“Studies on multiple unsaturated poly(urethane-ester) containing epoxy residues”

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In
Science
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(27th December, 2012)

Dedicated

To

My beloved

Family

Nirma University

Institute of Science

Declaration

I, **Mr. Patel Nikulkumar Navinbhai**, registered as Research Scholar, bearing Registration No. **09FTPHDS05** for Doctoral Programme under the Faculty of **Science** of Nirma University do hereby declare that I have completed the course work, pre-synopsis seminar and my research work as prescribed under R.Ph.D.3.5.

I do hereby declare that the thesis submitted is original and is the outcome of the independent investigations/ research carried out by me and contains no plagiarism. The research is leading to the discovery of new facts / techniques / correlation of scientific facts already known. This work has not been submitted to any university or body in quest of a degree, diploma or any other kind of academic award.

I do hereby further declare that the text, diagrams or any other material taken from other sources (including but not limited to books, journals and web) have been acknowledge and understanding.

Date: ___________________________________

Signature of the student

Abstract

The epoxy resins are used in a large number of fields, including surface coatings, in adhesives, reinforced with carbon fiber. The polyesters are most widely versatile materials and have broad spectrum of characteristics and wide applications ranging from aerospace to micro electronics. They are also important as laminating resins, molding composites, fibers, films, surface coating resins, fiber cushion. Polyurethanes are widely used in high resiliency flexible foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives and sealants, Spandex fibers, seals, gaskets, carpet underlay, and hard plastic parts (such as for electronic instruments).

Merging of all the four unsaturation, epoxy, ester and urethane segments into one polymer chain has not received attention academically and technically. Certain properties of thermoplastics may also be improved via blending or addition to an unsaturated resin is another possibility. In order to improve certain properties of such reported polymers their blending with commercial vinyl esters (epoxy resin) such as vinyl ester epoxy resin may afford a commercially important material for wide industrial applications. Hence the present report comprises synthesis of poly (urethane-ester) having epoxy residues.

Unsaturated polyesters were successfully synthesized using different aromatic diamines and diglycidyether of bisphenols. Unsaturated polyesters, vinyl ester and hexamethylene diisocyanates used for the production of unsaturated poly(urethane-ester).

All the produced polymer systems have been characterized by following techniques:

The C, H, and N contents were estimated by means of Thermofinagan 1101 flash elemental analyzer (Italy). The IR spectra were recorded in KBr pellets on a Nicollet 760 D spectrometer. The number average weights were estimated by non-aqueous conductometric titration followed by the method reported in the literature. Pyridine was used as a solvent and tetra-n-butyl ammonium hydroxide was used as a titrant. Curing of all blends was carried out on a differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. A universal V3 gTA DSC was used for this study. Unreinforced cured samples of blends were subjected to thermogravimetric analysis (TGA) on Du Pont 950 thermo gravimetric analyzer. The Flexural strength, Compressive strength, Impact strength, Rockwell hardness, Electrical strength was measured according to ASTM standards.

The values of C, H, N of each of the unsaturated polyesters and acrylated unsaturated polyesters were consistent with their predicted structures. The number average molecular weight of acrylated unsaturated polyesters were estimated by nonaqueous conductometric titration method and vapor pressure osmometric method. The results indicate that the degree of polymerization is about 6. The IR spectra were consistent with the ones expected from the structures of the unsaturated polyesters and poly(urethane-ester)s.The TGA data of all PUEs reveals that decomposition starts around 290°C, depending on the nature of the polymers. The rate of decomposition increases by increasing the temperature and it is the fastest between 400 °C and 550° C. It was observed that the weight loss is completed beyond 760 °C.

The results show that composites have good chemical resistant property, good mechanical and electrical strength. The results of these novel poly(Urethane-ester) resins suggest that these resins can be competitors to commercial unsaturated polyester resins.

Content

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List of abbreviations

atomic mass unit	a.m.u
And the rest	Et al.
Activation energy	Ea
American Society for Testing and Materials	ASTM
Benzoyl peroxide	BPO
Corrosion- glass	C-glass
Concentration	C
Centi Poise	cP
Centimeter	Cm
Diglycidylether of bisphenol-A	DGEBA
Diglycidylether of bisphenol-F	DGEBF
Diglycidylether of bisphenol-C	DGEBC
Differential scanning calorimeter	DSC
Density	P
Degree centigrate	^{o}C
Electrical -glass	E-glass
Fiber reinforced polymer	FRP
Fourier transformer infrared	FT-IR
glass fiber-reinforced composites	GFRC
Gram per centimeter	gm/cc
Gram per mole	gm/mole
Hertz	Hz
Heat of polymerization	ΔHp
Heat of vaporization	ΔHv
Hydroxyl value	OHV
Hexamethylene diisocyanate	HMDI
Hours	hrs

Unsaturated polyesters	UPEs
Acrylated unsaturated polyesters	AUPEs
Unsaturated poly(Urethane-ester)s	UPUEs
Initial temperature	Ti
Infrared	IR
Molecular weight	Mw
Millivolts	mV
Milligram	mg
Minute	min.
Millimeter	mm
Micrometer	2m
Melting piont	m.p.
Number average molecular weight	*Mn*
Namely	viz.
Order of reaction	*n*
Part per million	ppm
Per centimeter	cm-1
That is	i.e.
Thermogravimetric analysis	TGA
Temperature	Temp.
Ultraviolet	UV
Vapor pressure osmommetry	VPO
Viscosity average molecular weight.	*Mv*
Volume by volume	v/v
Versus	Vs
Weight average molecular weight	*Mw*
Weight by weight	w/w
Weight by volume	w/v

Acknowledgement

This Thesis is the end of my long journey in obtaining my degree. I have not traveled in vacuum in this Thesis journey. There are some people who made this journey easier with the word of encouragement and more intellectually satisfying by offering different place to look to expand my theories and ideas.

It is a pleasant aspect that I have now the opportunity to express my gratitude for all of them. I owe a debt of thank for their support over the research work.

First I would like to sincerely acknowledge my research supervisor ***Prof (Dr). P. N Dave*** *for suggesting in my opinion even though he has the busiest schedule of any professor I have met, he always found adequate time to oversee my studies and share his knowledge and expertise with me, without which this Thesis could not be produce in this present form. This was the constant motivating factor for me to complete this Thesis. I regard you sir, as an outstandingly good scientific supervisor and a very nice person to work with.*

The word is insufficient to express my deepest gratitude from bottom of my heart to my Father ***Navinbhai D Patel*** *and Mother* ***Induben N Patel****. The present work would have not been possible without their indispensable help, unlimited patience, moral and emotional support full of constant encouragement in all my endeavors. Affection and full of constant co-operation from my caring sister* ***Ripal N. Patel*** *and wife* ***Zalak*** *who has constantly provided emotional support, I would like to express my sincere thank to them.*

A special thanks to all teaching and non-teaching staff members, of the Institute of Science, Nirma University and Ph.D. section, Nirma University for their great help and co-operation. I am thankful to former Director, Institute of Science Prof. G Nareshkumar for financial assistance to participate in various conferences.

My acknowledgement would not be completed without expressing due regards and gratitude to all who had helped me directly or indirectly through, this study for their co-operation and patience without which this study would not have been possible.

- Nikul N Patel

Chapter-1

Introduction

1.1 Definition and statement of problem:

The recent age is of polymer materials. Today daily life is accomplished with the many polymeric items. They are in the form of plastics, fibers, rubbers, adhesives and surface coatings. As per properties the polymers they are classified into thermosets and thermoplasts. The well known thermoplasts are - polyethylene, polypropylene, nylons etc and thermosts are - polyester, epoxies, phenolics , polyurethanes etc. Out of these the unsaturated polyesters, epoxies and polyurethanes are versatile materials. These polymers possess unique preparations process, facile processing and exclusive properties for potential applications [1-4]. The goal of present research is in the direction of unsaturated polyester, epoxy and polyurethane types into one unit.

As these three polymers are independent and their brief introductions are given below

1.1.1 Unsaturated polyesters:

Among the four thermosetting resins such as, phenolic, amino, epoxy and unsaturated polyester (UP) (i.e. cross linkable) resins, the UP resins are the most important because of their ease of formation, transparency, thermal stability and good tackiness. They are synthesized in two steps. In first step, a low molecular weight polyester of about 700 – 4000, containing C=C is synthesized and then dissolved in a vinyl monomer followed by stabilization with an inhibitor. They are based on several components that can be combined in different ratios and their choice is decided by the properties needed for a particular application [5-7]. The categories of components are

a. Glycol 1,2-propylene glycol

b. Unsaturated acids and anhydrides like maleic acid and anhydride

c. Saturated modified acids and anhydrides . Isophthalic acid and succinic acid

d. Cross linking monomers diallyl phthalate and styrene

- **Curing and Applications**:

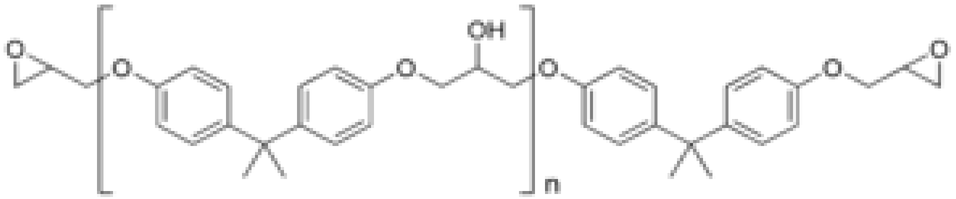
At normal temperatures USPE resins can be cured with peroxides and accelerators. The most important systems include hydroperoxides like methyl ethyl ketone peroxide, cyclohexanone peroxide with cobalt octanoate or vanadium octanoates or cobalt naphthenates, as well as benzoyl peroxide with aromatic amines. At elevated temperatures only peroxides are required for curing. USPE resins can also be cured in a few minutes by exposing them to UV light from high pressure mercury vapour lamps in the presence of photosensitizers.

Cured resins are thermosetting, infusible and insoluble materials. Their mechanical properties are maintained upto 100^{O}C and maximum upto 150^{O}C for reinforced general purpose resins. They are polar in nature.

They are mostly used as a matrix material for fabrication of glass fibre composites. The major applications of USPE resins are in automobile, marine and construction industries [8]. Common applications are for boat hulls, sports car bodies, truck cabs and public transport vehicles. They are also used for making decorative furniture castings, ornamental stone, buttons, trays, bowling balls, safety helmets, chemical processing equipments, missile shells and rocket motor cases.

1.1.2 Epoxy resins:

Epoxy or polyepoxide is a thermosetting polymer formed from reaction of an epoxide "resin" with polyamine "hardener". Epoxy has a wide range of applications, including fiber-reinforced plastic materials and general purpose adhesives.



Epoxy is a copolymer; that is, it is formed from two different chemicals. These are referred to as the "resin" and the "hardener". The resin consists of monomers or short chain polymers with an epoxide group at either end. Most common epoxy resins are produced from a reaction betweenepichlorohydrin and bisphenol-A, though the latter may be replaced by similar chemicals. The hardener consists of polyamine monomers, for example Triethylenetetramine (TETA). When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each -NH group can react with an epoxide group, so that the resulting polymer is heavily crosslinked, and is thus rigid and strong.

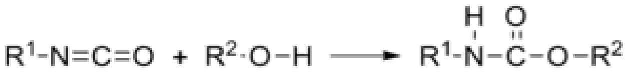
The process of polymerization is called "curing", and can be controlled through temperature and choice of resin and hardener compounds; the process can take minutes to hours. Some formulations benefit from heating during the cure period, whereas others simply require time, and ambient temperatures.

The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements (although polyester, vinyl ester, and other thermosetting resins are also used for glass-reinforced plastic). The chemistry of epoxies and the range of commercially available variations allow cure polymers to be produced with a very broad range of properties. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties. Many properties of epoxies can be modified (for example silver-filled epoxies with good electrical conductivity are available, although epoxies are typically electrically insulating). Variations offering high thermal insulation, or thermal conductivity combined with high electrical resistance for electronics applications, are available [9-10].

1.1.3 Polyurethanes:

A polyurethane (IUPAC abbreviation PUR, but commonly abbreviated PU) is any polymer consisting of a chain of organic units joined by urethane (carbamate) links. Polyurethane polymers are formed through step-growth polymerization by reacting a monomer containing at least two isocyanate functional groups with another monomer containing at least two hydroxyl (alcohol) groups in the presence of a catalyst.

generalized polyurethane reaction



$$R^1\text{-}N{=}C{=}O + R^2\text{-}O\text{-}H \longrightarrow R^1\text{-}\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}R^2$$

Polyurethane formulations cover an extremely wide range of stiffness, hardness, and densities. These materials include:

- Low-density flexible foam used in upholstery, bedding, and automotive and truck seating
- Low-density rigid foam used for thermal insulation and RTM cores
- Soft solid elastomers used for gel pads and print rollers
- Low density elastomers used in footwear
- Hard solid plastics used as electronic instrument bezels and structural parts
- Flexible plastics used as straps and bands

Polyurethanes are widely used in high resiliency flexible foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives and sealants, Spandex fibers, seals, gaskets, carpet underlay, and hard plastic parts (such as for electronic instruments) [11-12].

Polyurethane products are often called "urethanes". They should not be confused with the specific substance urethane, also known as ethyl carbamate. Polyurethanes are neither produced from ethyl carbamate, nor do they contain it.

1.2 Scope of the work:

The unsaturated polyester resins, epoxy and polyurethanes are independent candidates of polymers. All three have versatile properties for varieties of applications. Clubbing of unsaturated polyester, epoxy and polyurethane into one chain has not been received any attention academically and industrially. This may afford good materials for fabrication of composite and surface coating material. Hence, it was thought to undertake such study. Thus the present work comprises the studies on multiple unsaturated(urethane-ester) containing epoxy residues.

- Ease of preparation and processable
- Ease of curing with suitable crosslinking monomer
- Infisible, insoluble and thermally stable material
- Good adhesion with substrate
- Compatibility with inorganic fillers
- Flexibility with good elasticity
- May form rigid foam

1.3 Experimental:

1.3.1 Materials:

During whole study following materials were used:

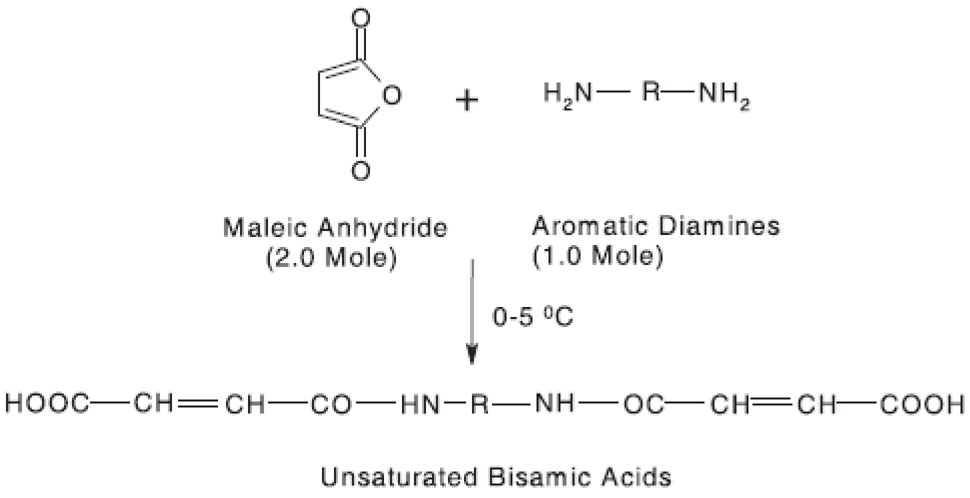
Allyl alcohol, maleic anhydride and diisocyanate were procured from local market.

Various Epoxy resin i.e. (Diglycidylether ether of bisphenols A (DGEBA), C (DGEBC) and F (DGEBF) were obtained from Synpole Product Pvt. Ltd., Ahmadabad, India. All other chemicals used were obtained from local market and were of laboratory pure grade.

1.3.2 Synthetic approach:

Various polymer systems have been prepared. The stepwise synthetic route from monomer to composite material is scanned as follows:

i. Various bisamic acids were prepared by reported method. The scanned procedure is as follows.



