime so as to 'hook' the glycol partially in order to avoid the loss of glycol through distillation. In the final stages, the temperature is raised to higher values (> 200°C) to accelerate the rate of the reaction. Therefore the kinetic data obtained under these conditions would be more relevant from a technological viewpoint.

In the present work, the reactions were carried out under nonisothermal conditions, following a pre-determined temperature-time cycle as described above, involving two isothermal plateau regions. The heating schedule was as follows :

- Heat from room temperature to 120°C in 30 minutes.
- Heat from 120°C to 180°C in 1 hour.
- Hold at 180°C for about 3 hours.

- Heat from 180°C to 200°C in 20 minutes
- Hold at 200°C till the end of the reaction.
- Cool to 110°C before styrene addition.

The kinetics were investigated at 180°C and 200°C.

These reactions were uncatalysed. The molar amount of the diol was in 10 % excess of the stoichiometric amount so as to give a hydroxyl to carboxyl ratio of 1.1. The progress of the reaction was monitored by determining the acid value of the reaction mixture from time to time. The reactions were carried out till the acid value reached about 32 mg of KOH/g. The reactions based on glycolysed PET were over in about 10 hours whereas the GP resin took about 25 hours to reach the same acid value. Figure - 15 shows the drop in acid value with time. The figure shows the slow drop in acid value of GP resin relative to the PET based systems.

Figure - 16 shows the increase in the extent of reaction 'p'with time. It is clear from the figure that in PET based systems the extent of reaction increases much more rapidly than in the GP resins. The extent of reaction in case of UVMW - 59 is less than UVMW - 58 at 180°C but increases rapidly at 200°C. At the end of the reaction the extent follows the order UVMW - 59 > UVMW-58 > UVMW -57 > GP resin.

The kinetic expression representing a stoichiometric reaction, need to be modified for the reactions involving nonstoichiometric amounts of reactants. However, in the present work, wherein, the excess is only 10 %, the kinetic data fits well with the equation proposed for stoichiometric amounts of the reactants, namely,

$$\frac{1}{(1-p)^2} = 2\,Co^2\,kt + \text{constant} \qquad (6)$$

The experimental data depicted in Tables 9 - 12 were used to generate plots of $1/(1-p)^2$ versus time (Figure - 17). The linear nature of the plots indicates that the reactions follow third order kinetics for both the temperature regimes. It is seen that the rate of reaction increases remarkably with temperature and this increase is more prominent in case of resins based on glycolysed PET waste, compared to GP resin.

The rate constants at 180°C and 200°C were calculated using equation -6 and Figure -17. The initial concentrations at 180°C and 200°C were calculated from acid values of the reaction mixture when it reached 180°C and 200°C respectively. The rate constants are given in Table - 13. The rate constants of the reactions based on glycolysed PET are much higher than that of phthalic anhydride based GP resin. The lower reactivity observed in the GP resin batch may be partly due to a secondary hydroxyl group of propylene glycol, which is partially replaced by ethylene glycol in the PET based resins.

Figure - 18 shows the drop in the rate of reaction with the extent of reaction. It is seen that the drop is more steep at 200°C. This is because of the higher extent of polycondensation reaction at 200°C leading to a higher viscosity which in turn makes the removal of water of reaction more difficult. The reaction equilibrium would thus shift to the reactant side thereby lowering the rate.

It is known that any imbalance in the stoichiometry of reactants reduces the degree of polymerization (DP). The quantitative expression of the lowering of DP can be represented as

$$DP = \frac{1 + r}{1 + r - 2p} \qquad (14)$$

where 'r' is the ratio of the reactant concentrations and is never less than unity. Figure - 19 shows the increase in DP with time. At any given time, the degree of polymerization is higher for the PET based resins than for the GP resin. Thus all the observations indicate that the PET waste based systems are much more reactive than the GP resin. The time required for synthesis of the GP resin is almost three times of that required for the glycolsed PET waste based system.

4.4 MECHANICAL PROPERTIES OF THE UP RESINS

The performance of any polymer, under static service conditions, can be well judged by testing its mechanical properties. However, for moulded FRP parts subjected to dynamic loading conditions, it is also necessary to investigate the dynamic mechanical response of the material over the temperature range of relevance to the end use. The static mechanical properties of interest include tensile strength, flexural strength, impact resistance, hardness and heat distortion temperature.

The polyesters made from glycolsed PET waste were tested for their static mechanical properties and compared with those of two commercially available unsaturated polyesters, namely, an ordinary grade, and an improved grade. The ordinary grade was obtained from a local supplier. The improved grade resin was supplied by Dr. Beck & Co. (India) Ltd.

It is well known that during high temperature polyesterification of maleic anhydride, a part of maleic (cis) unsaturation isomerizes into fumarate (trans) form. The extent of isomerization is a function of temperature and time of the polyesterification reaction (106). The isomerization has a profound effect on the mechanical properties of the unsaturated polyesters. The fumaric double bond reacts more readily with styrene than maleic double bond, thereby giving a higher crosslinking density than the corresponding maleic containing polyester. Thus fumarate double bonds give more rigid and hard product than maleic unsaturation. Therefore it is essential to determine the extent of cis-trans isomerization. The extent of isomerization can be determined by NMR analysis (107). In the present work, the base polyesters (without styrene) were dissolved in acetone - d_6, filtered, and analysed by FT NMR. The unsaturated polyesters show signals for maleate (cis) hydrogens at 6.4 δ and for fumarate (trans) hydrogens at 6.8 δ values (Figure - 20). Integration of these peaks gave the relative concentrations of the maleate and fumarate hydrogens. In all the resins the fumarate form was found to be above 96 % of the total unsaturation. It is interesting to note that in spite of the shorter reaction times for PET based resins the extent of isomerization is comparable to that in the GP resins. Therefore the probability of difference in the mecahnical properties due to maleate - fumarate isomerization can be eliminated.

The polyesters were cured using methyl ethyl ketone peroxide (MEKP) and cobalt naphthanate. The amount of the two chemicals used ranged between 0.5 to 1.5 % and 0.25 to 0.5 % respectively. The amounts of the initiator and the accelerator were carefully chosen so as to generate comparable exotherm profile (peak exotherm of about 110°C). The samples were then cast into the moulds conforming to the DIN specifications. The specimens were cured for 16 hours at room temperature followed by four hours at 80°C.

The following test methods were used for mechanical testing:

(i) Tensile Strength : - The tensile strength was measured as per DIN 53455. The specimens were cast to form dumble shaped strip as per specifications given in the test booklet.

(ii) Impact Strength : - The impact strength of the unnotched specimens was determined as per DIN 53453. The specimens were in the form of rectangular bars measuring 120 mm x 15 mm x 10 mm.

(iii) Flexural Strength : - Flexural strength was determined by three point method as per DIN 53452. The specimens were in the form of rectangular bars as specified for impact strength.

(iv) Hardness : - The hardness was measured as per DIN 53505, using Shore - D hardness tester.

(v) Heat Distortion temperature (HDT) : - The HDT was measured as per DIN 53458 using Martins method. The specimens used were similar to those discribed under impact strength.

The test results are summarized in Table - 14. The tensile strengths of the glycolsed PET based resins are comparable to that of the ordinary GP grade resin. The tensile strength of the improved grade is reported to be much higher than the other resins. This may be attributed to the higher molecular weight of the neat resin of improved grade (Table - 15). There is practically no change in the tensile strength of the three grades based on glycolysed PET waste.

The impact strength is found to be considerably sensitive to the change in the chemical composition. The impact strengths of the PET waste based resins are comparable to the ordinary grade. However, these are lower than that of the improved grade. Among the PET waste based systems, the impact strength increases with an increasing amount of the aliphatic moieties in the backbone of polymer (Table - 7).

The flexural strengths of the PET waste based polyesters are comparable to that of the ordinary GP grade of polyester. The value of flexural strength is found to be dependent on the molecular weight of the neat resins (Table-15), lower molecular weight polyester giving a more brittle product.

The hardness of all the polyester resins is in the range of 80 shore 'D'.

As expected the HDT of the PET based resins is much higher than both the grades of the orthophthalic based GP resins. This may be attributed to the better packing of the polyester chains having terephthalic acid moiety in the backbone.

The mechanical testing shows that the properties of the PET waste based polyesters are comparable to those of the commercially available systems. The properties of these resins can be further improved by increasing the molecular weight and by optimizing the chemical consituents of the resins. The amount of styrene is known to affect the properties of the cured resins. thus the styrene amount is also needed to be optimized in order to get optimum mechanical performance.

4.5 DYNAMIC MECHANICAL BEHAVIOR OF THE UP RESINS

Polymeric materials are viscoelastic in nature and their mechanical properties exhibit a pronounced dependence on temperature and time. The viscoelastic response to thermomechanical excitement can give valuable information regarding molecular motions and even polymer structure.

Under service conditions, most of the materials may be subjected to dynamic loading and not static stress conditions,as in simple tensile, compressive or flexural mode. Therefore, it is important to study the dynamic mechanical behavior of the material.

The viscoelastic response can be studied either by holding the time factor (frequency) constant and sweeping a temperature range or by keeping the temperature factor constant and scanning a frequency range. In usual practice the time factor is held constant and the viscoelastic response is studied for the desired temperature range. The frequency is then changed and the experiment is repeated.

The dynamic mechanical testing may be performed by many methods. The common ones are torsion pendulum, resonant rod, ultrasonic techniques and forced oscillation procedure. The method used in this work is a forced oscillation type. The sample is held rigidly by clamps at two ends one of which is connected to a stress guage and the other to strain guage. A sinusoidal strain is then applied to the polymer sample and the stress is recorded continuously(108).

The relation between strain 'ϵ' and frequency at any time 't' is given by

$$\epsilon = \epsilon_0 e^{i\omega t} \qquad (17)$$

where ϵ_0 is the strain amplitude and 'ω' is frequency.

The stress σ varies sinusoidally with the same frequency. However due to the viscous molecular processes, there exists a phase difference between the stress and strain. If the phase angle is represented by δ , the expression for stress is given as

$$\sigma = \sigma_0^{i(\omega t + \delta)} \tag{18}$$

where σ_0 is the stress amplitude.

The ratio of stress and strain gives the complex shear modulus

$$G^{*} = \frac{\sigma}{\epsilon} \tag{19}$$

Substituting the values of σ and ϵ the complex modulus can be represented as

$$G^{*} = G' + iG'' \tag{20}$$

where G' and G'' are termed as storage or real modulus and loss or imaginary modulus respectively. G' is related to the potential energy stored by the material under deformed condition, whereas G'', the loss modulus is associated with the dissipation of energy as heat, when material is deformed. The ratio of the two modulii can be represented as '$\tan \delta$'

$$\tan \delta = \frac{G''}{G'} \qquad (21)$$

The tangent, tan δ , is internal friction or damping and is referred as the loss factor.

All the three parameters defined above are related to the molecular motions and therefore yield useful information about the molecular structure as well as performance of the material. The viscoelastic response of the material at the frequency, corresponding to the end use, can provide a fairly good estimate of the material performance.

G' signifies the elastic modulus. Higher the value of G' more rigid is the material. The value of G' is dependent on the temperature. In a temperature sweep, beyond a particular temperature,the value of G' starts falling rapidly. Above this temperature the material acts as viscoelastic solid and is likely to undergo irreversible deformation leading to plastic flow. The temperature at which G' starts falling rapidly, corresponds to the maximum service temperature under the dynamic loading. Thus the variation of G' with temperature signifies the thermomechanical response.

G" signifies the viscous component of the material. The viscous segment of the polymer dissipates the energy by molecular motions, under deformation giving a peak in the value of G". The area under the peak, corresponds to the energy dissipated by molecular motions. Thus greater the area under the peak more would be the impact strength and crack resistance of the material.

The variation of tan δ with temperature, indicates the transitions in the material. The curve shows peak when the molecular motions are unlocked, due to thermal energy. Thus the transtions, due to mobility of pendent groups, amorphous segments, unlocking of Van der Waals forces and glass transition, can be observed in the tan δ curve. The tanδ curve also gives an idea about the damping characteristics of the material. Greater the value of tan δ and area under curve, more is the damping ability of the material.

Thus the viscoelastic data can be used as a tool to predict the behavior of the material under dynamic loading.

The measurements were done on a Rheometrics Dynamic Spectrometer, model RDS - 7700. The specimens were cast in a mould to form strips of dimensions - 60 mm x 12 mm x 2 mm. The casting was done as described in section - 4.4.

The dynamic mechanical behavior of PET waste based resins are compared with those of improved grade and the ordinary grade of GP resins.

The samples were subjected to a frequency sweep between 0.1 to 1000 rad/sec. at room temperature (25°C). The dependance of G', G" and tan δ was found to be insignificant for all the five resins. Therefore, the samples were then subjected to temperature sweep between 30° to 150°C.

The temperature sweeps were compared for correlating the structures of the polyesters. Figure - 21 shows the effect of temperature on the storage modulus. It is seen from the plots that the storage modulii of PET waste based systems are marginally lower than those of GP resins upto 65°C. However a rapid drop in the value of G' is observed in the case of conventional GP resins beyond 100°C. It is interesting to note that the temperature dependence of the G' is less in case of the PET waste based resins. Table -16, represents the temperatures at which the deviation in the value of G' starts appearing. The temperatures at which the value of G' drops to 8 x 10^9, 5 x 10^9 and 2 x 10^9 dynes / cm^2 are also represented in the same table. It may be noted from Figure-21 and Table - 16 that even though the initial value of G' is higher for GP resin it falls rapidly at higher temperatures. In case of improved grade GP resin the value of G' drops at 2 x 10^9 dynes / cm^2 at 133°C whereas in case of UVMW-58 and 59 the value does not drop down to that extent even at 150°C. The higher value of the storage modulus at high temperatures may be attributed to the higher extent of crosslinking$^{(109)}$. The chemical composition of UVMW-57 is comparable to that of GP resins. Thus, because of higher extent of linear structure and crosslinking PET based systems show lesser dependance on temperature of the storage modulus.

Figure - 22 shows the variation of G" with temperature at 100 rad / sec. The energy dissipation displays a maximum when the frequency of operation corresponds to the relaxation times of the molecular motions at that temperature. The value of G" goes through a maximum for GP resins. The value of G" at the maximum decreases for UVMW-57 and -58. This peak almost disappears in case of UVMW-59 and the value of G" is practically unchanged over the temperature range. As indicated earlier the area under G" curve signifies the impact strength. It is observed that the PET based systems have lower impact strength than the GP resins. UVMW-59 practically does not show any dissipation, thus would be most brittle in nature. These observations are consistent with the static mechanical properties discussed in section 4.4. Table - 17 indicates the peak value of G". The value of peak G", for improved grade GP resin is the highest. The peak value gradually decreases and the peak shifts to lower temperatures for UVMW-57 and -58. The peak almost disappears in case of UVMW-59. The drop in the value of G" at peak and the shift of the peak to lower temperatures for PET based resins may be attributed to the overall rigidity and brittleness.

Figure - 23 shows the variation in the dissipation factor, tan δ , with temperature, at 100 rad/sec. Again, only a marginal change is observed in case of UVMW-59. The behavior of UVMW-58 was intermediate to that of UVMW-59 and 57. Table - 18 gives the values of tan δ at 35°C, 65°C and 100°C. The relative insensitivity of UVMW-59 to temperature under dynamic testing is observed in this table too.

Thus the dynamic mechanical testing of the resins show that even though the PET based resins have better thermal stability, they exhibit poor impact resistance. The performance of the PET based resins can be improved by increasing the molecular weight and optimizing the amount of styrene. The effect of amount of styrene on the dynamic mechanical properties was studied. The improved grade of GP resin with varying amount of styrene was investigated. It is seen from Figure-24 that the dynamic mechanical properties are affected by the amount of styrene. The material becomes more brittle with increased styrene content. The data supports our view on need for optimization of styrene contents.

In many applications, the performance of the polymeric material is improved by incorporation of fillers. Besides improvement in performance, the fillers also reduce the cost of the material. The effect of fillers on properties of composites is dependent on the amount, chemical nature and physical state of the filler.

In the present work, talc, calcium carbonate and wollastonite were used as fillers. The three filers were chosen for their different particle shapes. The details regarding the fillers are summarized in Table-19(110).

Since the specific gravities of the three fillers were comparable, they were used on weight percent basis. 20 % fillers were incorporated in the resins for investigations. The samples were cast as described earlier. The samples were subjected to frequency sweep between 0.1 to 1000 rad / sec. at 25°C. The properties of filled samples did not show much variation from that of unfilled sample. The samples were then subjected to a temperature scan between 30° to 150°C at 100 rad/sec. The behavior of the materials was found to be dependent on the fillers. Figures-25 to 27 show the variation in values of G', G" and tan δ of UVMW-57 in unfilled and filled form. It is seen that the filled samples exhibit better thermochemical, and impact properties than the unfilled resins. The type of filler is also found to be affecting the properties of the polyester within a narrow range. Similar results were observed with improved grade and ordinary grade of GP resin.

Thus, it may be concluded from the above study, that the PET waste can be converted into value added unsaturated polyesters without any processing difficulty. The polyesterification of glycolysed PET with maleic anhydride, in the a absence of catalyst, follow third order kinetics. The rate of reaction is much higher for PET waste based resins than for GP resin. The reaction of PET based resins with styrene is faster than the reaction of corresponding orthophthalic based GP resin. The PET waste based resins exhibit slightly inferior mechanical properties than GP resin, which can be improved by optimizing molecular weight and styrene content. The PET based resins exhibit much better thermomechanical properties than the GP resins.

TABLE - 6

Characterization of the Unsaturated Polyester Resins

Sr. No.	Polyester code	Glycolysed product used	Analysis of resins without styrene			
			Carboxyl value mg KOH/g	Hydroxyl value mg KOH/g	$\overline{Mn}$ (end group)	$\overline{Mn}$ (VPO)
1.	UVMW - 57	UVWP - 1	32	74	1058	1045
2.	UVMW - 58	UVWP - 2	31	67	1145	1325
3.	UVMW - 59	UVWP - 3	32	57	1260	1269
4.	GP resin (control)	-	37	62	1333	1300

TABLE - 7

Composition of Unsaturated Polyester Resins

Sr. No.	Polyester	Weight % of different moieties before styrene addition				
		Terephthalic acid	Phthalic acid	Maleic acid	Ethylene glycol	Propylene glycol
1.	UVMW - 57	32	-	26	14	28
2.	UVMW - 58	23	-	32	11	34
3.	UVMW - 59	16	-	39	7	38
4.	GP resin	-	34	22	-	44

TABLE - 8

Gelation Behavior of UVMW-57 with 36 % Styrene

Sr. No.	MEKP %, w/w	Cobalt Naphthanate %, w/w	Gel time minutes	Peak exotherm °C
1.	1.5	0.2	52	120
2.	1.5	0.3	29	125
3.	1.5	0.4	20	130
4.	1.5	0.5	11	152
5.	1.25	0.5	26	120
6.	1.0	0.5	45	110
7.	0.75	0.5	80	105
8.	1.0	0.2	105	90

TABLE - 9

Kinetic Data of UVMW-57

Sr.No.	Time min	Acid value mg KOH/g	[COOH] eq./kg	p	DP	$1/(1-p)^2$
At 180°C						
1.	0	139.9	2.49	0.5596	2.141	5.156
2.	30	103.7	1.85	0.6735	2.789	9.381
3.	60	89.1	1.59	0.7195	3.177	12.710
4.	90	76.8	1.37	0.7583	3.599	17.118
5.	120	74.6	1.33	0.7652	3.687	18.137
6.	150	64.0	1.14	0.7985	4.175	24.629
7.	180	58.9	1.05	0.8146	4.460	29.092
At 200°C						
8.	0	55.0	0.98	0.8269	4.706	33.374
9.	120	47.0	0.84	0.8521	5.306	45.715
10.	180	38.0	0.68	0.8804	6.191	69.910
11.	210	36.4	0.65	0.8854	6.379	76.143
12.	240	35.8	0.64	0.8873	6.453	78.732
13.	270	32.0	0.57	0.8992	6.963	98.419

TABLE - 10

Kinetic Data of UVMW-58

Sr.No.	Time min	Acid value mg KOH/g	[COOH] eq./kg	p	DP	$1/(1-p)^2$
At 180°C						
1.	0	173.9	3.10	0.5806	2.237	5.685
2.	30	129.8	2.31	0.6875	2.896	10.240
3.	60	102.8	1.83	0.7525	3.529	16.325
4.	90	83.7	1.49	0.7985	4.175	24.629
5.	150	73.5	1.31	0.8231	4.627	31.955
6.	180	-	-	-	-	-
At 200°C						
7.	0	56.4	1.03	0.8642	5.651	54.225
8.	60	44.8	0.80	0.8921	6.650	85.893
9.	90	42.3	0.75	0.8982	6.917	96.495
10.	120	40.4	0.72	0.9027	7.128	105.627
11.	180	36.4	0.65	0.9124	7.631	130.314
12.	210	32.0	0.57	0.9229	8.261	168.225

TABLE - 11

Kinetic Data of UVMW-59

Sr.No.	Time min	Acid value mg KOH/g	[COOH] eq./kg	p	DP	$1/(1-p)^2$
At 180°C						
1.	0	194.6	3.47	0.6006	2.336	6.269
2.	30	150.0	2.67	0.6922	2.935	10.555
3.	60	127.6	2.27	0.7381	3.366	14.579
4.	120	103.9	1.85	0.7868	3.389	22.000
5.	180	83.6	1.49	0.8284	4.738	33.960
At 200°C						
6.	0	69.0	1.23	0.8584	5.480	49.874
7.	30	59.7	1.06	0.8775	6.087	65.762
8.	90	45.5	0.81	0.9066	7.322	114.632
9.	150	40.1	0.71	0.9177	7.936	147.639
10.	210	38.0	0.68	0.9220	8.203	164.365
11.	270	32.0	0.57	0.9343	9.075	231.670

TABLE - 12

Kinetic Data of GP resin

Sr.No.	Time min	Acid value mg KOH/g	[COOH] eq./kg	p	DP	$1/(1-p)^2$
At 180°C						
1.	0	233.8	4.17	0.5688	2.182	5.378
2.	30	209.1	3.73	0.6144	2.410	6.725
3.	60	198.3	3.53	0.6343	2.526	7.477
4.	120	175.1	3.12	0.6771	2.816	9.591
5.	180	161.1	2.87	0.7029	3.025	11.329
At 200°C						
6.	0	150.1	2.67	0.7232	3.212	13.052
7.	60	123.8	2.21	0.7717	3.773	19.186
8.	150	100.5	1.79	0.8146	4.460	29.092
9.	240	96.0	1.71	0.8229	4.623	31.883
10.	300	82.5	1.47	0.8473	5.180	42.877
11.	330	81.9	1.46	0.8489	5.221	43.800
12.	420	78.6	1.40	0.8550	5.385	47.562
13.	540	65.0	1.16	0.8801	6.180	69.568
14.	660	51.0	0.91	0.9059	7.287	112.933
15.	870	48.0	0.85	0.9115	7.581	127.677
16.	1110	46.0	0.82	0.9152	7.789	139.062
17.	1305	36.7	0.64	0.9341	9.051	230.266

TABLE - 13

Polyesterification Rate Constants at 180°C and 200°C

Sr.No.	Polyester Code	180°C			200°C		
		[COOH]* eq.mol/kg	Slope	Rate constant k, kg^2 $eq.mol^{-2}$ min^{-1}	[COOH]** eq.mol/kg	Slope	Rate constant k, kg^2 $eq.mol^{-2}$ min^{-1}
1.	UVMW-57	2.49	0.1133	9.14×10^{-3}	0.98	0.3513	18.28×10^{-2}
2.	UVMW-58	3.10	0.1788	9.30×10^{-3}	1.03	0.4825	22.70×10^{-2}
3.	UVMW-59	3.47	0.1555	6.46×10^{-3}	1.23	0.6944	22.90×10^{-2}
4.	G.P. resin	4.17	0.0370	1.06×10^{-3}	2.67	0.0926	0.65×10^{-2}

* = Concentration of carboxyl groups when temperature reached 180°C

** = Concentration of carboxyl groups when temperature reached 200°C

TABLE - 14

Static Mechanical Properties of the Unsaturated Polyesters

Test	UVMW-57	UVMW-58	UVMW-59	GP Improved	GP Ordinary
Tensile strenght, N/mm^2	23.3	23.3	23.9	51	19.6
Impact strength, kJ/m^2	1.7	2.1	2.5	4	2.2
Flexural strenght, N/mm^2	24.2	38.4	27.2	83	40.1
Hardness, Shore D	80	80	80	83	78
Heat distortion Temperature ^{o}C	85	82	81	65	55

TABLE - 15

Molecular Weight Data on Polyesters

Sr. No.	Polyester code	Styrene % , w/w	Molecular weight (VPO) $\overline{Mn}$
1.	UVMW-57	36	1045
2.	UVMW-58	36	1325
3.	UVMW-59	36	1269
4.	GP Ordinary	32	1300
5.	GP Improved	30	1977

TABLE - 16

Viscoelastic Behavior of Polyesters - Elastic Component

Sr. No.	Polyester code	Temperature when deviation in G′ starts, °C	Temperatures at different values of G′, °C		
			G′ = 8 x 10^9 dynes / cm^2	G = 5 x 10^9 dynes / cm^2	G′= 2 x 10^9 dynes / cm^2
1.	UVMW-57	57	77	90	112
2.	UVMW-58	57	77	96	> 150
3.	UVMW-59	62	87	126	> 150
4.	GP Improved	62	91	115	133
5.	GP Ordinary	57	90	103	118

TABLE - 17

Viscoelastic Behavior of Polyesters - Viscous Component

Sr. No.	Polyester code	Value of peak G" dyne / cm^2	Temperature range for peak G", ^{o}C
1.	UVMW-57	9.0×10^{8}	80-97
2.	UVMW-58	7.5×10^{8} (small hump)	80-88
3.	UVMW-59	6.0×10^{8} (no peak)	-
4.	GP Improved	12×10^{8}	97-109
5.	GP Ordinary	1.1×10^{9}	90-101

TABLE - 18

Viscoelastic Behavior of Polyesters - Loss Factor

Sr. No.	Polyester code	Values of tan δ at different temperatures, dynes/cm^2		
		35°C	65°C	100°C
1.	UVMW-57	3.4×10^{-2}	5.2×10^{-2}	2.6×10^{-1}
2.	UVMW-58	3.7×10^{-2}	5.2×10^{-2}	1.6×10^{-1}
3.	UVMW-59	4.3×10^{-2}	5.1×10^{-2}	7.7×10^{-2}
4.	GP Improved	1.9×10^{-2}	3.5×10^{-2}	1.4×10^{-1}
5.	GP Ordinary	2.5×10^{-2}	3.9×10^{-2}	2.0×10^{-1}

TABLE - 19

Properties of the Fillers

Sr.No.	Filler	Specific gravity	Shape of particles	Particle size
1.	Talc	1.49	Platelike	150-300 mesh
2.	Calcium-Carbonate	1.48	Prismatic	150-300 mesh
3.	Wollastonite	1.51	Fibrous	150-300 mesh

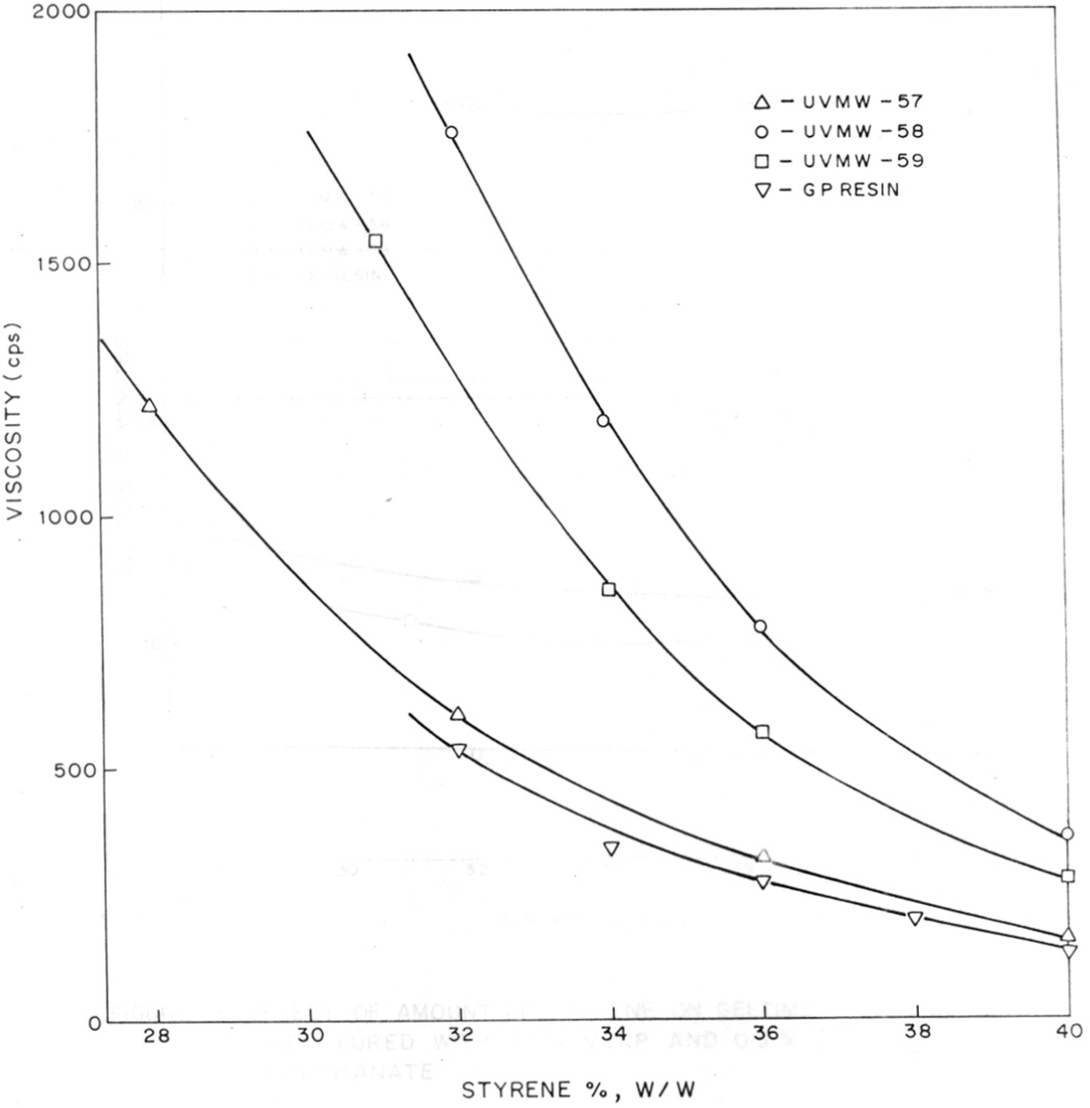


FIGURE 12 : EFFECT OF AMOUNT OF STYRENE ON VISCOSITY OF UP RESINS

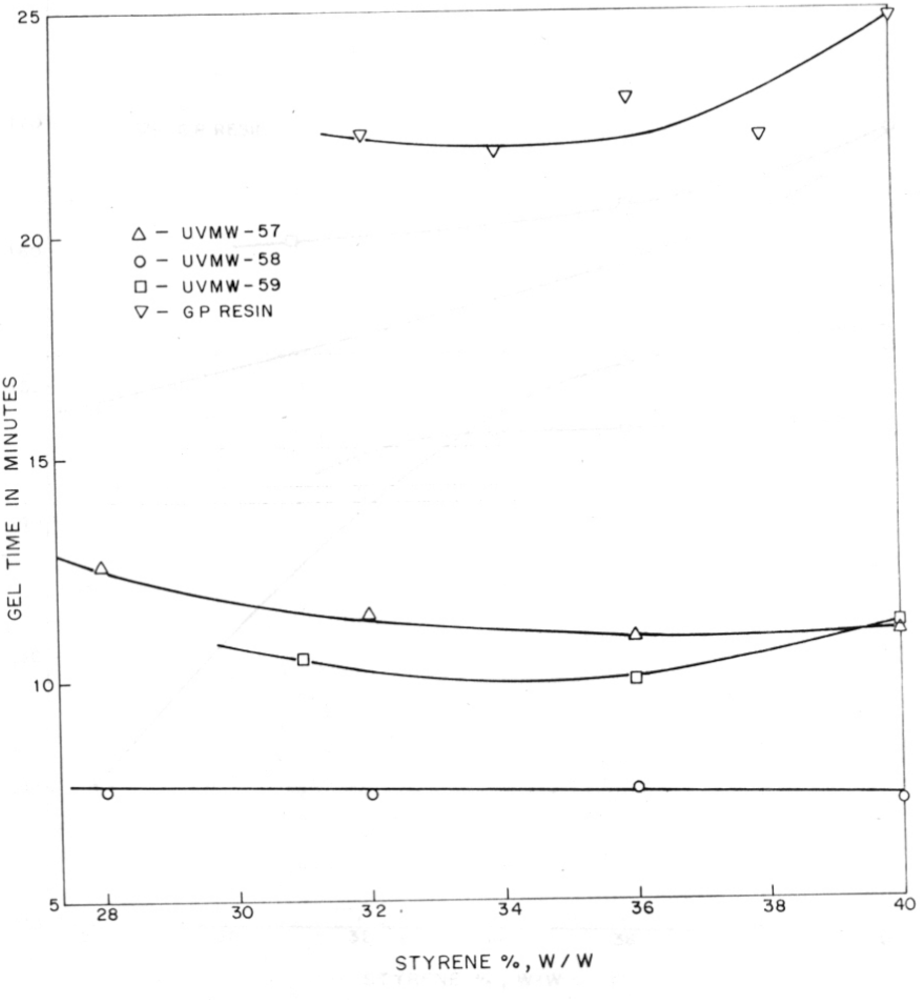


FIGURE 13: EFFECT OF AMOUNT OF STYRENE ON GELTIME OF UP RESINS WHEN CURED WITH 1·5% MEKP AND 0·5 % COBALT NAPHTHANATE

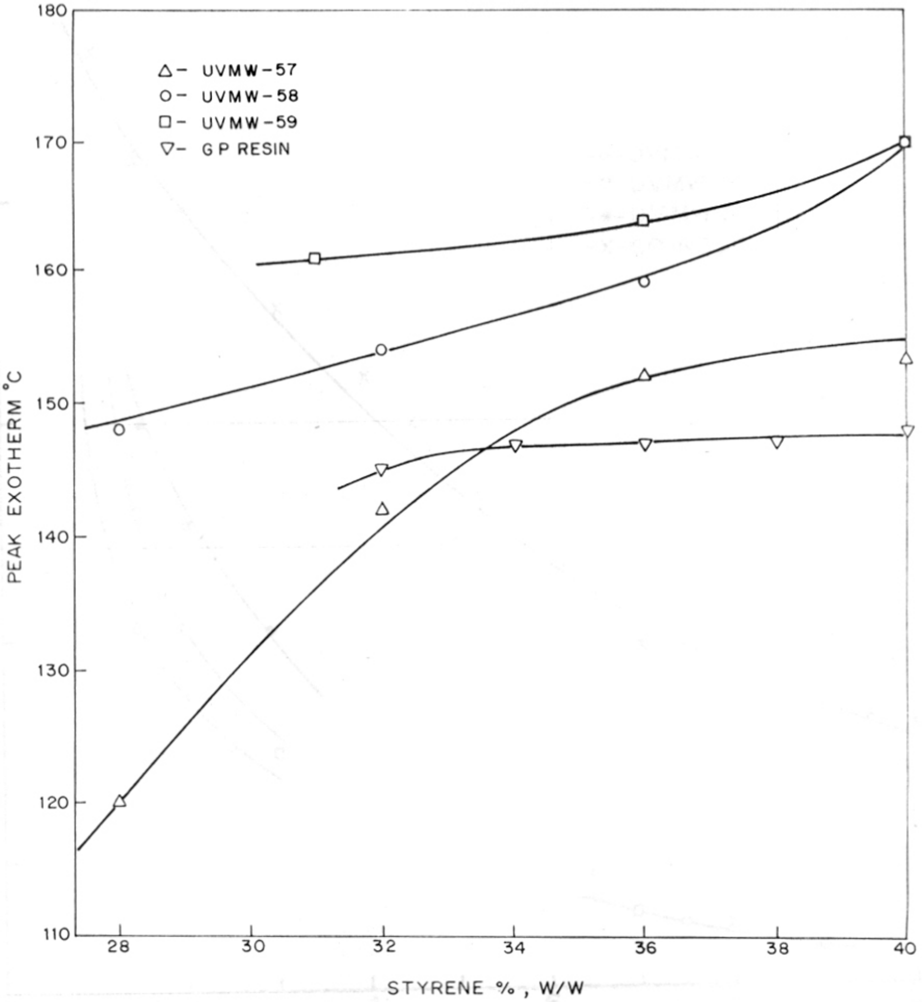


FIGURE 14: EFFECT OF AMOUNT OF STYRENE ON PEAK EXOTHERM TEMPERATURE OF UP RESINS, WHEN CURED WITH 1·5% MEKP AND 0·5% COBALT NAPHTHANATE