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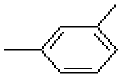
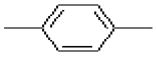


(Ia)



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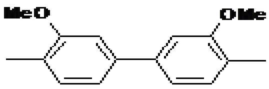

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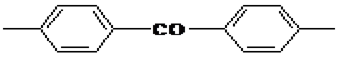

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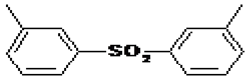

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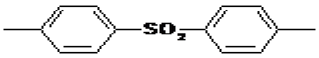

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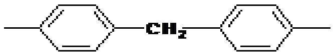

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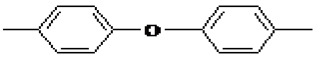

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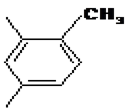

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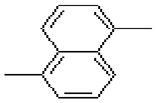
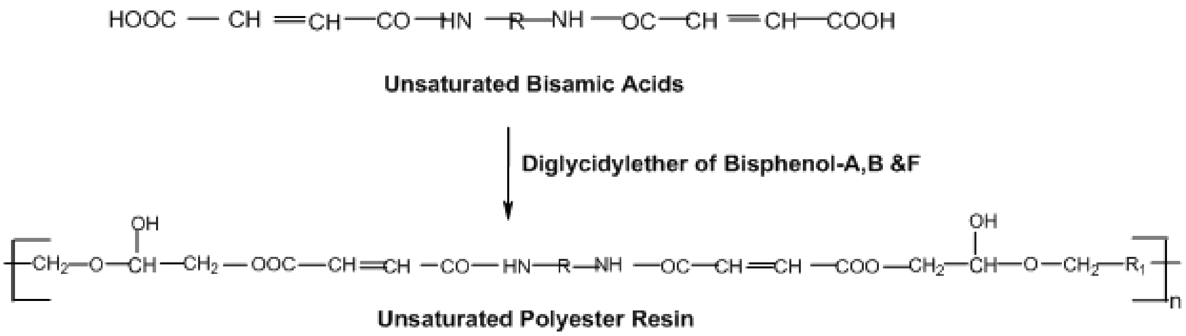
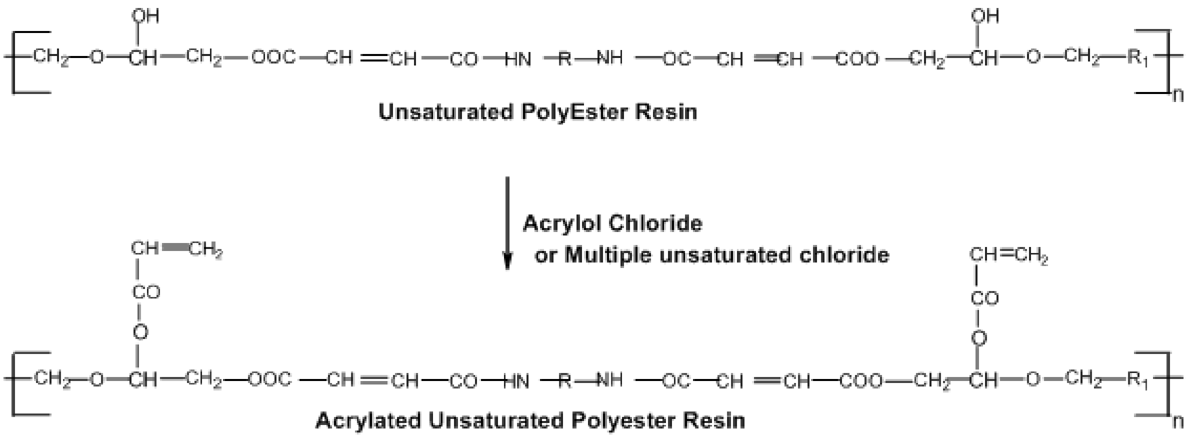


(Ij)

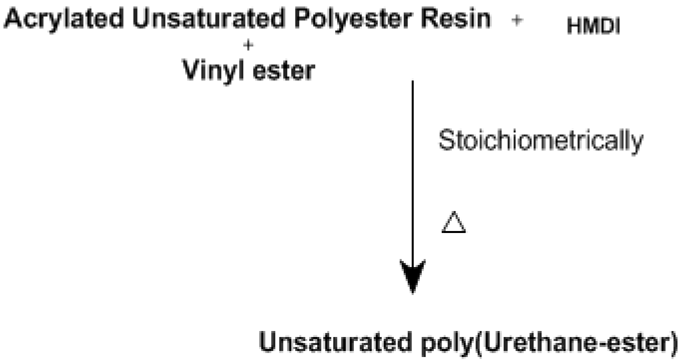
ii. All the bisamic acids were purified for next step, reaction as follows:



iii. All the unsaturated polyesters were then acrylated by multiple unsaturated chloride.



iv. All acrylated Unsaturated polyester, vinyl ester and Hexa methylene diisocyanate were blended stoichiometrically to form urethane linkage.



1.4 Objectives:

The objectives of the present work are:

a. To study multiple unsaturated poly(urethane-ester) containing epoxy residues.

b. To study appropriate material applications like composites, surface coatings etc.

1.5 Research Methodology:

During the course of produced research work various methods and techniques have been used these are as follows:

As per objectives the research work was designed. Various type of research design has been surveyed by literature. For this present candidate go through the literature regarding polymer composite in chemical abstract, recent books, e-books and latest industrial products. Looking to the advantages of potential applications of polyester, epoxy and polyurethane, the research topic has been selected. The net system has also been surfed for the latest technological development of composite and coating material that we thought.

Thus according to these surveys experimental procedures were designed. The high qualities of materials were procured. The well established experimental techniques were adopted. Micro scale and batch scale preparation of composite and coating were attempted.

Various measurement techniques like different mechanical properties were used to characterize the produced composite materials. The resultant data were than analysed and interpreted. The work was published in referred journals.

1.6 Outline of thesis:

All the polymer composites and coated steel panels were then characterized duly. This work has been bifurcated into five Chapters in the thesis.

The chapter-2 represents the review of literature of unsatutared polyesters, polyurethanes, epoxies and clubbing of these polymers.

The Chapter-3 contains the synthesis and characterization of polymers and it is divided into three sections.

- Section-1 deals with the details about the synthesis of unsatutrated polyesters, Acrylated multiple unsaturated polyesters and unsaturatedpoly(urethane-ester)s.
- Section-2 deals about techniques and instruments used for the whole study like molecular weight determination, inftrared spectroscopy, differential scanning calorimetry and Thermogravimetric analysis.
- Section-3 describes with fabrication of glass reinforced composites and surface coating on steel panel.

The Chapter-4 comprises the result and discussion of synthesized polymers.

Finally, the concluding remarks will be illustrated in Chapter-5 under heading of summary and conclusion.

Chapter-2

Review of Literature

The title of the present thesis proposes the research work on Unsaturated poly (Urethane-ester)s resins containing epoxy residues. Therefore, it would be prior to review briefly the features of polyesters, polyurethanes, epoxy and poly (urethane-esters).

2.1 Polyesters:

Polyesters are one of the most versatile synthetic copolymers. Polyesters are produced in high volume that exceeds 30 billion pounds a year worldwide. They are widely used commercially as fibers, plastics, composites and for coating applications [13-14]. They are heterochain macromolecules that possess carboxylate ester groups as an integral component of their polymer backbones. They differ from other ester containing polymers (such as polyacrylates and cellulose esters) in that the ester functionality is part of the backbone and not a pendant group. Polyesters have received a great deal of attention since the early work of Carothers, who initiated study on many step growth polymerizations [15].

Nowadays large numbers of polyesters are commercially available. These polyesters are mainly classified as follows:

a. Linear saturated polyesters

b. Polycarbonates

c. Alkyd resins

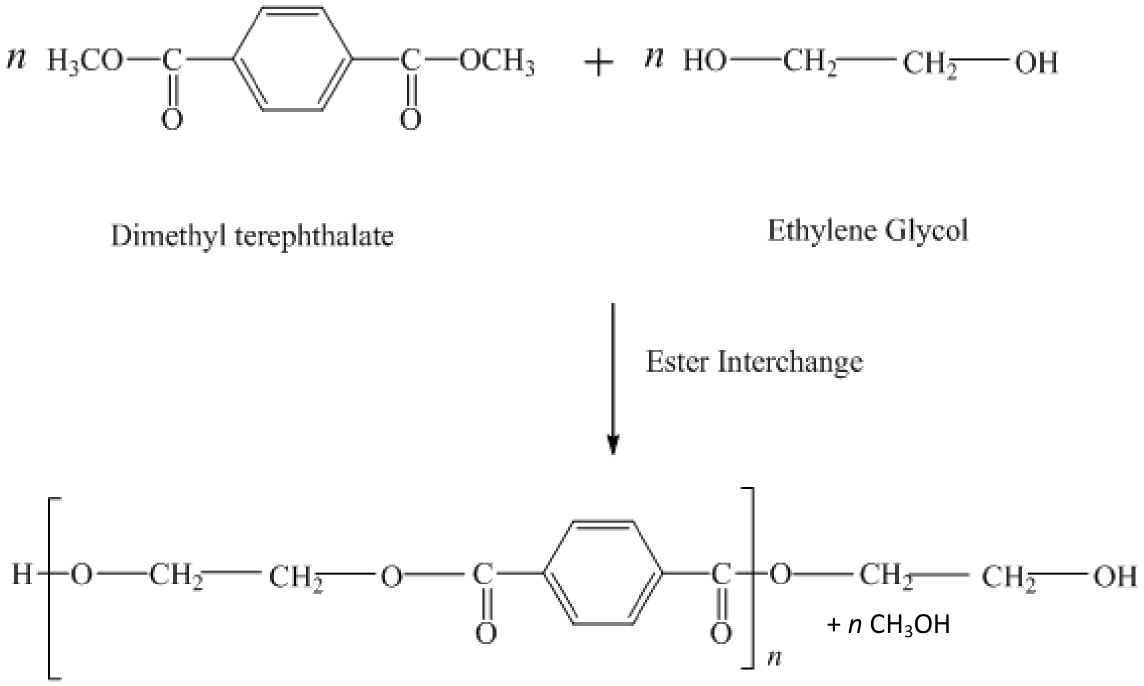
d. Linear unsaturated (i.e. cross-linkable) polyesters

These are deliberated briefly as follow:

a. Linear Saturated Polyesters:

Linear saturated polyesters are produced by polycondensation of diols and dibasic acids with aliphatic/aromatic combinations. But out of all polyesters, the poly(ethylene terephthalate) (PET) is the most prominent include in this class of polyesters and by far the most important linear saturated polymer of the present time. It is manufactured by polycondensation of dimethylterephthalate and ethylene glycol [16].

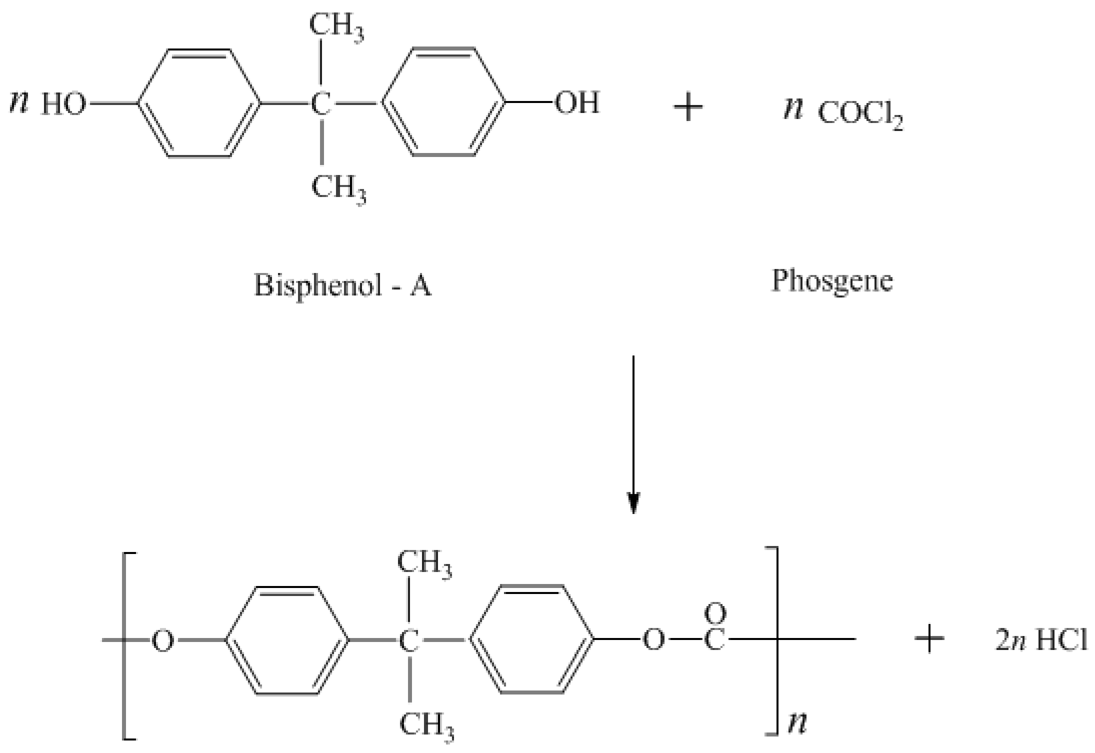
PET is synthesized by the ester interchange reaction between ethylene glycol and dimethyl terephthalate.



It is of high molecular weight and heat deflection temperature is about 155°C. PET has good mechanical and chemical resistance properties and is used to produce gas tight bottles, automotive parts and fibers [17].

b. Polycarbonates:

Polycarbonates (PC) are high performance thermoplastic engineering polymers. They are the reaction products of diols and phosgene. One of the commercially available polycarbonate is synthesized by interfacial polymerization of bisphenol-A and phosgene.



Polycarbonate

Its molecular weight is in the range of 20,000 – 50,000 and heat deflection temperature is about 130°C. It has excellent optical property. Polycarbonates are mainly used as a bulletproof material, hygienic plastics for feeding baby food items and compact disk (CD) of computers.

c. Alkyd Resins:

Alkyds are oil-modified polyesters. Alkyds are the reaction products of polyhydric alcohols with fatty acids followed by the reaction with dibasic acids. They are largely used in paint and printing ink industries **[18-19]**. Three major components are employed to prepare an alkyd resin, namely;

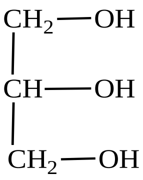
(i) Polyols

(ii) Dibasic acids or anhydrides

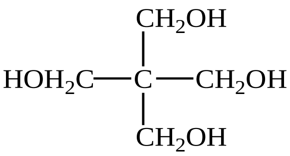
(iii) Modified oils

(i) Polyols:

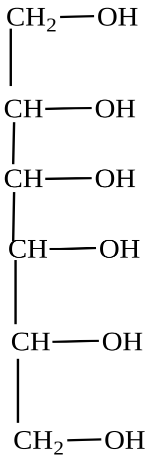
Glycerol (1) is by far the most used polyol. Other polyols like pentaerythritol (2), sorbitol (3) and trimethylolpropane (4) are occasionally employed.



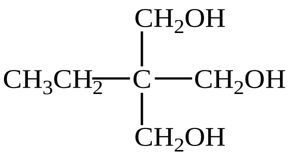
$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$



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



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

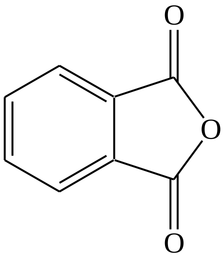


$$\begin{array}{c} CH_2OH \\ | \\ CH_3CH_2-C-CH_2OH \\ | \\ CH_2OH \end{array}$$

(1) (2) (3) (4)

(ii) Dibasic acids or anhydrides:

Phthalic anhydride (5) is the most commonly used for synthesis of dibasic acid. For special purposes pyromellitic dianhydride (6), trimellitic acid (7), maleic anhydride (8), sebacic and adipic acids are also used.



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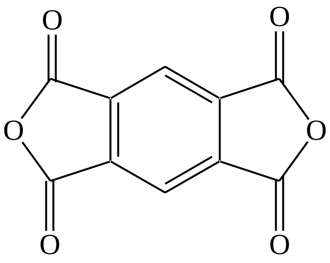

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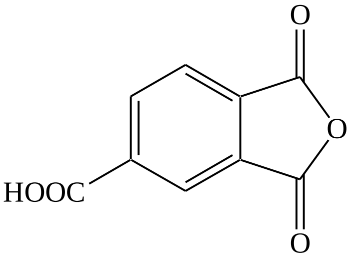

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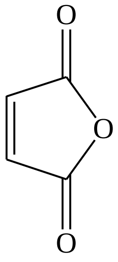

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(iii) Modified oils:

The drying, semi-drying and occasionally non-drying oils are used as modified oils depending on the application of resins. Drying oils such as linseed oil contains triglycerides of unsaturated fatty acids whereas non-drying oils such as castor or olive oil contains saturated fatty acids.

- **Synthesis**

They can be prepared by two different processes namely, fatty acid and alcoholysis process.

In fatty acid process, the oil is first hydrolyzed to free fatty acids and is mixed with glycerol and phthalic anhydride. Poly-condensation takes place by heating the mixture at 200 – 240 °C under an inert gas flow that removes water from the reaction. In alcoholysis process, the oil is trans-esterified by heating with glycerol at 240°C to give monoglyceride that is then heated with phthalic anhydride either in the presence or absence of a solvent, such as in the above process.

The formation of final cross-linked network is based on the polymerization of the double bonds of unsaturated acids contained in the oil. Alkyd resins are mainly used for formulating surface coatings [20].

d. Unsaturated Polyesters:

Among the four thermosetting resins such as, phenolic, amino, epoxy and unsaturated polyester (UP) (i.e. crosslinkable) resins, the UP resins are the most important because of their ease of formation, transparency, thermal stability and good tackiness. They are synthesized in two steps. In first step, a low molecular weight polyester of about 700 – 4000 mol/wt, containing -C=C- is synthesized and is then dissolved in a vinyl monomer and further stabilized with an inhibitor. They are based on several components that can be combined in different ratios and their choice is decided by the properties needed for a particular application **[21-22]**. The categories of components are:

(i) Glycol

(ii) Unsaturated acids and anhydrides

(iii) Saturated modified acids and anhydrides

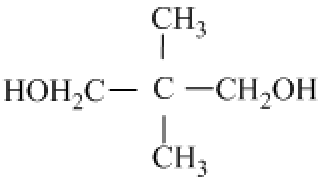
(iv) Cross-linking monomers

(i) Glycol:

1,2-propylene glycol is the most widely used diol. Other diols are used for special requirements. Diethylene (1) and triethylene glycols impart greater flexibility. 2,2’-dimethyl-1, 3-propanediol (2) gives resin with improved thermal and UV resistance. The resistance to alkali is enhanced by glycols with large molecules like bis-glycol (3).

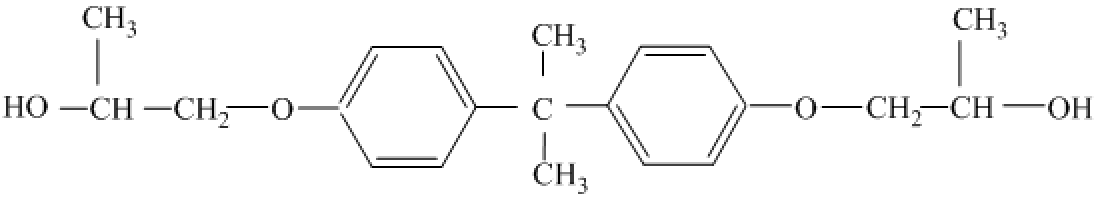
$$HO-CH_2-CH_2-O-CH_2-CH_2-OH$$

(1)



$$HOH_2C-C(CH_3)_2-CH_2OH$$

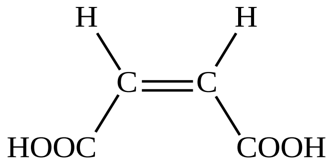
(2)



(3)

(ii) Unsaturated acids and anhydrides:

Maleic acid (4) or more usually anhydride (5) or fumaric acid (6).



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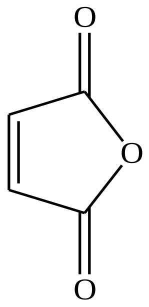

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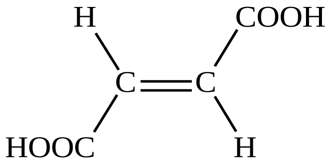
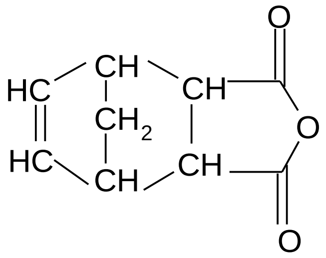


(6)

(iii) Saturated modified acids and anhydrides:

These are employed in order to increase the distance between the double bonds along the polymer chain. Hence,the resins have reduced cross-linking density and consequently are less brittle. Phthalic anhydride is the widely used compound. Isophthalic acid is used where higher heat deflection temperature and better alkali resistance are required. Succinic anhydride, adipic and sebasic acids are used for more flexible cured resins for coating. Nadic anhydride (7) gives resin with improved heat and chemical resistance. Flame resistant resins are prepared by using tetrachlorophthalic anhydride (8) or chlorendic acid (9).



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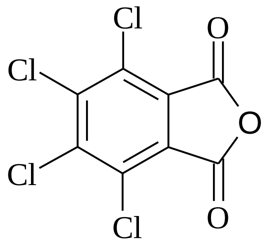

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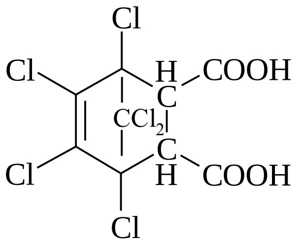
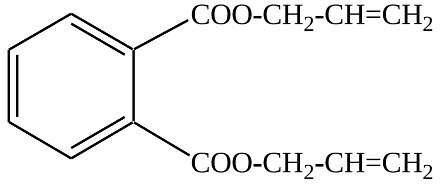


(9)

(iv) Cross-linking monomers:

Styrene is the most widely used cross linking monomer. It serves as solvent to reduce the viscosity of the resin and to facilitate the impregnation of glass fibre. Monomers such as divinyl benzene can replace styrene. Other monomers are employed for special property resins. Methyl methacrylate in 50% mixtures with styrene gives better weather resistant and translucent products. Improvements in heat resistance are also obtained by replacing styrene with diallyl phthalate (10) or by triallyl cyanurate (11).



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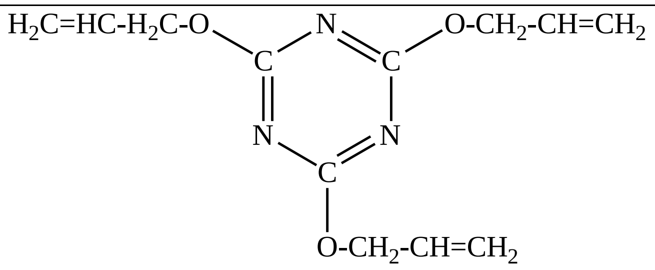


(11)

- ***Synthesis***

Unsaturated polyesters (USPE) are usually produced by batch wise condensation of dicarboxylic acids or anhydrides with diols. Dicarboxylic acids are esterified with diols at 180 – 230 °C under nitrogen atmosphere in thermostat with stirring. Esterification is generally being performed with a slight excess (upto 10 %) of diols. The water formed in the reaction is distilled off. The end point of the condensation is determined by measuring the acid number and possibly, also the hydroxyl number and the viscosity. Commercial resins have a mean molecular mass of 2000 – 4000 mol/wt. The liquid melt is cooled and then dissolved. The styrene contains inhibitors such as hydroquinone or tert-butylcatechol added.

- ***Classification of Unsaturated Polyester Resin***

On the basis of their properties unsaturated polyester resin can be classified as follows:

1. General purpose Polyester Resin

2. Flexible Polyester Resin

3. Chemical Resistant Polyester Resin

4. Resilient Polyester Resin

5. Speciality Polyester Resin

6. Fire Resistant Polyester Resin

7. Electrical Resistant Polyester Resin

- ***Curing and Applications***

At normal temperatures USPE resins can be cured with peroxides and accelerators. The most important systems include hydroperoxides like methyl ethyl ketone peroxide, cyclohexanone peroxide with cobalt octanoate or vanadium octanoates or cobalt naphthenates, as well as benzoyl peroxide with aromatic amines. At elevated temperatures only peroxides are required for curing. USPE resins can also be cured in a few minutes by exposing them to UV light from high pressure mercury vapour lamps in the presence of photosensitizers like benzoin ether.

Cured resins are thermosetting, infusible and insoluble materials. Their mechanical properties are maintained upto 100°C and maximum upto 150°C for reinforced general purpose resins. They are polar in nature.

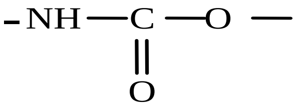
They are mostly used as a matrix material for fabrication of glass fibre composites. The major applications of USPE resins are in automobile, marine and construction industries [20]. Common applications are for boat hulls, sports car bodies, truck cabs and public transport vehicles. They are also used for making decorative furniture castings, ornamental stone, buttons, trays, bowling balls, safety helmets, chemical processing equipments, missile shells and rocket motor cases.

2.2 Polyurethanes:

The polyurethanes are widely used in the fields of daily life due to its excellent wear resistance, toughness, mechanical properties and chemical resistance. It is an important class of block polymer in which the properties of the end product can be designed according to the user need. Due to potential large volume of applications combined with high versatility in the properties, these materials require a thorough understanding of synthesis and properties as well as update of knowledge.

The ability of a synthetic chemist to maneuver numerous possibilities and combinations ideally suits the synthesis of polyurethanes and their development. Polyurethane comprises a class of materials ranging widely in their properties and this versatility is associated with a greater than normal complexity in manufacture. Indeed the manufacture of polyurethanes involves a greater degree of control of chemical reactions than most other polymers. Their properties range from liquid, soft and rubbery solid to rigid thermoplastics and thermoset materials [23-26].

Polyurethanes are long chain molecules in which different chemical fragments are linked by the below linkage.



$$-NH-\underset{\underset{O}{\|}}{C}-O-$$

The chemical term for the unit is an ester of carbonic acid but the whole of this polymer is called polyurethane, which is a misnomer that arose from the compound ethyl carbamate ($H_2NCOOC_2H_5$), which has been known for many years by the simple term “Urethane”.

There are wide ranges of raw materials; both active hydrogen containing compounds as well as isocyanate bearing monomers, available to design the polyurethane building blocks. The resulting oligomers / polymers can be obtained for tailor-made performance in surface coatings. In fact the polyurethane resins have proven high performance film forming binders for variety of industrial coating applications. This is due to their inherent characteristics in terms of

(a) Wide range of flexibility coupled with toughness

(b) High chemical and abrasion resistance and

(c) Low temperature cure .

The usual coating compositions are polymer solutions in organic solvents and like all solvent borne coatings they suffer from shortcomings such as high volatile organic content (VOC) and flammability. To overcome these limitations of solvent borne coatings, the current trend is towards Radiation (UV) curable coatings. Urethane acrylate oligomers are important building blocks for such systems which find wide industrial acceptance because they impart the toughness, abrasion resistance and elastomeric properties inherent in PU coating [27]. These PU Oilgomers / polymers therefore cover a wide range of industrial applications, including binders for magnetic media, vehicles for inks, and coatings for vinyl floor tiles, optical fibers and paper [28-29].

The workability and properties of finished urethane acrylate are strongly governed by chemical nature, structure and molecular size of reactants i.e. isocyanates, polyol and hydroxy alkyl acrylate. The relative ratios of these three components can also be varied. These stoichiometric changes allow variations in molecular weight, degree of unsaturation and urethane content, which in turn leads to possibility of exploring the same for varied coating and ink applications.

2.2.1 Isocyanate:

The modern polyurethane industry is based on Isocyanate chemistry. This organic functional group is capable of a surprisingly diverse range of chemical reactions. As the foundation of the polyurethane industry, Isocyanates are among the most heavily produced specialty organic chemicals.

The first synthetic route for isocyanate is reported by Wurtz in 1848 by reacting organic sulphates with cynic acid salts. The work of Wurtz clearly demonstrated the preparation of monoisocyanates and the subsequent formation of urethanes and substituted urea linkages by reaction of the isocyanate group with a primary alcohol and a secondary amine respectively. Following efforts by Hoffmann, Curtius, and Hentschel pioneered alternative synthetic approaches. These efforts highlighted the phosgene-amine approach.

$$R_2\ S\overline{O_4} + 2KCNO \longrightarrow 2RNCO + K_2SO_4$$

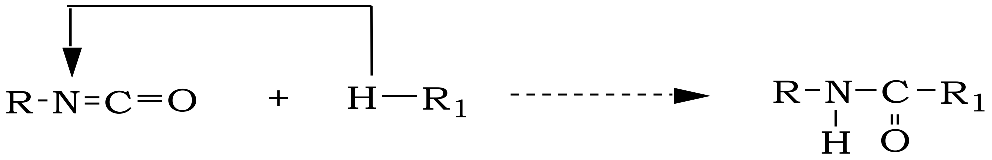
Staudinger elucidated the structural similarities between isocyanate and ketenes and stimulated interest in this class of compounds. However, it was not until 1945, when the world was pressed for an alternative to natural rubber, that synthetic routes to isocyanates become an area of commercial importance. Since then, sources of different reactions of organic isocyanates have been described in the chemical literature. Most of these have been used experimentally for the synthesis of polymeric materials; however, only a handful has reached industrial significance. The actions at isocyanates fall into two broad categories:

(a) Active hydrogen donors

(b) Nonactive hydrogen reactions

The most important category comprises reactions involving active hydrogen. This category of reactions requires at least one co-reagent containing one or more hydrogen that are potentially exchangeable (or labile) under the conditions of reactions. The familiar reaction of isocyanates with polyol, to form polycarbonates, is of the active hydrogen type. The active hydrogen groups are, in this case the hydroxyl groups on the polyol. Non-active hydrogen reactions constitute the second broad category. These include cycloaddition reaction and linear polymerizations.

The isocyanate functionality (-N=C=O) is highly reactive towards proton-bearing nucleophiles. This reaction occurs by nucleophilic addition across the carbon nitrogen double bond. Aromatic isocyanates are generally more reactive then aliphatic isocyanates. The classical *"active hydrogen"* reaction involves compounds containing replaceable hydrogen i.e. hydrogen replaced by sodium in the active hydrogen reaction, the hydrogen becomes attached to the isocyanate nitrogen, and the remainder of the active radical ($R^{\bullet}$) becomes covalently attached to the carbonyl carbon, according to the reaction shown below:



Isocyanates are colorless liquid and highly toxic in nature and care should be exercised during their usage.

- ***Monoisocyanates:***

Monoisocyanates are used to synthesize mono-functional urethanes, which are used to improve adhesion to difficult substrates and to improve the flexibility. These materials show very low viscosity e.g. methyl isocyanate.

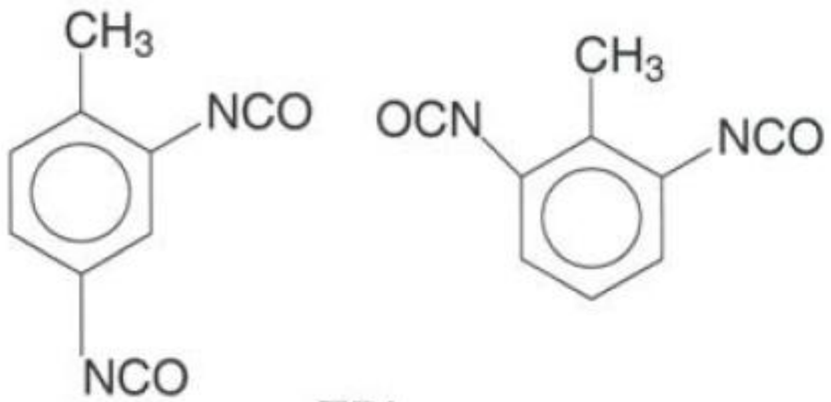
- ***Diisocyanates*:**

They are most widely used in urethane synthesis and are further divided in two categories such as: aliphatic diisocyanates and aromatic diisocyanates.