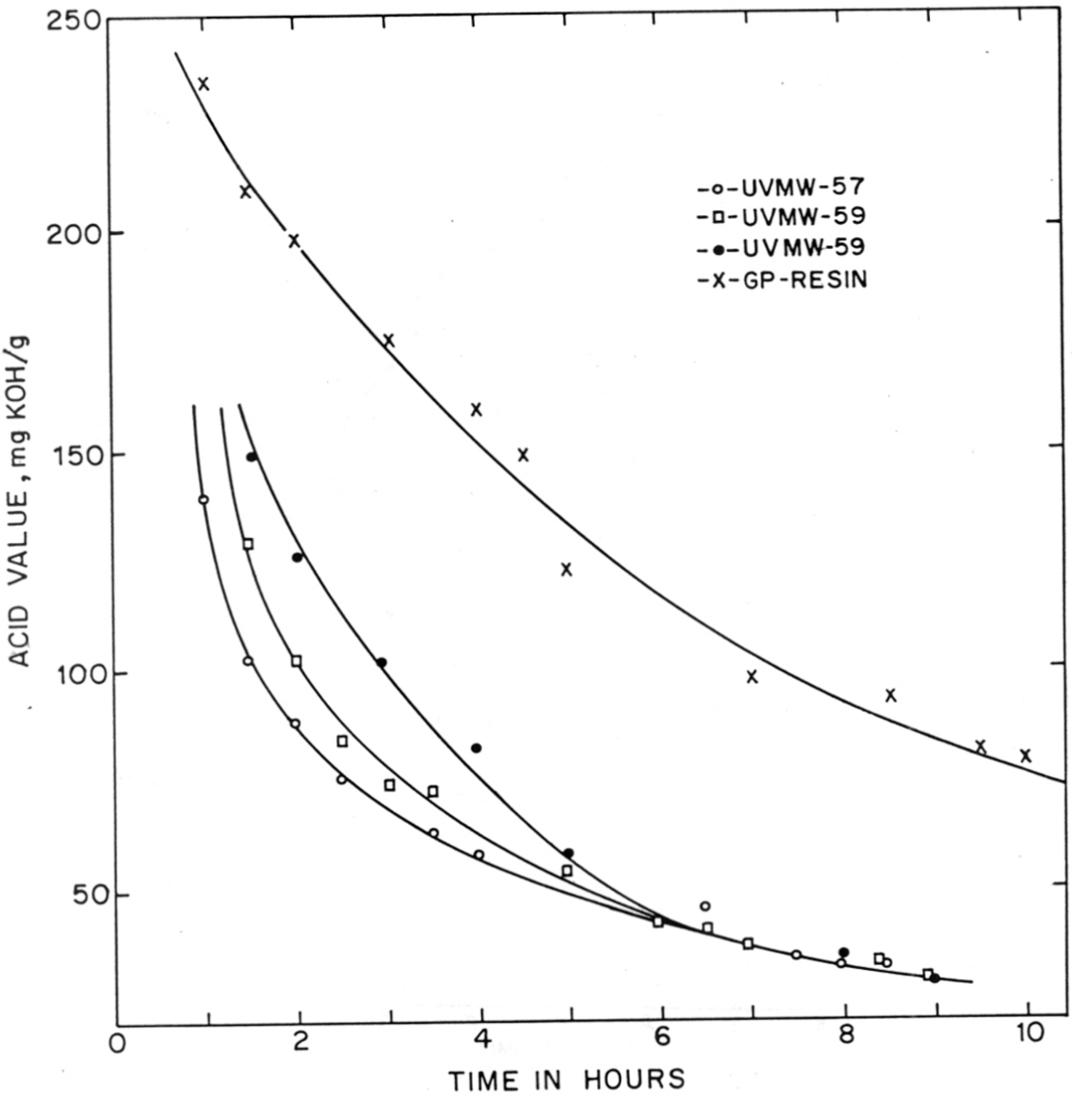


FIGURE 15: CHANGE IN ACID VALUE WITH REACTION TIME

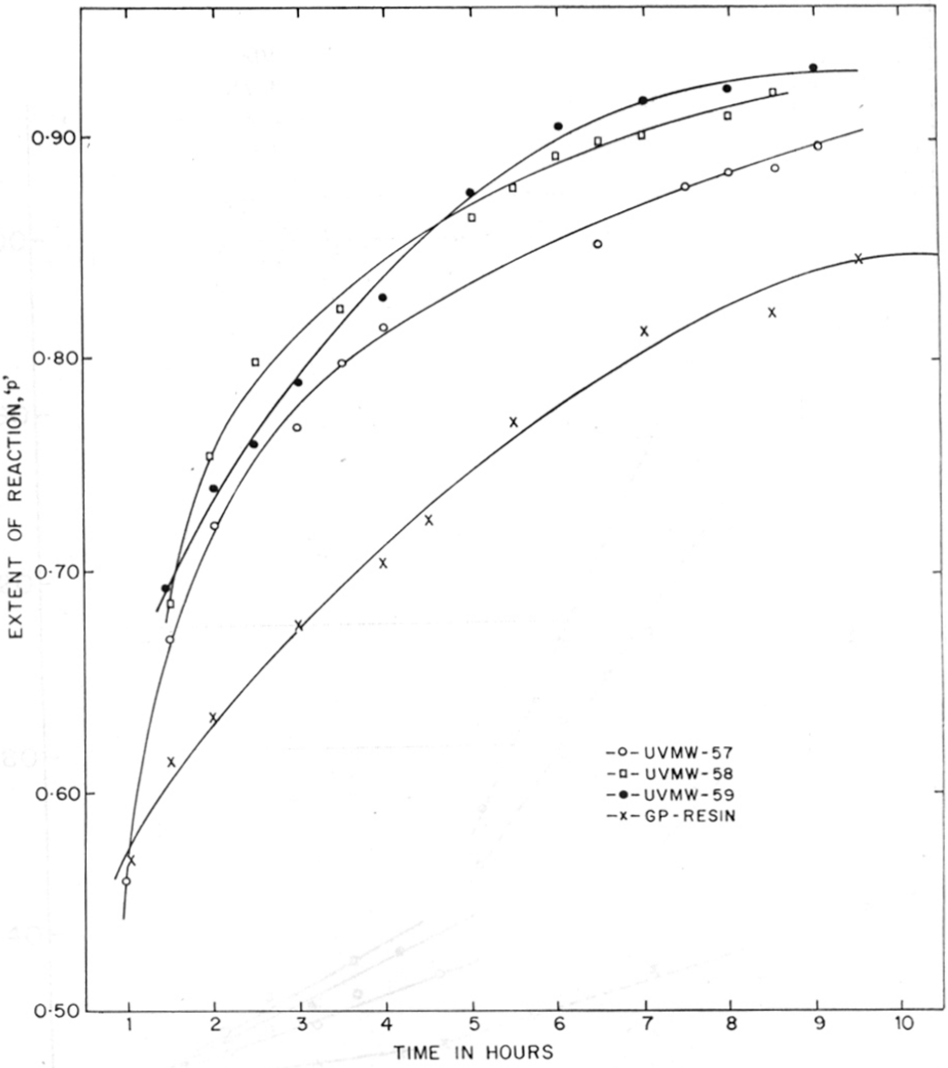


FIGURE 16 : INCREASE IN THE EXTENT OF REACTION WITH REACTION TIME

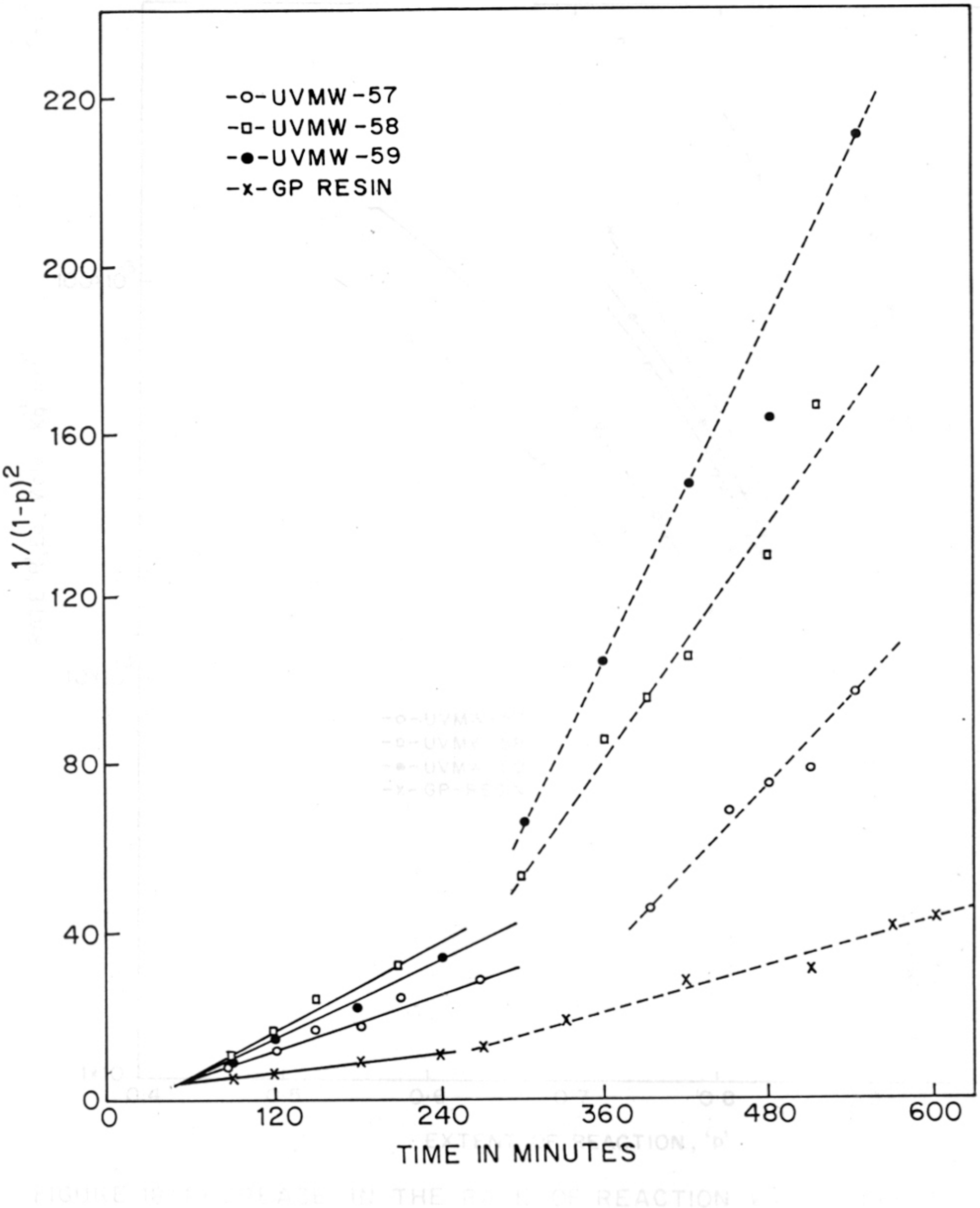


FIGURE 17: PLOT OF $1/(1-p)^2$ VERSUS TIME AT 180°C (—) AND AT 200°C (----)

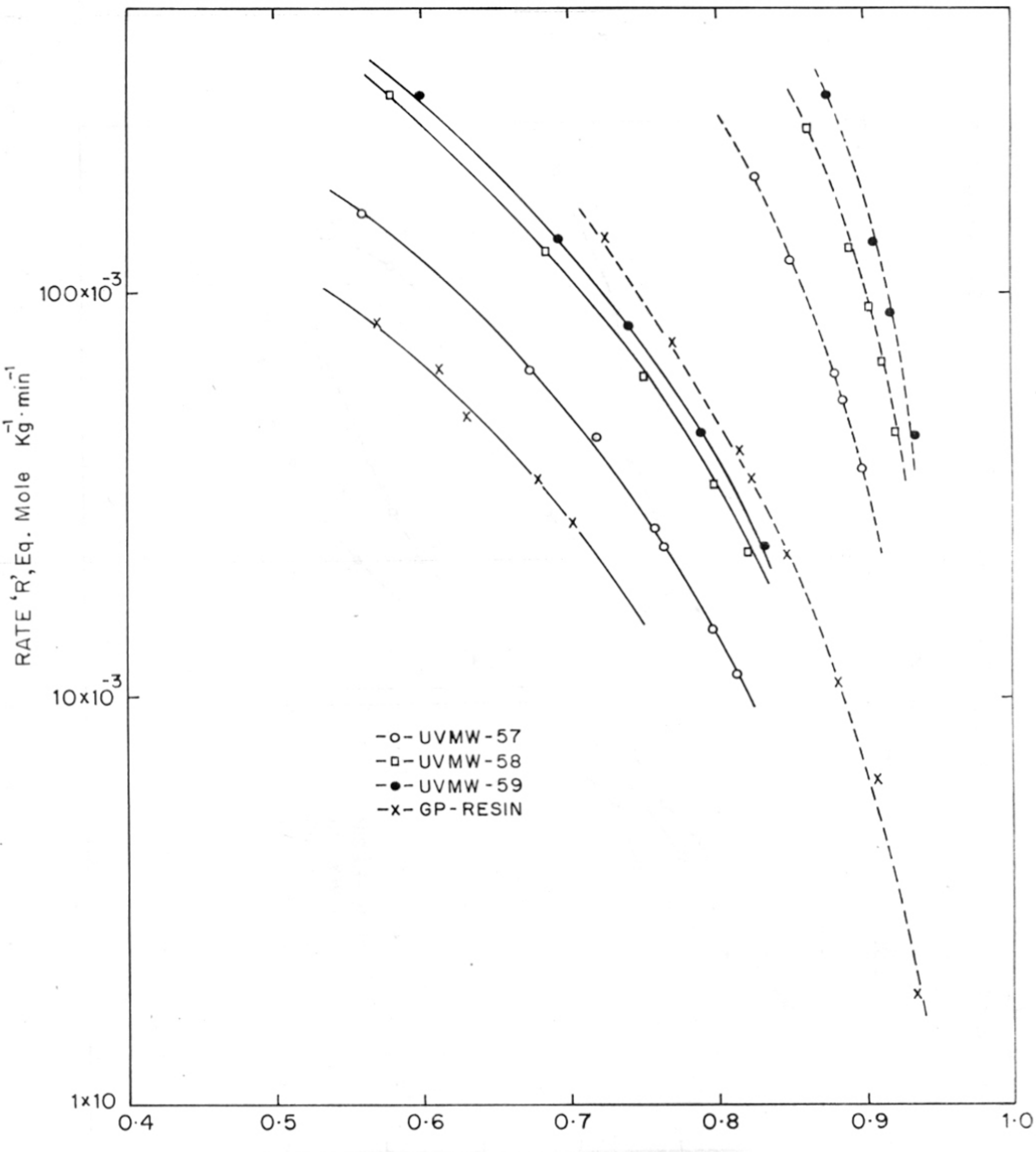


FIGURE 18: DECREASE IN THE RATE OF REACTION WITH EXTENT OF REACTION AT 180°C (—) AND AT 200°C (----)

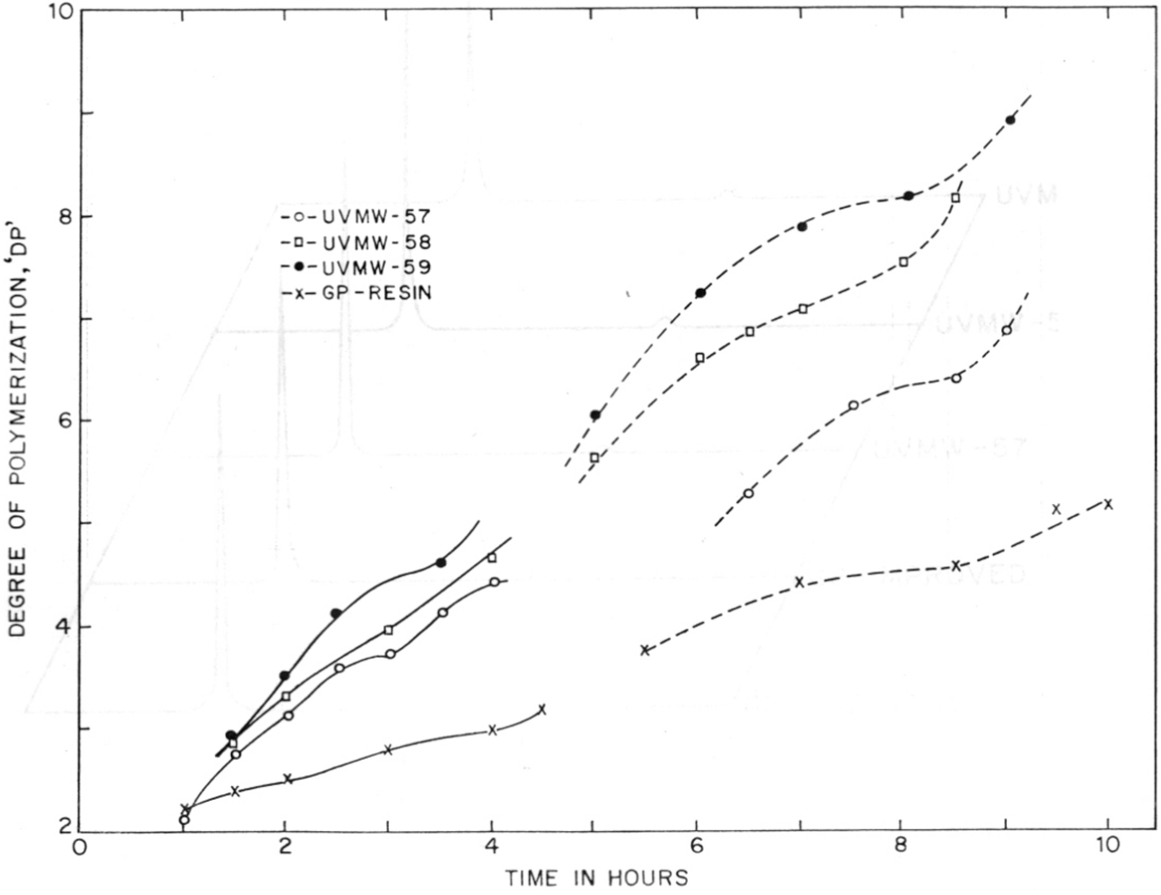


FIGURE 19: INCREASE IN DEGREE OF POLYMERIZATION WITH TIME AT 180°C (——) AND AT 200°C (- - - -)

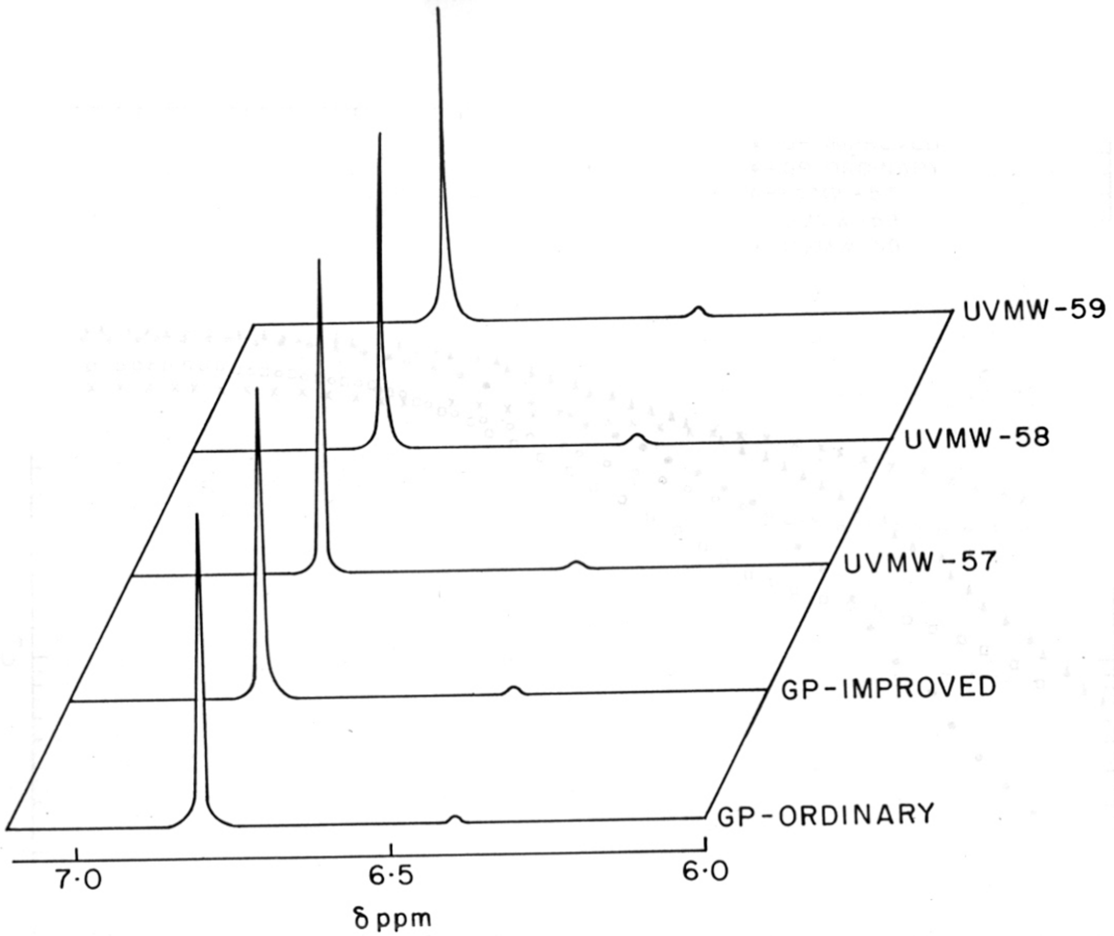


FIGURE 20: NMR SPECTRUM OF UP RESINS INDICATING FUMARATE-MALEATE ISOMERIZATION

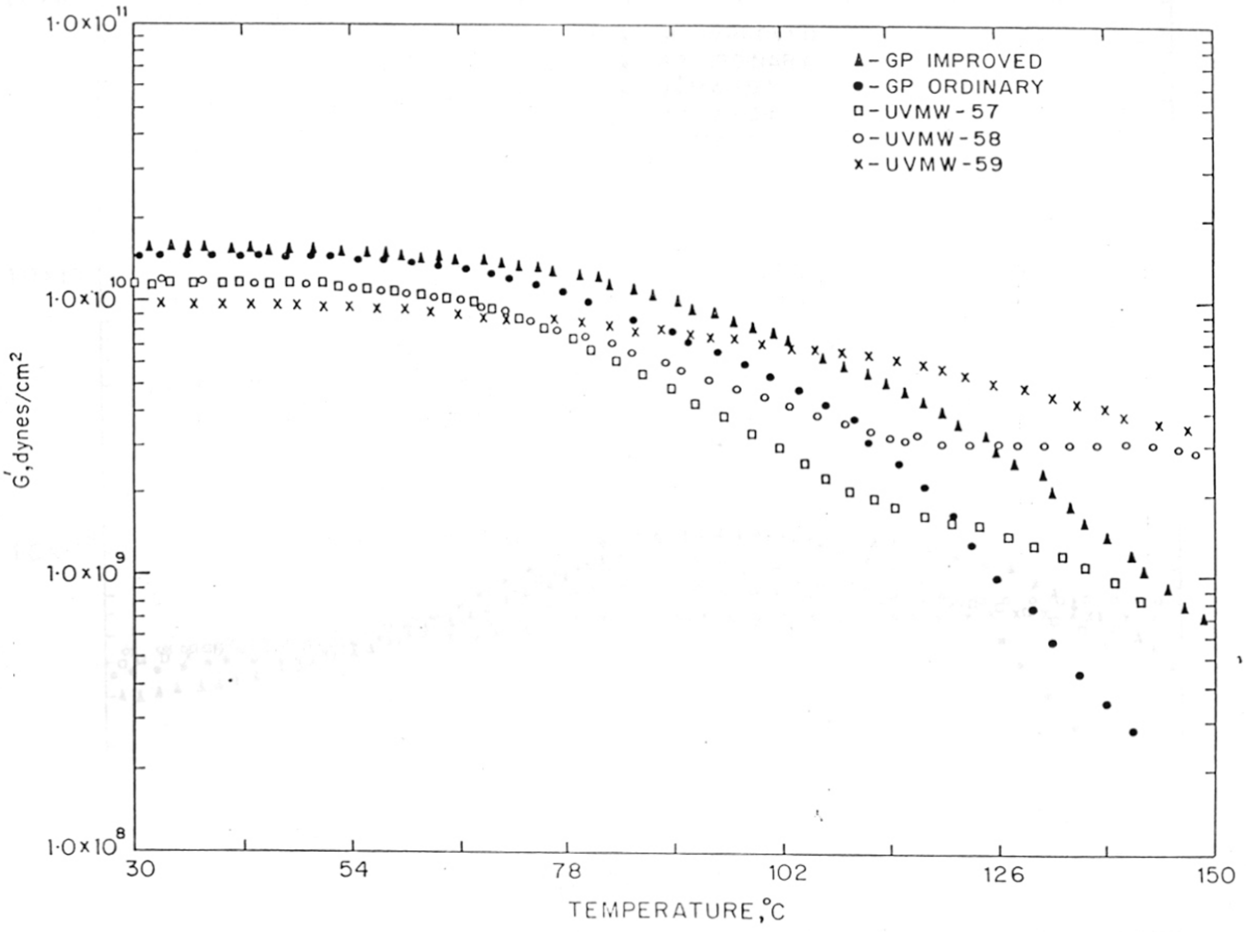


FIGURE 21: EFFECT OF TEMPERATURE ON STORAGE MODULUS OF UNSATURATED POLYESTERS

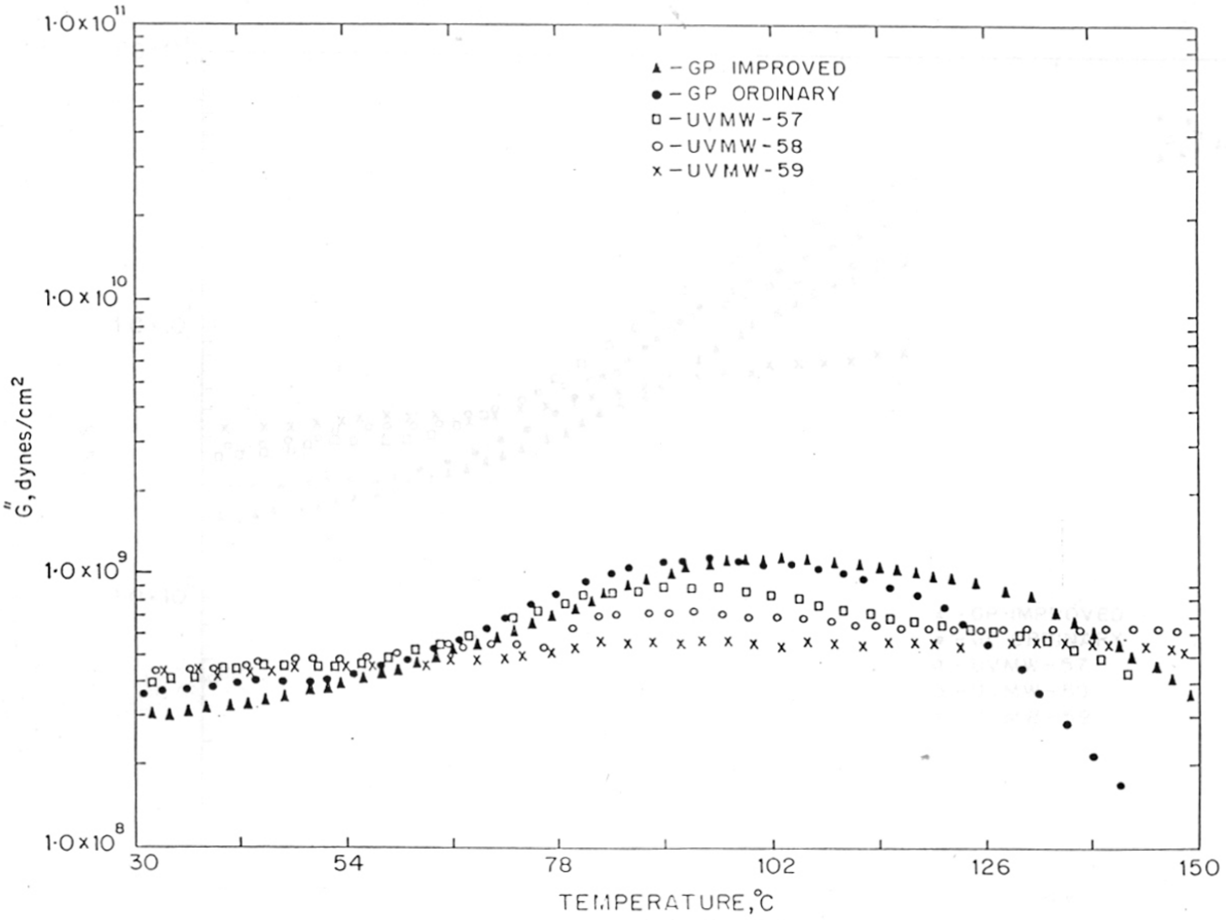


FIGURE 22: EFFECT OF TEMPERATURE ON LOSS MODULUS OF UNSATURATED POLYESTERS

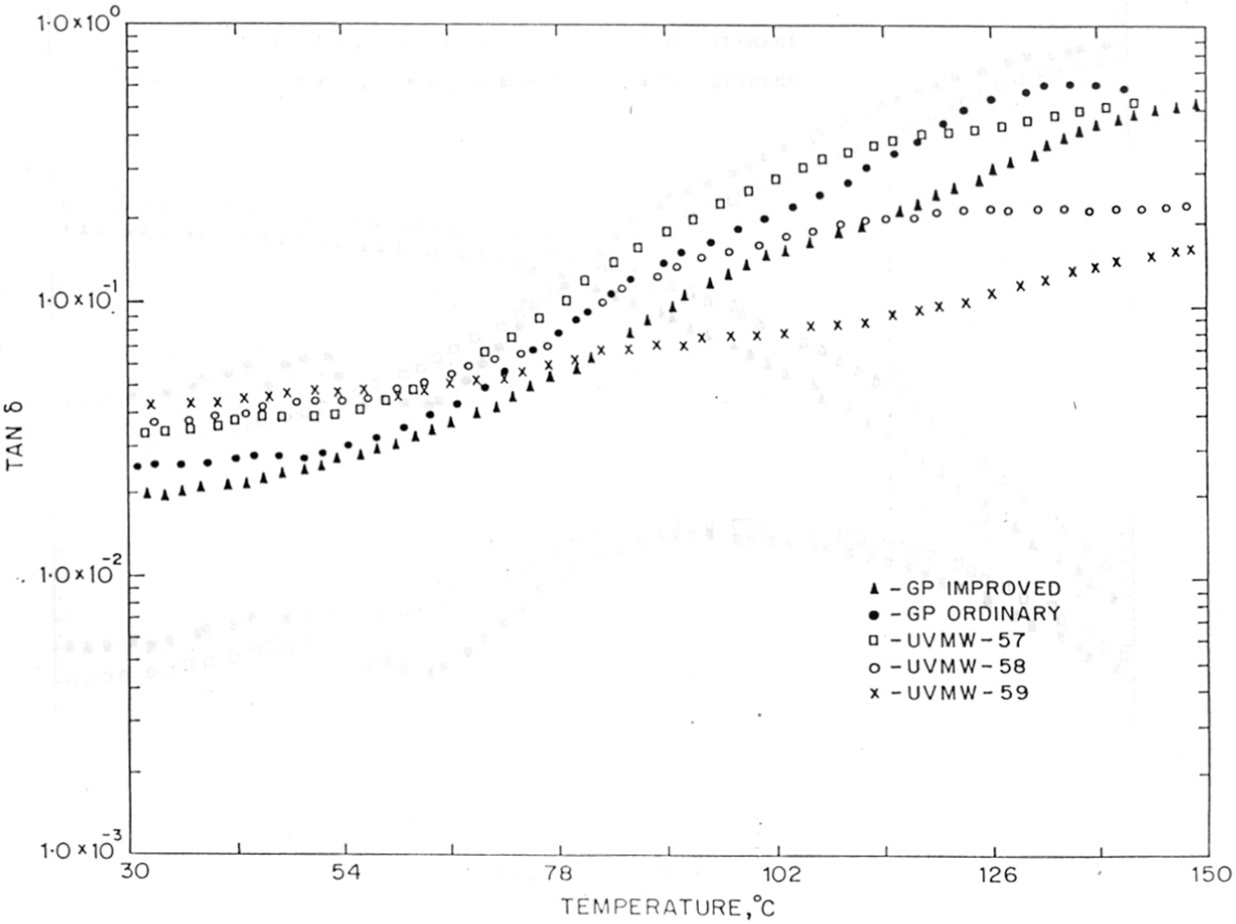


FIGURE.23: EFFECT OF TEMPERATURE ON LOSS FACTOR OF UNSATURATED POLYESTERS

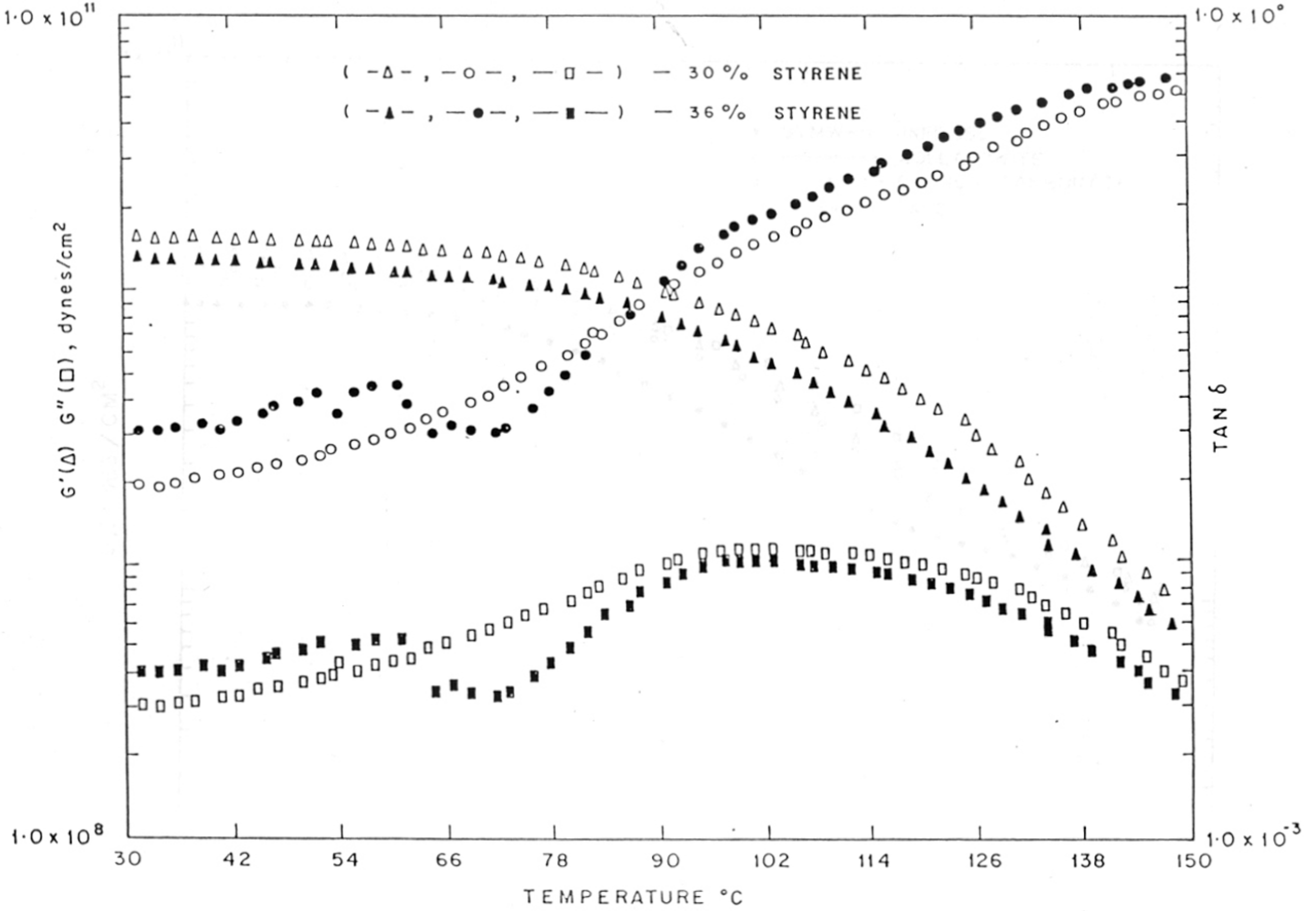


FIGURE 24: EFFECT OF STYRENE CONTENT ON VISCOELASTIC BEHAVIOR OF UNSATURATED POLYESTER

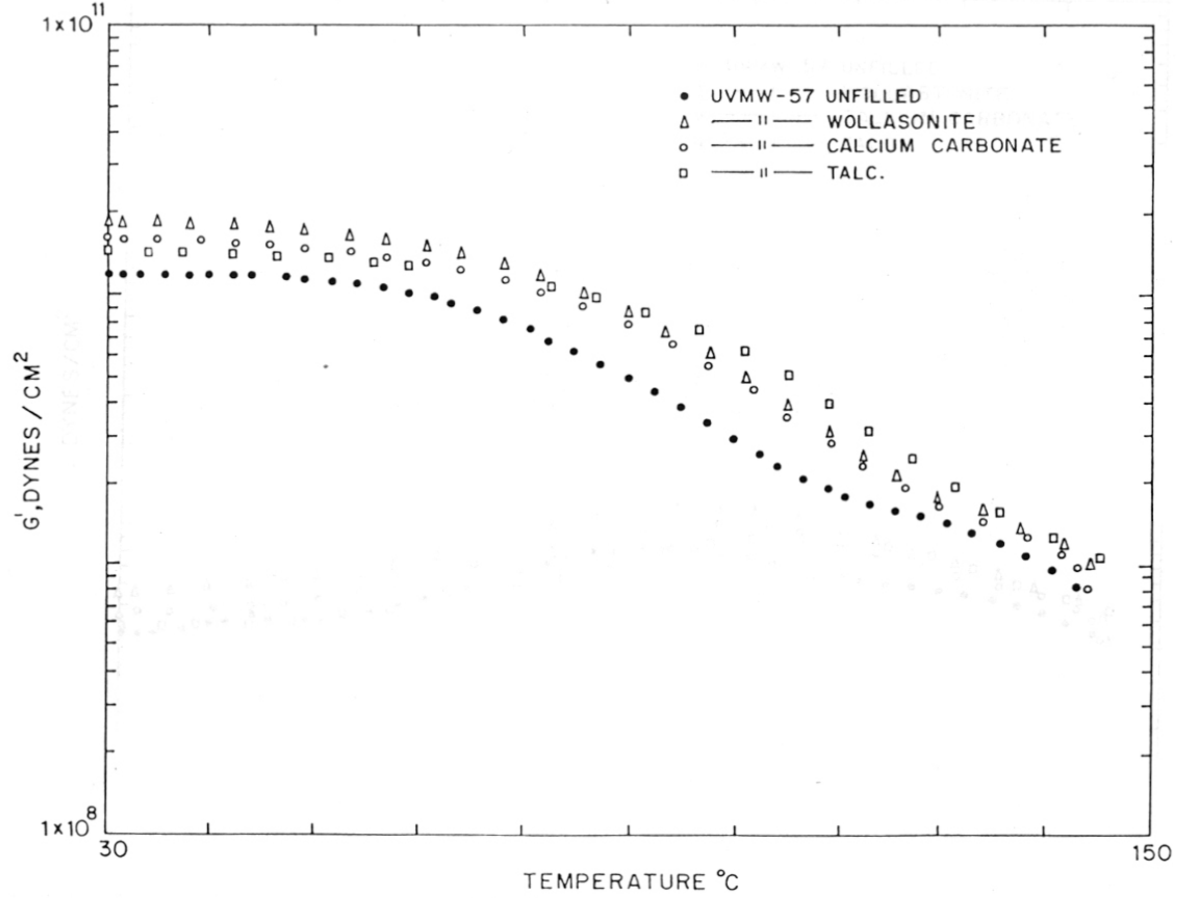


FIGURE 25: EFFECT OF FILLERS ON THE STORAGE MODULUS OF PET WASTE BASED UNSATURATED POLYESTER

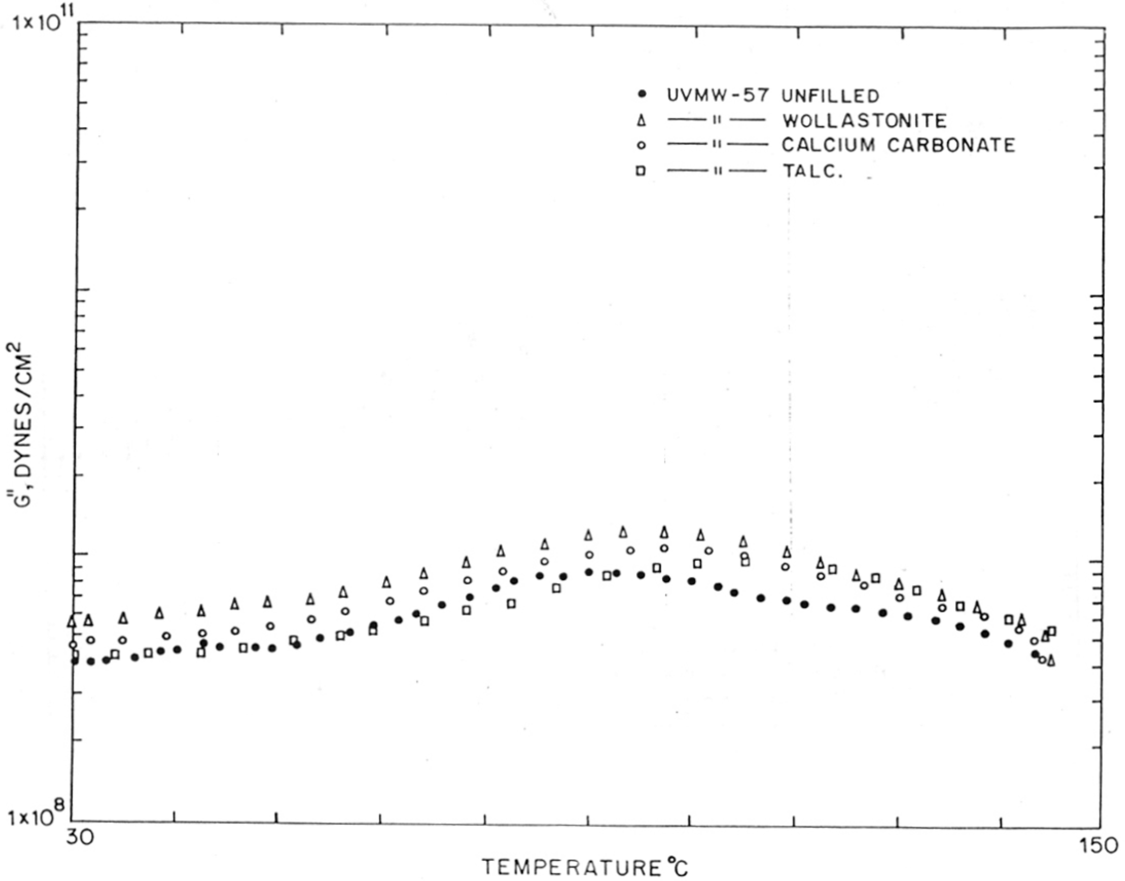


FIGURE 26: EFFECT OF FILLERS ON THE LOSS MODULUS OF PET WASTE BASED UNSATURATED POLYESTER

SUMMARY OF CONCLUSIONS AND RECOMMENDATION FOR FURTHER WORK

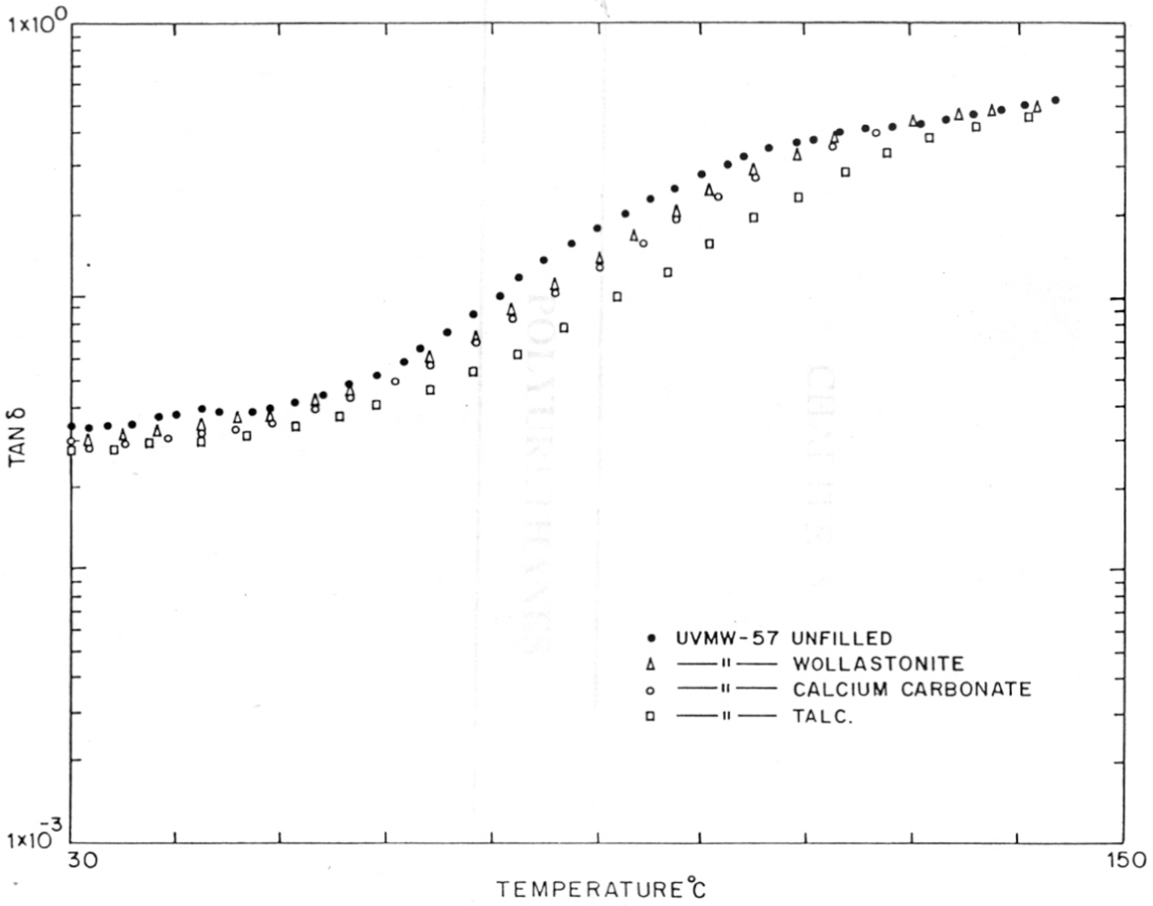


FIGURE 27: EFFECT OF FILLERS ON THE LOSS FACTOR OF PET WASTE BASED UNSATURATED POLYESTER

Polyurethanes are a versatile class of materials which can be tailor made to suit performance requirements by molecular engineering of the polyol backbone and proper choice of the polyisocyanate component.

The most commonly used polyols are polyether polyols which are used mostly in flexible foams and coatings. The other class of polyols termed polyester polyols are mainly used in elastomers, rigid foams and adhesives applications because of the wide range of properties that can be achieved by proper selection of monomers. The structure property relationships in polyurethane systems are discussed in section-2.3.

The use of aromatic diacid,as one of the comonomers, improves the thermomechanical properties of the resulting polyurethane material. Thus the incorporation of the terephtalic acid moiety would improve both thermal and mechanical performance in view of the linear structure. This can be achieved by using the glycolysed PET waste in the synthesis of polyester polyols. The low molecular weight terephthalate diols, obtained by the glycolysis of PET with different glycols, can react with any diacid to form the polyester polyol. In the present work, the terephthalate diols obtained by glycolysis of PET waste with EG, PG and DEG (described in Chapter -3) are reacted with adipic acid to form polyols of different molecular weights. These polyols, when reacted with PMDI, give elastomers and rigid foams. The details of the polyol synthesis, polyurethane formulations and properties of elastomers and rigid foams are discussed in this chapter.

5.1. PREPARATION OF POLYESTER POLYOLS

5.1.1. Materials : -

(i) The oligomeric diols used for polyol synthesis are tabulated below :

Code	Type of glycol in glycolysis	PET : Glycol	Hydroxyl value mg/KOH
UVWE - 1	EG	62.5 : 37.5	610
UVWE - 2	EG	50.0 : 50.0	870
UVWE - 3	EG	37.5 : 62.5	1070
UVWP - 3	PG	37.5 : 62.5	933
UVWD - 3	DEG	37.5 : 62.5	650

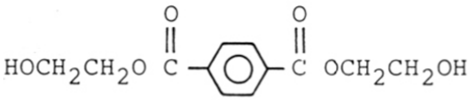
The details of the above mentioned diols are given in Chapter - 3. The free glycol present in these glycolysed PET waste products (oligomeric diols) was not removed, and the hydroxyl value is that of the total glycolysed product.

(ii) Adipic acid : -

Molecular formula	$HOOC(CH_2)_4COOH$
Molecular weight	146
Melting point	153°C

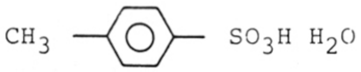
Adipic acid was obtained from M/s. High Purity Chemicals, Delhi.

(iii) Bis (2-hydroxy ethyl) terephthalate [BHET] : -

Molecular formula	
Molecular weight	254
Melting point	109°C

BHET was isolated from UVWE - 3 by extraction with hot water followed by recrystallization.

(iv) Para toluene sulfonic acid monohydrate (PTSA) : -

Molecular formula	
Molecular weight	190.22
Melting point	104°C

PTSA used as polyesterification catalyst was obtained from M/s Sisco Chemicals, Bombay.

5.1.2. Synthesis Details :-

The polyesterification reactions were conducted in a round bottom glass reactor having a thermowell, a gas bubbler, a distillation condenser and the stirring assembly. The heating was done using a heating mantle and temperature controller. The reaction mixture was heated from room temperature to 110°C in half an hour and then raised from 110°C to 170°C in one hour. It was then held at 170°C for three hours. Finally the temperature was raised to 200°C in half an hour and held till the end of the reaction. The water of reaction was removed continuously by distillation. Nitrogen was bubbled through the reaction mixture to prevent oxidative degradation. The flow of nitrogen gas also helped to remove the water of reaction thus promoting the reaction. The progress of the reaction was monitored by withdrawing samples periodically and analysing them for acid value.

Initially three polyesters were prepared from UVWE-1, UVWE-2 and UVWE-3 with adipic acid at a OH/COOH ratio of 1.8. The polyesters prepared from UVWE-1 and UVWE-2 formed polyols which were in the form of nonflowing, semisolid pastes whereas the one based on UVWE-3 was a free flowing liquid at room temperature. Since the polyesters based on UVWE-1 and UVWE-2 were not suitable for room temperature casting because of their high viscosities, only UVWE-3 was used for further investigations.

Thus three polyesters were prepared by reacting UVWE-3 with adipic acid as per the following quantity inputs :

Polyester code	weight of UVWE-3, g	weight of adipic acid, g	OH/COOH 'r'
UVAW-78	68.2	73.0	1.3
UVAW-79	78.7	73.0	1.5
UVAW-80	94.5	73.0	1.8

Since the diol used above is a mixed diol comprising mainly of ethylene glycol and BHET, the polyesters were also prepared by reacting these monomeric diols in pure form with adipic acid. Thus following two polyesters were prepared for interpretation of kinetic data.

Polyester code	type of diol	weight of diol g	weight of adipic acid g	OH/COOH 'r'
UVAE-77	EG	58.2	91.4	1.5
UVAB-74	BHET	108.8	41.7	1.5

In order to see the effect of the type of diol on the kinetics of polyesterification, two more polyesters were prepared by reacting PG based UVWP-3 and DEG based UVWD-3 with adipic acid, using the following reactant amounts :

Polyester code	type of diol	weight of diol g	weight of adipic acid g	OH/COOH 'r'
UVAW-81	UVWP-3	90.0	73.0	1.5
UVAW-82	UVWD-3	129.0	73.0	1.5

5.2. CHARACTERIZATION OF POLYESTER POLYOLS

5.2.1. Viscosity :-

The viscosity measurements were carried out at constant temperature (30°C) using a Brookfield viscometer. The data are given in Table-20.

5.2.2. Hydroxyl Value Determination :-

The hydroxyl value was determined using the rapid (perchloric acid catalysed) method which is already discussed in Chapter-3. The results are shown in Table-20.

5.2.3. Acid Value Determination :-

The acid value was determined by titrating the solution of a weighed quantity of the resin with standard alcoholic KOH. The results are given in Table-20.

5.2.4. Number Average Moleculer Weight (VPO) :-

$\bar{M}n$ was determined using a 'Knauer vapor pressure osmometer'. Ethyl acetate was used as solvent and benzil as standard. The chamber temperature was kept at 50°C. The other details are discussed in earlier chapter. The results of VPO analysis are given in Table-20.

It is seen from Table-20 that the viscosity and molecular weight of the polyester polyols based on EG glycolysed PET product decreases with increasing value of the OH/COOH ratio. When the ratio is fixed at 1.5 and the reaction is carried out using PG and DEG glycolysed PET (UVWP-3 and UVWD-3 respectively), the hydroxyl values of the polyesters drop down. This decrease is expected because the $\bar{M}n$ of the three diols (glycolysed PET) follow the order UVWE-3 < UVWP-3 < UVWD-3 (see Chapter-3). The viscosity and molecular weight of UVAW-81 (based on PG glycolysed PET) is higher than that of UVAW-82 (based on DEG glycolysed PET). This may be attributed to the fact that the synthesis of UVAW-81 was carried out under vacuum (in the final stages) for a prolonged duration in order to achieve low acid value. This experimental change had to be instituted to account for the relatively lower reactivity of the secondary hydroxyl group on PG. The prolonged application of vacuum at high temperature might have distilled out a small amount of PG, along with the water of reaction thereby leading to a higher molecular weight and viscosity. The significantly higher viscosity of UVAW-81 may also be due to broader MWD of PG glycolysed PET or polyol.

Though the OH/COOH ratio was 1.5 for both EG based (UVAE-77) and BHET based (UVAB-74) polyesters, the resins were in solid form at room temperature, because of the crystalline nature of the polymers.

5.3. KINETICS OF POLYCONDENSATON

The polyesterification is a reversible reaction. The reaction is caried out at high temperature (> 160°C). The kinetic equations governing the polyesterification rate under different conditions are discussed in Chapter-2. The kinetics was investigated under reaction conditions comparable to those employed on commercial scale.

As indicated in the discussion on the kinetics of unsaturated polyesters, in polyesterification, the reaction temperature should be slowly increased to a temperature below the boiling point of the glycol and held there for some period so that half-ester formation takes place, thereby minimizing any glycol loss in subsequent high temperature processing.

In the present work, the temperature of the reaction mixture was increased from room temperature (30°C) to 110°C in half an hour and then from 110^{o}C to 170^{o}C in one hour. The temperature was maintained at 170^{o}C for three hours and then raised to 200^{o}C in half an hour. The reaction was carried out at 200^{o}C till the acid value dropped below 2 mg KOH/g. The kinetics was investigated for the two isothermal regions at 170^{o}C and 200^{o}C. The progress of the reaction was monitored by estimating the carboxyl contents of the reaction mixture periodically. The concentration of hydroxyl groups was computed from acid value, assuming one to one reaction of carboxyl and hydroxyl groups.

The kinetics was investigated in two sets of experiments. In the first set, polyesterification of ethylene glycol based UVWE-3 with adipic acid, was investigated at three different OH/COOH ratios. In the second set, EG based UVWE-3, PG based UVWP-3 and DEG based UVWD-3 were reacted with adipic acid at OH/COOH ratio of 1.5

Since the reactions were catalysed using non-stoichiometric quantities of the reactants (excess glycol), the following kinetic equation may be applied.

$$\ln \frac{[OH]}{[COOH]} = \ln r + [COOH]_0 \ (r - 1)\ kt \qquad (13)$$

where $[COOH]_0$ is the initial concentration of carboxyl groups, [COOH] is the concentration of carboxyl groups at any time 't', [OH] is the concentration of hydroxyl groups at time 't' and 'r' is the ratio of the hydroxyl to carboxyl groups. For the reaction to be of second order, the plot of $\ln \frac{[OH]}{[COOH]}$ versus time should be linear.

The zero time for the reaction was taken to be that when the reaction temperature reached 170°C. The extent of reaction was calculated from the following formula :

$$p = \frac{[COOH]_0 - [COOH]}{[COOH]_0} \qquad (4)$$

where $[COOH]_0$ is initial concentration of carboxyl groups in eq/kg and [COOH] is the concentration for carboxyl groups in eq/kg, at any given time.

The degree of polymerization was calculated from the following relationship :

$$DP = \frac{1 + r}{1 + r - 2p} \qquad (14)$$

where 'r' is the ratio of hydroxyl to carboxyl group concentration and 'p' is the extent of reaction.

Initially the data of UVAW-78, UVAW-79 and UVAW-80, having different values of 'r', were analysed for kinetic behavior. These three resins were synthesized from UVWE-3 which contained mixture of free EG, BHET and some higher oligomers. Therefore, their kinetic data are compared with the kinetics of polyesters based on pure monomers EG (UVAE-77) and BHET (UVAB-74).

The kinetic data for the polyesterification reactions are given in Tables - 21 to 25.

Figure - 28 depicts the plots of $\ln \frac{[OH]}{[COOH]}$ versus time for UVAW-78, UVAW-79 and UVAW-80. The plots are fairly linear at 170°C for all the three resins, but at 200°C, considerable deviation from linearity is observed. This could be attributed to the presence of a number of diol structures in the reaction system, with different reactivities towards adipic acid.

In order to confirm this hypothesis polyester polyols were prepared by reacting pure monomers, namely, EG and BHET with adipic acid at OH/COOH equal to 1.5. For both the systems UVAB-74 and UVAE-77, the plots of $\ln \frac{[OH]}{[COOH]}$ versus time are linear (Figure - 29) over both the isothermal regions. The reactivity of EG based system was observed to be much higher than the BHET based systems. The difference in the reactivities of EG and BHET based systems may explain the non-linear kinetic behavior of the mixed systems based on glycolysed PET waste.

The variation of the extent of reaction, 'p', with time for the five polyesters is shown in Figure - 30. From the Figure, it is clear that the rate of reaction of the glycolysed PET based systems are comparable. The reactivity of the pure EG based system is the highest in the initial stages but drops down in the later stages beyond a conversion of 0.96, at 200°C. The BHET based system exhibits the lowest reactivity throughout the course of the reaction.

The plots of $\ln \frac{[OH]}{[COOH]}$ versus time are fairly linear at 170°C for the glycolysed PET based systems and also for polyols from EG and BHET. Therefore, the rate constants could be calculated from slopes of the lines using equation-13. Table-26 presents the rate constants at 170°C. The initial concentrations of the reactants were calculated from the acid value of the reaction mixture, when the temperature reached 170°C. Thus the starting point (t = 0) for kinetic analysis was assumed to be the time when the temperature of the reaction mixture reached 170°C. Since each system had undergone different extent of reaction during the initial heating period upto 170°C (Figure - 30 and Table-26), it is more logical to compare the rates of reaction at equivalent extent of reaction, than to compare the rate constants. Referring to Figure - 31, which depicts the variation of the rate of polymerization with extent of reaction at 170°C for the five systems, it is apparent that the reactivity of EG based system is the highest and that of BHET based system is the lowest. The three polyester polyols, based on EG glycolysed PET waste have comparable reactivity indicating practically no effect of the reactant ratio on rate over the range of 1.3 to 1.8 studied. These three systems exhibit kinetic behavior intermediate to those of the EG and BHET based systems.

At 200°C the plots of $\ln \frac{[OH]}{[COOH]}$ versus time are linear for the BHET (UVAW-74) and EG (UVAE-77) based polyols. Therefore the rate constants could be calculated from the slopes. However, for the glycolysed PET based systems, large deviations from linearity were observed. Therefore, it was difficult to calculate the precise values of the rate constants. Table - 27 shows the approximate values of the rate constants of PET based systems, calculated from the mean straight lines as shown in Figure - 28.

The variation of the reaction rate at 200°C with the extent of reaction for the five polyester polyols is shown in Figure - 32. The data indicate that the glycolysed PET (UVWE-3) based systems are more reactive, at 200°C, than the BHET and EG based systems. The reactivities of the UVWE-3 based systems are comparable. The rates of reaction of EG and BHET based systems were lower at 200^{o}C than at 170^{o}C. This may be related to the difficulty in removal of reaction water from the reaction mixture in case of the BHET based system and to the loss of EG at high temperatures in case of the EG based polyol. It is known that, in the later stages of the polyesterification reaction, the efficiency of removal of reaction water influences the rate of reaction (111). The viscosity of the pure BHET based polyester was found to be very high even at high temperature (see Table-28), which would make the removal or water through the bulk of reaction mixture very difficult. In the case of the EG based polyester, though the polyol viscosity was not as high as that of BHET based polyol, the glycol started distilling at 200^{o}C. Therefore, the stirring and nitrogen flow had to be reduced which might have adversely affected the removal of water from the reaction mixture. Similar problem was also observed in UVWE-3 based systems with increasing value of 'r'. Therefore there is no remarkable difference observed in the reactivity of the three systems with varying ratios of OH/COOH. However, the rate shows a slight increase with increasing value of 'r' at conversions below 97 % .

In order to elucidate the effect of the type of glycol on the kinetics of polyesterification, the reactions of glycolysed PET waste obtained from glycolysis with EG (UVWE-3), PG (UVWP-3) and DEG (UVWD-3), with adipic acid at a fixed reactant ratio of 1.5 were compared. The diols used were prepared by glycolysing PET waste with EG, PG and DEG respectively at a fixed weight ratio of PET/glycol (37.5/62.5). As discussed in Chapter-3, the extent of depolymerization was maximum in UVWE-3 followed by UVWP-3 and UVWD-3. In other words, UVWP-3 and UVWD-3 contained a relatively higher concentration of high molecular weight oligomers. Though the assumption of constant reactivity irrespective of the molecular size of the reacting species is widely accepted, in a number of systems, a difference in the reactivity of the monomer compared to its oligomeric species has been reported (112,113). This is also seen from the data discussed earlier concerning the kinetics of EG and BHET based polyols versus those of the mixed diol systems.

The kinetic data of UVAW-81 and UVAW-82 are given in Tables - 29 and 30. Figure-33 shows the variation of the extent of polyesterification reaction with time, for the polyester polyols made from UVWE-3 (UVAW-79), UVWP-3 (UVAW-81) and UVWD-3 (UVAW-82). For plotting the data, the zero time has been taken to be the time at which the reaction temperature reached 170°c. For the initial period, the increase in the extent of reaction for UVAW-79 and UVAW-82 is comparable. The rate of reaction of the PG glycolysed product with adipic acid (UVAW-81) is comparatively lower. However, at 200°C there is a marked increase in the rate of reaction of UVAW-79, whereas UVAW-81 and UVAW-82 proceed at relatively lower rates.

Figure - 34 illustrates the plots of $\ln \frac{[OH]}{[COOH]}$ versus time as per equation-13. It is seen that inspite of the presence of monomers and oligomers of different sizes in the reaction mixture, the plots, for UVAW-81 and UVAW-82, are fairly linear. Thus the reactions follow second order kinetics. The slight nonlinearity in the initial stages at 170°C may be attributed to the large changes in the concentration of the reactive groups and polarity of the reaction medium.

The rate constants of the reactions were calculated for the two regions at 170°C and 200°C as described earlier. The values of rate constants are summarized in Table-31. At 170°C, covering the extent of reaction from 0.4 to 0.9, the DEG based system exhibits the highest rate constant, followed by EG based and then the PG based system. This trend is consistent with the reported observations that the reactivity of DEG is higher than that of EG (114) and that the presence of secondary hydroxyl group on PG reduces its reactivity(115). At 200°C there is an increase in the values of the rate constants as expected. However, the increase is maximum for the EG based glycolysed product.

As stated earlier, a more logical way to compare the reactivity is to follow the variation in the rate of reaction with the extent of reaction. Figure - 35 illustrates the change in the rate of reaction with the extent of reaction at 170°C. Though the rate constant of UVAW-82 (DEG based) is higher than the UVAW-79 (EG based), because of a higher concentration of free functional groups (see Figure-36) in UVAW-79, its rate is higher than that of UVAW-82. The rates of UVAW-81 and UVAW-82 are identical. The reactivity of diethylene glycol (monomer) is higher than that of ethylene glycol. However, the mole percent of free DEG present in UVAW-3 is less than the mole percent of free EG present in UVAW-3. Thus the lower percent of free glycol and the presence of higher oligomers in UVWD-3 may cause the reaction, in case of UVAW-82, to proceed at a slower rate. Though the concentration of hydroxyl group in UVWP-3 is higher than that of UVWD-3, the presence of a secondary hydroxyl groups of PG would reduce the overall reactivity.

Figure - 37 represents the change in the reaction rate with the extent of reaction at 200°C. Again the same trend is observed in the reaction rates. The rates are higher than the corresponding rates at 170°C. The lower rate of reaction of UVAW-82 is observed in this region also. This may again be attributed to the lower concentration of functional groups (see Figure-38) and higher concentration of large sized oligomers.

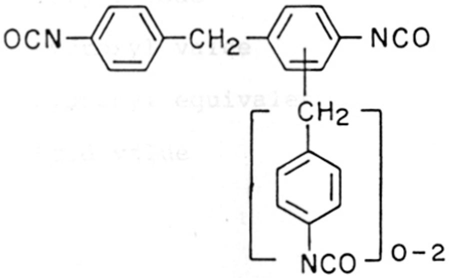
Thus it is seen that the rate reaction depends on the amount and type of oligomers present in the beginning of polyesterification reaction. The rate is greatly affected by efficiency of water removal. Any process parameter, such as stirring speed, the rate of nitrogen sparge or heating which influences the removal of water of reaction would govern the rate of reaction.

5.4. POLYURETHANE FORMULATION DEVELOPMENT

The polyester polyols synthesized were reacted with polymeric 4,4'-diphenyl methane diisocyanate (PMDI) to get polyurethane elastomers and rigid foams.

The said isocyanate was obtained from M/s BASF under the trade name Lupranate with the following specifications :

NCO %	31 - 32
NCO equivalent	130 - 140
Average functionality	2.7
Chemical structure	



5.4.1. **Preparation of PU Elastomers** :-

The specifications of the polyols used for synthesis of elastomers are summarized in Table - 32. The polyols were mixed with PMDI at four different NCO/OH ratios. For practical purpose the NCO/OH ratio may be expressed in terms of isocyanate index as follows :

$$\text{Isocyanate Index} \quad (\text{II}) = \frac{[\text{NCO}]}{[\text{OH}]} \times 100.$$

The four values of Isocyanate Indices investigated are : 79,87,95 and 103. The reaction mixtures were degassed in a reactor equiped with vacuum line & stirrer and then cast into the moulds for further testing. The specimens were allowed to cure at room temperature for 24 hours and were then further cured at 80°C for 4 hours.

5.4.2. **Preparation of Polyurethane / Urea Rigid Foams** :-

A polyol was prepared by reacting adipic acid with EG glycolysed PET waste (UVWE-3), at a hydroxyl to carboxyl ratio of 2.08. The specifications of the polyol are given below :

Polyol code	UVAW-83
Hydroxyl value	360 mg KOH/g
Hydroxyl equivalent	180
Acid value	1 mg KOH/g

Moisture content	1 %
Silicone surfactant	0.2 %
Viscosity, @ 30^{o}C	2000 cps

The polyol was reacted with PMDI at NCO to OH ratio equal to one. The same polyol was mixed with 10 % glycerol, by weight and then reacted with PMDI at NCO to OH (from polyol and glycerol) ratio equal to one. The formulations are summarized in Table-33.