- ***Aromatic isocyanates:***

(i) Diisocyanato toluene / toluene Diisocynate (TDI)*:*

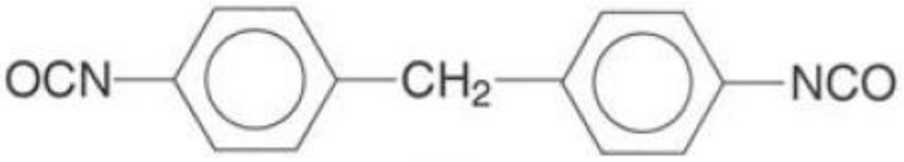
In the industrial use of the polyurethane, the toluene derivative (TDI) has been key of importance in the coating sector. Toluene diisocynate is chiefly used as a mixture of the 2, and 2,6- isomers in the ratio of 80:20 and less commonly as 65:35 and pure 2,4 compound. The different reactions of the *ortho* and *para* NCO group are exploited specifically for the particular application. At temperatures below 100°C the NCO group in the para positions is more reactive than the NCO group in the ortho position. This important fact allows the variation of reaction by offering the isomer mixture one advantage, for example is possibility to produce the derivatives with a narrow molecular weight distribution that can be achieved with equal reactive NCO group.



TDI

(ii)Diisocyanato diphenylmethane / Diphenyl methane diisocyanate (DMDI):

The second most important aromatic diisocyanate used in the coating is 4-4’-diphenylmethane diisocyanate. It is also supplied as a standard product by many manufacturers,usually mixed with homologues (approximately 30-70% bicyclic, 15-40% tricycilic and 15-30% polycyclic). These supply forms have the advantage that unlike pure MDI, these are liquid at ambient temperature and therefore easy to handle and derivative.



MDI

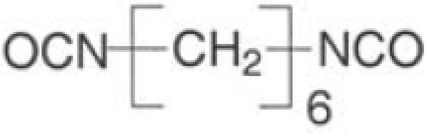
Isomer mixture such as 60% 2,4 MDI and 40$ 4,4 MDI are of less significance in coating application.

MDI has special role in formulation of coating, as unlike all the other diisocynate used in the coating sector it requires no further derivation before use. This is possible because of its relatively low vapor pressure that allows safe handling even at an ambient temperature.

Aromatic isocyanates are used to synthesize harder urethanes which show excellent scratch resistance. Aromatic isocyanates are also available at significantly lower cost than aliphatic isocyanates. The major drawback of aromatic urethanes is that they turned to yellowish in color and therefore they are less appropriate for long term applications on white colored substrates.

- ***Aliphatic diisocynate:***

(i) 1,6-Diisocyanatohexane /Hexamethylene diisocyanate (HDI): since its introduction in the coating sector in the early 1960's1, 6 HDI has become by far the most important base product for aliphatic derivatives.

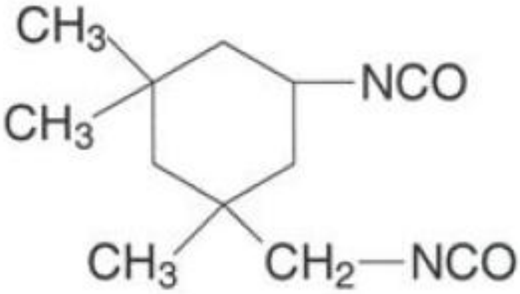


$OCN-[CH_2]_6-NCO$

HDI

Coatings based on these substances have set a standard of quality that even today remains unrivalled.

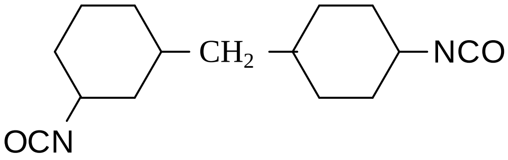
(ii) 3,5,5'- Trimethyl-cyelohexyl isocyanate/ isophorone diisocynate (IPDI): this aliphatic diisocynate is usually a mixture of approximately 75% cis and 25% trans isomers.



IPDI

IPDI has an unusual characteristic for individually available aliphatic diisocynate which makes in extremely valuable for custom modification synthesis. IPDI has two isocynate group of differing reactivity exceptionally perhaps from sterical reason the secondary cycloaliphatic NCO group being many times more reactive than the primary and secondary NCO groups can be increased selectivity. This allows a balancing or even a reversibility of the reactivity of the two NCO groups.

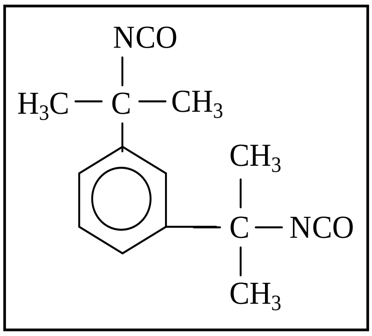
(iii) 4-4'-Diisocynate Diucychlohexyl Mehtane (H_{12} MDI):- H_{12} MDI is equivalent in formula to dehydrated MDI. The cycloaliphatic is supplied asan isomer mixture (approximately 30% cis/cis, approximately 50% cis/trans, approximately 20% trans/trans)



H_{12}

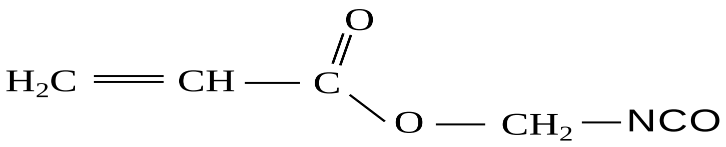
The following diisocynate are of this significance but also used as building for light fast polyurethanes.

(iv) M-Tetra methyl xylylens Diisocynate (TMXDI):- Although this substances has on aromatic ring. The NCO groups are not bonded directly to this ring.



(v) Trimethyl Hexamethylens Diisocynate (TMDI):-

For the sake of completeness, mention should be made of special monoisocynates with a second functionality in the form of unsaturated polyurizable groups. Because of their two chemically different bonding principles, these polymer building blocks provide interesting synthetic option. These can be used to manufacture copolymer with NCO groups from e.g.acrylis or methylacrylate monomers or to synthesize polymerizable polyurethanes. These have a minimal role in the coating sector because of their high price and are found only in special application eg. Special monoisocynates is the acrylate with double carbon bond shown in following formula.



$$H_2C{=}CH{-}C({=}O){-}O{-}CH_2{-}NCO$$

Urethanes synthesized from aliphatic diisocyanates are termed as aliphatic urethanes. They are used to synthesize flexible urethanes. They offer non-yellowing property and therefore can be used for long lasting applications [30-34], on white or colored substrates. They also offer good weathering properties.

2.3 Epoxy resins:

2.3.1 Introduction:

Epoxy resins represent an important class of polymers primarily due to their versatility. High degree of cross linking and the nature of the interchange bonds give cured epoxies many desirable characteristics. These characteristics include excellent adhesion to many substrates, high strength (tensile, compressive and flexural), chemical resistance, fatigue resistance, corrosion resistance and electrical resistance [35]. In addition, processing is simplified by the low shrinkage and lack of volatile by-products. Properties of the uncured epoxy resins, such as viscosity, which are important in processing [36], as well as final properties of cured epoxies such as mechanical strength or electrical resistance can be optimized by appropriate selection of the epoxy monomer and the curing agent or catalyst [38]. Because of the ease of application [37] and desirable properties, epoxies are widely used for coatings, corrosion protectants , electronic encapsulants, fiber optic sheathing, flooring and adhesives. Given so many everyday uses, every hardware store carries a wide selection of epoxy adhesives and coatings [39-45].

Epoxy resins are the most versatile class of contemporary plastics. Due to tendency of undergoing variety of chemical reactions, it became material of choice for researchers for several years. By the help of reactions like co-polymerization, chain extension by reactive diluents, side chain modification, incorporation of variety of fillers and structure modifiers, the resin structure can be modified. The capabilities of undergoing vast chemical reactions of the resins the desire properties can be achieved. Epoxy resins are widely used as a matrix in composites in different applications where chemical, mechanical, thermal, and dielectric properties are necessary. In addition, epoxy resins are versatile crosslinked thermosetting polymers with an excellent chemical resistance and good adhesion properties to different substrates. Due to these properties, they are used as adhesives and coatings [46-50].

Epoxy is best for laminates in combination with glass fiber to achieve excellent electrical insulators. Use of epoxy resins in composite matrix in high technology areas are limited, as these areas require material with inherent low thermal expansion coefficients and high toughness and better heat and moisture stability. Recently, a lot of research work has been done to improve the required parameters of epoxy resins through modifications in both the backbone and pendant groups.

The properties which result in successful adhesives and coatings also made epoxies the obvious choice for matrices in fiber-reinforced composites [51-58]. Today glass fiber-reinforced epoxies are commonly the major components in boats, aircraft, automobiles, medical prostheses and sports equipment. Epoxies and fiber-reinforced epoxy composites have influenced sports equipment, especially for common leisure sports such as tennis, but perhaps more importantly, in high visibly sports, including Olympic [59-64].

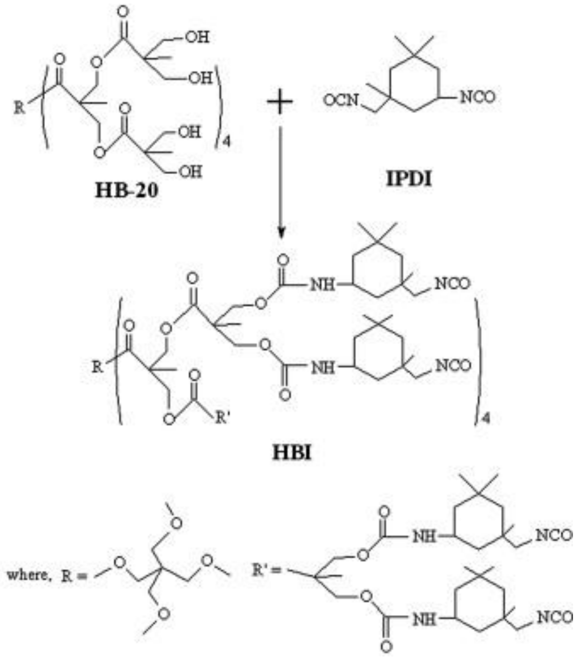
Unsaturated polyesters, polyurethanes and epoxies discussed above have particular individual properties and applications. Hence, many researchers have synthesized co-poly (urethane-ester)s from different raw materials in order to obtain the properties and applications of the individual ones into single segment. Some of the poly(urethane-ester)s and clubbing of unsaturated polyesters, polyurethanes, epoxy and polyamide by different researchers are briefly outline below.

2.4 Poly(urethane-ester)s:

Rasmika H. Patel et al prepared flame retardant coatings from poly(ester-urethane) from phosphorous-containing polyester polyols and different isocyanates like toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HMDI). The flame-retardant properties of cast films were determined by limiting oxygen index analysis and UL-94 test methods. The physical and mechanical properties of polyester-urethane coatings such as pot life, drying properties, scratch hardness, pencil hardness, impact resistance, adhesion, and flexibility were investigated. In addition, the chemical resistance properties of coatings were also determined. The data reveal that polyesterurethanes hold promise for use as effective flame-retardant coatings [65].

Przemyslaw Czech et al. formulated polyurethane chain in networks cross-linked by hyperbranched polyester. Several non-conventional polyurethane (PU) networks cross-linked with hyper branched polyesters were synthesized with an aim to determine an influence of the PU chain length on molecular relaxations in such systems. The PU chain length was regulated by changing the macrodiol length or by changing the number of the repeating macrodiol/diisocyanate units *n*. Molecular dynamics were investigated by broadband dielectric spectroscopy and by dynamic mechanical analysis. It was found that the macrodiol length has a strong influence on the glass transition and the α-relaxation, and also on the crystallization. By contrast, the changes of *n* practically do not affect the molecular relaxations [66].

Jie Zhang et al. has synthesized Aliphatic polyester-based polyurethane (PU) elastomers with hyperbranched polyester segments were synthesized from polyester diol, hydroxyl-terminated hyperbranched polyester (HB-20), isophorone diisocyanate (PDI) and 1,4-butanediol. The crosslinking density of the PU elastomer was calculated by using Flory–Rehner equation. The experimental results showed that the PU elastomers containing small amount of HB-20 exhibited the enhanced hydrogen bonding and mechanical properties. As compared with the comparable PU specimen, the tensile strength of the polyester-based aliphatic PU containing 6 wt% HB-20 increased by 71.2 times, up to 36.1 MPa, and the elongation at break was still as high as 333.1%, resulting from the dual effects of the hydrogen bonding and the crosslinking density in the PU system [67].



Ludovic Valette et al. prepared hybrid networks of Polyurethane and unsaturated polyester and studied the Influence of hard domains on mechanical properties. The influence of hard domains on the mechanical and thermomechanical properties of polyurethane and unsaturated polyester hybrid networks has been investigated. The hybrid networks consist of a polyurethan linkage formed by reacting unsaturated polyester polyol with polymeric 4,4′-diphenylmethane diisocyanate (MDI) and free-radical crosslinking through styrene monomer and vinylene groups in the unsaturated polyester. Hard segments were formed by condensing two different types of chain extender, ethylene glycol (EG) and 1,6-hexanediol (HD), with MDI. Incorporation of chain extenders in the hybrid networks varied from 0% to 12% by weight based on the weight of unsaturated polyester polyol. The thermomechanical properties of the polyurethane and unsaturated polyester hybrid networks were characterized by heat distortion analysis and by dynamic mechanical analysis. The hybrid network had improved mechanical properties when more hard segments were added into it without creating the phase-separated hard domains. A dramatic drop in mechanical properties was observed for the sample with a two-phase structure [68].

F. J. Hua et al. produced Interpenetrating polymer networks of epoxy resin and urethane acrylate resin. A series of simultaneous interpenetrating polymer networks composed of epoxy resin (epoxy) and urethane acrylate resin (UAR) with different compositions were synthesized and the polymerization kinetics of both network formations was monitored by using a Fourier transform infrared spectroscopy for the potential application in the reaction injection molding process to prepare the toughened epoxy materials. It was found that during the course of synthesis the polymerization rate for formation of both pure networks has almost no dependence on the concentration of reactants, especially at the early stage of reaction and the two pairs of reactants interfere with each other significantly, although they followed different polymerization mechanisms. All these unusual polymerization kinetics behaviors observed could be correlated well with the changes of viscosity and morphology of the systems [69].