The specimens were cast into closed moulds to get densities of 0.3 and 0.43 g/cc. The moulds were preheated to 60^{o}C. The initial curing was done at room temperature for 30 minutes followed by high temperature curing at 80^{o}C for 4 hours.

5.5. MECHANICAL PROPERTIES OF POLYURETHANES

5.5.1. Elastomers :-

(i) Hardness :-

The hardness was measured as per ASTM-D 2240 by shore A/D durometers. The elastomers were cast into a mould to form a circular specimen of about 1 cm thickness and 6 cm diameter.

(ii) Tensile Strength :-

The tensile strength was determined as per ASTM-D790. The specimens were cast into moulds, as per specifications given in the method. The testing was done on a Instron mechanical tester, model - 1122.

The results of the testing are summarized in Table-34. The polyol used for the synthesis of PU elastomers were bifunctional. Therefore, the crosslinking was contributed only by PMDI. The extent of crosslinking can be determined by swelling studies of the sample in a solvent (116-119). When a polymer is placed in a solvent, it swells, and the extent of swelling depends on solvent-polymer interaction. The swelling would be maximum in the solvent whose solubility parameter (δ) matches that of the polymer. Similarly the swelling also depends on the polarity of the solvent. Polymers having polar groups swell to a greater extent in polar solvent. The extent of swelling of the polymer would decrease with the increase in crosslinking.

In the present work, samples of dimension 3 mm x 20 mm x 20mm were weighed accurately, enclosed in wire mesh, and immersed in benzene (δ = 9.2, non polar), ethyl acetate (δ = 9.1, moderately polar) and dimethyl formamide (δ = 12.1, highly polar), for 24 hours. The sample lost the mechanical integrity in DMF because of excessive swelling. Therefore, samples immersed in benzene and ethyl acetate were further investigated for swelling estimation. The polymer samples were weighed immediately after removal from the solvent bath. The difference in the weight gave the amount of solvent absorbed by the sample. The samples were then dried under vacuum at 100 °C for 24 hours to remove the absorbed solvent. The difference in the weight of sample, from the original weight gives the weight of sol fraction of the polymer which is extracted out of the gel part (116). It is seen from Tables-35 and 36 that the amount of sovent absorbed and the sol fraction decreases with increasing isocyanate index, indicating increase in the crosslinking. Similarly the crosslinking density is also found to increase with decrease in the molecular weight of polyol.

It is seen from the Table - 34 that for any polyol the hardness and tensile strength increases with increasing isocyanate index, in the given range. In the case of polyols, made from UVWE-3, namely, UVAW-78 , UVAW-79 and UVAW-80, the tensile strength and hardness increase with decreasing molecular weight at a fixed isocyanate index. This may be attributed to higher crosslinking density, that is a lower average molecular weight, M_c, between points of crosslinking, obtained in the network by using low molecular weight polyols.

Figure - 39 shows the variation in the tensile strength and elongation at break with isocyanate index. The tensile strength increases and elongation decreases with isocyanate index. The increase in the strength is the most notable with the polyol UVAW-80, which has the lowest molecular weight.

Polyols coded UVAW-79, UVAW-81 and UVAW-82 are made from glycolysed PET products UVWE-3 (EG based) UVWP-3 (PG based) and UVWD-3 (DEG based) respectively, at OH/COOH ratio equal to 1.5. These resins may be compared to see the effect of the type of glycol on the properties. As indicated in the synthesis of polyols, the molecular weight of UVAW-81 is slightly higher than the one expected theoretically. This resulted from the loss of PG during polyesterification due to excessive heating under vacuum which was essential to complete the reaction, involving slow reacting PG and its oligomers. Though the molecular weight is slightly higher, the polyol may be used for comparison with UVAW-79 and UVAW-82. It is seen that the tensile strength decreases with the increasing chainlength of glycol,the tensile strength is the maximum for EG based system and minimum for DEG based system. The elongation is maximum for PG based systems probably because of the higher molecular weight of the polyol.

During mechanical testing, it was noted that the elastic recovery of the tensile specimens after deformation was about 98-100 % in most of the cases. The stress strain curves of all the samples, except UVAW-80, were linear, even when the % elongation ranged from 180 to 300 %, indicating their elastic nature. UVAW-80 exhibited a yield point at higher isocyanate indices. Figures-40 to 43 depict the stress-strain curves at four isocyanate indices (79,87,95 and 103), for polyol UVAW-80. The elongation is drastically reduced from 215 % to about 5 % when the isocyanate index is increased from 79 to 103. The specimens start exhibiting a clear yield point above isocyanate index of 87. Though there is not much of difference in the value of tensile strength at the break above isocyanate index of 87, the stress-strain curves show that the yield point shifts to higher values of stress with increasing isocyanate index. At the lower isocyanate indices one can observe the oriention hardening effect beyond the yield point. The orientation of polymer chains is possible at lower isocyanate index due to lower crosslinking. However at NCO/OH ratio 1.03, beyond the yield point one can observe a constant stress indicating plastic flow for a short strain before the break. The plastic flow would arise due to the increase in the temperature of the test specimen due to high stress generated during the testing. At the isocyanate index of 103, the sample is sufficiently crosslinked to prevent the orientation of the chains. Therefore, no orientation hardening could be observed.

Thus it can be seen that the ultimate tensile strength and hardness increases with increaing isocyanate index, crosslinking and decreasing M_c.

Thus the PET waste based polyols may be used to produce elastomers exhibiting a broad spectrum of properties by varying the composition. The effect of the incorporation of extenders/crosslinking agents on the properties of the elastomers also needs to be studied.

5.5.2. **Rigid Foams** :-

(i) Tensile strength :-

The tensile strength was measured as per ASTM-1627. The samples were foamed into cylindrical dumbells conforming to the specifications given in the test method. The testing was done on a Instron tensile tester machine, model - 1122.

(ii) Compressive strength :-

The compressive strength was determined as per ASTM-D1621. The samples were foamed in a cylindrical mould of diameter 2.5" and height 1.5". The compressive stength is denoted as stress at 10 % deflection. The testing was performed on the Instron machine.

(iii) Flexural strength :-

The flexural strength was determined as per ASTM - D790. The samples were foamed to form slabs which were cut to form specimens of 6" x 1" x 1" (ASTM - D2341). The testing was done on the Instron machine. The loading nose and supports were in the form of cylindrical rods with 1 cm diameter.

A set of test specimens were prepared from UVAW-83 and PMDI to get densities of 0.30 and 0.43 g/cm^3. Another set was prepared using 10 % w/w glycerol as extender with UVAW-83 and a NCO/OH ratio equal to 1.0. (refer Table-33).

The results of the testing are summarized in the Table-37. The internal variation in the samples was about + 10 % as indicated in parantheses after each value. Therefore it can be concluded that the incorporation of glycerol has no significant effect on the properties in relation to the effect of density. As expected, the mechanical properties improve to a great extent with increase in the density. The data given in the Table -37 can be used as a rough estimate of the performance of the material. However before arriving at any specific conclusions, many more experiments in a wider density range are required to be conducted.

Figure - 44, shows the stress-strain data in tensile mode. It is seen that the performance of the foam improves with the increase in the density. The effect of extender is more pronounced at higher density. At the foam density of 0.43 gm/cc, though the ultimate tensile strengths of the extended and nonextended systems are comparable, the extended foam is more rigid than the nonextended foam.

Figure - 45 shows stress-strain data under compression. Both nonextended and extended formulation exhibit yield point at about 4 % deflection. It is clearly seen that density improves the compressive strength remarkably. Though the stress-strain curve shows slight improvement with the incorporation of glycerol, the sample to sample variation is of the same order. Therefore, for practical purpose it may be concluded that the behavior of extended and nonextended foam is comparable over the density range studied.

Similar behavior is observed in flexural testing also. Therefore it can be concluded that the properties are affected to a greater extent, by variation of density, than the incorporation of glycerol extender. The mechanical properties of the polyurethane foams also depend on the cell size and cell size distribution. The cell structure of the rigid foams, derived from PET waste (UVAW-83) was investigated by electron microscopy. A Cambridge model 'Steroscan 150' scanning electron microscope was used for these studies. The photographs in Figure-46 show the cell size distribution with variation in density and incorporation of glycerol extender. The cell size ranges from 150 to 250 μ. Figure-47 shows the cell size and shapes at higher magnification. It is seen that the cells are smaller with thinner cell walls (1 to 2 μ)at a density of 0.3 g/cc, than at 0.43 g/cc. Among the extended and nonextended foams, no significant difference in the cell size or wall thickness is observed.

The cells are spherical in shape for all the formulations. The dark spots on the cell walls indicate that the cells are interconnected to each other.

The electron micrographs of cut and fractured surface did not show any difference in the shape or size.

However the testing with respect to cell size and structure should be conducted carefully, in a broader range of density to establish the precise behavior of the foams. There is also scope for further improving the cell structure in terms of finer cell size and narrower size distribution, which could lead to better mechanical performance.

Thus the rigid foams having a wide range of properties can be made from PET waste by properly selecting the structure of polyol, molecular weight of the polyol, isocyanate index, the type and amount of extender and the density.

5.6 DYNAMIC MECHANICAL PROPERTIES OF PU ELASTOMERS

The theory and significance of dynamic mechanical analysis, are discussed in section 4.5. The influence of polyurethane structure on its physical and mechanical properties has been reported in a number of publications (120-125). The polyurethanes are reported to undergo γ, β and α transitions depending on the structure (116). These transitions correspond to the 'unlocking' of different intermolecular associations arising due to the polar groups present in the polymer chain. The α transition corresponds to the glass transition temperature, Tg. Because of the large number of variables such as type of segments (soft / hard), extent of crosslinking, multiplicity of groups and molecular weight between crosslinks (M_c), associated with the chemical structure of PU, a wide range of trends in properties are observed. Normally, the thermomechanical performance improves with an increase in the fraction of hard segments and the crosslinking, while an increase in the fraction of soft segments improves the damping characteristics of the material.

The different systems investigated in the present work are tabulated in Table-38.

The samples were cast in the mould to form strips of dimension 2mm x 12mm x 60mm. The dynamic mechanical analysis was performed on Rheomatrics Dynamic Mechanical Spectrometer, model RDS-7700. The measurements were taken over a temperature range of $-40^{\circ}C$ to about $100^{\circ}C$ with 0.1 % strain at 100 rads/sec. The specimens were tested in triplicate and the average data are used for interpretation.

The different molecular parameters of the PU network investigated in the present work are :

i. Molecualr weight of polyol
ii. Isocyanate index (II)
iii. Type of glycol
iv. Rigid and Soft segment

These variables could be correlated to the dynamic mechanical performance of PU elastomers. The dynamic mechanical parameters are illustrated in Figure-48 a.

(i) Molecular weight of polyol :-

Figure-48 illustrates the effect of molecular weight of UVWE-3 based polyols on the value of temperature at tan δ peak. It is seen that the tan δ peak temperature increases significantly with decrease in the molecular weight of the polyol. The difference in the temperatures at varying isocyanate indices is marginal, indicating that the effect of molecular weight is more significant than that of the isocyanate index.

The variation of G', the shear modulus, for UVAW-78, UVAW-79 and UVAW-80 having different $\overline{M}n$, but same isocyanate index (II = 87), with temperature is shown in Figure-49. The plot shows that the value of G' and temperature at which G' starts deviating, Td, decrease with increasing molecular weight. The increase in the value of G' with the decrease in the molecular weight of polyol may be attributed to the decrease in the average molecular weight between crosslinks, M_c. Thus for the same isocyanate index the hard segment content of the network increases with decreasing molecular weight. The decrease in the value of M_c would restrict the mobility of the molecules thereby increasing the transition temperature. These results are consistant with results of Seefried et. al.(124), who observed a substantial decrease in the shear modulus with the increase in the molecular weight of polycaprolactone polyol.

(ii) Isocyanate index :-

The data obtained for the polyol UVAW-79 ($\overline{M}n$ = 747), at isocyanate index values of 79,87,95 and 103, can be used to study the effect of isocyanate index on the properties. Since the isocyanate, used in the present study, PMDI, has an average functionality of 2.7 it leads to crosslinking. Thus an increase in the isocyanate index would increase the crosslinking density.

Figure-50 depicts the variation of tan δ with temperature for the polyol UVAW-79 at different isocyanate indices. It is noted that the temperature of tan δ peak shifts to a progressively higher value with increasing isocyanate index. However, there is no significant change in the nature of the tan δ peak. Figure-51 shows the variation of G" with temperature. It is seen that the increase in the isocyanate index increases the glass transition temperature and also the span of temperature over which the energy dissipation occurs. The values are tabulated below :

Sr. No.	isocyanate index	transition temperature, °C	temperature span of relaxation, °C
1.	79	31	40
2.	87	38	45
3.	95	42	55
4.	103	47	70

The temperature dependence of the dynamic storage modulus, G' of UVAW-79 at varying isocyanate index is shown in Figure-52. The temperature at which G' starts dropping increases with increasing isocyanate index. The value of G' is constant upto 20°C for isocyanate index of 103 whereas for isocyanate index of 87, it starts dropping at about 0°C. The increase in the thermomechanical stability at higher isocyanate index may be attributed to the increase in the molecular weight of the polymer and greater crosslinking. Similar observations are noted in the case of UVAW-78 and UVAW-79, (Figures 53 - 58).

(iii) Type of glycol in polyol :-

UVAW-79, UVAW-81 and UVAW-82 made from EG, PG and DEG glycolysed PET, respectively, can be compared to see the effect of the type of glycol on dynamic mechanical properties of the PU elastomer.

The temperature dependance of the shear modulus G' for samples UVAW-79. UVAW-81 and UVAW-82 at isocyanate index equal to 103 are presented in Figure-59. The storage modulus G' remains almost constant upto -5^{o}C for DEG containing and about 20^{o}C for EG and PG containing samples. The lower themomechanical performance of UVAW-82 may be attributed to the additional ether linkage in DEG, which forms more flexible segment than EG. However, the effect of methyl group substitution i.e. use of PG does not seem to have a significant effect on the storage modulus.

The dynamic loss modulus G'' versus temperature is shown in Figure-60. The transition temperature shifts to a higher value as the flexibility of the glycol decreases. Similarly tan δ peak also shifts to a higher value, in

Figure-61. Thus EG and PG based samples behave in identical manner whereas the DEG based sample exhibits lower Tg and thermomechanical behavior.

(iv) Fraction of Hard and Soft segments :-

The dynamic mechanical behavior of the polyurethanes can also be related to the fraction of soft and hard segments. The soft segments include the flexible part of the polymer chain structure responsible for the relaxation phenomena, whereas the hard segments are those which restrict the movement of polymer chains because of their rigid chemical structure.

The weight percentages of the different chemical moieties in the polyurethane network are indicated in Table-38. The hard segments are represented by terephthalic acid and PMDI moieties and the soft segments include glycol and adipic acid moieties. The relative amounts of the hard and soft segments may be represented by a parameter λ, defined as :

$$\lambda = \frac{\text{wt. \% of terephthalic acid + wt.\% of PMDI}}{\text{wt. \% of glycol + wt. \% of adipic acid}}$$

The variation of the transition temperature, that is $\tan\delta$ peak temperature with λ is shown in Figure-62. It is interesting to note that the experimental points can be represented by a single straight line. The effect of the molecular weight of polyol becomes insignificant when the transition temperatures are correlated to λ. This relation indicates that the variation of the transition temperature for EG based systems can be predicted on the basis of the weight fractions of the hard and soft segments. Thus depending on the application, the polymer structure may be pre-designed to suit a specific transition temperature.

The temperature at which the storage modulus G' deviates from the initial constant value Td, is plotted as a function of λ value, in Figure-63. Td also varies linearly with λ. Thus the λ parameter can be used as a tool in molecular engineering for designing synthesis experiments.

Thus it is seen that the elastomers with a wide range of properties can be synthesized from PET waste. The thermomechanical properties are imporved by increase in the crosslinking density or amount of hard segments. However, this increase is accompanied by decrease in the flexibility. The amount of hard segments and soft segments can be used as a guideline to predict the properties of the polymer.

TABLE - 20

Characterization of Polyester Polyols

Sr. No.	Polyester code	Diol used	OH/COOH ratio	Viscosity cps (30°C)	Hydroxyl value mg KOH/g	Acid value mg KOH/g	$\overline{Mn}$ Endgroup	$\overline{Mn}$ VPO
1.	UVAW-78	UVWE-3	1.3	Paste	70	0.6	1603	1550
2.	UVAW-79	UVWE-3	1.5	4000	150	0.5	748	800
3.	UVAW-80	UVWE-3	1.8	2900	263	0.5	426	490
4.	UVAB-74	BHET	1.5	Solid	-	-	-	-
5.	UVAE-77	EG	1.5	Solid	-	-	-	-
6.	UVAW-81	UVWP-3	1.5	12500	110	0.8	1020	1002
7.	UVAW-82	UVWD-3	1.5	4100	125	0.5	898	910

TABLE - 21

Kinetic Data of UVAW-78

Sr. No	Time min	Acid Value mg KOH/g	[COOH] eq/kg	[OH] eq/kg	p	DP	ln [OH]/[COOH]
At 170°C							
1.	0	186.1	3.317	5.441	0.5314	1.859	0.4949
2.	30	110.4	1.968	4.092	0.7220	2.687	0.7320
3.	60	85.0	1.515	3.639	0.7860	3.159	0.8762
4.	90	70.3	1.253	3.377	0.8230	3.517	0.9914
5.	120	59.8	1.066	3.190	0.8494	3.826	1.0961
6.	150	51.8	0.923	3.047	0.8696	4.101	1.194
7.	180	47.6	0.848	2.292	0.8801	4.262	1.254
At 200°C							
8.	210	38.7	0.690	2.814	0.9025	4.648	10.256
9.	240	27.0	0.481	2.605	0.9320	5.276	14.706
10.	270	21.7	0.387	2.511	0.9454	5.620	18.315

11.	330	18.0	0.321	2.445	0.9547	5.888	22.075
12.	390	12.6	0.224	2.348	0.9683	6.328	31.546
13.	450	9.6	0.171	2.295	0.9758	6.603	41.322
14.	510	3.7	0.066	2.190	0.9907	7.218	107.527
15.	600	1.3	0.023	2.147	0.9967	7.503	303.030
16.	660	1.0	0.018	2.142	0.9974	7.540	384.600

TABLE - 22

Kinetic Data of UVAW-79

Sr. No.	Time min	Acid Value mg KOH/g	[COOH] eq/kg	[OH] eq/kg	p	DP	ln [OH]/[COOH]
At 170°C							
1.	0	178.1	3.175	6.469	0.5182	1.708	0.7119
2.	30	101.1	1.800	5.095	0.7268	2.389	1.4003
3.	60	80.3	1.431	4.726	0.7828	2.675	1.1945
4.	90	63.1	1.125	4.420	0.8293	2.971	1.3685
5.	120	54.2	0.966	4.261	0.8534	3.151	1.4840
6.	150	46.0	0.820	4.115	0.8756	3.338	1.6131
7.	180	40.3	0.718	4.013	0.8910	3.482	1.720
At 200°C							
8.	210	34.8	0.620	3.915	0.9058	3.632	1.842
9.	240	21.5	0.383	3.678	0.9418	4.056	2.261
10.	270	15.1	0.269	3.564	0.9591	4.289	2.583

11.	300	8.8	0.157	3.452	0.9762	4.565	3.091
12.	330	4.6	0.082	3.377	0.9875	4.763	3.718
13.	360	3.6	0.064	3.359	0.9902	4.812	3.958
14.	390	2.9	0.052	3.346	0.9921	4.848	4.170
15	450	2.0	0.035	3.330	0.9946	4.894	4.537
16	490	1.5	0.027	3.322	0.9959	4.920	4.822

TABLE - 23

Kinetic Data of UYAW-80

Sr. No.	Time min	Acid value mg KOH/g	[COOH] eq./kg	[OH] eq./kg	p	DP	ln [OH]/ [COOH]
At 170°C							
1.	0	170.9	3.046	7.822	0.4897	1.5380	0.9430
2.	30	93.0	1.670	6.446	0.7202	2.059	1.350
3.	60	76.2	1.358	6.134	0.7725	2.231	1.507
4.	90	58.0	1.034	5.810	0.8268	2.442	1.726
5.	120	47.9	0.854	5.630	0.8570	2.578	1.886
6.	150	40.5	0.722	5.498	0.7891	2.687	2.030
7.	180	34.4	0.613	5.389	0.8973	2.785	2.173
At 200°C							
8.	210	23.0	0.410	5.186	0.9313	2.987	2.537
9.	240	16.0	0.285	5.061	0.9522	3.126	2.876
10.	270	11.8	0.210	4.986	0.9647	3.216	3.166
11.	300	9.4	0.167	4.943	0.9720	3.271	3.385

12.	330	6.4	0.114	4.890	0.9810	3.340	3.758
13.	360	4.0	0.071	4.847	0.9880	3.398	4.219
14.	420	2.9	0.052	4.827	0.9913	3.426	4.537
15.	480	1.2	0.021	4.797	0.9964	3.469	5.413
16.	540	1.0	0.018	4.794	0.9970	3.474	5.594
17.	600	0.8	0.015	4.791	0.9975	3.478	5.768

TABLE - 24

Kinetic Data of UVAE-77

Sr. No	Time min	Acid value mg KOH/g	[COOH] eq./kg	[OH] eq./kg	p	DP	ln [OH]/[COOH]
At 170°C							
1.	0	44.1	0.786	2.683	0.7928	2.734	1.227
2.	30	32.1	0.572	2.469	0.8492	3.119	1.462
3.	60	28.1	0.501	2.398	0.8680	3.273	1.566
4.	90	22.5	0.401	2.298	0.8943	3.515	1.745
5.	120	16.2	0.289	2.186	0.939	3.834	2.024
6.	150	13.1	0.233	2.130	0.9384	4.013	2.211
7.	180	11.8	0.210	2.107	0.9446	4.093	2.304
At 200°C							
8.	210	10.5	0.187	2.084	0.9507	4.177	2.410
9.	270	9.2	0.164	2.061	0.9568	4.264	2.531
10.	300	8.3	0.148	2.045	0.9610	4.326	2.626

11.	360	7.1	0.126	2.023	0.9666	4.412	2.772
12.	390	6.9	0.123	2.020	0.9676	4.427	2.799
13.	450	5.1	0.090	1.988	0.9760	4.563	3.085
14.	540	3.8	0.068	1.965	0.9821	4.668	3.367
15.	600	2.7	0.044	1.941	0.9882	4.776	3.774

TABLE - 25

Kinetic Data of UVAB-74

Sr. No	Time min	Acid value mg KOH/g	[COOH] eq./kg	[OH] eq./kg	p	DP	ln [OH]/[COOH]
At 170°C							
1.	0	131.3	2.340	4.237	0.3833	1.442	0.593
2.	30	98.9	1.763	3.652	0.5354	1.749	0.730
3.	90	67.7	1.207	3.104	0.6820	2.201	0.944
4.	120	56.2	1.002	2.898	0.736	2.432	1.062
5.	150	48.4	0.863	2.760	0.7726	2.619	1.163
6.	180	42.5	0.757	2.654	0.8004	2.780	1.254
At 200°C							
7.	210	32.7	0.583	2.480	0.8464	3.097	1.448
8.	240	23.7	0.422	2.319	0.8886	3.460	1.703
9.	300	17.5	0.312	2.209	0.9178	3.763	1.957
10.	360	14.4	0.258	2.155	0.9319	3.930	2.121

11.	420	13.8	0.246	2.143	0.9352	3.971	2.164
12.	480	11.9	0.212	2.109	0.9441	4.087	2.297
13.	540	9.5	0.169	2.066	0.9554	4.243	2.501
14.	660	7.6	0.135	2.032	0.9643	4.376	2.708
15.	720	6.1	0.109	2.006	0.9713	4.487	2.915

TABLE - 26

Rate Constants at the First Isothermal Region at 170°C

Sr. No.	Polyester code	Extent of reaction, p*	[COOH] eq./kg	Rate constant, k kg/eq./min
1.	UVAW-78	0.5314	3.317	3.2×10^{-3}
2.	UVAW-79	0.5182	3.174	2.9×10^{-3}
3.	UVAW-80	0.4897	3.046	2.2×10^{-3}
4.	UVAB-74	0.3833	2.340	3.0×10^{-3}
5.	UVAE-77	0.7928	0.786	32.3×10^{-3}

* Extent of reaction when temperature reached 170°C.

TABLE - 27

Rate Constants at Second Isothermal Region at 200°C

Sr. No	Polyester code	Extent of reaction, p*	[COOH] eq./kg	Rate constant, k kg/eq/min
1.	UVAW-78	0.9025	0.690	36.8×10^{-3}
2.	UVAW-79	0.9058	0.620	34.8×10^{-3}
3.	UVAW-80	0.9313	0.410	30.8×10^{-3}
4.	UVAB-74	0.8464	0.583	8.0×10^{-3}
5.	UVAE-77	0.9506	0.187	14.8×10^{-3}

* Extent of reaction when temperature reached 200°C.

TABLE - 28

Visosity of Polyester Polyols at 140°C

Sr.No.	Polyester code	Viscosity, cps
1.	UVAW-78	73
2.	UVAW-79	37
3.	UVAW-80	19
4.	UVAB-74	nonflowing paste
5.	UVAE-77	75

TABLE - 29

Kinetic data of UVAW-81

Sr. No.	Time min	Acid value mg KOH/g	[COOH] eq./kg	[OH] eq./kg	p	DP	ln [OH]/[COOH]
At 170°C							
1.	0	202.7	3.613	6.680	0.4111	1.490	0.614
2.	30	123.1	2.194	5.261	0.6423	2.057	0.874
3.	60	92.1	1.642	4.709	0.7324	2.415	1.053
4.	90	72.7	1.296	4.363	0.7888	2.710	1.214
5.	120	63.3	1.128	4.195	0.8161	2.881	1.313
6.	150	55.2	0.984	4.051	0.8396	3.046	1.415
7.	180	50.78	0.904	3.971	0.8527	3.146	1.480
At 200°C							
8.	210	40.6	0.724	3.791	0.8820	3.397	1.655
9.	240	29.7	0.529	3.596	0.9137	3.717	1.916
10.	270	24.9	0.444	3.511	0.9276	3.877	2.068
11.	330	20.2	0.360	3.427	0.9413	4.049	2.253

12.	390	18.5	0.329	3.396	0.9462	4.114	2.334
13.	450	15.1	0.269	3.336	0.9561	4.253	2.5198
14.	510	13.0	0.232	3.299	0.9622	4.343	2.654
15.	570	12.0	0.214	3.281	0.9651	4.387	2.730
16.	630	10.0	0.718	3.245	0.9709	4.478	2.902

TABLE - 30

Kinetic Data of UVAW-82

Sr. No.	Time min	Acid value mg KOH/g	[COOH] eq./kg	[OH] eq./kg	p	DP	ln [OH[/[COOH]
At 170°C							
1.	0	131.3	2.340	4.815	0.5272	1.729	0.721
2.	30	77.5	1.381	3.856	0.7209	2.362	1.027
3.	60	57.4	1.023	3.498	0.7933	2.737	1.229
4.	120	40.4	0.720	3.195	0.8545	3.160	1.490
5.	180	32.3	0.576	3.051	0.8837	3.412	1.667
At 200°C							
6.	210	21.8	0.388	2.863	0.9215	3.805	1.999
7.	240	19.8	0.353	2.828	0.9287	3.890	2.081
8.	270	16.1	0.287	2.762	0.9420	4.058	2.264
9.	330	14.3	0.255	2.730	0.9485	4.146	2.371
10.	390	12.1	0.215	2.690	0.9564	4.257	2.526

11.	450	11.1	0.198	2.673	0.9600	4.310	2.602
12.	480	10.5	0.187	2.662	0.9656	4.395	2.656
13.	600	8.0	0.142	2.617	0.9712	4.483	2.914

TABLE - 31

Rate Constants of Polyesterification Reactions Based on Different Types of Glycols

Sr. No.	Polyester code	Type of diol used for polyestrification	170°C		200°C	
			[COOH]* eq./kg	Rate constant, k kg/eq/min	[COOH]** eq./kg	Rate constant, k kg/eq/min
1.	UVAW-79	UVWE-3 (EG based)	3.174	2.9×10^{-3}	0.620	34.8×10^{-3}
2.	UVAW-81	UVWP-3 (PG based)	3.613	2.4×10^{-3}	0.724	10.5×10^{-3}
3.	UVAW-82	UVWD-3 (DEG based)	2.340	3.7×10^{-3}	0.388	10.5×10^{-3}

* Concentration of carboxyl groups when reaction reached 170°C.

** Concentration of carboxyl groups when reaction reached 200°C.

TABLE - 32

Specifications of Polyols used for Synthesis of PU Elastomers

Sr. No.	Polyol code	Type of diol	OH/COOH	Hydroxyl value mg KOH/g	$\overline{Mn}$	Viscosity cps,@ 30°C
1.	UVAW-78	UVWE-3 (EG based)	1.3	70	1603	pasty (1350 @ 45°C)
2.	UVAW-79	UVWE-3 (EG based)	1.5	150	748	4000
3.	UVAW-80	UVWE-3 (EG based)	1.8	263	426	2900
4.	UVAW-81	UVWP-3 (PG based)	1.5	110	1020	12500
5.	UVAW-82	UVWD-3 (DEG based)	1.5	125	898	4100

TABLE - 33

PU Rigid Foam Formulations

Sr.No.	PU Foam code	Polyol used	NCO/OH*	Density,g/cc
1.	0.3	UVAW-83	1.0	0.30
2.	0.43	UVAW-83	1.0	0.43
3.	0.3 EX	UVAW-83 + 10 % glycerol	1.0	0.30
4.	0.43 EX	UVAW-83 + 10 % glycerol	1.0	0.43

* The amount of isocyanate is calculated considering both moisture and extender (glycerol).

TABLE - 34

Properties of PU Elastomers

Sr.No.	Polyester code	Molecular weight of polyol	NCO/OH	Hardness, Shore	Tensile strength kg/cm^2	Elongation %
1.	UVAW-78	1603	0.79	very soft	-	-
			0.87	very soft	-	-
			0.95	A - 20	9.21	300
			1.03	A - 26	11.00	234
2.	UVAW-79	748	0.79	A - 34	15.13	233
			0.87	A - 40	18.76	183
			0.95	A - 60	33.03	176
			1.03	A - 70	68.15	180
3.	UVAW-80	426	0.79	A - 60	61.12	180
			0.87	A - 96	305.32	113
			0.95	D - 68	352.6	80
			1.03	D - 85	395.67	5
4.	UVAW-81	1020	1.03	A - 60	54.34	250
5.	UVAW-82	898	1.03	A - 50	23.43	144

TABLE - 35

Swelling Behavior of PU Elastomer in Benzene

Sr. No.	Polyol code	NCO/OH	Weight of sample g	Weight of swollen sample, g	Solvent absorbed %	Weight of dry sample g	Sol %	Gel %
1.	UVAW-78	0.95	1.4228	2.5281	77.7	1.2168	14.5	85.5
2.	UVAW-78	1.03	1.4466	2.5901	79.0	1.2863	11.1	88.9
3.	UVAW-79	0.79	1.2180	2.1266	74.6	1.0879	10.7	89.3
4.	UVAW-79	0.87	1.3980	2.0242	44.8	1.3255	5.2	94.8
5.	UVAW-79	0.95	1.4379	2.0394	41.8	1.3919	3.2	69.8
6.	UVAW-79	1.03	1.5326	2.0180	31.7	1.5125	1.3	98.7
7.	UVAW-80	0.79	1.3993	1.6464	17.6	1.3600	2.8	97.2
8.	UVAW-80	0.87	1.4376	1.6264	13.1	1.4407*	-	100.0
9.	UVAW-80	0.95	1.4588	1.5853	8.7	1.4608*	-	100.0
10.	UVAW-80	1.03	1.3386	1.4384	7.4	1.3390*	-	100.0
11.	UVAW-81	1.03	1.5602	3.0292	94.4	1.4819	5.0	95.0
12.	UVAW-82	1.03	1.3602	2.0257	48.9	1.2765	6.1	93.9

* The small increase in the weight, even after drying was observed, indicating high crosslinking which prevented the total removal of absorbed solvent.

TABLE - 36

Swelling Behavior of PU Elastomer in Ethyl Acetate

Sr. No.	Polyol code	NCO/OH	Weight of sample g	Weight of swollen sample, g	Solvent absorbed %	Weight of dry sample g	Sol %	Gel %
1.	UVAW-78	0.79	1.5958	4.0395	153.1	1.1424	28.4	71.6
2.	UVAW-78	0.87	1.5271	3.6741	140.6	1.1900	22.1	87.9
3.	UVAW-79	0.79	1.4160	2.6243	85.3	1.1449	19.1	80.9
4.	UVAW-79	0.87	1.2689	2.2935	80.7	1.0986	13.4	86.6
5.	UVAW-79	0.97	1.3446	2.3406	74.1	1.2354	8.1	91.9
6.	UVAW-79	1.03	1.5136	2.4367	60.1	1.4913	2.2	97.8
7.	UVAW-80	0.79	1.4168	2.2285	57.3	1.2703	10.3	89.7
8.	UVAW-80	0.87	1.5907	2.3060	45.0	1.5642	1.6	98.4
9.	UVAW-80	0.95	1.3553	1.8990	40.3	1.3475	0.4	99.6
10.	UVAW-80	1.03	1.3712	1.7190	25.3	1.3926*	-	100.0
11.	UVAW-81	1.03	1.4013	3.176	126.6	1.2900	7.9	92.1
12.	UVAW-82	1.03	1.2953	2.1191	63.6	1.1642	10.1	89.9

* The small increase in the weight, even after drying indicated the high crosslinking which prevented the total removal of absorbed solvent.

TABLE - 37

Mechanical Properties of Rigid PU Foams

Sr.No.	Formulation	Density g/cc	Tensile strength kg/cm^2	Copressive strength kg/cm^2	Flexural strength kg.cm^2
1.	0.3	0.30	32.8 (±4)	31.7 (±3)	63.7 (±3)
2.	0.43	0.43	58.6 (±7)	69.3 (±10)	97.0 (±5)
3.	0.3 EX	0.30	38.5 (±2)	38.7 (±4)	50.1 (±5)
5.	0.43 EX	0.43	59.3 (±6)	63.3 (±5)	140 (±7)

TABLE - 38

PU Elastomer Formulations Analyzed by Dynamic Mechanical Analysis

Sr.No.	Polyol used	Molecular weight of polyol (end group)	Isocyanate Index (II)
1.	UVAW-78	1603	87
2.	UVAW-78	1603	95
3.	UVAW-79	748	79
4.	UVAW-79	748	87
5.	UVAW-79	748	95
6.	UVAW-79	748	103
7.	UVAW-80	426	79
8.	UVAW-80	426	87
9.	UVAW-80	426	95
10.	UVAW-81	1020	103
11.	UVAW-82	898	103

TABLE - 39

Weight Composition of the Different Chemical Moieties in PU Network

Sr.No.	Polyol code	NCO/OH	Weight % of Moieties			
			Terephthalic	Adipic	Glycol	PMDI
1.	UVAW-78	0.87	12.69	39.88	35.01	12.47
2.	UVAW-78	0.95	12.55	39.38	34.62	13.45
3.	UVAW-79	0.79	11.59	33.12	33.59	21.70
4.	UVAW-79	0.87	11.34	32.42	32.88	23.36
5.	UVAW-79	0.95	11.10	31.74	32.19	24.97
6.	UVAW-79	1.03	10.88	31.09	31.53	26.50
7.	UVAW-80	0.79	11.04	25.37	30.89	32.70
8.	UVAW-80	0.87	10.69	24.58	29.92	34.81
9.	UVAW-80	0.95	10.36	23.82	29.00	36.82
10.	UVAW-81	1.03	12.57	31.68	35.82	20.93
11.	UVAW-82	1.03	13.92	23.45	39.51	23.12

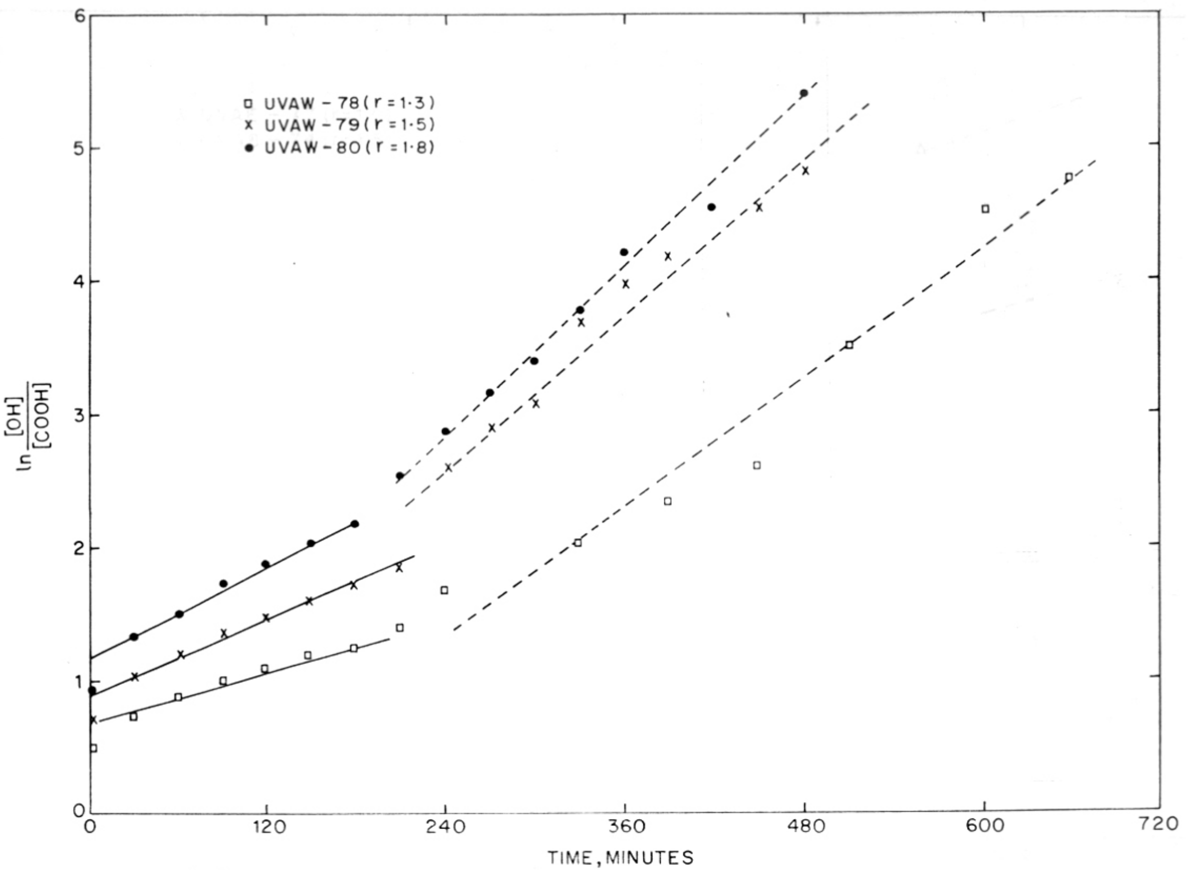


FIGURE 28 : $\ln\frac{[OH]}{[COOH]}$ VERSUS TIME FOR POLYESTERIFICATION OF UVWE-3 AT DIFFERENT REACTANT RATIOS AT 170°C (——) AND 200°C (- - - -)

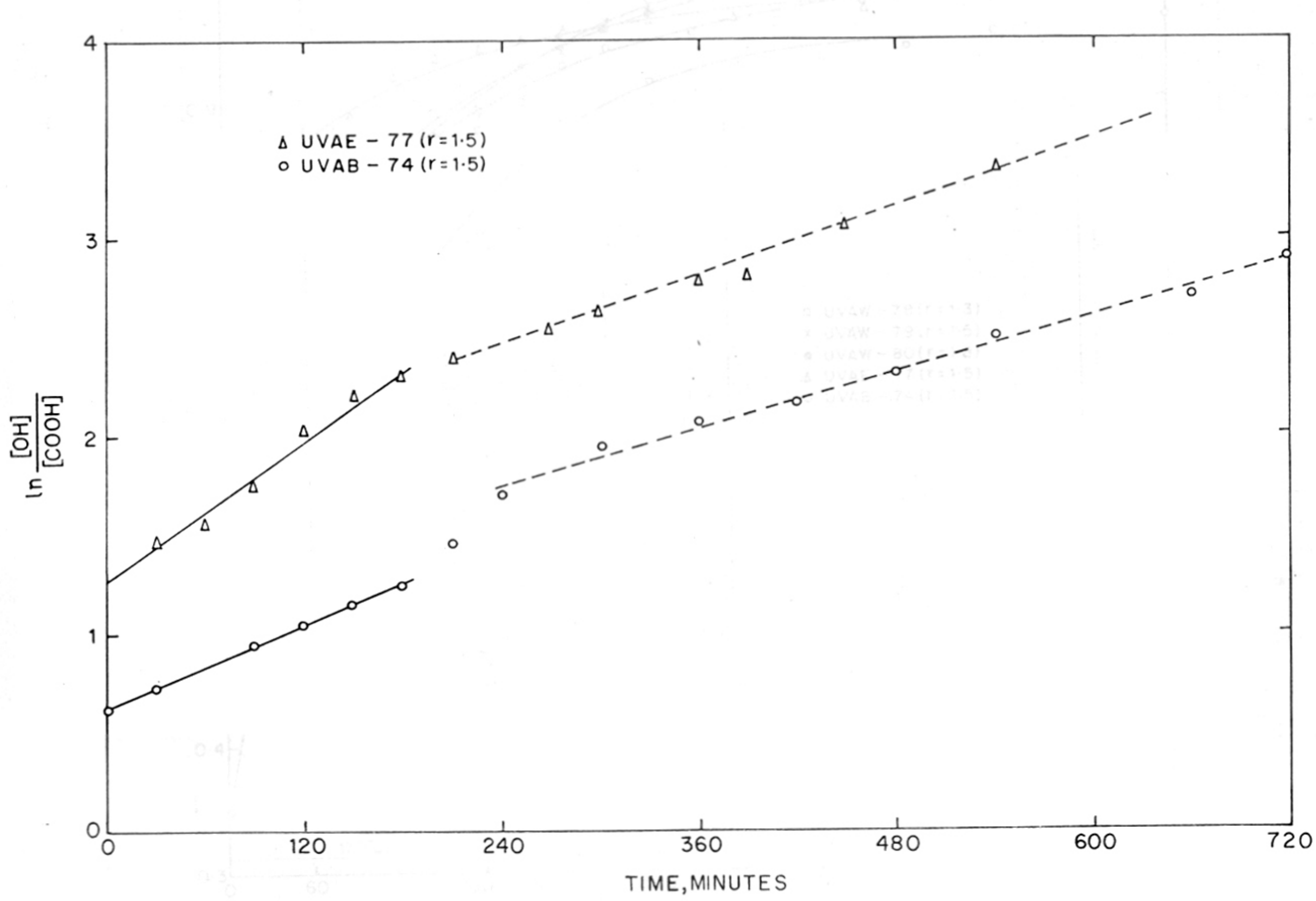


FIGURE 29: $\ln\frac{[OH]}{[COOH]}$ VERSUS TIME FOR POLYESTERIFICATION OF EG AND BHET AT FIXED REACTANT RATIO, AT 170°C (—) AND 200°C (----)

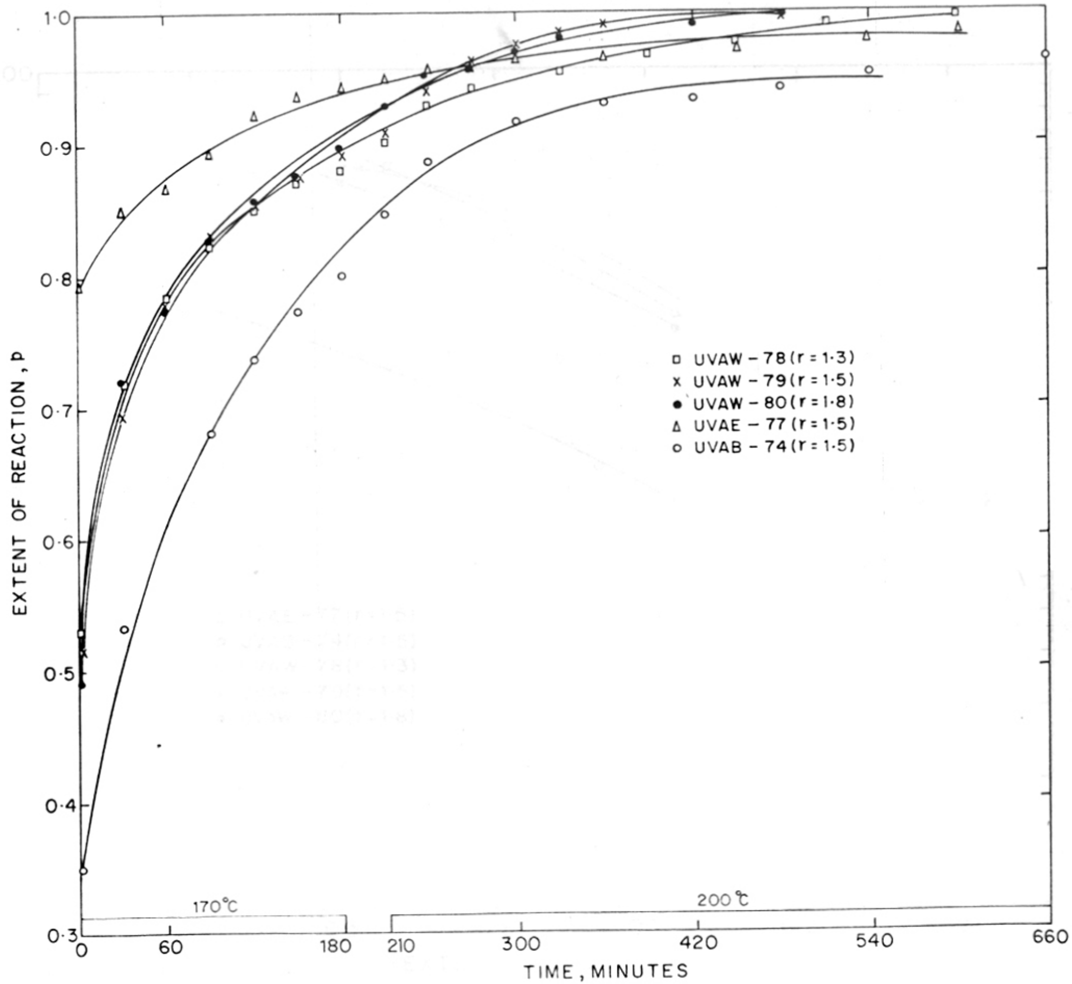


FIGURE 30: CHANGE IN THE EXTENT OF REACTION WITH TIME FOR POLYESTERIFICATION OF UVWE-3, EG AND BHET WITH ADIPIC ACID

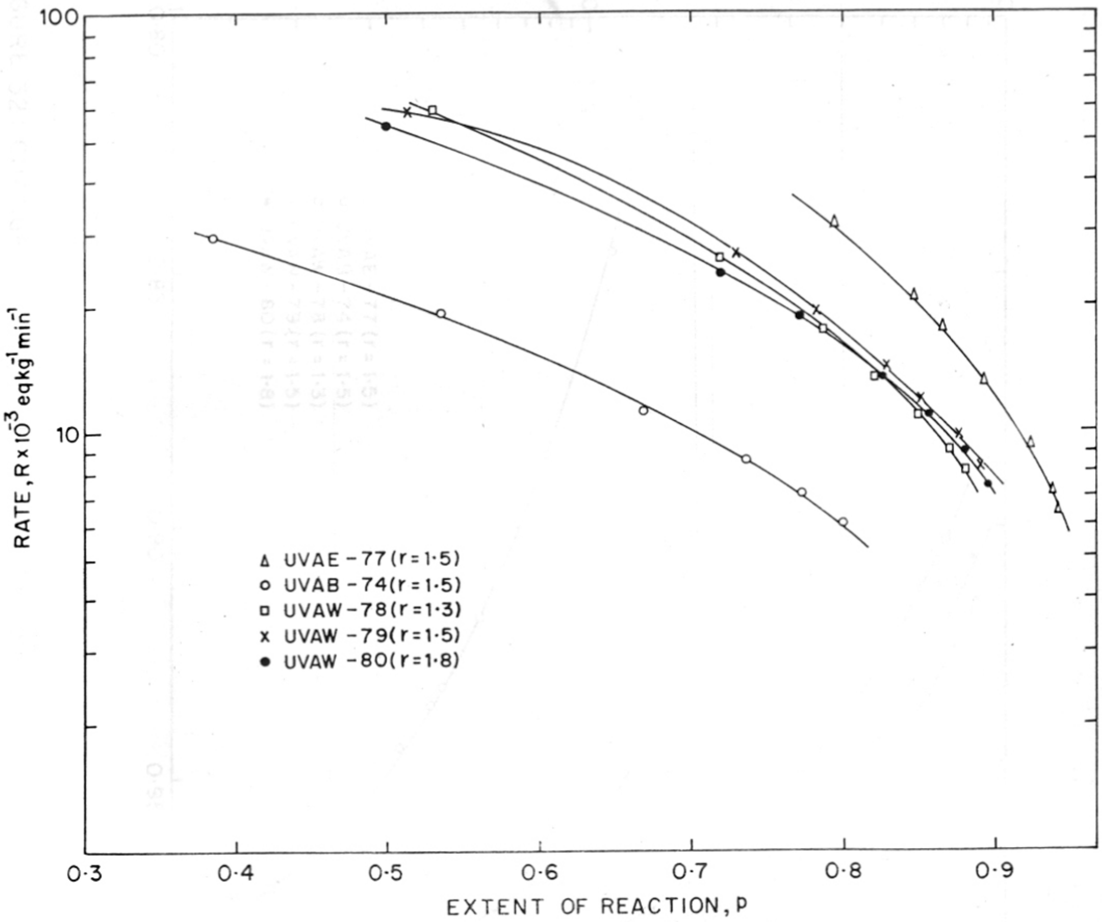


FIGURE 31: CHANGE IN RATE OF REACTION WITH EXTENT OF REACTION AT 170°C

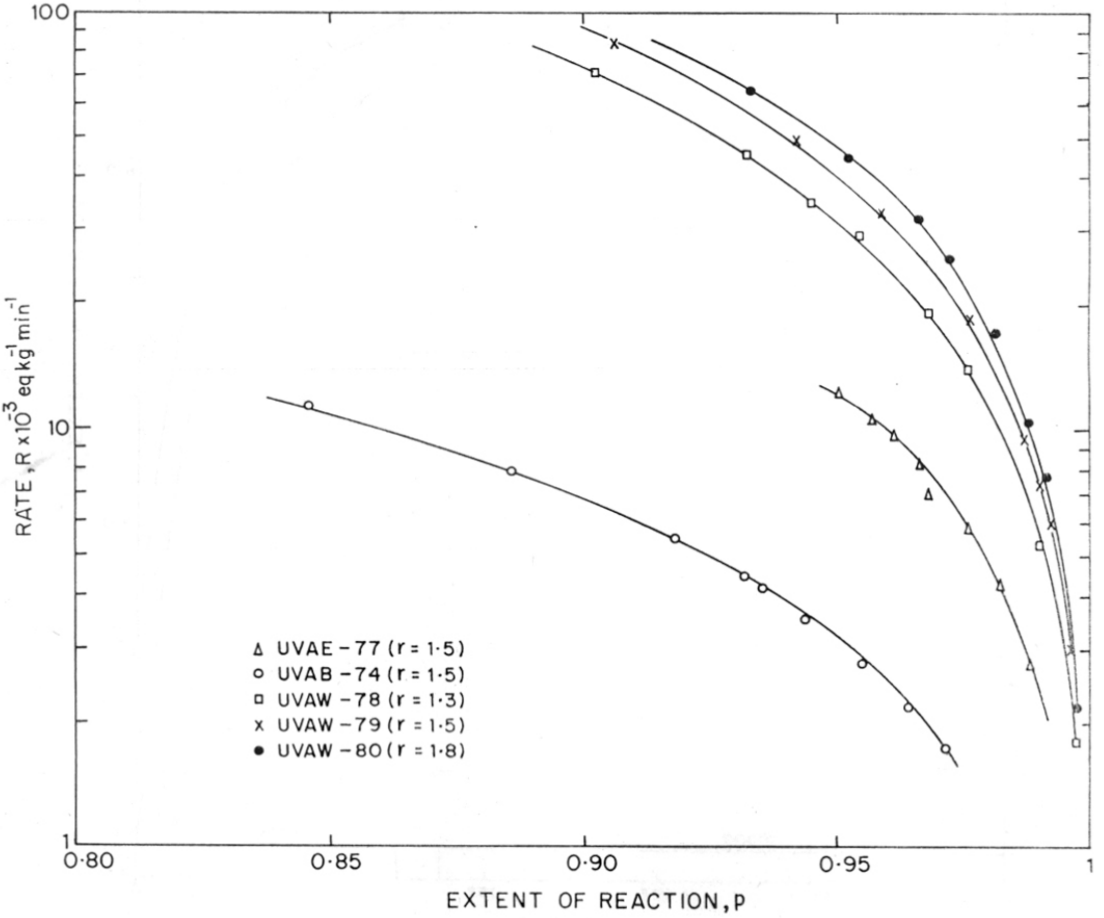


FIGURE 32: CHANGE IN RATE OF REACTION WITH EXTENT OF REACTION AT 200°C

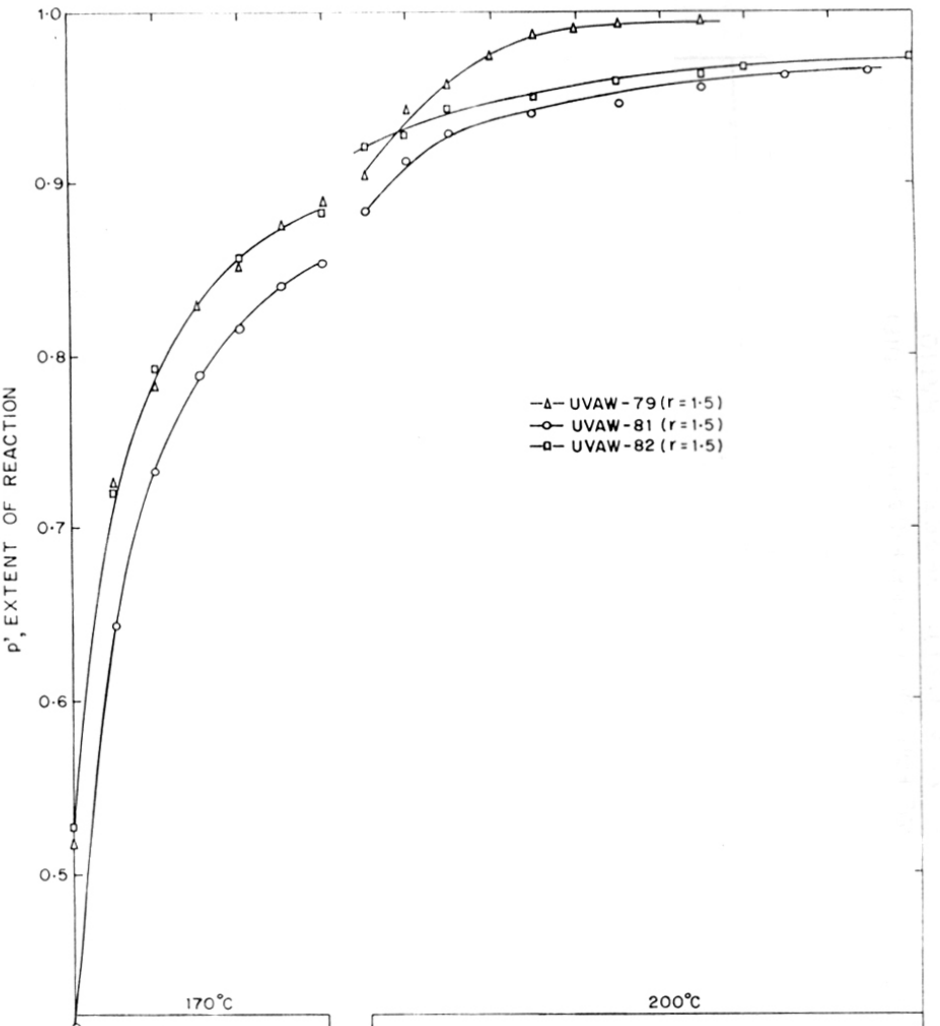


FIGURE 33: INCREASE IN THE EXTENT OF REACTION WITH TIME FOR POLYESTERIFICATION OF DIFFERENT TYPES OF GLYCOLS

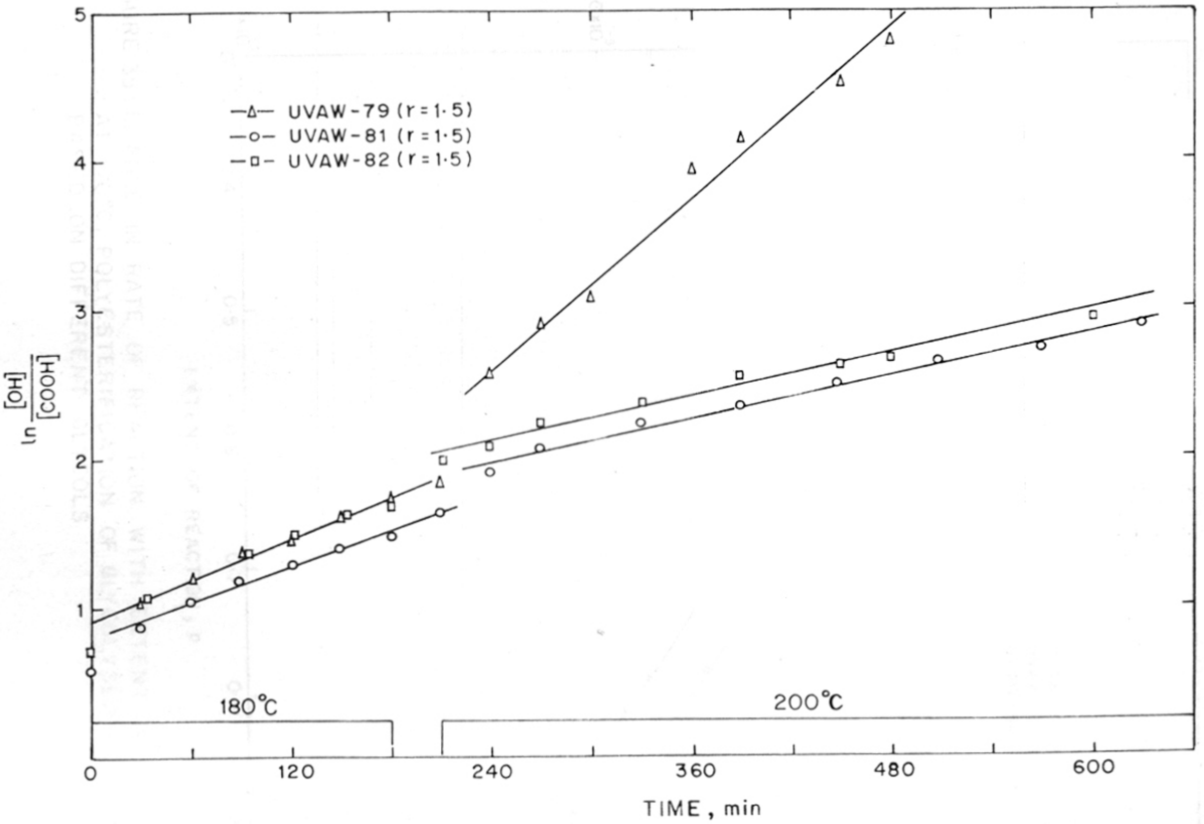


FIGURE 34: $\ln \frac{[OH]}{[COOH]}$ VERSUS TIME FOR POLYESTERIFICATION OF DIFFERENT TYPES OF GLYCOLS AT A FIXED REACTANT RATIO

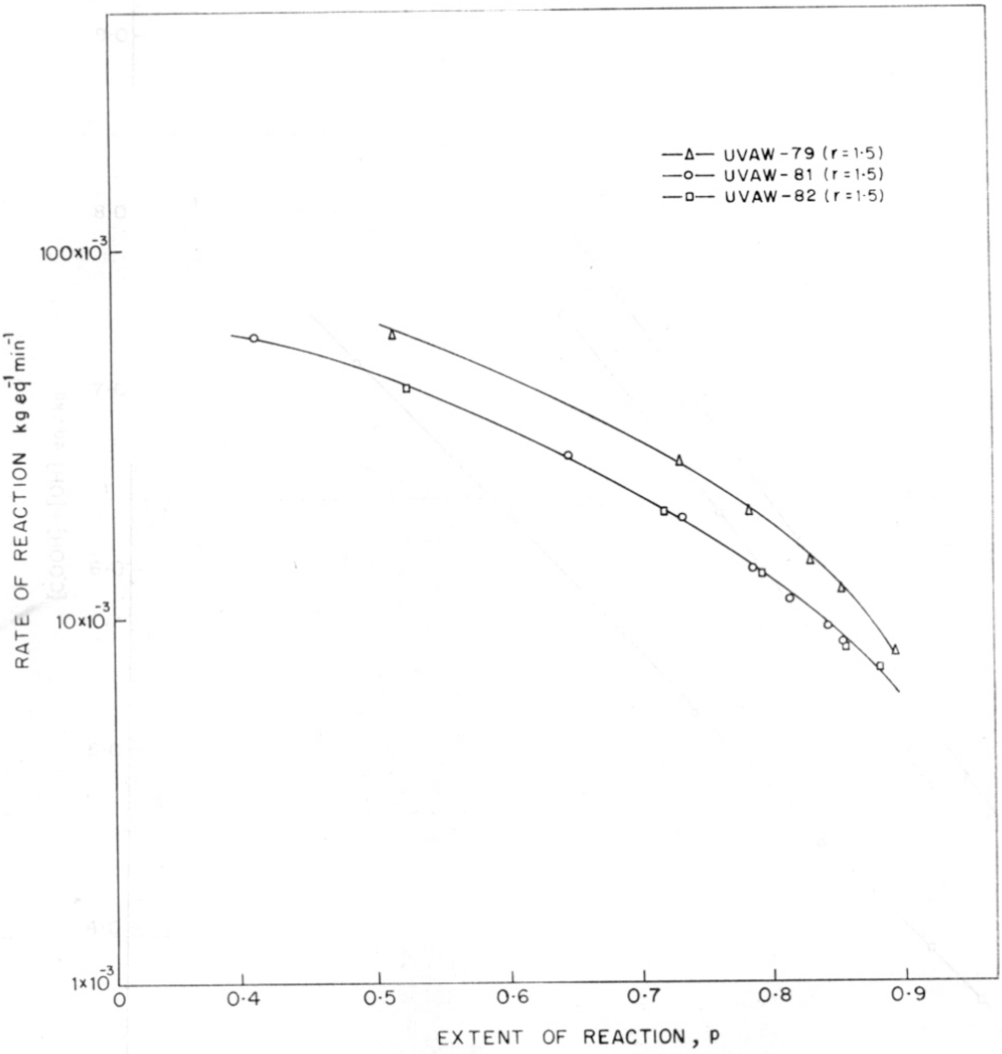


FIGURE 35 : CHANGE IN RATE OF REACTION WITH EXTENT OF REACTION AT 170°C, POLYESTERIFICATION OF GLYCOLYSED PET WASTE, BASED ON DIFFERENT GLYCOLS

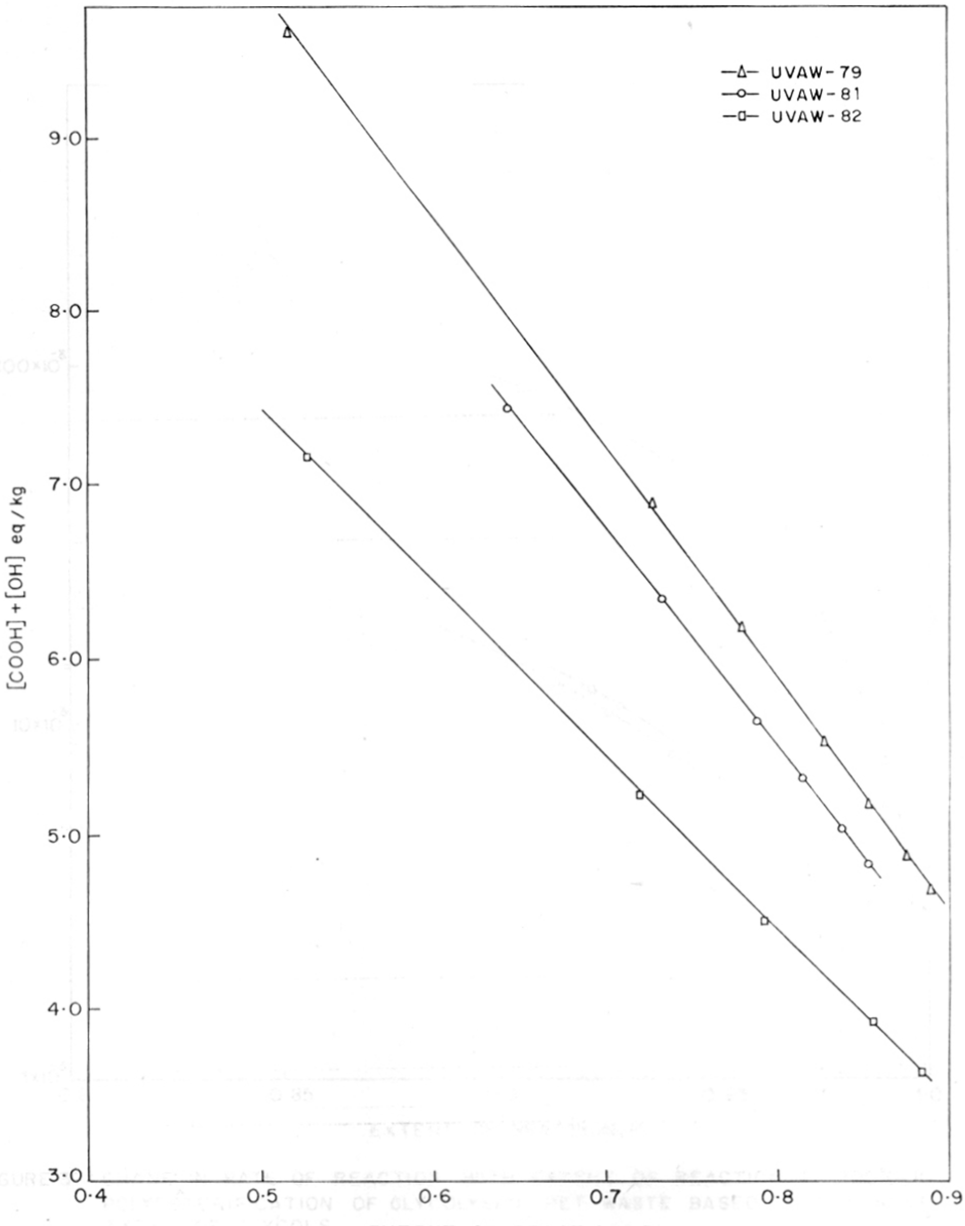


FIGURE 36 : VARIATION IN CONCENTRATION OF FUNCTIONAL GROUPS WITH TIME AT 170°C IN POLYESTERIFICATION OF GLYCOLYSED PET WASTE BASED ON DIFFERENT GLYCOLS

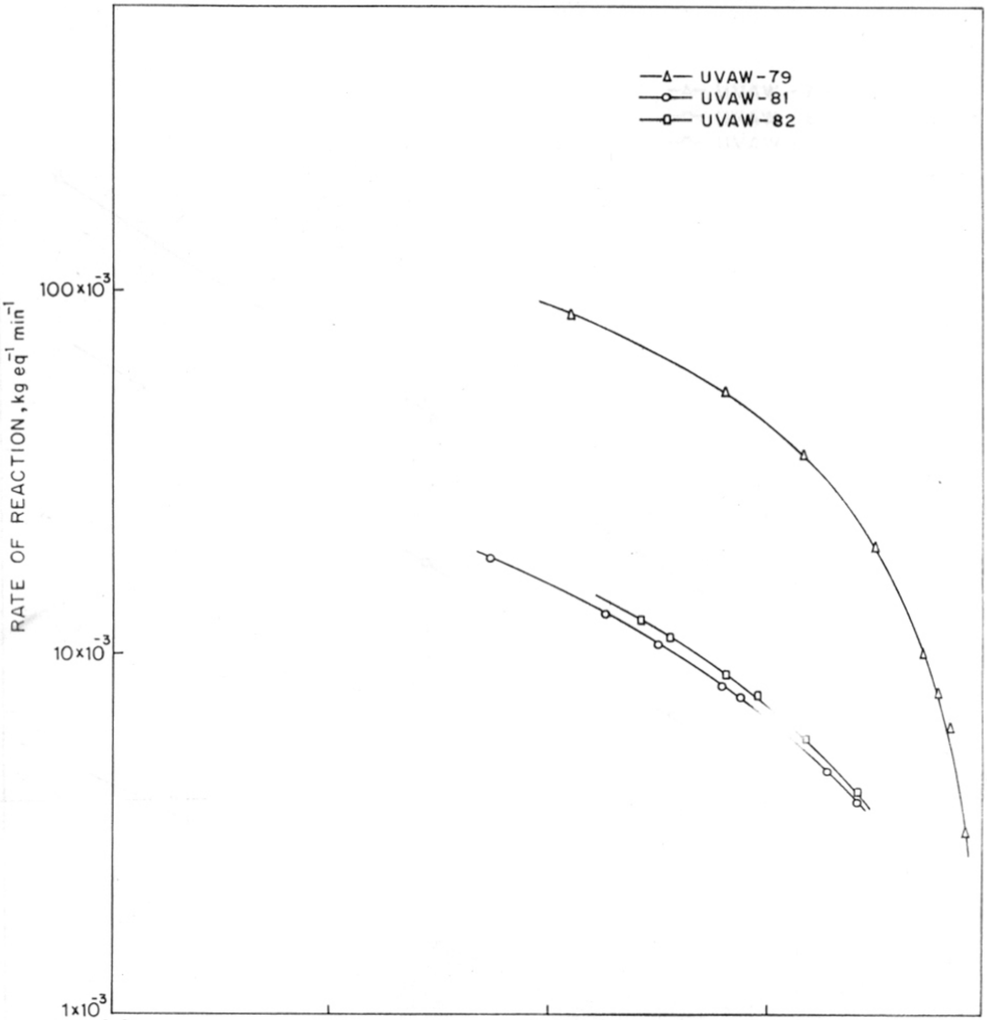


FIGURE 37 : CHANE IN RATE OF REACTION WITH EXTENT OF REACTION AT 200°C, IN POLYESTERIFICATION OF GLYCOLYSED PET WASTE BASED ON DIFFERENT TYPES OF GLYCOLS