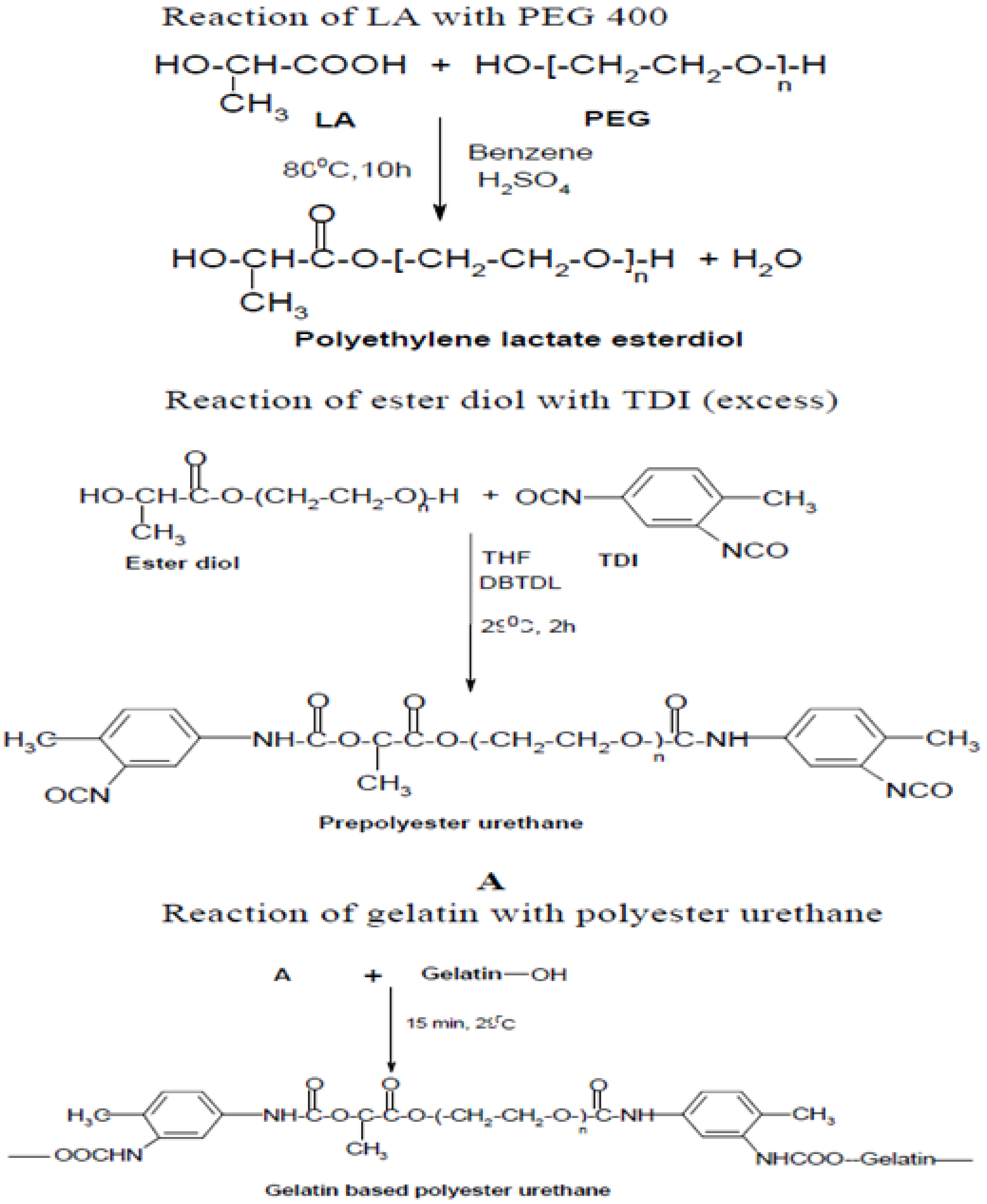
L Irusta et al. prepared Aromatic poly(ester–urethanes) from Photooxidation of 4,4’-methylene bis(4-phenylisocyanate) and toluene diisocyanate and studied the effect of the polyol molecular weight on the photochemical behavior. The results have been related to the hard/soft segment phase mixing, studied by differential scanning colorimetry [70].

Lina Zhang et al derived cross-linked materials from poly(ester-urethane) and nitrochitosan. They have prepared poly(ester-urethane) from Poly(ethylene glycol adipate) and TDI.The extent of the photolysis reaction in the urethane linkage is more relevant in higher soft segment molecular weight based polymers. The phase separated structure is a critical factor which must be taken into account in order to study the extent of the photodegradation of the hard segments in aromatic poly(ester–urethanes) [71].

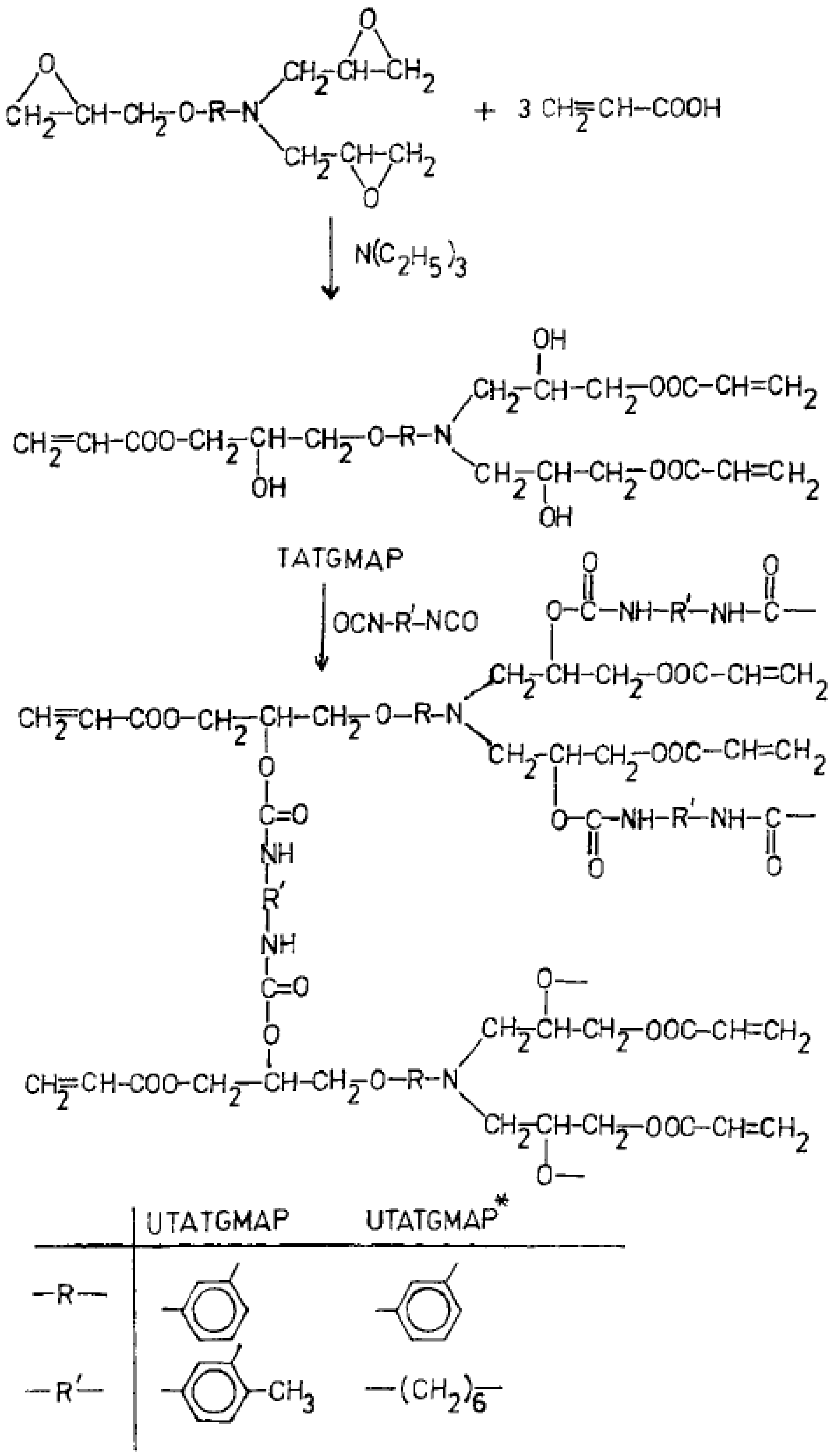
Interpenetrating polymer networks (IPNs) were prepared by K. H. Hsieh from polyurethane (PU) crosslinked epoxy and polyurethanes based on the mixture of polydiol and polytriol by the one-shot method. The mechanical properties, dynamic mechanical properties, morphology and damping behaviour were investigated. The results show that the damping ability and mechanical strength are enhanced through the introduction of PU cross-linked epoxy into the PU matrix to form the IPN structure. As the epoxy content increases, the tensile strength of the two types of the IPNs decrease in low composition, then increase in high composition. The damping properties of the PU (polyether type) cross-linked epoxy/PU IPNs are much better than those of the PU (polyester type) cross-linked epoxy/PU IPNs, but the mechanical properties reveal an opposite tendency. The sample with 20 wt% epoxy content in the PU cross-linked epoxy/PU IPNs shows particleĐmatrix morphology and exhibits good damping properties [72]

S. Oprea prepared Polyurethane network films using polyester urethane acrylate (PUA) having terminal double-bond functional groups and acrylated epoxidized soybean oil (AESO). PUA elastomers were prepared by reacting polyester diol with diisocyanates, hexamethylene diamine, and acrylic acid. PUA/AESO network blends are synthesized by a simultaneous thermal polymerization process. The physical and thermal properties of the polymer networks obtained from the blend of AESO and polyester urethane urea acrylate were studied using FTIRATR, the thermal degradation behavior was studied by thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical analysis, and tensile properties measurements being applied. The measurements were compared to the results for elastomers made from the PUA. The weight ratios of PUA/AESO affected the thermal and mechanical properties [73]

B Adhikari et al prepared gelatin based polyester urethane scaffolds of different compositions from lactic acid, polyethylene glycol 400 (PEG 400) and characterized by FTIR, XRD for their mechanical and morphological properties using SEM and optical microscopic analyses. Degradation and swelling studies of gelatin based polyester urethane scaffolds in phosphate buffer saline (PBS) were performed [74].



Dipak K. Raval et al. developed glass-fibre-reinforced composites of a vinyl ester resin from triglycidyl- m-aminophenol and its urethane derivatives. The fabricated laminates were characterized by their mechanical properties and chemical resistance. The incorporation of vinyl monomer styrene in the resin system was found to improve some properties of composites remarkably [75].


+ 3 CH2=CH-COOH
N(C2H5)3
TATGMAP
OCN-R'-NCO
UTATGMAP
UTATGMAP*
—R—
—R'—
CH3
—(CH2)6—

2.5 Poly(ester-amide)s:

Kamal I. Aly et. al. developed a new category from poly(ester-amide)s based on diarylidenecyclohexanone in the main chain via interfacial polycondensation technique of two monomers namely: 2,6-bis (4- hydroxybenzylidene) cyclohexanone and 2,6- bis (4-hydroxy-3-methoxybenzylidene) cyclohexanone with diacid chlorides. The model compounds were synthesized by reacting one mole of compound with the two monomers. The structure of the model compounds was confirmed by correct elemental and spectral analyses [76].

A. K. Mow and co-workers synthesized novel biocomposites from a cheap, renewable natural fiber, coir (coconut fiber) as reinforcement with a biodegradable polyester amide (BAK 1095**)** matrix**.** In order to have better fiber-matrix interaction the fibers are surface modified through alkali treatment, cyanoethylation, bleaching and vinyl grafting. The effects of different fiber surface treatments and fiber amounts on the performance of resulting biocomposites are investigated. Among all modifications, cyanoethylated coir-BAK composites show better tensile strength (35.50 Mpa) whereas ***7%*** methyl methacrylate grafted coir-BAK composites show sigdicant improvement in flexural strength (87.36 MPa).The remarkable achievement of the present investigation is that a low strength coir fiber, through optimal surface modifications, on reinforcement with BAK show an encouraging level of mechanical properties. Moreover, the elongationat break of BAK polymer is considerably reduced by the incorporation of coir fibers [77].

J. Puiggal et al. derived crystalline structure of two sequential poly(ester amide)s from glycine, terephthalic acid, and 1,6-hexanediol or 1,12-dodecanediol has been investigated using X-ray and electron diffraction and real space electron microscopy. Crystal packing shows features of both polyamides and polyesters. The structures of the two studied poly(ester amide)s are characterized by the establishment of strong hydrogen-bond interactions along a single direction. The morphology of lamellar crystals has been investigated, their high aspect ratio being consistent with the existence of a preferential crystal growth direction. A deviation from an all-trans conformation has been detected for both polymers. Differences in crystal packing have been found depending on the number of aliphatic methylene groups. In this way, orthorhombic and triclinic unit cells have been deduced for the dodecanediol and the hexanediol derivatives, respectively. Their structures are based on a different arrangement of sheets constituted by hydrogen-bonded molecular chains [78].

Wenjeng Guo prepared two naphthalene-ring-containing bis(ester-amine)s, 2,3-bis(4-aminobenzoyloxy)naphthalene (p-2) and 2,3-bis(3-aminobenzoyloxy)naphthalene (m-2), from the condensation of 2,3-dihydroxynaphthalene with 4- nitrobenzoyl chloride and 3-nitrobenzoyl chloride, respectively, followed by catalytic hydrogenation. The novel aromatic poly(ester-amide)s and poly(ester-imide)s having 2,3-linked bis(benzoyloxy)naphthalene units have been synthesized from the polycondensation reactions of bis(ester-amine)s (p- 2 and m-2) or an equimolar mixture of 4,4′-oxydianiline and p-2 or m-2 with various aromatic dicarboxylic acids and dianhydrides. The synthesis of the poly(ester-amide)s was achieved by the phosphorylation polyamidation reaction by means of triphenyl phosphate, and the synthesis of the poly (ester-imide)s included ring-opening polyaddition to give poly(amic acid)s followed by chemical imidization to polyimides. Most of the poly(ester-amide)s were readily soluble in various organic solvents.[79]

Sharif ahmad created melamine modified polyester amide (MPEA) by the reaction of linseed oil fatty amide. The resin was further cured at room temperature by polystyrene comaleic anhydride (SMA) in different phr (30–80) to obtain MPEA coatings. The probable structure of MPEA was confirmed by FT-IR, 1H-NMR and 13C-NMR spectroscopic techniques. The physico-chemical characterization of these resins viz. iodine value, saponification value, refractive index, inherent viscosity were carried out by standard methods. MPEA (40 wt%) solution in ethylene glycol monomethyl ether (EGME) was applied on a mild steel strip of standard sizes to study their physicomechanical and chemical resistance properties. It was found that coatings of MPEA with 60 parts per hundred of the resin (phr) of SMA showed the best performance in physico-mechanical and alkali resistance properties.[80]

2.6 Poly(Ester-Amide)s containing epoxy residues:

Bisamic acids have been prepared using different diamines and maleic anhydride. Poly(ester-amide)s (PEAs) have been prepared by the reaction between bisamic acids and epoxy resins . The prepared poly(ester-amide)s were characterized by elemental analysis, IR-spectral study, molecular weight determination carried out by non-aqueous conductometric titration method and by thermal analysis. Interacting blends of the prepared poly(ester-amide)s have also been prepared using methyl methacrylate monomer. Glass fiber reinforced composites for both poly(ester-amide)s and poly(ester-amide)s-methyl methacrylate monomer blends have been laminated and characterized for their chemical, mechanical and electrical properties [81].

2.7 Research gaps about Poly(Urethane-ester)s:

As per available literature and technical reports, it is well known that epoxy resins, polyurethane and unsaturated polyester resins (UPEs) are independent polymer candidates for a wide range of industrial applications like microelectronics to aerospace.

Merging of all three i.e. Urethane, unsaturated esters and epoxy segments into single polymer chains has not received attention academically and technically. Assimilation of all three segments and unsaturation into the single polymer chain may alter the property landscape. Therefore, this hypothesis is interesting to undertake the novel multiple unsaturated poly (urethane-ester) resins.

Thus aim of the present work is:

“Studies on multiple unsaturated poly(urethane-ester)s containing epoxy residues”

Chapter-3

Synthesis and characterization Techniques

The present chapter alienated into three sections.

The section-1 accord with the experimental details about the synthesis of acrylated multiple polyesters, acrylated polyesters and unsaturated poly(urethane-ester)s.

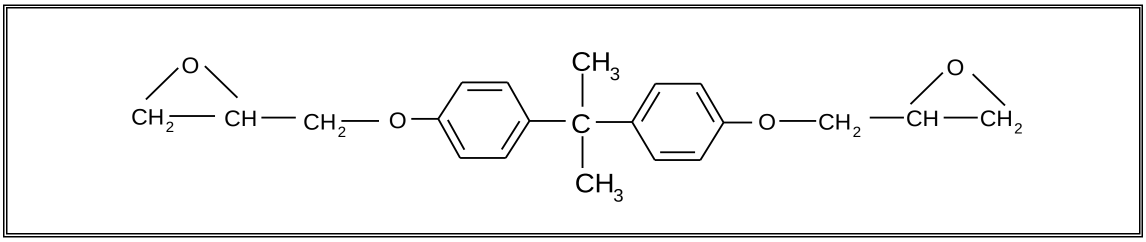
3.1.1 Materials:

Maleic Anhydride, acryloyl chloride, hexamethylene diisocyanate were obtained from Chiti Chem., Baroda, Gujarat (India).

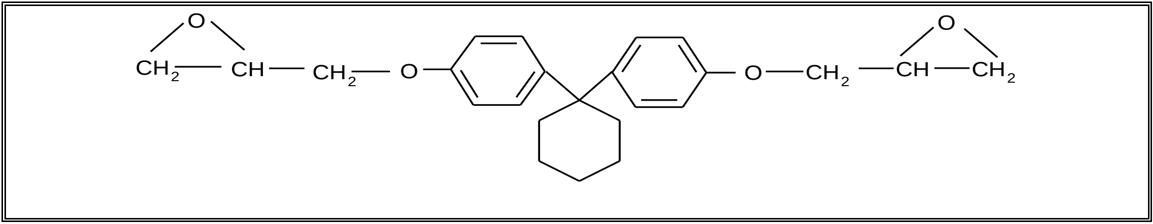
Diamines: All the diamines (listed in Table 3.1.1) were obtained as pure grade from Chiti Chem., Baroda. They were used without purification.