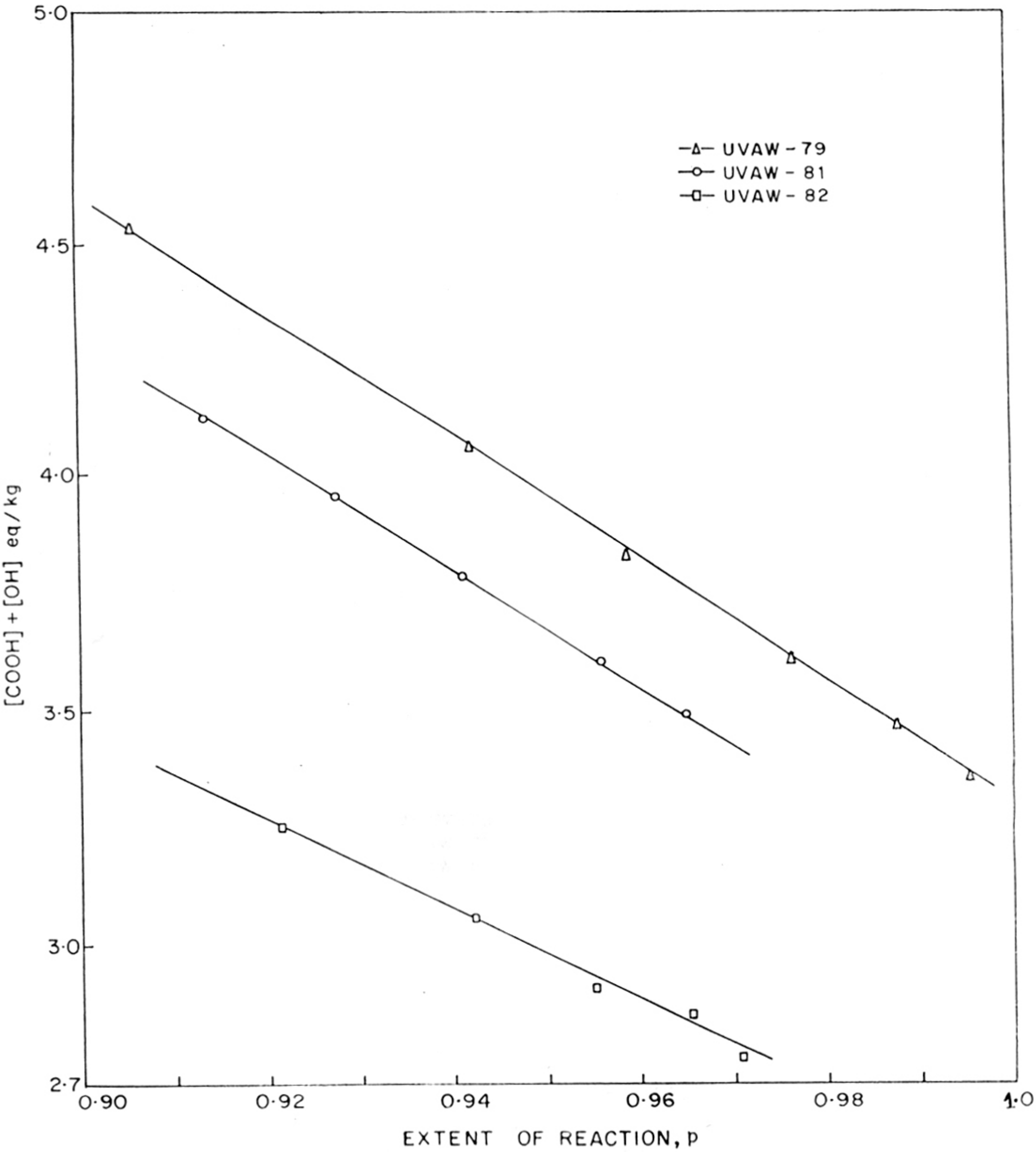


FIGURE 38: VARIATION IN CONCENTRATION OF FUNCTIONAL GROUPS WITH TIME AT 200°C, IN POLYESTERIFICATION OF GLYCOLYSED PET, BASED ON DIFFERENT GLYCOLS

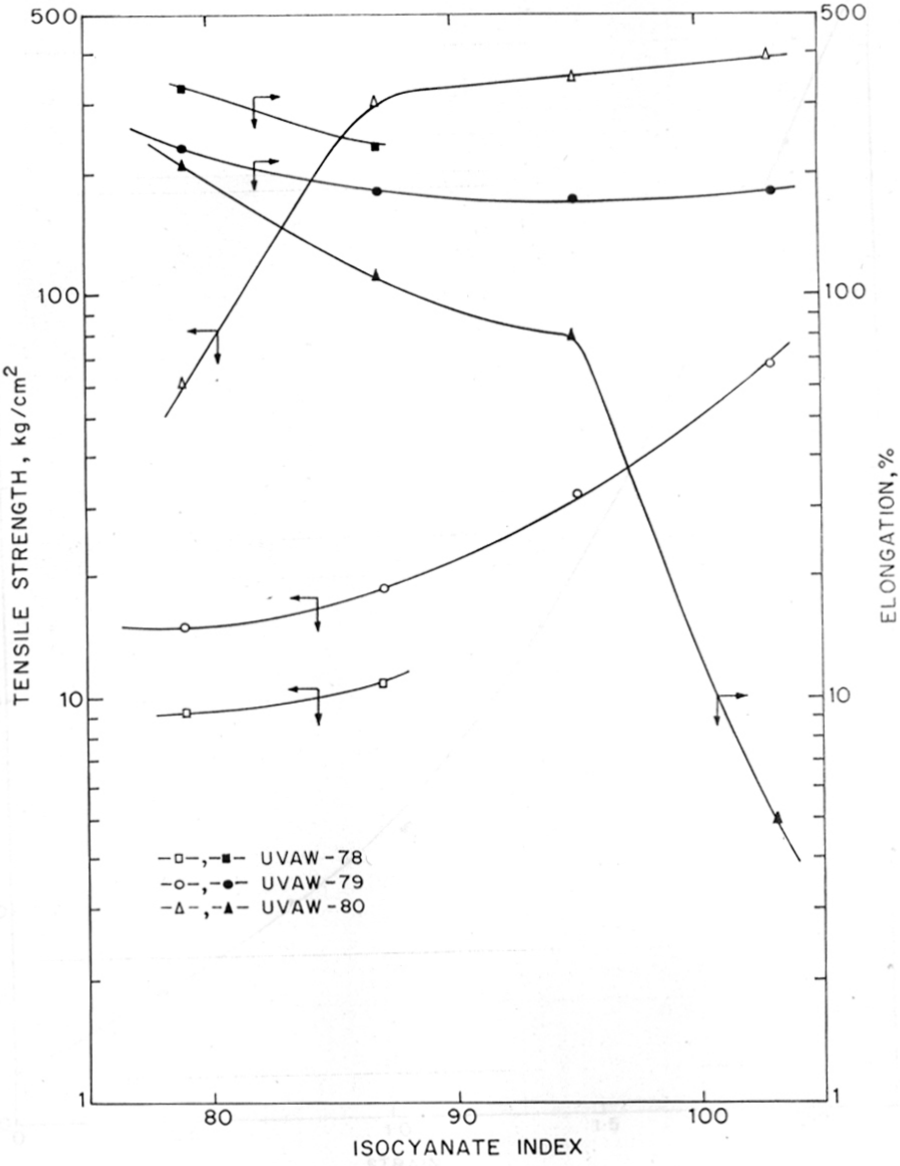


FIGURE 39: VARIATION IN TENSILE PROPERTIES OF PU ELASTOMERS, WITH ISOCYANATE INDEX

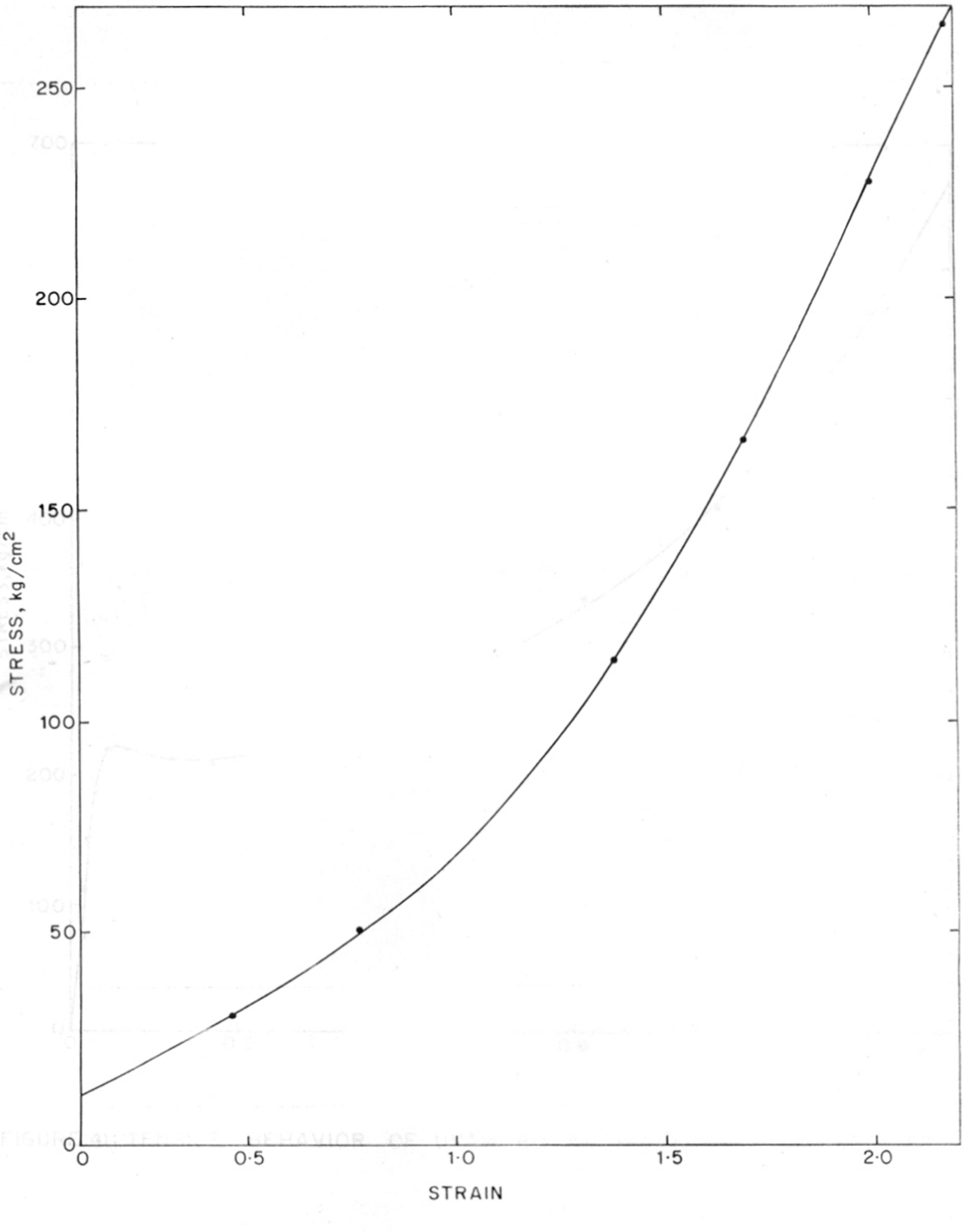


FIGURE 40: TENSILE BEHAVIOR OF UVAW-80 AT ISOCYANATE INDEX OF 79

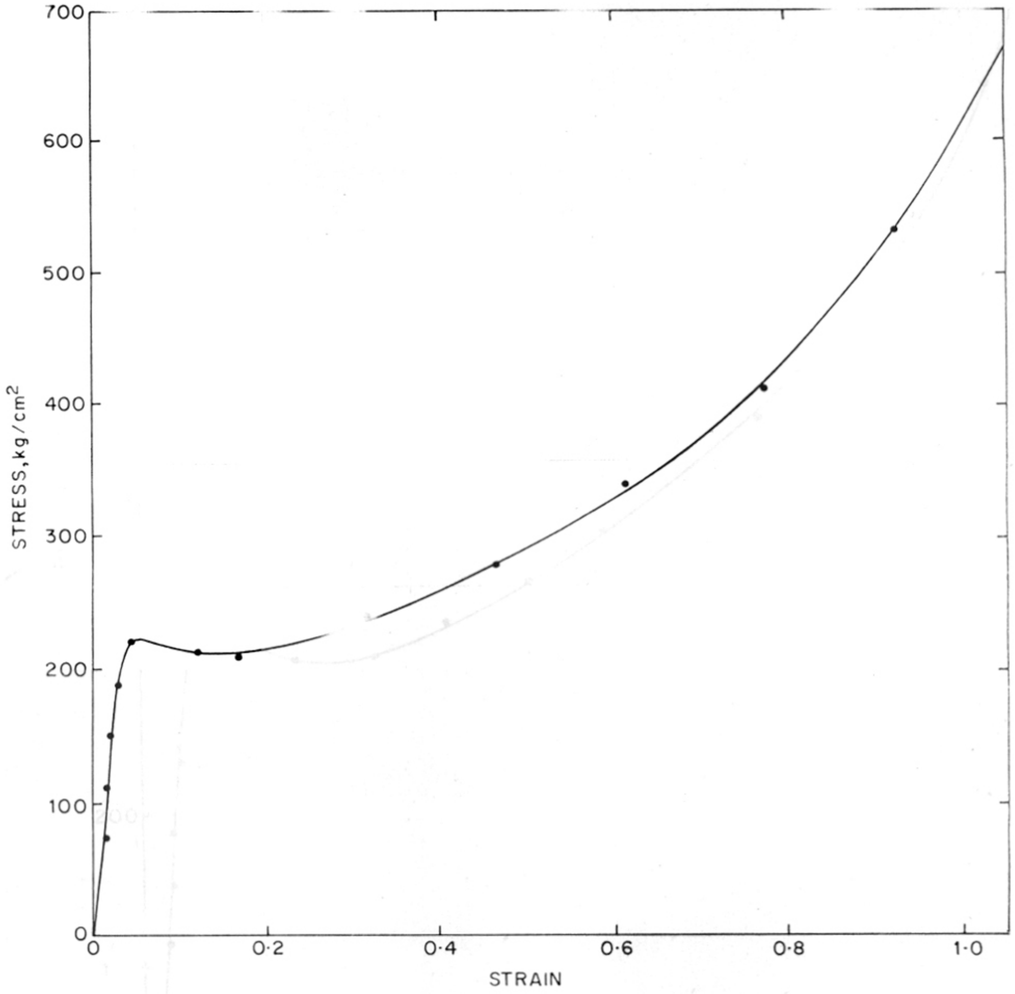


FIGURE 41: TENSILE BEHAVIOR OF UVAW-80 AT ISOCYANATE INDEX OF 87

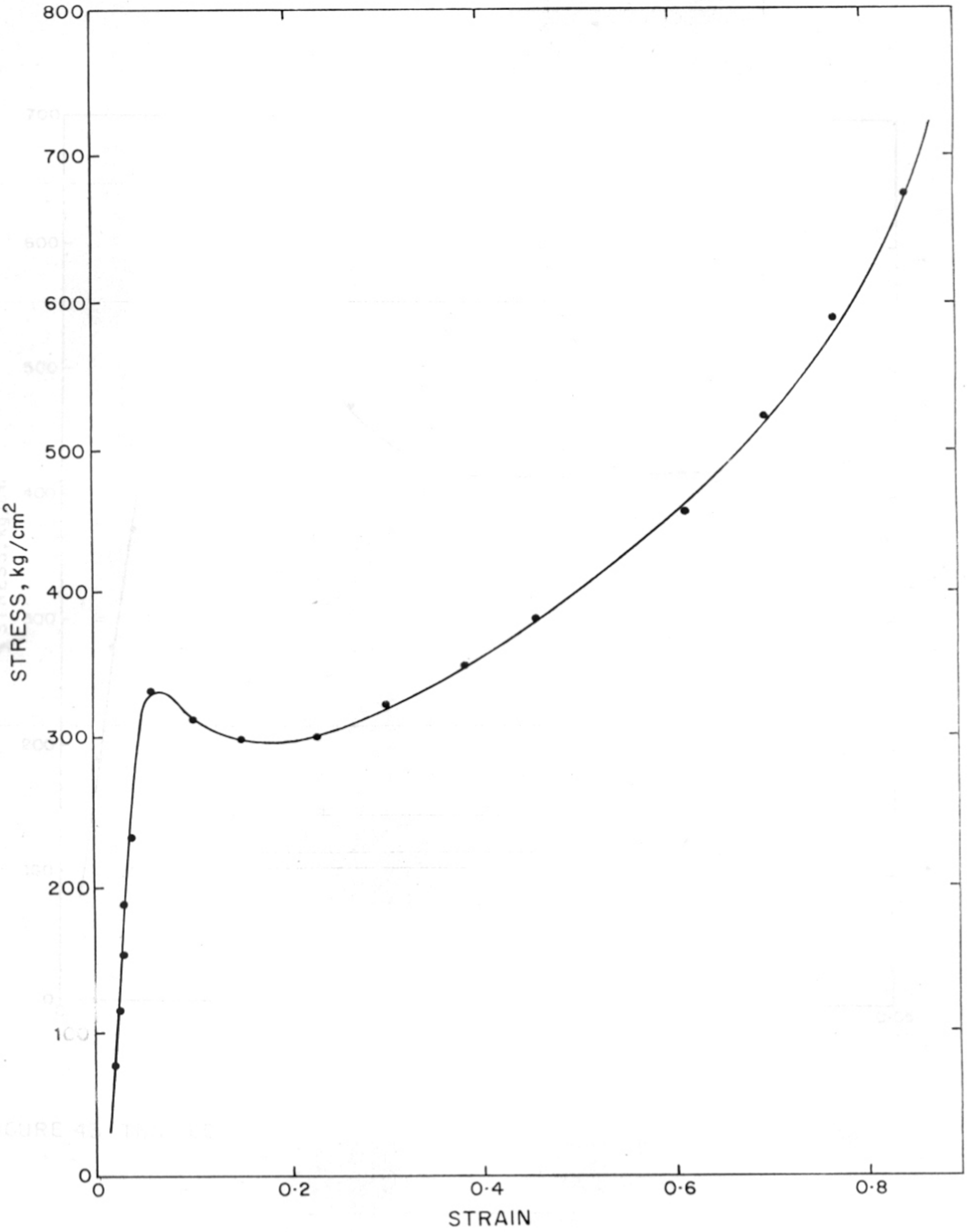


FIGURE 42: TENSILE BEHAVIOR OF UVAW-80 AT ISOCYANATE INDEX OF 95

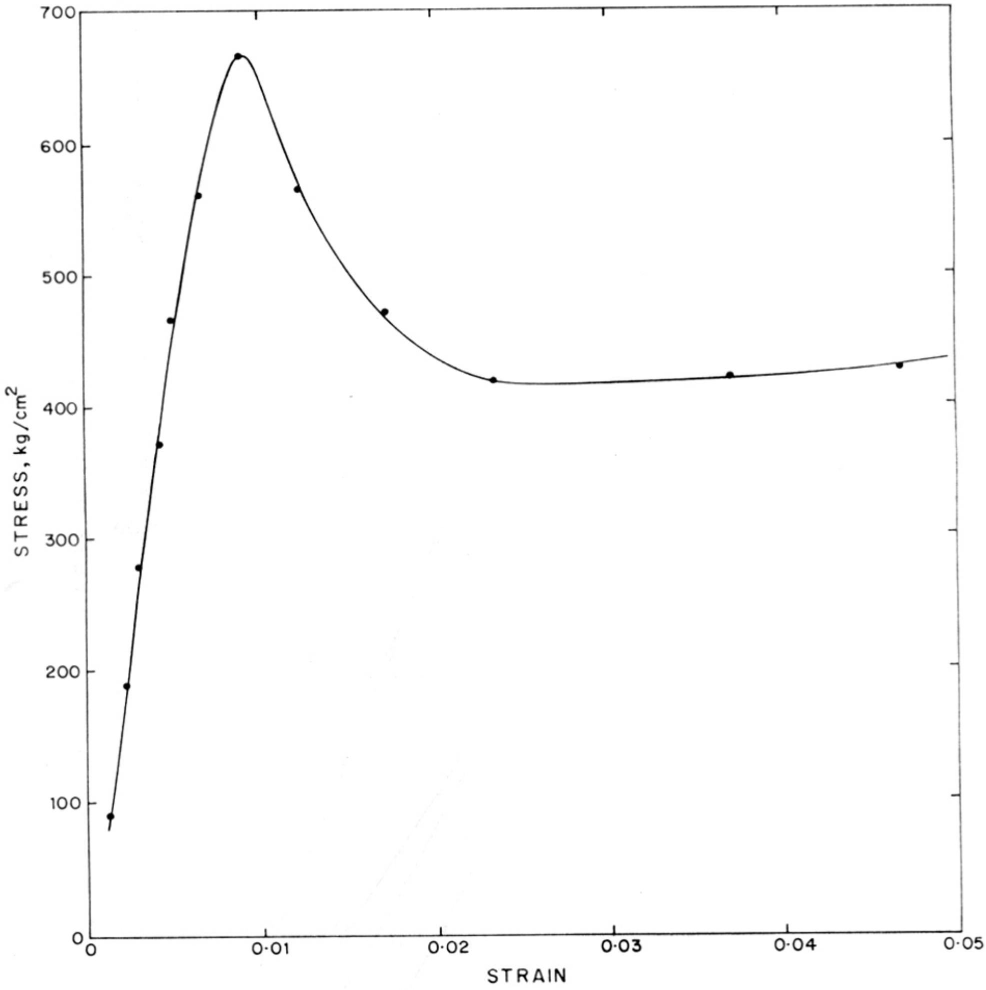


FIGURE 43: TENSILE BEHAVIOR UVAW-80 AT ISOCYANATE INDEX OF 103

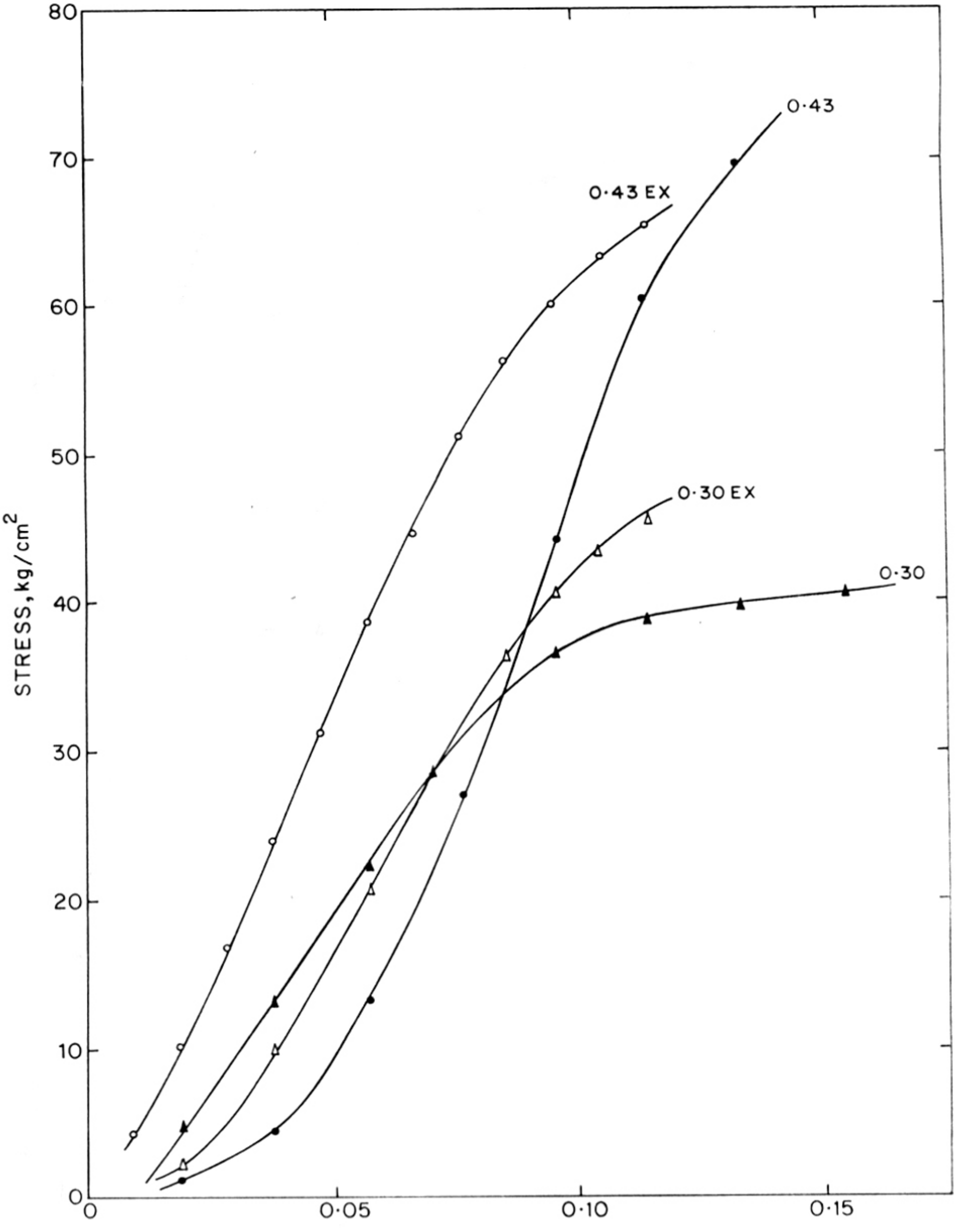


FIGURE 44: TENSILE BEHAVIOR OF RIGID FOAMS

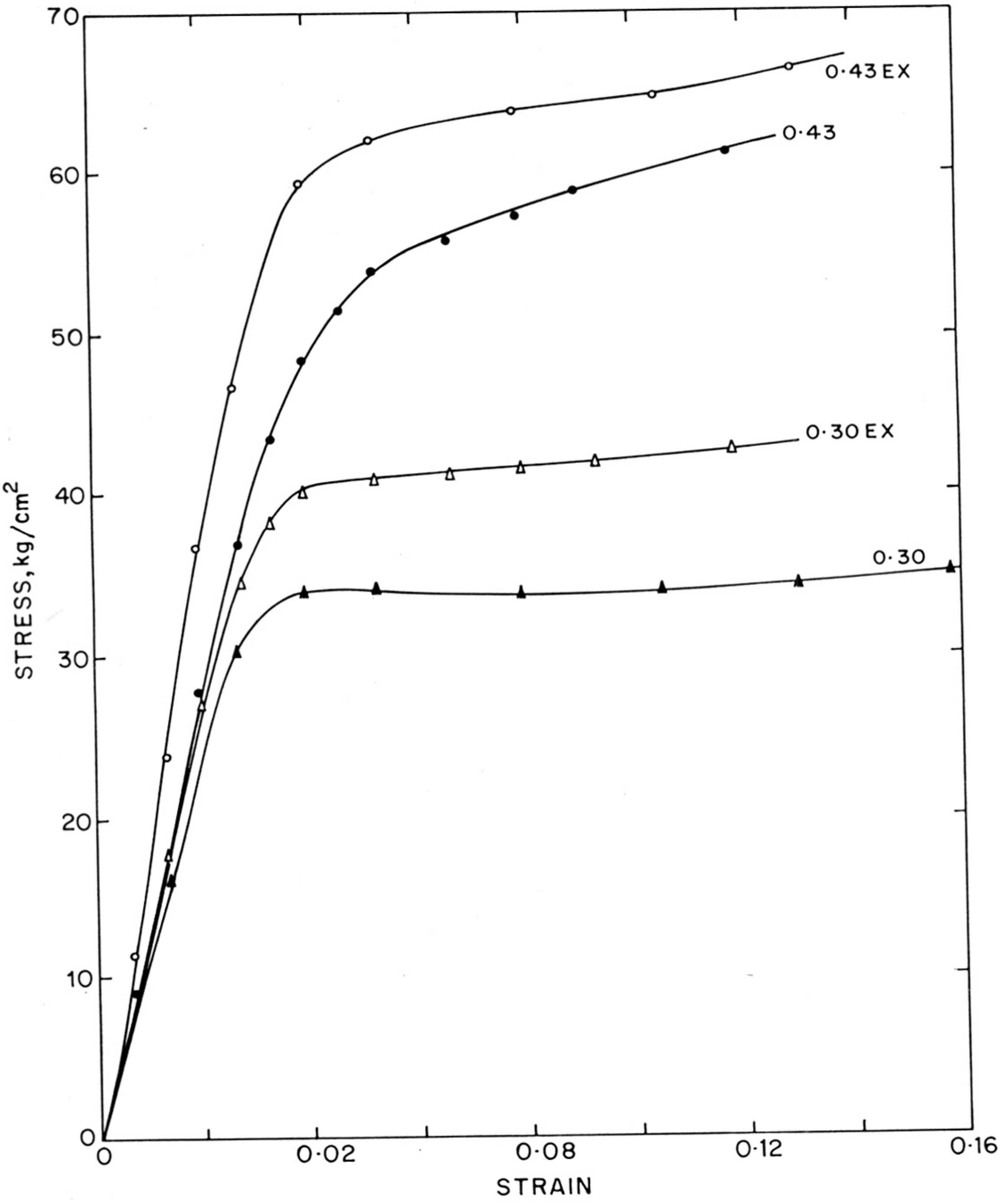
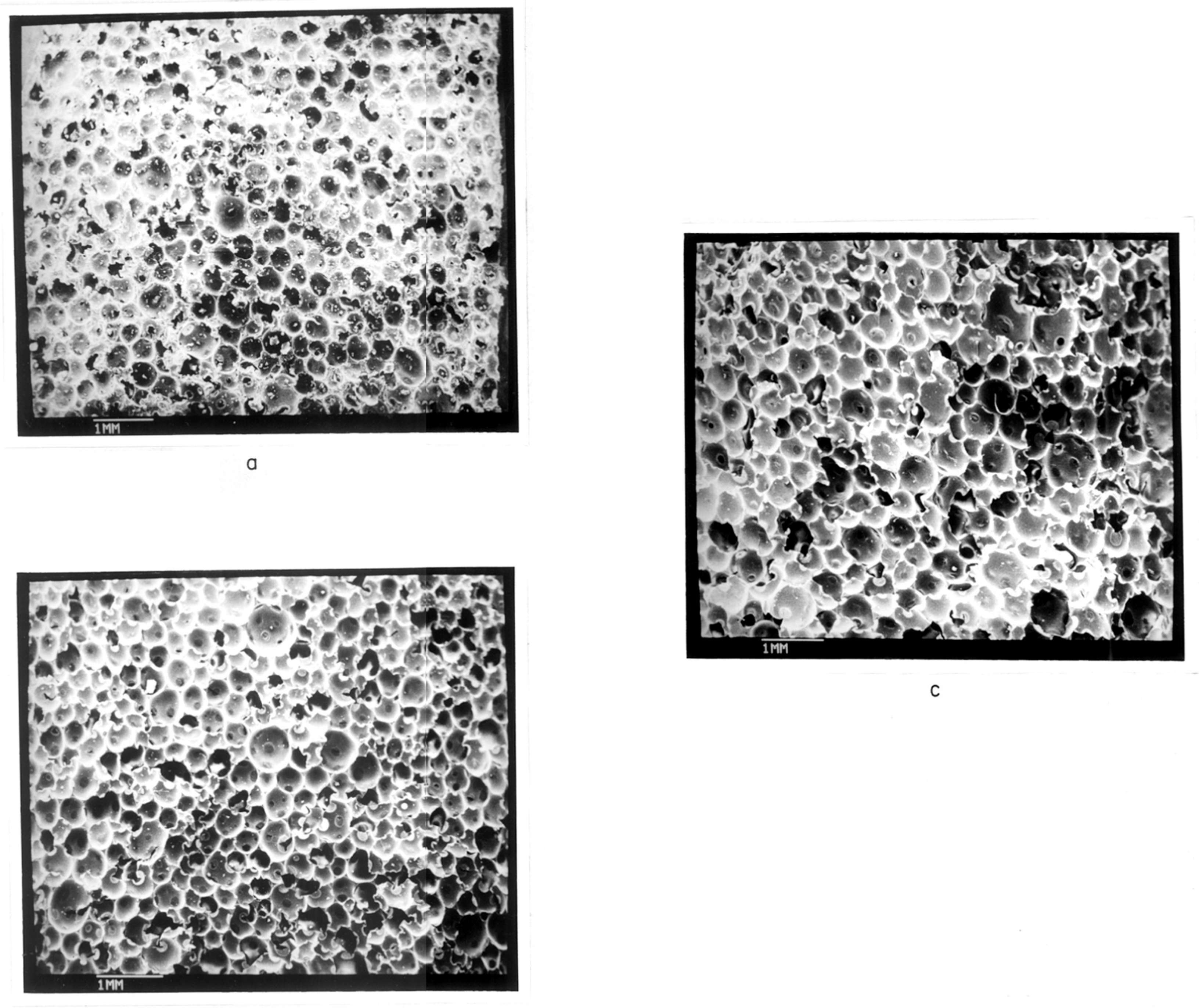


FIGURE 45: COMPRESSIVE BEHAVIOR OF RIGID FOAMS



a

b

c

FIGURE 46: MICROGRAPHS OF RIGID POLYURETHANE FOAMS DEPICTING THE CELL SIZE DISTRIBUTION: (a) 0·3, (b) 0·43, (c) 0·43 EX.

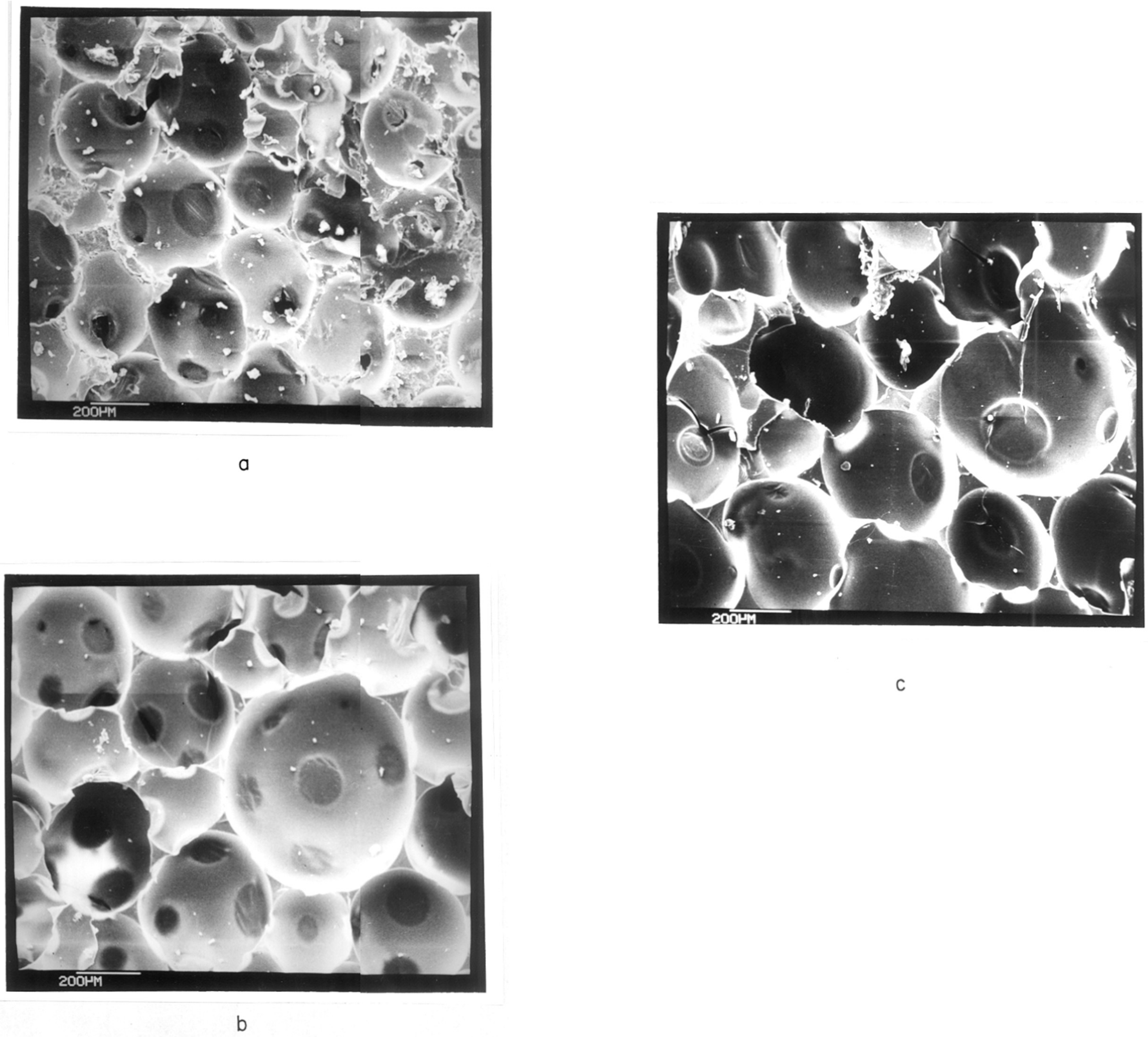


FIGURE 47: MICROGRAPHS OF RIGID POLYURETHANE FOAMS DEPICTING THE CELL SIZE (a) 0·3, (b) 0·43, (c) 0·43Ex

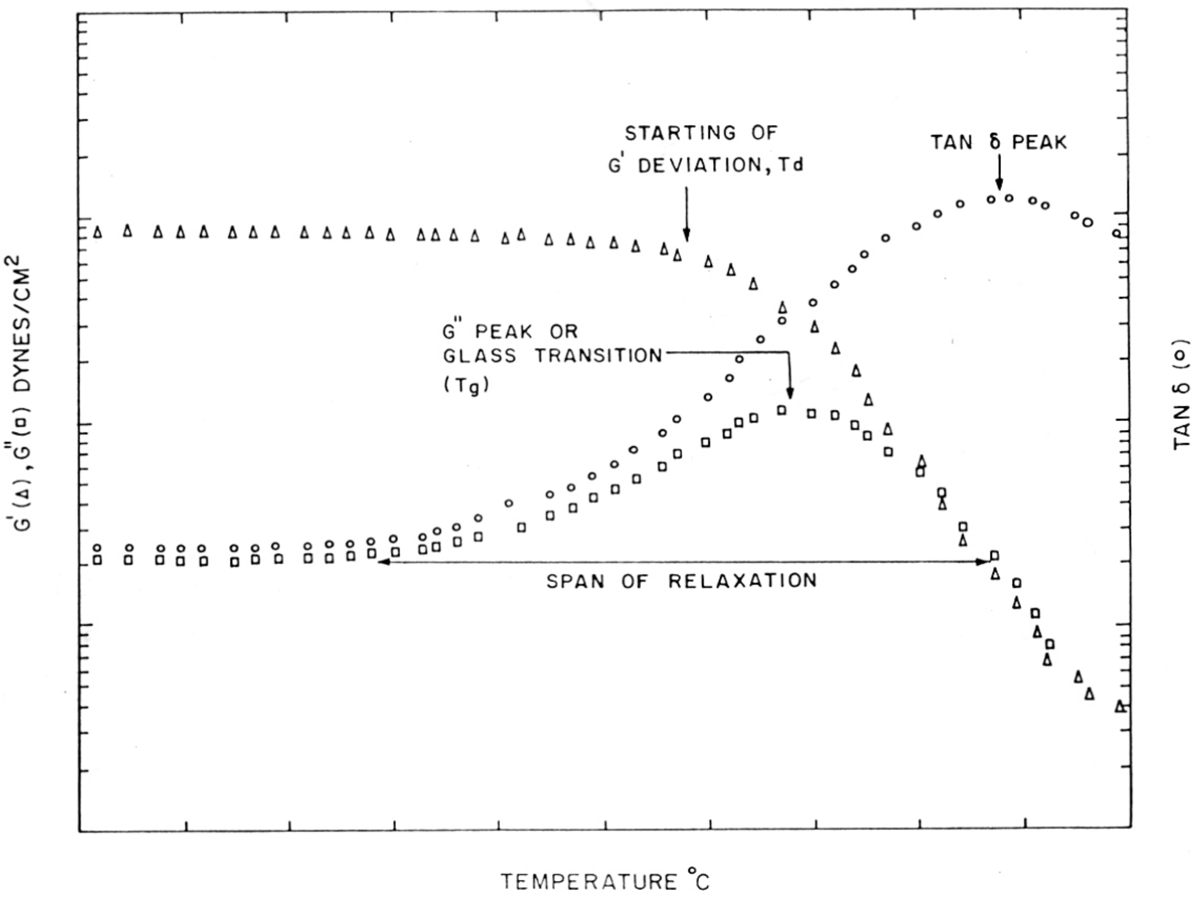


FIGURE 48a : TYPICAL VISCOELASTIC SPECTRUM ILLUSTRATING THE DYNAMIC MECHANICAL PARAMETERS

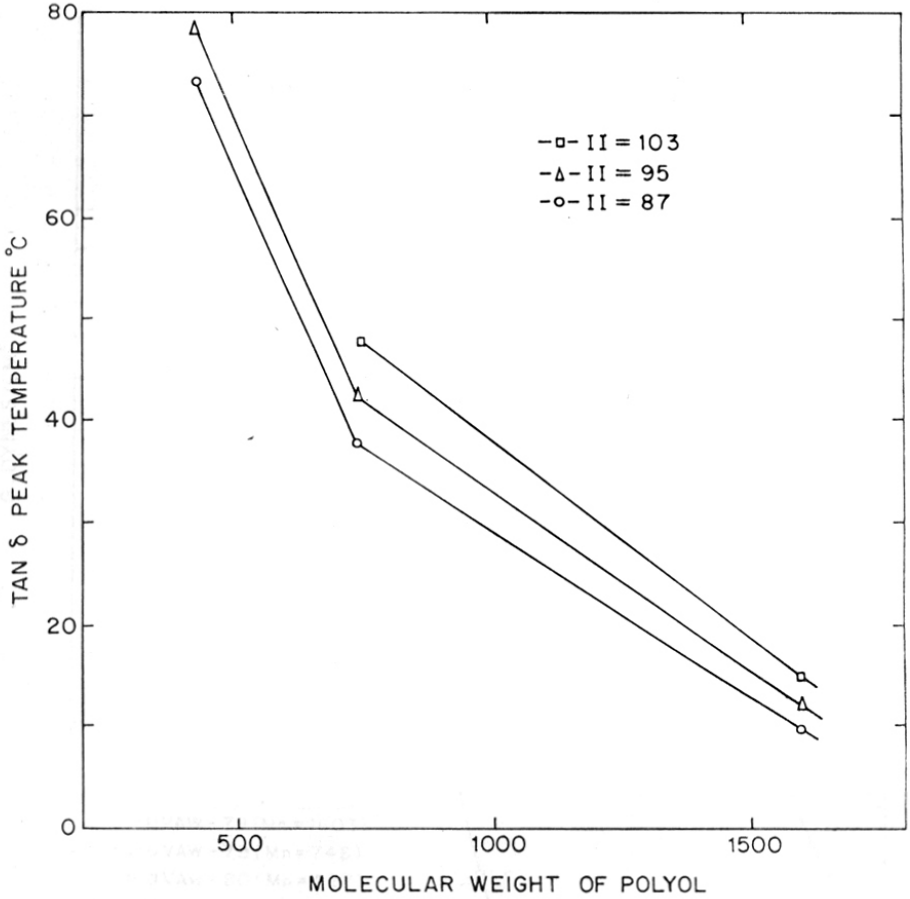


FIGURE 48: EFFECT OF MOLECULAR WEIGHT OF POLYOL ON THE TAN δ PEAK TEMPERATURE OF PU ELASTOMERS

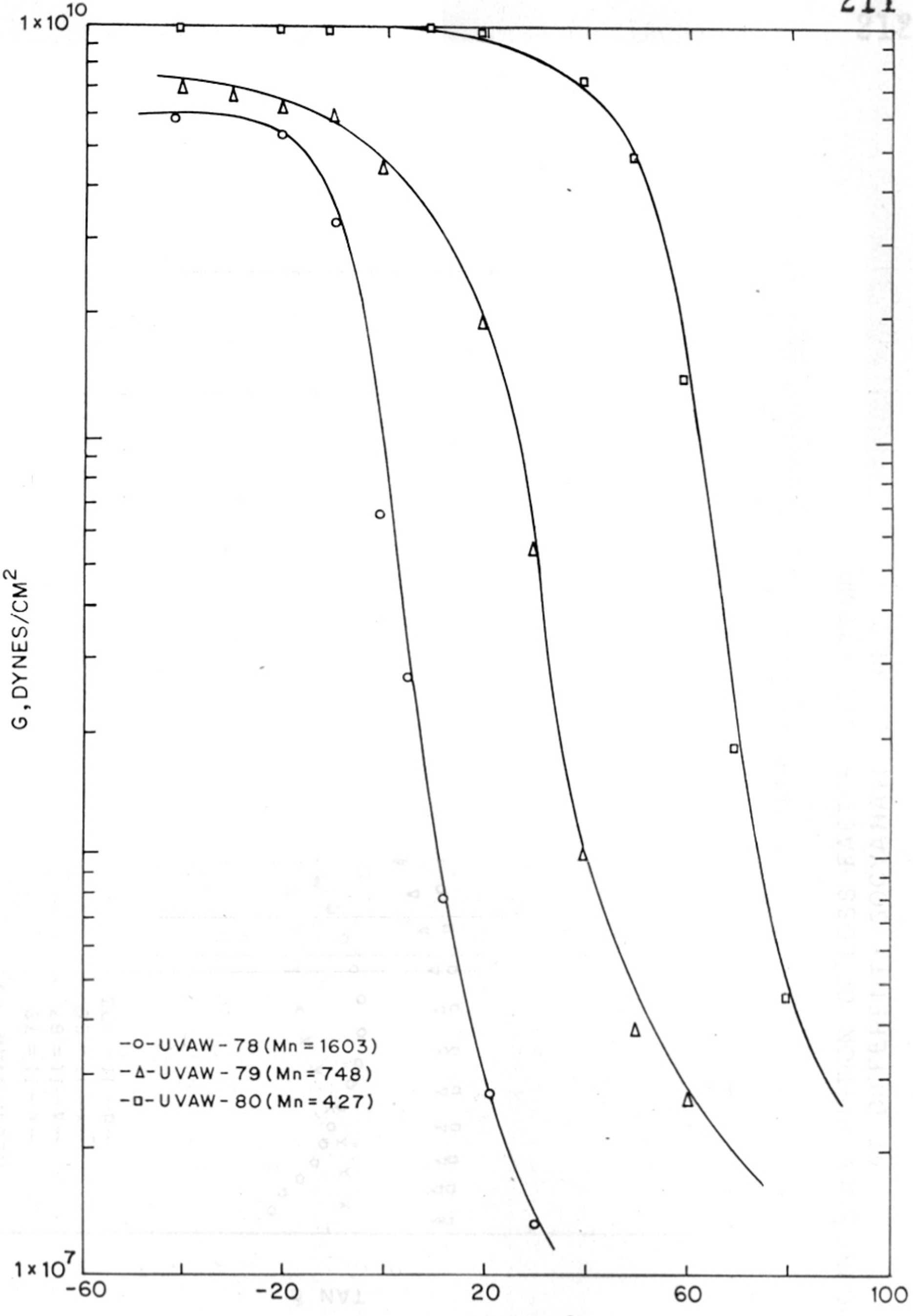


FIGURE 49: EFFECT OF MOLECULAR WEIGHT OF POLYOL ON STORAGE MODULUS OF PU ELASTOMERS AT ISOCYANATE INDEX OF 87

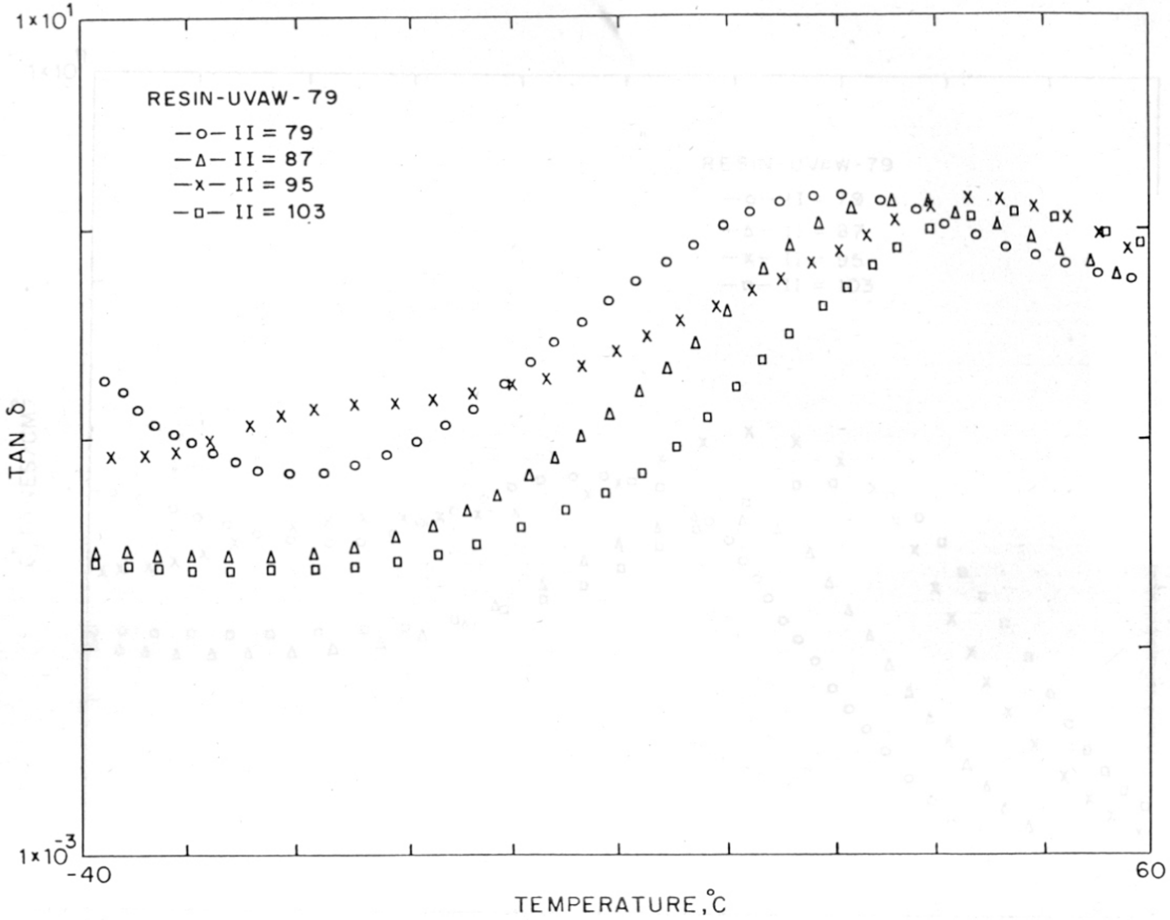


FIGURE 50: VARIATION OF LOSS FACTOR WITH TEMPERATURE FOR UVAW-79 AT DIFFERENT ISOCYANATE INDICES

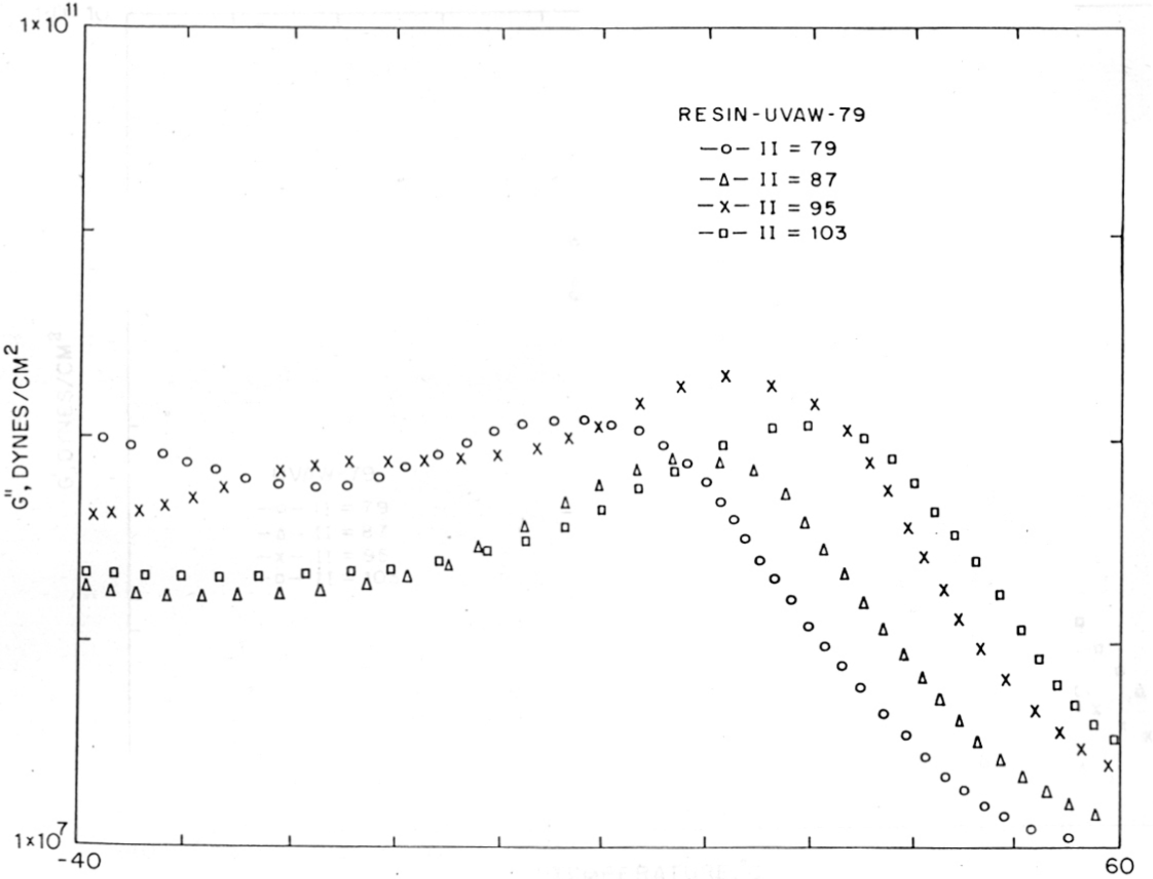


FIGURE 51: VARIATION OF LOSS MODULUS WITH TEMPERATURE FOR UVAW-79 AT DIFFERENT ISOCYANATE INDICES

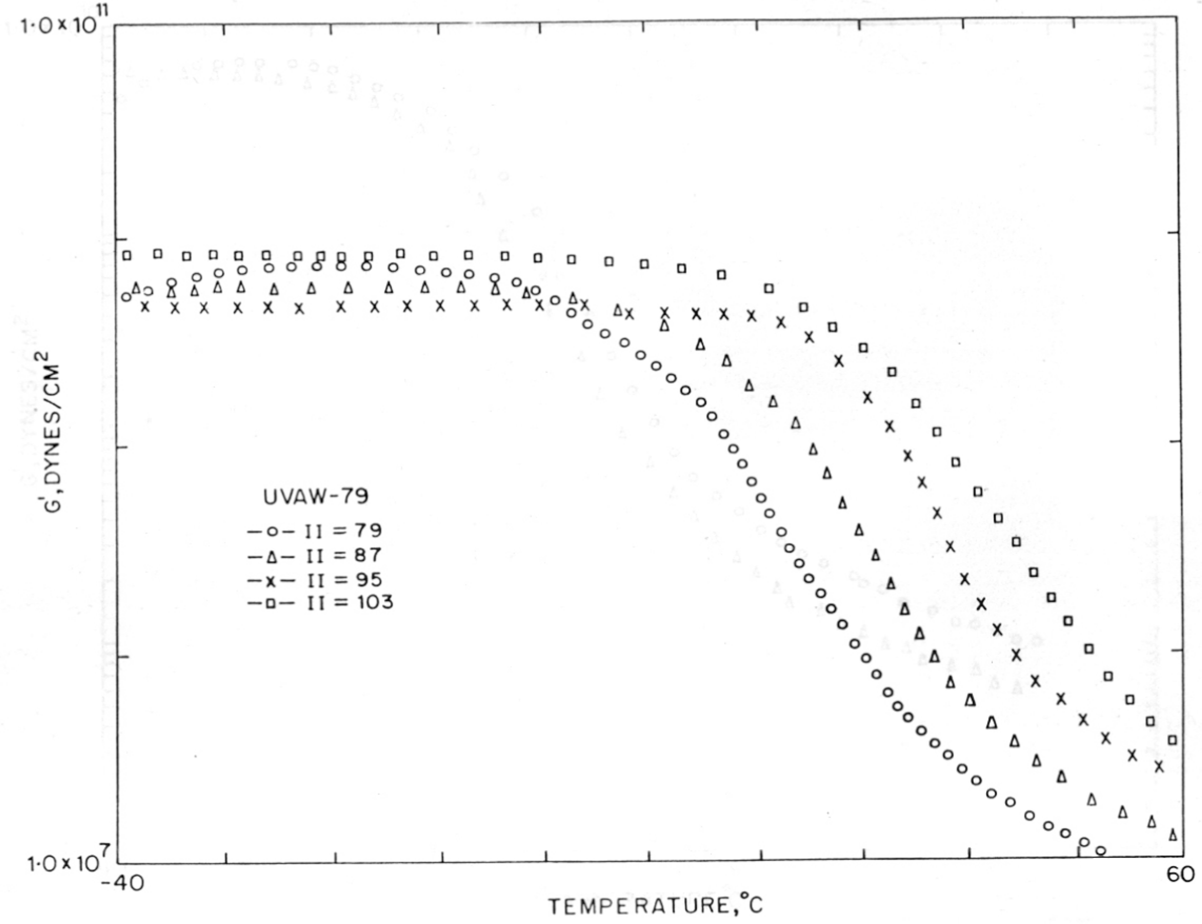


FIGURE 52: VARIATION OF STORAGE MODULUS WITH TEMPERATURE FOR UVAW-79 AT DIFFERENT ISOCYANATE INDICES

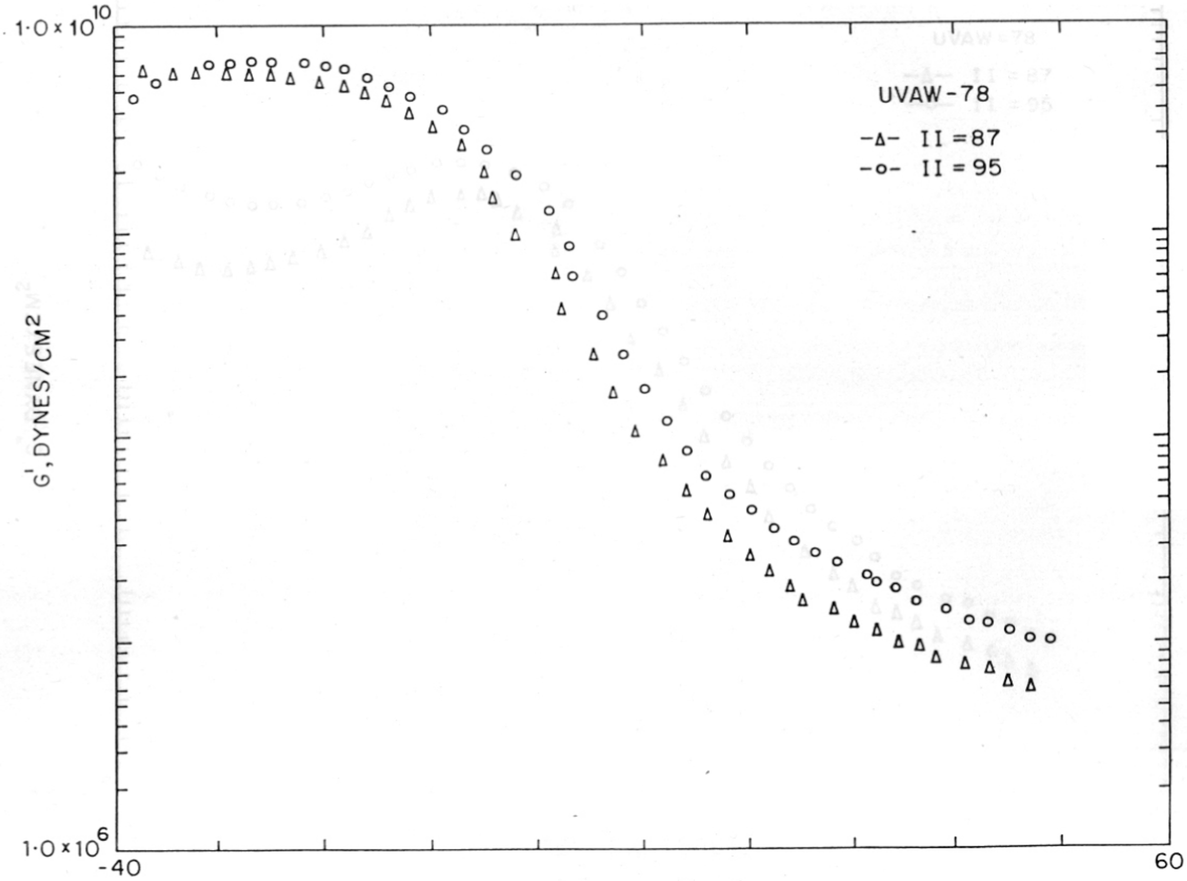


FIGURE 53: VARIATION IN THE STORAGE MODULUS WITH TEMPERATURE FOR UVAW-78 AT DIFFERENT ISOCYANATE INDICES

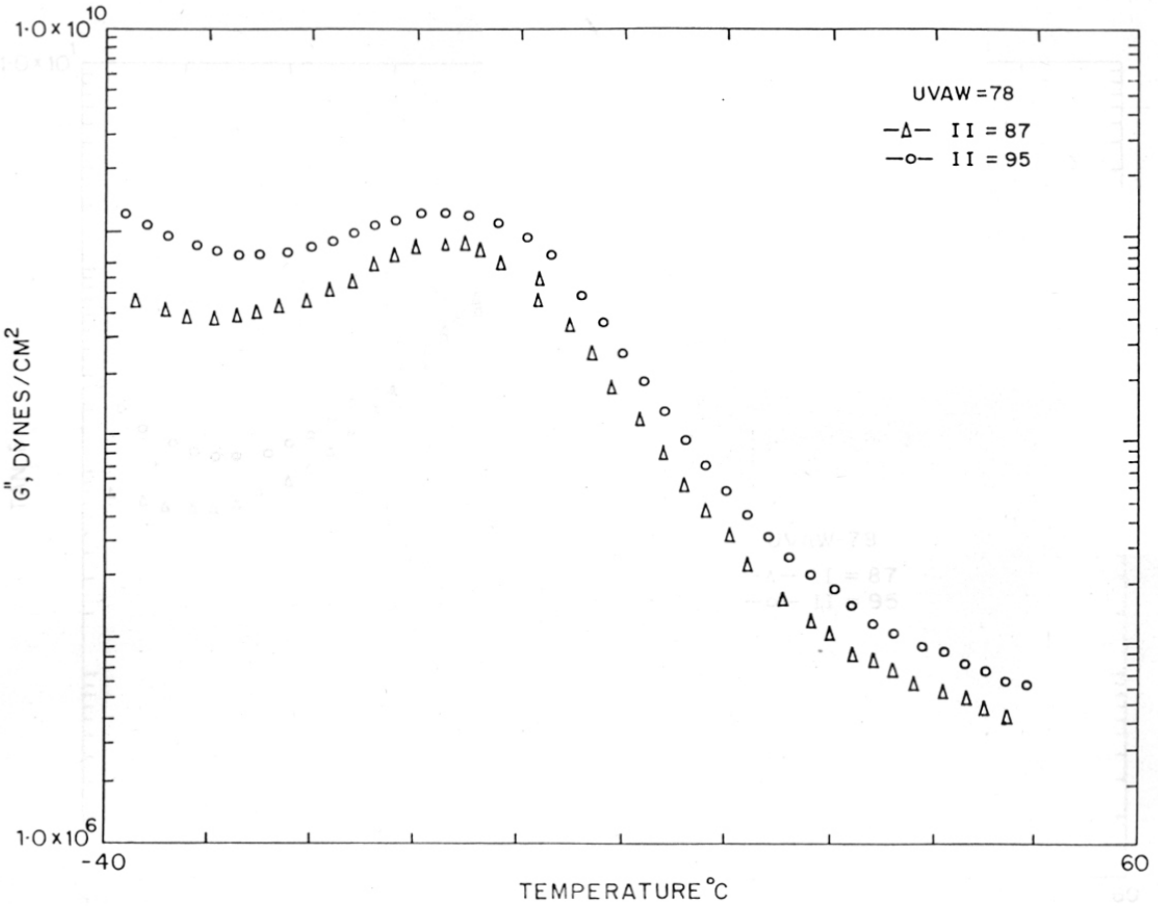


FIGURE 54: VARIATION IN THE LOSS MODULUS WITH TEMPERATURE FOR UVAW-78 AT DIFFERENT ISOCYANATE INDICES

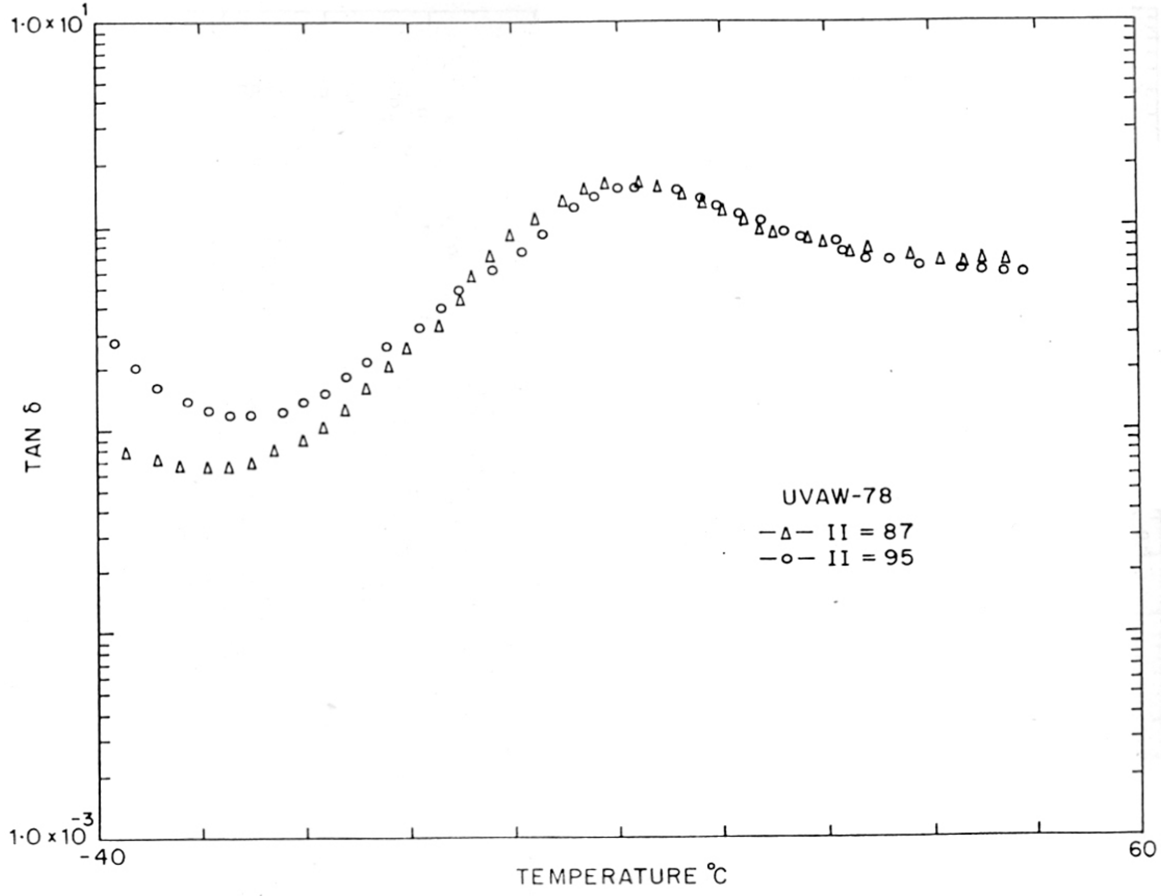


FIGURE 55: VARIATION IN THE LOSS FACTOR WITH TEMPERATURE FOR UVAW-78 AT DIFFERENT ISOCYANATE INDICES

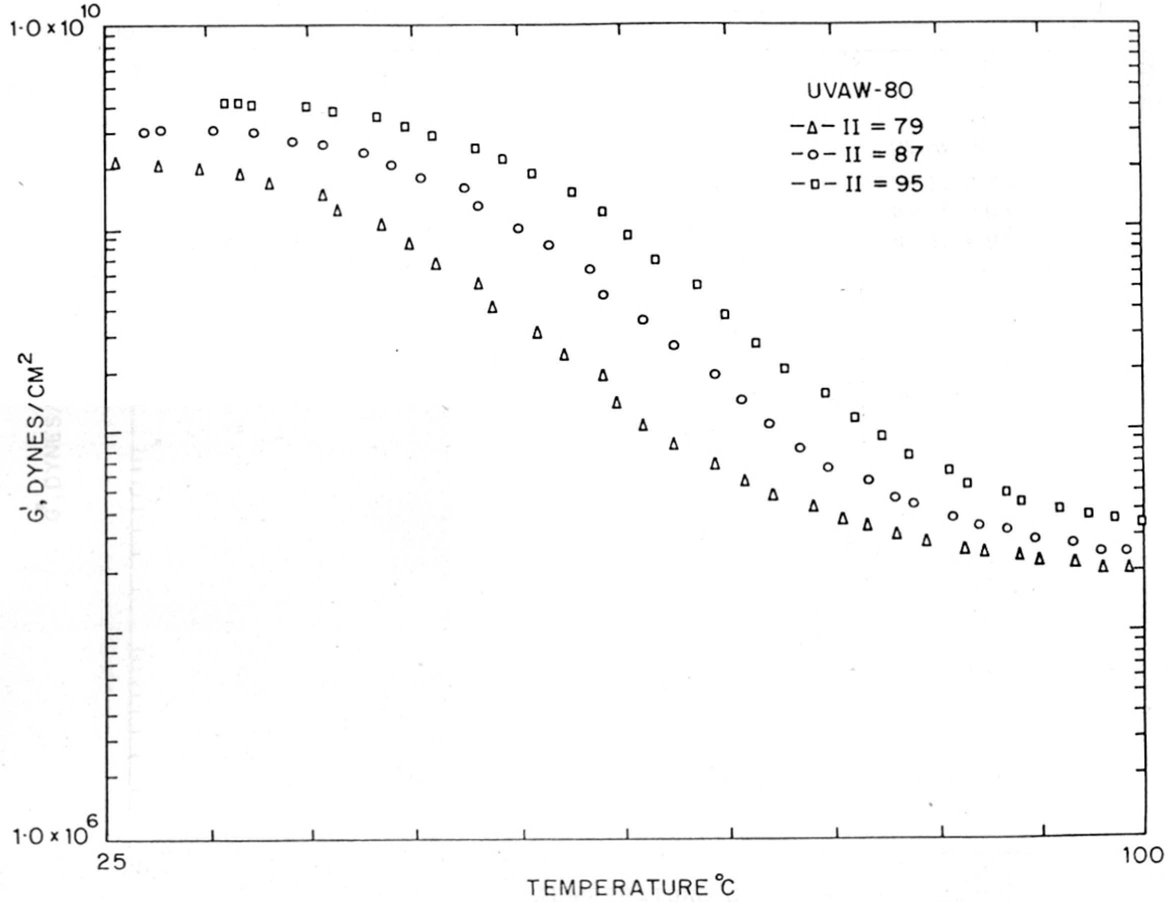


FIGURE 56: VARIATION OF STORAGE MODULUS WITH TEMPERATURE FOR UVAW-80 AT DIFFERENT ISOCYANATE INDICES

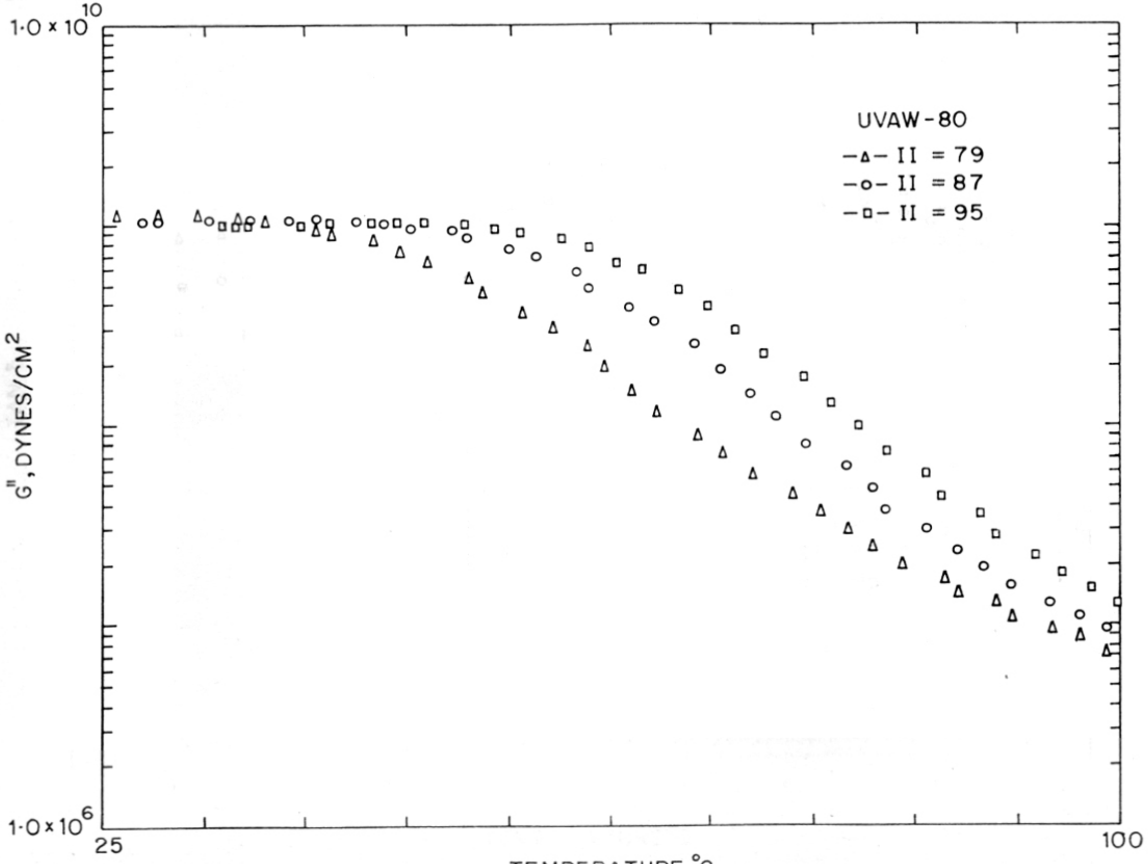


FIGURE 57: VARIATION OF LOSS MODULUS WITH TEMPERATURE FOR UVAW-80 AT DIFFERENT ISOCYANATE INDICES

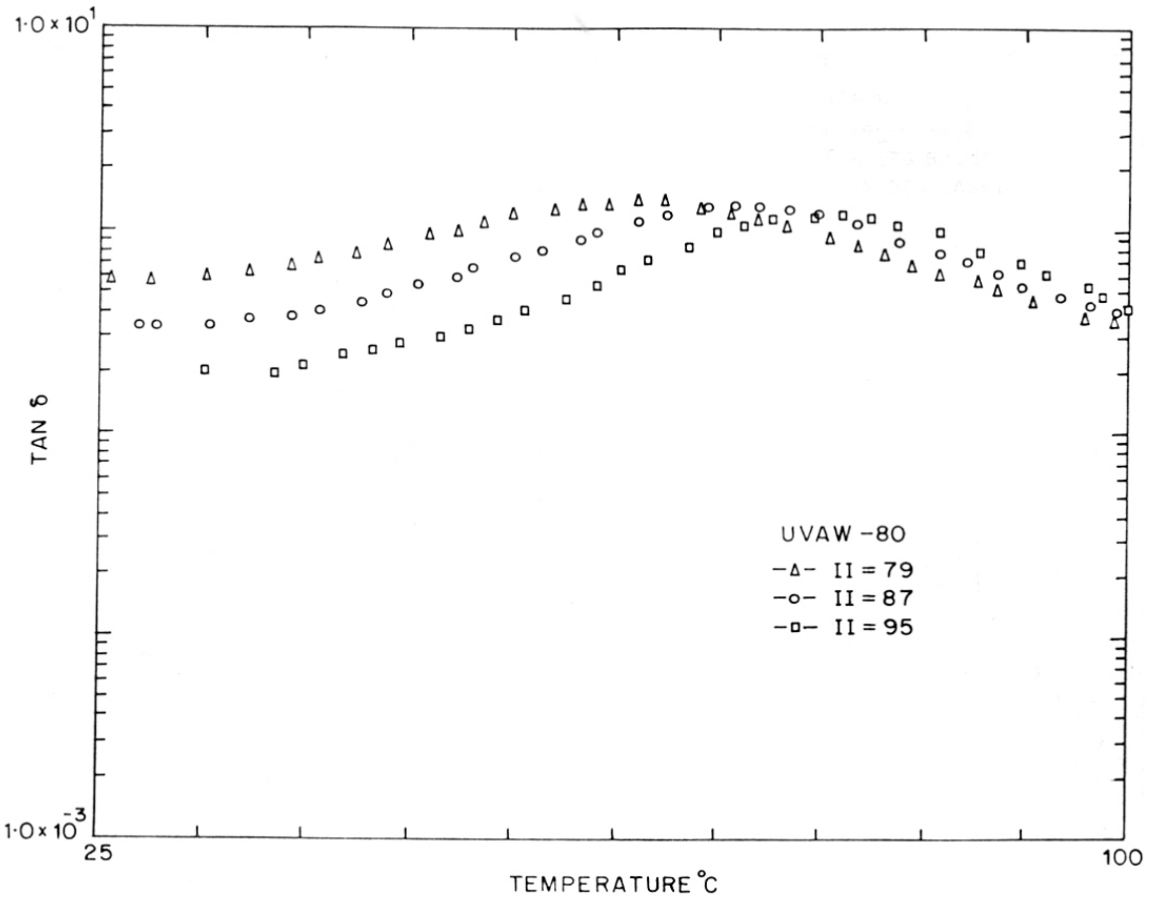


FIGURE 58: VARIATION OF LOSS FACTOR WITH TEMPERATURE FOR UVAW-80 AT DIFFERENT ISOCYANATE INDICES

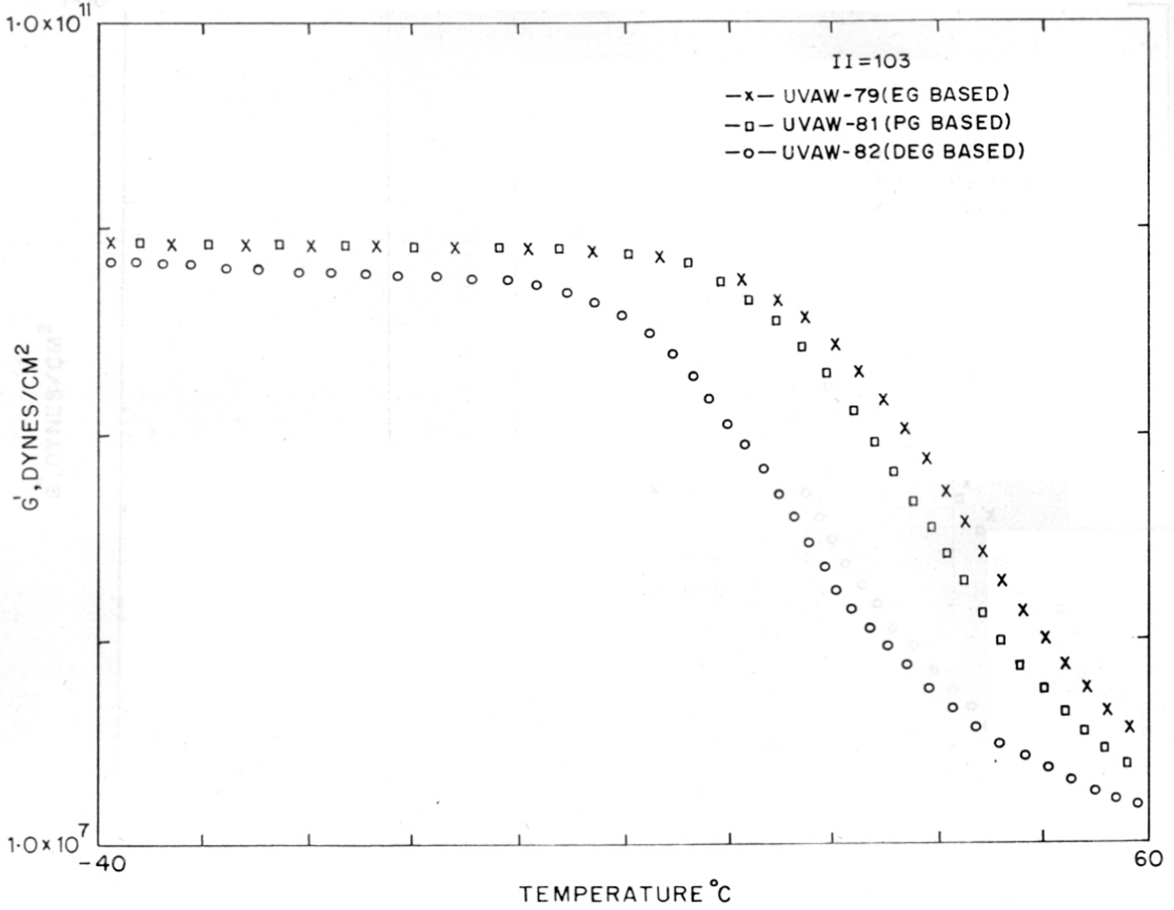


FIGURE 59: VARIATION OF STORAGE MODULUS OF PU ELASTOMERS MADE FROM GLYCOLYSED PET, BASED ON DIFFERENT GLYCOLS, AT ISOCYANATE INDEX OF 103

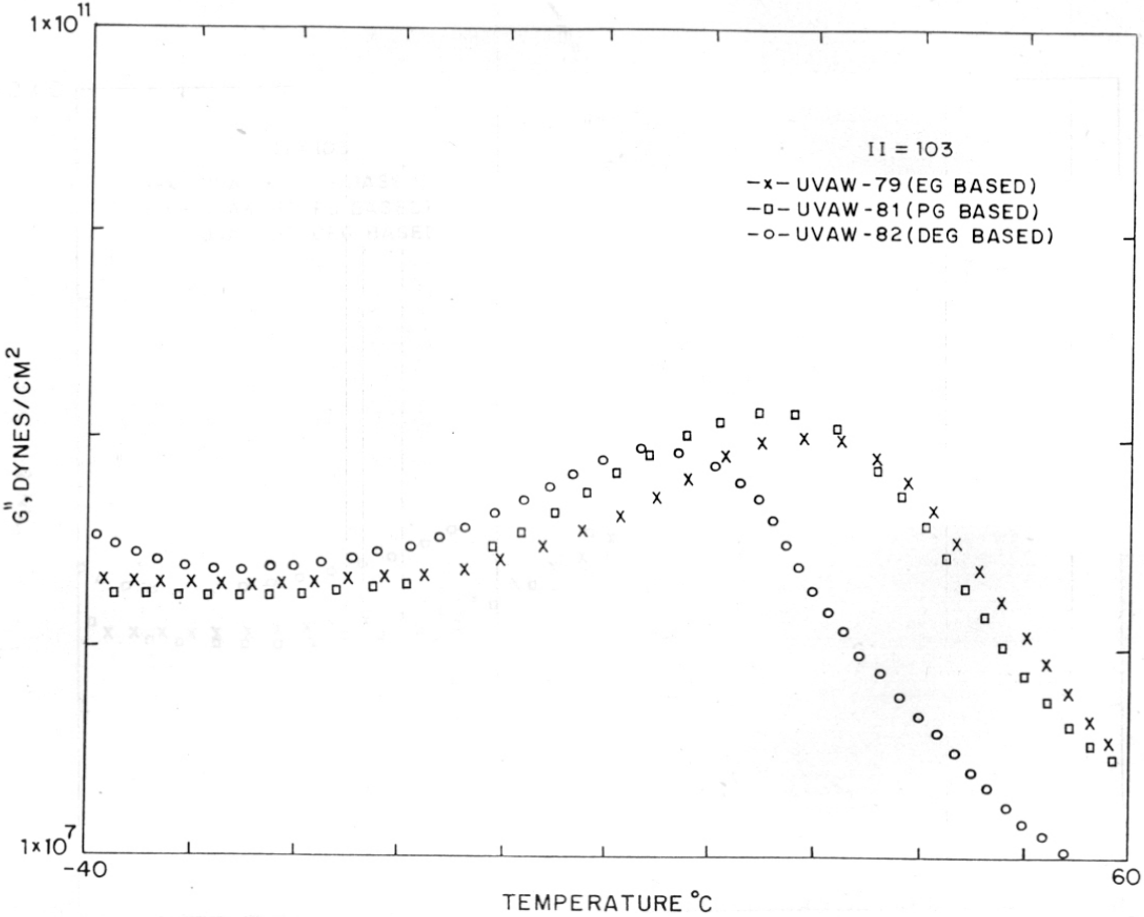


FIGURE 60: VARIATION IN LOSS MODULUS OF PU ELASTOMERS MADE FROM GLYCOLYSED PET WASTE BASED ON DIFFERENT GLYCOLS, AT ISOCYANATE INDEX OF 103

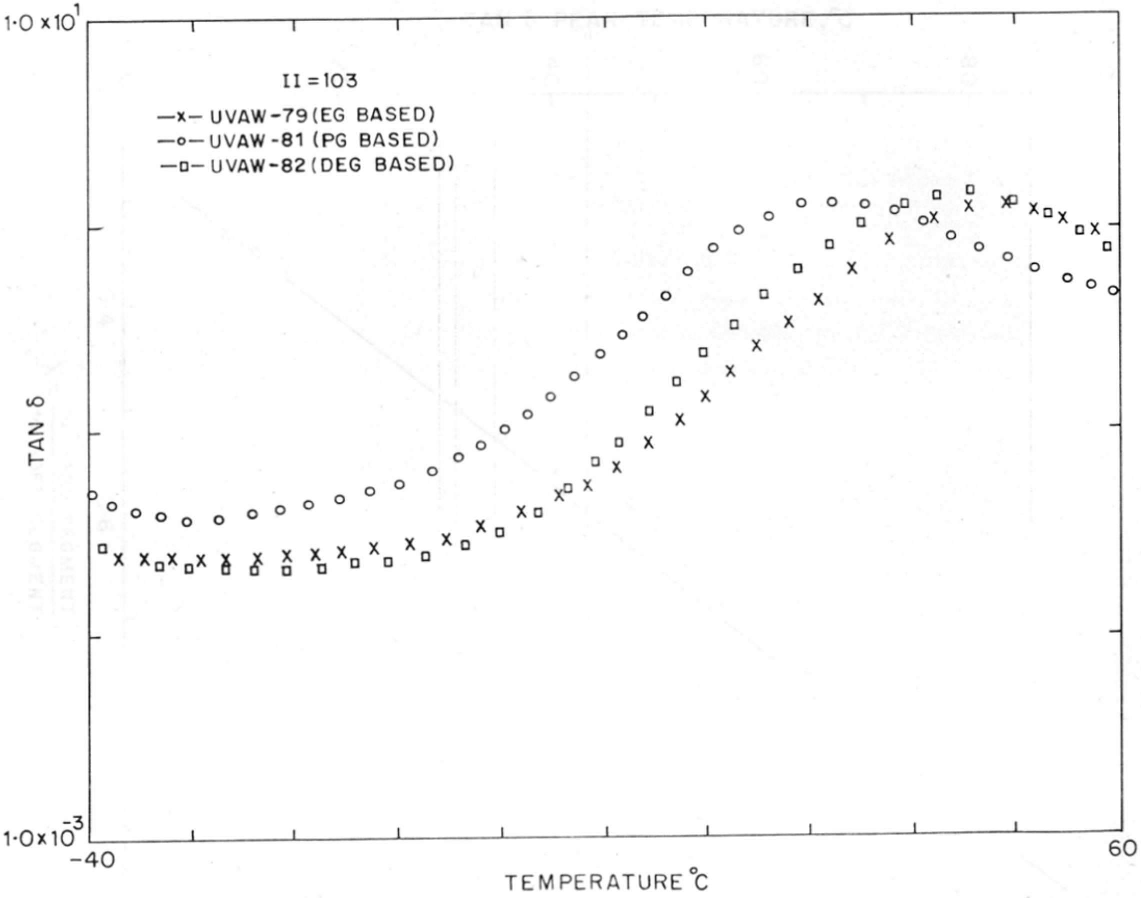


FIGURE 61: VARIATION IN LOSS FACTOR OF PU ELASTOMERS MADE FROM GLYCOLYSED PET BASED ON DIFFERENT GLYCOLS, AT ISOCYANATE INDEX OF 103

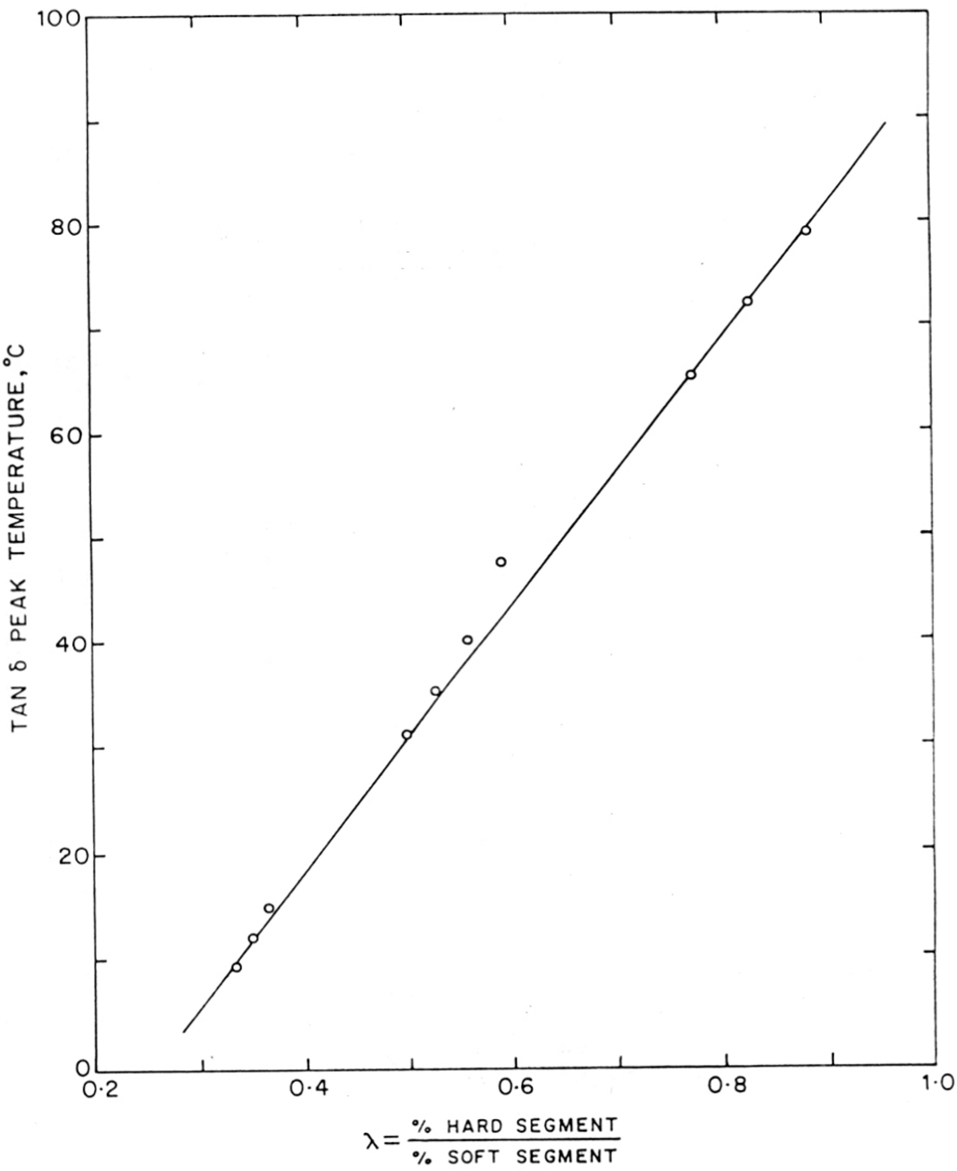


FIGURE 62: DEPENDANCE OF TAN δ PEAK TEMPERATURE ON RELATIVE AMOUNTS OF HARD AND SOFT SEGMENTS, IN PU ELASTOMERS BASED ON EG GLYCOLYSED PET

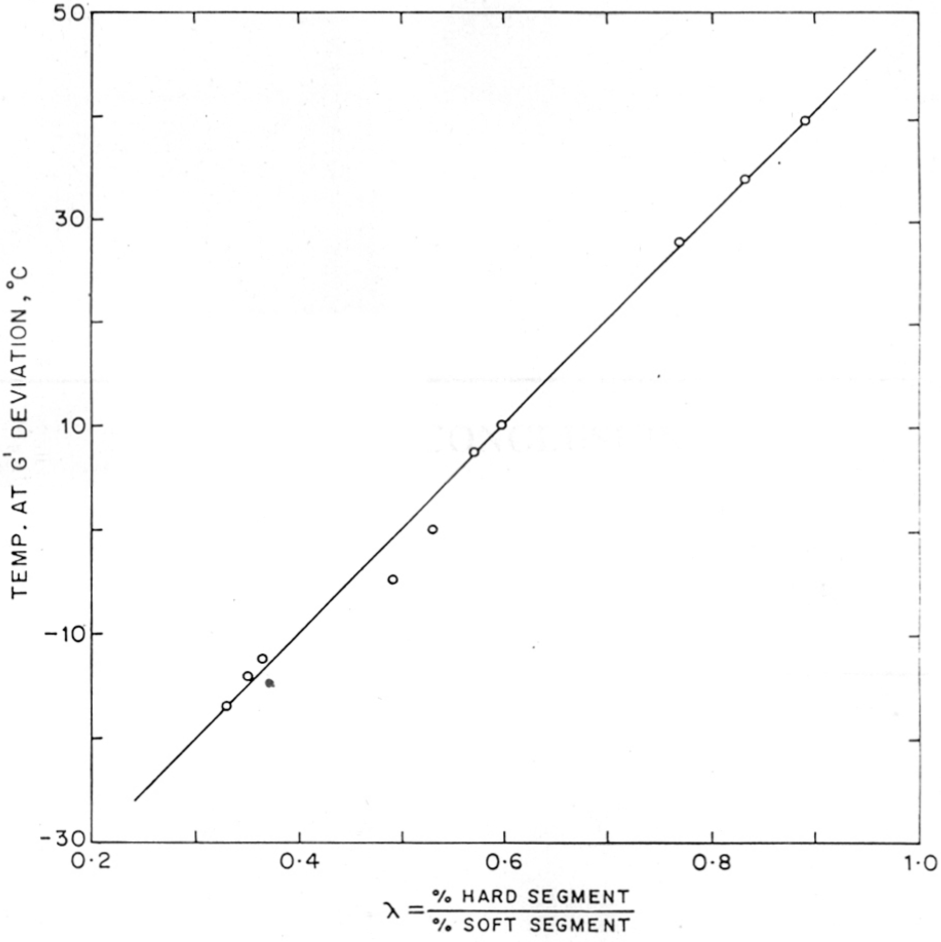


FIGURE 63: DEPENDANCE OF STORAGE MODULUS DEVIATION TEMPERATURE ON RELATIVE AMOUNTS OF HARD AND SOFT SEGMENTS IN PU ELASTOMERS BASED ON EG GLYCOLYSED PET

SUMMARY OF CONCLUSIONS
AND
RECOMMENDATION FOR FURTHER WORK

SUMMARY OF CONCLUSIONS

The fiber grade PET waste could be depolymerized by glycolysis using various glycols like ethylene glycol (EG), propylene glycol (PG) and diethylene glycol (DEG). The extent of depolymerization was found to be a function of the amount of glycol. However, use of glycol in excess of 70 % (w/w) of the reaction mixture would lead to almost complete depolymerization of PET to BHET. The extent of depolymerization was the maximum for ethylene glycol. The oligomers obtained after glycolysis were separated by HPLC. The oligomers of ethylene glycol glycolysed PET could be well separated, whereas those based on propylene glycol and diethylene glycol did not separate effectively due to the presence of a large number of similar species. The concentration of high molecular weight oligomers decreased with increasing amount of glycol in glycolysis. When glycolysed with 62.5 %, 50.0 % and 37.5 % glycol, the PG based product showed wider MWD for product with 50.0 % glycol based on HPLC results. It may be noted that the UP resin made from this oligomer, gave abnormally high viscosity and a gelation behaviour inconsistent with other UP resins.

The glycolysed PET waste when reacted with maleic anhydride, gave unsaturated polyesters. The UP resins based on ethylene glycol were not miscible with styrene.

Therefore, only the PG glycolysed waste was used for synthesis of UP resins. The viscosities of these resins were slightly higher than the orthophthalic based general purpose (GP) resin. The comparatively higher molecular weight and viscosity of the polyester made from 50 % PG glycolysed product was attributed to the higher concentration of high molecular weight species in glycolysed PET. The PET based UP resins were more reactive than the orthophthalic based GP resin. The geltime and peak exotherm could be manipulated by changing the amounts of the initiator and the accelerator.

The kinetics of polyesterification was investigated under conditions comparable to those employed in commercial scale production. The heating cycle comprised of two isothermal regions, first at 180°C and second at 200°C. The reactions followed third order kinetics. The glycolysed PET based reactions proceeded at a much higher rate than the phthalic anhydride based GP resin.

The mechanical and dynamic mechanical properties of the PET based resins were found to be comparable to those of the ordinary grade GP resin ($\overline{M}n = 1300$). However, the properties of imporved grade GP resin with a higher molecular weight ($\overline{M}n=1977$) exhibited better mechanical and dynamic mechanical properties. It was interesting to note that the thermomechanical properties of PET based resins were much superior to both ordinary and improved grade GP resins. The higher thermal performance of PET based resins is attributed to the close packing of polymeric chains with para-para linkages of terephthalic acid. The incorporation of fillers improved the dynamic mechanical performance of the polyesters. The mechanical performance of the PET based resins may be further improved by optimizing their molecular weights and the styrene contents.