Epoxy Resins: Three epoxy resins were used. They were:

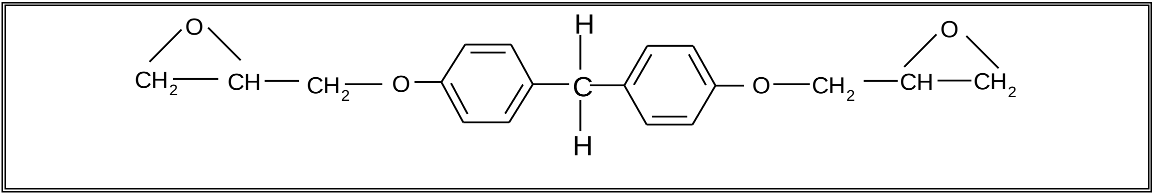
(1) Diglycidylether of Bisphenol-A (DGEBA): (IIa)



(2) Diglycidylether of Bisphenol-C (DGEBC): (IIb)



(3) Diglycidylether of Bisphenol-F (DGEBF): (IIc)



Out of three resins, two resins IIa and IIc (DGEBA and DGEBF) were obtained from ATUL Ltd , Valsad, Gujarat (India). The epoxy resin IIb (DGEBC) was synthesized by reported Method [82]. The specifications of three epoxy resins are furnished in Table 3.1.2. All the other chemicals used were of laboratory grade.

Table 3.1.1

List of Diamines used for synthesis of Bismaleicamic Acids

No.	Diamines	Molecular Formula	Melting Point (°C)
A	1,3-Phnylenediamine	$C_6H_8N_2$	**64-66 °C**
B	1,4-Phnylenediamine	$C_6H_8N_2$	**143-145 °C**
C	3,3’-Dimethoxybenzidine	$C_{14}H_{16}N_2O_2$	**137 °C**
D	3,3’-Diaminobenzophenon	$C_{13}H_{12}N_2O$	**150-151 °C**
E	3,3’-Diaminodiphenylsulfone	$C_{12}H_{12}N_2SO_2$	**170-173 °C**
F	4,4’-Diaminodiphenylsulfone	$C_{12}H_{12}N_2SO_2$	**175-177 °C**
G	4,4’-Diaminodiphenylmethane	$C_{13}H_{14}N_2$	**89-90 °C**
H	4,4’-Diaminodiphenylether	$C_{12}H_{12}N_2O$	**186-187 °C**
I	4-Methyl-1,3-phenylenediamine	$C_7H_{10}N_2$	**97-101 °C**
J	1,5-Diaminonaphthalene	$C_{10}H_{10}N_2$	**185-187 °C**

Table 3.1.2

Specifications of Epoxy Resins

No.	Epoxy Resins	*EEW	Viscosity (cps)
IIa	Diglycidylether of Bisphenol-A (DGEBA)	190	**40-100 at 25 °C**
IIb	Diglycidylether of Bisphenol-C (DGEBC)	210	**55-100 at 30°C**
IIc	Diglycidylether of Bisphenol-F (DGEBF)	160	**30-90 at 25 °C**

*EEW: Epoxy Equivalent Weight

3.1.2 Synthesis of Bismaleicamic Acids:

The bismaleicamic acids were synthesized by a simple addition reaction of maleic anhydride with different diamines (listed in Table 3.1.1) following the method reported in literature [83]. The general procedure for the synthesis of bismaleicamic acid is as followed:

To a well stirred solution of maleic anhydride (2.0 mole) in dry acetone, the solution of diamine (a-j) (1.0 mole) (as listed in Table 3.1.1) in dry acetone was gradually added at room temperature within 30 minutes. After complete addition of the diamine solution, the reaction mixture was further stirred for one hour at room temperature. The resulting bismaleicamic acid was then filtered, washed with dry acetone and air-dried.

All the bismaleicamic acids (I a-j) were obtained in the form of free flowing powder. All the acids were analyzed for their acid value by determining the carboxyl groups. The reaction scheme for the synthesis of bismaleicamic acid is shown in Scheme 3.1.

3.1.3 Synthesis of 1,1-bis(4-hydroxy phenyl) cyclohexane (Bisphenol-C):

This was prepared by method reported in literature [84].

3.1.4 Synthesis of Unsaturated Polyesters Resins (UPEs):

Epoxy resins (IIa-c) (1.0 mole) and bismaleicamic acids (Ia-j) (1.0 mole) were charged in three necked flask equipped with a mechanical stirrer. To this 8.0% of the total weight of above, triethylamine (TEA) was added as a base catalyst. The reaction mixture was slowly heated up to 85°C with continuous stirring. The reaction temperature was maintained at 85°C and at regular interval the samples were taken to check the acid value employing carboxyl end group analysis method. The reaction was continued till the acid value fell below 60 mg KOH/gm. The resin was then discharged to give Unsaturated polyesters (UPEs). It was in the form of pasty mass [85].

3.1.5 Synthesis of Acrylated Unsaturated Polyesters Resins (AUPEs) i.e. Multiple unsaturated polyesters:

Acrylation of Unsaturated Polyesters Resins have been carried out using acryloyl chloride as per method reported. The general procedure is as follows:

Unsaturated Polyesters Resins and acryloyl chloride both were taken in a 1:2 mole ratio, 1.008 g of hydroquinone and 1.67 g of imidazole were placed. The reaction content was heated in an oil bath at 100°C while stirring continuously. The reaction was carried out approximately for 7-8 h still the acid value was found to be between 2 to 5 [94].

The reaction route for the synthesis of acrylated Unsaturated Polyesters Resins using bismaleicamic acids and three different epoxy resins is shown in scheme 3.1. The details of the Unsaturated Polyesters Resins (UPEs IIIa-j, IVa-j and Va-j) and Acrylated unsaturated Polyesters Resins (AUPEs VIa-j, VIIa-j and VIIIa-j) are furnished in results and discussion.

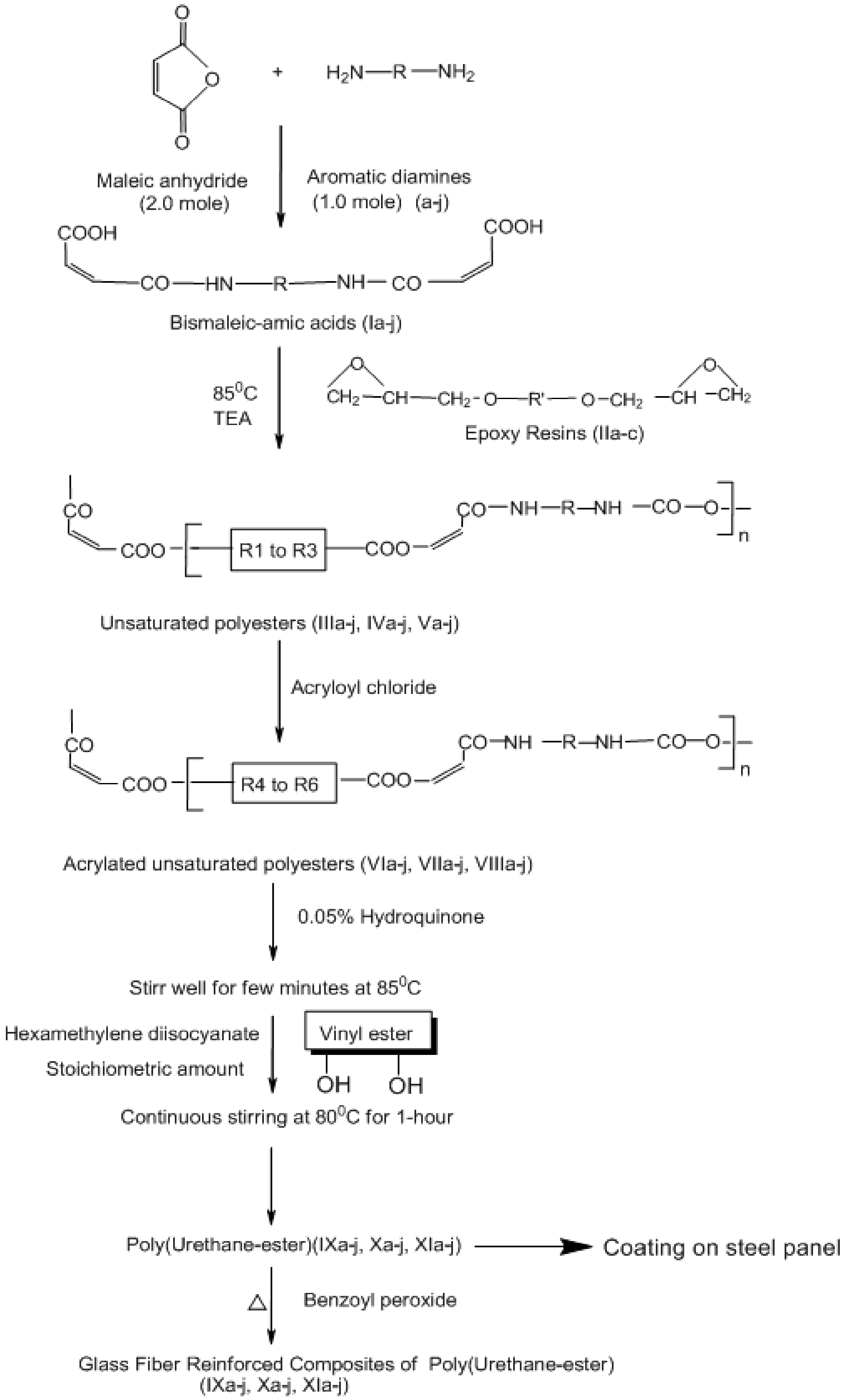
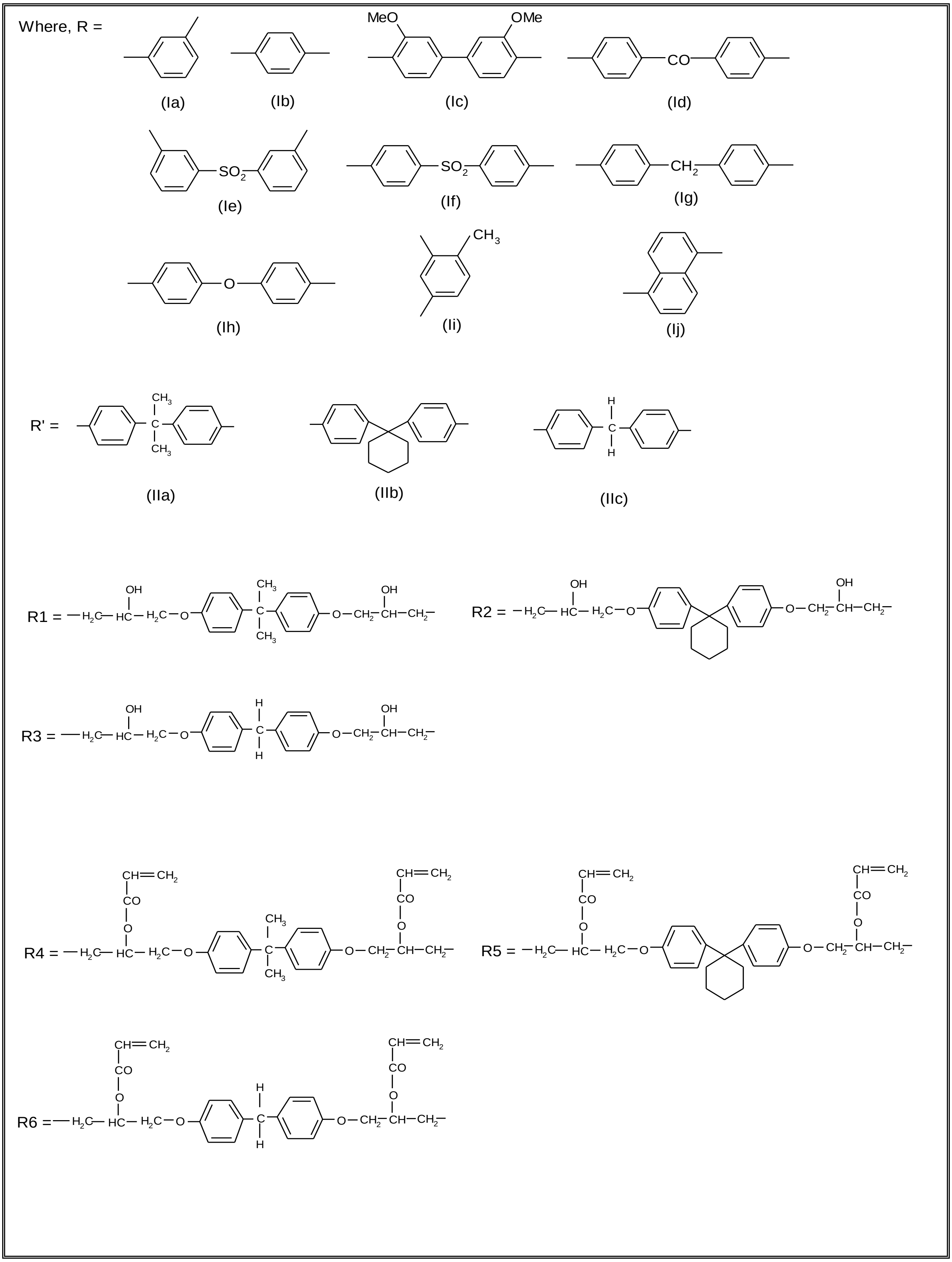
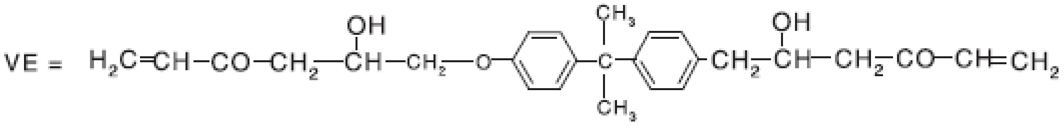


Figure 3.1: Scheme of Synthesis


Where, R =
(Ia)
(Ib)
MeO
OMe
(Ic)
CO
(Id)
SO2
(Ie)
SO2
(If)
CH2
(Ig)
O
(Ih)
CH3
(Ii)
(Ij)
R' =
CH3
C
CH3
(IIa)
(IIb)
H
C
H
(IIc)
R1 = —H2C— HC— H2C—O
OH
CH3
C
CH3
O—CH2—CH—CH2—
OH
R2 = —H2C— HC— H2C—O
OH
O—CH2—CH—CH2—
OH
R3 = —H2C— HC— H2C—O
OH
H
C
H
O—CH2—CH—CH2—
OH
R4 = —H2C— HC— H2C—O
CH=CH2
CO
O
CH3
C
CH3
O—CH2—CH—CH2—
CH=CH2
CO
O
R5 = —H2C— HC— H2C—O
CH=CH2
CO
O
O—CH2—CH—CH2—
CH=CH2
CO
O
R6 = —H2C— HC— H2C—O
CH=CH2
CO
O
H
C
H
O—CH2—CH—CH2—
CH=CH2
CO
O

- **Structure of Vinyl ester:**



3.1.6 Synthesis of poly(urethane-ester)s:

- **Materials:**

Commercially available vinyl ester and hexamethylene diisocyanate was obtained from local market. AUPEs VI - VIIIa-j were prepared according to the reported method. All other chemicals used were of pure grade.

- **Experimental:**

When the acid value of AUPEs VI - VIIIa-j fell below 60 mg KOH / gm, 0.05 % of the total weight of the above, hydroquinone was added as an inhibitor. The whole reaction mixture was stirred well for few minutes maintaining the temperature at 85°C. Then the temperature was lowered to 80°C and 50 % of the total weight of the above, vinyl ester and hexamethylene diisocyanate was added stoichiometrically. The reaction mixture was then continuously stirred at 80°C for one hour. It is then discharged to give the poly(urethane-ester)s. They were in the form of viscous resinous syrup [86].

Chapter 3, Section 2

Characterization Techniques

Section–2 of Chapter-3 contains analytical measurement techniques used for the characterization of the synthesized polymer.

3.2.1 Elemental Analysis:

The majority of organic compounds are composed of a comparatively small number of elements. The most important ones are: carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine, etc. Elementary quantitative organic analysis is used to determine the content of carbon, hydrogen, nitrogen and other elements in the molecule of the polymer. The C, H, N and S contents of all samples were estimated by using Thermofinagan 1101 flash elemental analyzer (Italy).

3.2.2 Infrared Spectroscopy:

Infrared spectroscopy gives information on molecular vibration or more precisely on transition between vibrational and rotational energy levels in molecules. This information is of immense help to organic chemists because it can be directly related to molecular structure.

Absorption of radiation in the infrared region results in the excitation of bond deformation, either stretching or bending. Various stretching and bending vibrations occur at certain quantized frequencies. When infrared light of that frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased.

An infrared spectrum is obtained when the frequency of molecular vibration corresponds to the frequency of the infrared radiation absorbed. The material under study is usually in the form of a solid, a neat liquid or a solution. Sometimes, however, a compound in the gas or vapour phase is studied. Under these conditions, in addition to changes in vibrational energy, simultaneous changes in rotational energy can occur and consequently some fine structures may be observed on the vibrational band.

The normal range of an infrared spectrum, used by organic chemists for structural study, extends from 4000cm^{-1} to 667cm^{-1}. The shorter wavelength region (12500-4000cm^{-1}) is referred to as near-infrared region and contains absorption bands due to harmonic overtones of fundamental bands and combination bands. The region extending from 667cm^{-1} to 50cm^{-1}

is referred to as far infrared region. The normal and far infrared regions contain absorptions due to fundamental harmonic and combination bands.

The use of linear-in-frequency instruments results in a considerable expansion of the high frequency end of the infrared region, resulting in an increased ability to resolve bands and define their positions. The position of absorption in the spectrum is usually expressed in terms of wave number (cm^{-1}) of the absorbed light.

The infrared spectrum is the simplest, most rapid and often most reliable means for assigning a compound to its class. It can also provide a variety of information on structure, symmetry, purity, structural and geometrical isomers and hydrogen bonding [87].

- ## IR Spectral Properties of Polymers :

As a consequence of the sensitivity of IR to change the dipole moments of the vibrating groups under examination, it is considered as one of the useful method for providing information regarding chemical and physical nature of the polymers. In principle IR spectroscopy furnishes the qualitative and quantitative information of structural units, type and degree of branching and end groups present in a polymer of interest. However, the quality of IR spectroscopy of a polymer primarily depends upon the correct sampling of polymer, otherwise a considerable amount of information may be lost or misinterpreted. Hence the thorough knowledge of sampling techniques for different forms of polymers, such as films, solid, solution, powder, pellet, granules, fiber etc. is very essential [88].

The polymer samples which are insoluble in common solvents do not give good IR spectra i.e. fine IR spectrum is not observed. Only few bands are easily detectable and in the major part of the spectrum it becomes difficult to observe the characteristic bands. In such cases the IR spectral data do not serve this purpose of even a comparative study.

The reliability of IR spectral data can be further improved by using computer supported IR spectral data, which can be easily added or subtracted from the selected data [89-90]. The most probable structure and chemical nature of the polymer of interest may be readily obtained from the certain characteristic group frequencies and their comparison with the IR data published as IR library. Henniker published the IR spectral data for many industrial polymers. These data can be used as references for identification of new polymers and plastics. An infrared library including monomers and polymers is commercially available from the Sedtler Research Lab.

The features of the IR spectra are usually observed in the region from 3500-2900 cm^{-1} for X-H stretching, in the region from 1800-1500 cm^{-1} for X=Y stretching. In X-H stretching region, bands are observed in the order of decreasing frequency as OH > NH > CH. Among C-H bands; SP C-H, SP^2 C-H and SP^3 C-H bands can be distinguished because of their different placements. In certain cases, bands due to C-H stretching of $–COCH_2–$ are observed and can be distinguished.

It is reported that the characteristic absorption of amines is due to N-H stretching vibrations in the region 3500-3200 cm^{-1}. The spectrum of primary amine shows absorption caused by free N-H stretching vibrations at 3597 cm^{-1} and 3497 cm^{-1}.

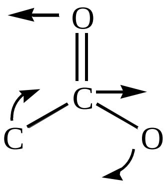
The strong absorption of the keto (>C=O) stretching of conjugated aryl appears at 1720-1660 cm^{-1}. The nature of groups decides the position of >C=O band in the IR spectrum.

The skeletal stretching vibrations due to –C=C– of the aromatic rings are observed in the region around 1580 to 1450 cm^{-1}. They are diagnostic of the presence of the aromatic system. Generally four bands are observed around 1615, 1580, 1465 and 1450 cm^{-1}. The latter band is often mixed up with the aliphatic C-H bending vibration band. The region from 1200-1000 cm^{-1} comprises many bands including the bands due to C-O and C-N stretching vibrations. The decision of the assignment of a band due to C-O and C-N stretching is difficult because the position of the band is variable and a band may get mixed up with other bands in the finger print region.

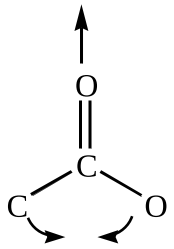
The region from 1010 to 610 cm^{-1} contains certain bands. Generally the spectra of all the compounds containing aromatic systems exhibit easily discernible bands in the region from 820 to 710 cm^{-1}. These bands are of particular interest because they are characteristic of the substitution pattern of the aromatic nucleus. It is a usual practice to examine this part of the spectrum to decide the presence of an aromatic system and to get, if possible, indications about the substitution pattern in organic system [91-95].

• IR Spectral Features of present polymer:

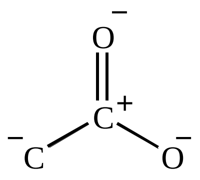
The IR spectra of polyesters have been studied extensively. If we consider the ester group as a plane, three-pointed star, then this "molecule" of four atoms is able to perform the following vibrations (wave numbers in brackets for gaseous acetone).



B$_1$ (530 cm^{-1})



A$_1$ (390 cm^{-1})



B$_2$ (490 cm^{-1})

The first one is asymmetric with respect to C=O axis and a degenerate vibration. During this vibration all atoms of the group perform non-linear movements in the plane of the ester group. In a first approximation, the single bonded C and O describe circles. The second one is a bending vibration symmetric to the C=O axis, the third one is an out of plane deformation vibration of the group. The above assignments were given by Mirone for gaseous acetone. The first of these vibrations is especially sensitive to mechanical coupling and inductive effects and may be found in the region between 650 cm^{-1} and 500 cm^{-1}. Also, the intensity has been found to vary strongly. The other two bands are frequently found near 350 cm^{-1} and 450 cm^{-1} respectively.

The far infrared spectra of styrene free samples of unsaturated polyesters from maleic acid show the characteristic band of maleic acid esters at 650 cm^{-1}, together with bands of other components at 670, 640 and 563 cm^{-1}. However, this picture may change considerably from one type of unsaturated polyester to another.

Polyamides are widely used thermoplastics. They contain sequences of secondary amide groups and aliphatic groups. IR spectra of polyamides have been studied extensively by polymer scientists. It shows amide bands have planar α - and β - forms compared with the corresponding bands of the non-planar γ - form. The polyamides in the α - or β - forms can be easily identified by the bands near 690 cm^{-1} and 580 cm^{-1}. The same polyamides in γ - form, absorb near 710 cm^{-1} and 625 cm^{-1}.

A very valuable fact is the sensitivity of the infrared spectrum of polyamides against polymorphism, which shows the >C=O band of –CO-NH at 1640 cm^{-1}.

The IR spectral study of unsaturated poly (ester-amide)s have not been studied so far. So we thought that it must consists the characteristic bands of the unsaturated polyesters and polyamides.

• IR Spectral Characteristics:

It is usually found that, the bands in the IR spectra of polymer samples are not so distinct as compared to the bands in the spectra of the normal molecules. This presents a major difficulty in understanding and deriving crucial details about all the structural features of the polymer molecules. The bands falling in the region of other strong bands, are not so easily discernible in the spectra of polymers. Hence in the present case the positions of all the easily discernible bands of spectra are noted. Even the positions of inflections at certain characteristic positions are also noted. Anticipated IR spectral features of UPEs samples are furnished in Table 3.2.1

Table: 3.2.1

Anticipated IR spectral features

No.	Group	IR Characteristics (cm^{-1})
A	Esters α,β - unsaturated >C=O Stretching	1730 – 1715
B	>C=O stretching NH bending NH stretching	1700 – 1670 1550 – 1510 3320 – 3140
C	C – O stretching (Ar–O–Ar / R)	1270 – 1250
D	Aromatic C – H stretching (Phenyl) Ring breathing modes (Phenyl)	 3500 – 3300 1600 – 1450
E	Aliphatic C – H stretching (Sym.) C – H stretching (Asym.)	 2870 – 2845 2940 – 2915
F	Hydroxy >CH–OH (OH stretch) O – H bending C – O stretching	3600 – 3200 (s) 1350 – 1250 (s) 1120 – 1030 (s)
G	Alkene Cis R-CH=CH-R,C=C stretching	1655-1660.

- **Experimental:**

IR spectra of the polymer samples were recorded in KBr. Carefully purified and dried KBr was used for purpose. The pellet for the IR study was prepared by mixing uniformly 2-3 mg of polymer sample with 1gm of pure crushed KBr. This mixture is compressed to a disc at a pressure of 15,000 psi in vacuum. The spectrum of pellet was scanned on “Nicolet 760D” IR spectrometer. IR spectra of UPEAs are shown in results and discussion chapter.

3.2.3 Molecular Weight Determination of Acrylated unsaturated polyesters:

The molecular weight determination of Acrylated unsaturated polyesters was done by end group analysis and by vapor pressure osmometry (VPO) method. The non-aqueous conductometric titration method was employed to determine the carboxyl group.

- **Introduction:**

The molecular weight characterizes the size of a molecule. While for low molecular weight substances have certain uniform molecular weight, it is their characteristic. All synthetic and many natural macromolecular substances are polydisperse in their molecular weight. It means that they have a range of molecular weight distribution. Keeping this in mind, the concept of average molecular weight is adopted for polymers.

Various definitions of the molecular weight of a polymer have been formulated depending on the method employed in the measurement of the molecular weight of the polymer. The general criteria used in the estimation of average molecular weight of the polymer is either to determine number average molecular weight ($\overline{Mn}$), weight average molecular weight ($\overline{Mw}$) or viscosity average molecular weight ($\overline{Mv}$). Their definitions are as follows:

(1) Number average molecular weight ($\overline{Mn}$):

$$(\overline{Mn}) = \frac{\sum n_i M_i}{\sum ni} = \frac{\sum W_i}{\sum W_i / M_i}$$

The methods employed for the estimation of $\overline{Mn}$ are end group analysis, non-aqueous conductometric titration or the methods based on the estimation of colligative properties of polymer like vapour pressure osmometry (VPO).

(2) Weight average molecular weight **(**$\overline{Mw}$**)** ***:***

$$\overline{Mw} = \frac{\sum n_i M^2_i}{\sum n_i M_i} = \frac{\sum W_i M_i}{\sum W_i}$$

The weight average molecular weight is usually determined by the sedimentation equilibrium method or by light scattering method.

(3) Viscosity average molecular weight **(**$\overline{Mv}$**):**

It is determined by viscosity measurements (by Ostwald Fenske Viscometer or Brooke Field Viscometer or Mooney Viscometer) and is to be used in the following equation, assuming that the intrinsic viscosity and the molecular weight relationship of the sample follow the Staudinger's equation.

$$[\eta] = KMa$$

Where 'a' is a constant dependent upon the polymer-solvent system, [η] is a Intrinsic viscosity, M is a molecular weight of polymer.

$$\overline{Mn} = [\sum W_i M_i]^{½} \left(\frac{\sum n_i M_i^{a+1}}{\sum n_i M_i} \right)^{1/a}$$

When 'a' equals unity, the viscosity average reduces to the weight average. The value of $\overline{Mv}$ is intermediate between $\overline{Mn}$ and $\overline{Mw}$. The order is $\overline{Mn} < \overline{Mv} < \overline{Mw}$.

In these relations n_i, W_i, and M_i respectively are the number of moles, weight fraction and molecular weight of the i^{th} type of the molecule present in the polymer sample. The ratio of $\overline{Mw}$ / $\overline{Mn}$gives the polydispersity index and is a measure of the polydisperse nature of the polymer sample.

The average molecular weight of a polymer plays a very important role in deciding the specific end application of a polymer and hence its estimation is considered as one of the essential property for the polymer characterization. Different methods have been developed for the estimation of average molecular weight of a polymer. Individual methods of molecular weight determination can be distinguished qualitatively according to the statistical averages obtained and also according to the relationship between quantity to be measured and molecular weight. A distinction is made between:

→ Absolute Methods

→ Equivalent Methods and

→ Relative Methods

With absolute methods, the quantity to be measured is directly related to the molecular weight without having to make any assumptions about chemical and / or physical structures. For equivalent methods, the chemical structure must be known. Relative methods measure properties which depend both on chemical and physical structure, and which is required for evaluation of a calibration relationship between quantity to be measured and molecular weight.

Table 3.2.2 summarizes the most important methods of determining molecular weight and divides them into absolute (A), equivalent (E) and relative methods (R).

Table: 3.2.2

Principal methods of determining molecular weight

No.	Method	Type	Molecular Weight range (g/mol)	Mean values of the Molecular Weight
1	Membrane osmometry	A	10^4…..10^6	$\overline{Mn}$
2	Ebullioscopy	A	$< 10^4$	$\overline{Mn}$
3	Cryoscopy	A	$< 10^4$	$\overline{Mn}$
4	Isothermal distillation	A	$< 10^4$	$\overline{Mn}$
5	Vapour pressure osmometry	A	$< 10^4$	$\overline{Mn}$
6	End group determination	E	$< 10^5$	$\overline{Mn}$
7	Light scattering	A	10^2…..10^8	$\overline{Mw}$
8	Sedimentation equilibrium	A	$< 10^6$	$\overline{Mw}$
9	Sedimentation equilibrium with density gradient	A	$> 10^5$	$\overline{Mn}$, $\overline{Mw}$
10	Combination of sedimentation / diffusion coefficient	A	10^3…..10^8	$\overline{Mn}$, $\overline{Mw}$
11	Solution viscosity	R	10^2…..10^8	$\overline{Mv}$
12	Melt viscosity	R	10^2…..10^7	$\overline{Mw}$
13	Gel permeation chromatography	R	10^2…..10^7	$\overline{M_{GPC}}$

Light scattering method determines not only the weight average molecular weight but can also provide information on molecular geometry, size, macromolecular interactions and thermodynamic parameters of polymer solutions. In an analogous manner, X-ray scattering can be used to determine the size and shape of dissolved polymer molecules. Molecular weight determination by electron microscopy is highly effective where a very dilute polymer solution and the individual molecules are then counted. Sedimentation and diffusion of macromolecules in solvents are also dependent on molecular weight and can be measured in an ultracentrifuge and utilized for molecular weight determination.

A simple low cost commonly used method of investigating molecular weights of polymers is that of viscosity measurements. Certain more specific methods have been employed for the estimation of the molecular weight of aromatic and mixed aromatic-aliphatic polymers which are either polycarboxylic acids, polyphenols or polyamines. These methods are conductometric or potentiometric titration in non-aqueous media.

Thus, the measurement of $\overline{Mn}$of AUPEs VIa-j, VIIa-j has been carried out by the –COOH end group analysis employing non-aqueous conductometric titrations. The $\overline{Mn}$ determination of AUPEs has also been done by vapour pressure osmometry method.

- **Molecular weight determination by End group analysis:**

End group analysis is aimed at determining the end group content quantitatively. It takes advantage of the fact that the groups at the end of polymer chain are frequently of different constitution to the “internal” chain links and are thus accessible to quantitative analytical determination. Examples include –COOH and –NH_2 groups in polyamides, –COOH and –OH groups in polyesters or terminated prepolymers, -SH groups and terminal double bonds and certain heteroatoms provided that the molecular weights of the polymers are less than 5×10^4 g / mol [96].