The oligomers obtained after glycolysis of PET waste with different glycols were reacted with adipic acid to form polyols of different molecular weights. The polyesterification reactions catalysed by PTSA followed second order kinetics. The slight non-linearity in the plots of ln [OH] / [COOH] versus time was attributed to a large number of reacting species with different reactivities. Among the EG glycolysed PET based reactions, the rate slightly increases with the increasing ratio of glycol/acid (r). Among different types of glycols, PG glycolysed product is the slowest reacting compared to EG and DEG glycolysed PET. This is attributed to the presence of secondary hydroxyl group. The rates of EG and DEG based products were comparable. The factors affecting the removal of water of reaction, such as stirring, viscosity and flow of nitrogen gas, were found to alter the rate of reaction significantly.

The elastomers made by reacting these polyols with PMDI exhibited a wide range of properties. The hardness and tensile strength increased with an increase in the isocyanate index and a decrease in the M_c (molecular weight between the crosslinks). It was interesting to note that all the elastomer samples recovered to within 98 % of the original length after breaking under tensile load.

The rigid foams made from PET based polyols exhibit good mechanical properties. The effect of density was more significant than the effect of glycerol extender. Increase in the density from 0.30 g/cc to 0.43 g/cc improved the properties significantly. The size of spherical cells was in the range of 150 to 250 μ .

The dynamic mechanical testing revealed interesting correlations. The Tg and storage modulus increased with an increase in the isocyanate index and a decrease in the M_c. A linear relationship was found between the peak tanδ temperature, the temperature at which value of storage modulus starts falling down and the ratio of the hard to soft segments for EG based polyols. Such a relationship would be useful for molecular engineering of PU networks to meet specific end properties.

A list of publications in international technical journals, based on the Ph. D. Research is attached.

RECOMMENDATIONS FOR FURTHER WORK

The glycolysis of the PET waste using different glycols should be investigated by studying of the kinetics of glycolysis. The progress of glycolysis may be monitored either by observing the change in the viscosity of the melt during reaction or by chemical analysis, in terms of hydroxyl value. Since the glycolysis reaction is accompanied by glycol and ester exchange reactions, the MWD changes with time. It would be interesting to follow the change in the MWD with time till an equilibrium is attained. The MWD can be monitored by HPLC/GPC analysis. The separation of oligomers by HPLC/GPC can be further improved by derivatization of the oligomers, for example by synthesizing acetyl derivative. The structural elucidation can be better achieved by the use of shift reagents in NMR analysis and by the use of mass spectra.

The brittle nature of the unsaturated polyesters made from these oligomeric diols (PG based) can be improved by the use of small quantity of phthalic anhydride and high impact polystyrene (HIPS). The anamalous behavior, in terms of a high viscosity and $\overline{M}n$ of UP resin made from 50 % PG glycolysed PET, need to be investigated further. The focus should be on the effect of molecular weight distribution of glycolysed PET used as a reactant on the viscosity and other characteristics of the resulting UP resins. The use of other unsaturated monomers like acrylates should also be studied.

There is considerable scope for exploring synthesis of polyurethanes from PET waste. In the present work, only one diacid (adipic) and isocyanate (PMDI) were used. Similarly other diacids and diisocyanates may be used with varying types and amount of the glycolysed PET. Though the viscosity of polyols based on higher PET waste content was found to be higher, these may be processed by high temperature Reaction Injection Moulding (RIM). The elastomers with various extenders and crosslinking agents are likely to give much better mechanical properties.

The rigid foams with different formulation parameters, namely, molecular weight of polyol, functionality, NCO/OH ratio and aromatic/aliphatic segments should be synthesized over a broader range of density. The incorporation of fillers was found to improve the mechanical properties to a great extent. Thus, a study of the mechanical properties of rigid foams with varying extender amounts, densities and fillers would reveal interesting information for the development of formulations.

The PET waste may be depolymerized by aminolysis using diamines. The oligomers having amine and hydroxyl end groups may then be reacted with either diacids or diisocyanates. The incorporation of amide/urea linkages would improve the thermomechanical properties of the product.

The use of polyurethane rigid foams made from glycolysed PET waste in various wood replacement applications may be explored. In this context, we are evaluating the foam for use as an ankle block in place of wood laminate in the famous artificial foot, Jaipur Foot.

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LIST OF PUBLICATIONS

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1. Unsaturated polyester resins from PET waste: I Synthesis and characterization; Industrial and Engineering Chemistry - Research, Vol. 26, 194, 1987.

2. Unsaturated polyester resins form PET waste: Kinetics of polycondensation; Journal of Applied Polymer Science, Vol.54, No.1, July, 1987.

3. Unsaturated polyester resins from PET waste: II Mechanical and dynamic mechanical properties; Industrial and Engineering Chemistry - Research, (In press).

4. Polyester polyols for polyurethane from PET waste: Kinetic of polycondensation; Journal of Applied Polymer Science, Vol.35, 775, 1988.

5. Polyester polyols from glycolysed PET waste: Effect of glycol type on kinetics of polyesterification; Journal of Applied Polymer Science, (In press).

6. Polyurethane elastomers from PET waste, (To be communicated).

7. Polyurethane rigid foams from PET waste, (To be communicated).