The technical importance of end group analysis in the manufacture of polyesters, polyurethanes, liquid rubber and other products is obvious. Under favorable conditions, end group analysis can also be used for determining molecular weight since the latter can be obtained if the number of end groups in a given weight of polymer is known. End group analysis is therefore an equivalent method for obtaining the number average molecular weight $\overline{Mn}$.

$$\overline{Mn}_{end} = \frac{q.\,m}{n_{end}} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

Where,

q = Number of end groups

m = Weight of the polymer in gm.

n_{end} = Number of moles of the end groups in 'm' gram of polymer

Determination of $\overline{Mn}$ this amount to determine the molecular concentration of end groups [97]. This, however, calls for a knowledge of the type and number of all end groups and their quantitative determination. Since the number of moles of end groups decreases with increasing molecular size, the sensitivity of the $\overline{Mn}_{end}$ determination diminishes. With the usual analytical methods, the upper limit is about 5×10^4 gm / mol. whereas radiochemical methods enable molecular weights upto 10^6 gm / mol. to be determined reliably. When comparing $\overline{Mn}$ values obtained by end group analysis and osmotic methods conclusions can sometimes be drawn regarding molecular branching and thus, the mechanism of formation. Because of the great number of possible side reactions, such results require confirmation by other methods. In spite of such reservations end group analysis has become routine practice – not least because of its simplicity.

Functional end group content in polymers can be determined by chemical, radiochemical and physical methods. The choice depends largely on the sensitivity of the method and hence the range of molecular weights which can be determined. In the present study the end group analysis was performed by chemical method for –COOH end group determination employing non-aqueous conductometric titrations [98].

Chemical determination of end groups is based on the complete reaction of reactive end groups with low molecular weight reagents and measurements of reagent consumption by common analytical methods. In a polymer, the end groups behave as similar groups in low molecular weight compounds as long the solutions are very dilute and the solvents or neighboring groups do not exert any influence or cause degradation. Chemical determination of functional end groups can be effected directly or after conversion to a substance that can be analyzed more conveniently. Examples of direct end group determination include –COOH, –

NH_2, –SH groups in polyamides, polyesters or liquid thioplasts. Indirect methods are used primarily for determining –OH groups.

COOH end group content can be determined universally by direct titrating with sodium alkoxide solutions in anhydrous media. When using alcoholic potassium hydroxide with hydrolysable substances such as polyesters, saponification or hydrolysis reactions may also occur since water is formed in the neutralization of the –COOH groups. Water containing solvent mixtures are only used when free dicarboxylic acid / anhydrides are present because the latter react with water to form the respective dicarboxylic acids [99].

Separate determination of COOH end groups and dicarboxylic acid / anhydrides in polyesters, requires two titrations – one in a water free medium for the detection of COOH end groups and any free acid, and the other in an aqueous medium after heating for determination of anhydride. Consequently solvent selection and test conditions are substance specific. Titration end points can be determined using an indicator or by potentiometric or conductometric techniques.

Hence the number average molecular weights of AUPEs were determined by COOH end group analysis employing non-aqueous conductometric titrations.

- **Non-aqueous Conductometric Titration of AUPEs:**

As mentioned above the number average molecular weight ($\overline{Mn}$) determination of AUPEs was carried out by non-aqueous conductometric titration in pyridine against sodium methoxide as a titrant base.

Experimental

** Purification of pyridine :*

Pyridine was purified by refluxing it over potassium hydroxide for about 6 hours and then distilled carefully . The anhydrous pyridine has a boiling point of 115°C.

** Preparation of sodium methoxide :*

1.5 gm pure sodium metal was carefully added to 40 ml absolute methanol. The resulting solution was diluted to 500 ml with pyridine. The turbidity formed during the dilution was removed by the addition of required quantity of methanol. This solution of titrant base was standardized against 0.1 M benzoic acid using phenolphthalein as an indicator.

**** Conductometric titration :***

A weighed amount of resin sample (50 gm) was dissolved in 50 ml of anhydrous pyridine. This solution was then allowed to stand for overnight for the complete dissolution and was then filtered. This solution was then transferred to a conductance cell and it was then stirred magnetically. The base sodium methoxide was added to the conductance cell at a regular interval of 0.1 ml of titrant base beyond the stage of equivalence. The conductance measurement was carried out by allowing the lapse of 2 –3 minutes with stirring after the addition of each volume of titrant base. During titration the temperature of the solution was maintained constant at $25\pm0.1^{\circ}C$. When the point of equivalence exceeded, a continuous increase in conductance was observed on addition of every additional aliquot of sodium methoxide indicating the stage of neutralization of the –COOH end group in the given amount of resin sample. The volume of base added is converted into millimoles of sodium methoxide required for 100 gm of resin. A plot of specific conductance against milli equivalent sodium methoxide per 100 gm of resin sample was plotted. The inspection of the plot revealed that there is one break in the plot. Beyond this break there is a continuous increase in conductance on further addition of the base titrant. The break in the plot corresponds to the neutralization of the –COOH end group.

- **Molecular Weight ($\overline{Mn}$) Determination by Vapour Pressure Osmometry (VPO):**

This technique is based on the principle that at a given temperature, the vapour pressure of a solution is less than that of the pure solvent. Now, when a drop of each of a pure solvent and the solution is kept in the atmosphere saturated with solvent vapour (continuously supplied from a large reservoir of solvent), since the vapour phase pressure of a solution is lower than that of pure solvent, condensation of the solvent takes place from saturated vapour phase on to the solution droplet, whereas practically nothing happens as far as the solvent droplet is concerned. The solution droplet, therefore starts getting diluted as well as heated up by the latent heat of condensation of the solvent condensing on it. Owing to the temperature rise and increased concentration of the solvent, the vapour pressure of the solvent and the vapour pressure of the solution droplet increases steadily. The process of condensation and resultant temperature rise continues till the vapour pressure of the solution droplet at a new elevated temperature becomes equal to that of the pure solvent at the original temperature. The total rise in temperature ΔT, will be proportional to the mole fraction of the solute (n) in the solution, as per the following equation,

$$\triangle T = \frac{RT^2 n}{\triangle Hv}$$

Where,

ΔH_v is the heat of vaporization of solvent,

R = Gas Constant,

T = Temperature of solution (°C).

A drop of solvent and that of the solution of the solute (standard or unknown) in the same solvent are placed on two thermistor beads. They are suspended by fine wires in a closed chamber saturated with solvent used for the experiment and maintained at constant temperature. When equilibrium is established due to vaporization on one bead and condensation on other, the difference in the temperature on the two beads - which is a function of concentration – is noted as a change in voltage measured in millivolts, say mV. This bridge output mV is noted. Such experiments are carried out using three other solutions.

$$V = \left(k_1 - \frac{M_1}{1000g}\right)\left(\frac{C}{M}\right)$$

$$= K\left(\frac{C}{M}\right)$$

Where, k_1 is constant dependent on the experimental conditions of the experiment. M_1 is the molecular mass of the solvent. Hence the factor in the first bracket is constant, say K. The terms C and M are concentration of solution in grams of solute per kilograms of solvent and M is the molecular mass of solute [100-102].

Experimental

The estimation of $\overline{Mn}$ by VPO method was carried out on a Hewlett Packard–Vapour Pressure Osmometer using DMF as a solvent. Here only AUPEs VIIIa-j were analyzed for their $\overline{Mn}$ by employing VPO technique.

Estimation of $\overline{Mn}$ by VPO comprises of two steps as;

- **Estimation of Calibration constant 'K':**

The constant 'K' was estimated by using polystyrene of known molecular weight. Solutions of four different concentrations of polystyrene were prepared in DMF. The concentrations were 5, 10, 15 and 20 gm / kg respectively. The experiment was carried out following the instructions in the instrument manual. The bridge output voltage; in milli volts (mV) which is proportional to the vapour pressure lowering was measured for each concentration. The plot of mV → C was plotted and was found to be linear passing through the origin. The slope was measured and hence 'K' was calculated. 'K' was found to be 1.7×10^4.

- **Estimation of $\overline{Mn}$ of AUPEs:**

Solutions of four different concentration of each of UPEs were prepared in DMF. The concentrations were about 1.1, 2.7, 3.7 and 5.8 gm. / kg. of DMF. The VPO measurements for all the AUPEs for each concentration were carried out and for each concentration their corresponding bridge output voltage (mV) were noted. The plots of mV → C were plotted for all the UPEs and were found to be linear passing through the origin. From the plots the slopes were determined for each of the AUPEs From the values of the slope and 'K'. $\overline{Mn}$ of all the AUPEs were estimated.

Table 3.2.3

Calibration experiment using polystyrene- Estimation of VPO constant K

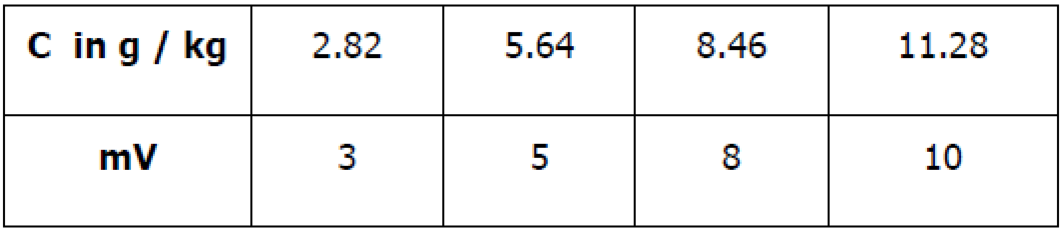
Sample : Polystyrene (Mn =4000 g / mole)

Solvent : Dimethyl formamide (DMF)

Temperature : 90 ˚C

Time interval : 15 minutes

(For steady state)



C in g / kg	2.82	5.64	8.46	11.28
mV	3	5	8	10

From the plot of mV→ C

Slope = 2.8

K=Mn x slope

= 4000 x 0.75

=3000 mV kg /mole

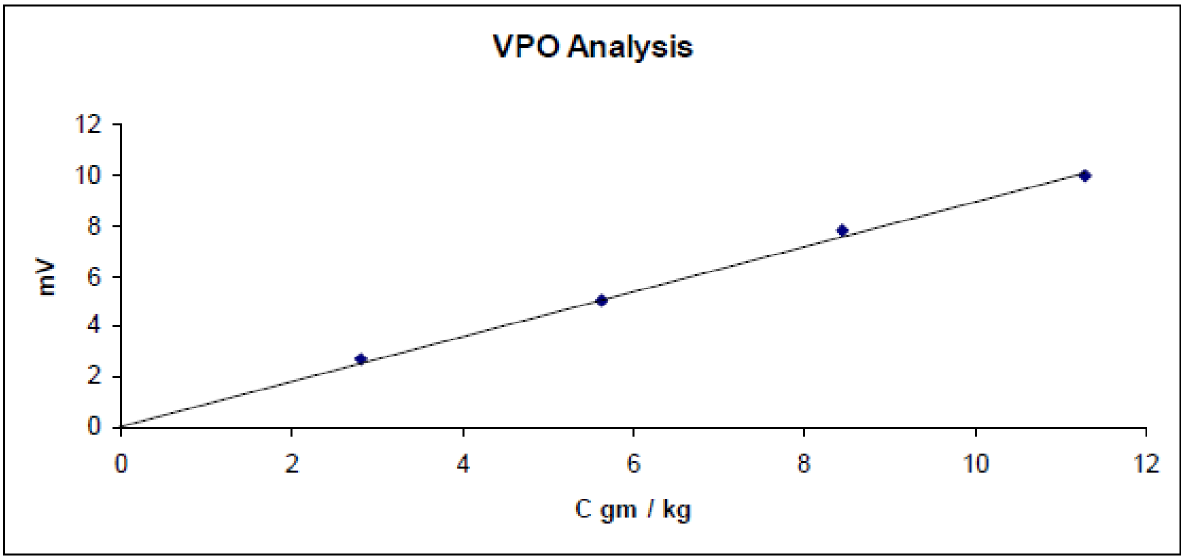


Figure 3.2: Plot of mV → C

3.2.4 Curing study of UPUEs by Different Scanning Calorimeter (DSC):

This method is employed to study the curing reaction of UPUEs using benzoyl peroxide as a catalyst, which is an important stage in the application of these resins. The cross linked network of cured resin furnishes desirable properties for the fabrication of fiber reinforced composites and for the formulation of structural adhesives. There are many reports about the curing of unsaturated polyesters [103].

The curing reaction is associated with the formation of insoluble substances with the evolution of heat during the reaction. For a given resin sample the amount of curing agent decides the curing time and the amount of heat liberated in a given time.

DSC is an excellent thermal method used for the estimation of the kinetic parameters such as activation energy (Ea), order of reaction (n), heat of polymerization (ΔH_p) and the extent of curing reaction of the polymers.

Various methods have been developed to estimate the kinetic parameters of the polymers by analyzing the DSC curves. Some of the methods developed are as follows;

(A) Borchardt and Daniel Method.

(B) Barrett et. al. method

(C) Rogers and Smitle method

(D) Ellerstein method

Among all the above, Borchardt and Daniel method is widely used for the estimation of curing parameters such as activation energy (Ea), order of reaction (n) and heat of polymerization (ΔH_p).

- **Scanning experiment**

The Universal V3.0GTA Instrument was employed to obtain the data of the exothermic curing reactions. The differential scanning calorimeter was calibrated using a standard material i.e. Indium metal with known heat of fusion (ΔH= 28.45 Jg^{-1}) according to the instrumental manual.

The calibration constant ‘E’ was computed by employing the following relation,

$$\Delta H\ \frac{m \times cal.}{mg} = \frac{Ea\ (\Delta Ts)\ Ts}{Mb}$$

Where,

E = Calibration co-efficient $cal.deg^{-1}.min^{-1}$.

A = Peak area in square inch.

ΔTs = Y-axis sensitivity $deg.inches^{-1}$.

M = Sample mass in mg.

b = Heat rate $deg.min^{-1}$.

Ts = X-axis sensitivity $deg.inches^{-1}$.

The values of ‘E’ were estimated for different standard materials using the given cell. The total area under the exotherm, at which the exotherm commences and terminates, is obtained from the DSC thermogram [104-109].

- **Analysis of the DSC Scan**

The equation derived by H. J. Borchardt and F. Daniels correlating the shape of differential thermal analysis (DTA) curve to the degree of reaction (rate constant- K) can also be applied to the curve obtained from the DSC. The well known relation used for studying the reaction kinetics of various thermosetting resins is deduced by Barrett on the lines and assumptions made by Borchardt and Daniels.

The Barrett relation can be described as;

$$K = \frac{d\alpha / dt}{A - a} = \frac{dh / dt}{A - a}$$

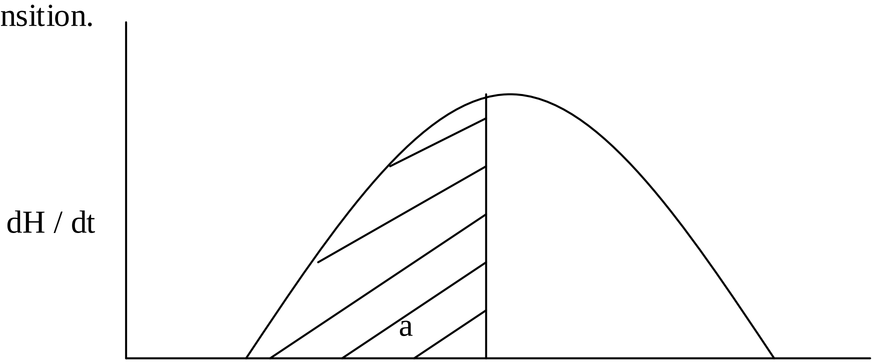
Where,

α = Fractional conversion

A = Total area

a = Area at a particular temperature (t)

The exothermic peak obtained in the scan was analyzed to obtain a heat flow data relative to the base line drawn manually by joining the points of start and completion of the exothermic transition.



Temperature °K

From the data obtained for the heat flow as a function of temperature and time, the overall rate constant K at different temperatures were estimated using the Barrett relation. After obtaining the rate constant K at different temperatures, the plot of ln K vs 1/T was made directly by the linear computation programme installed in the instrument, which directly gives the values of activation energy (Ea) and the order of reaction (n). Assuming that the curing reaction obeys Arrhenious type kinetics.

$$\ln K = \frac{Ea}{R \times T} + \ln A$$

Where,

K = Rate Constant

Ea = Activation energy

R = Gas constant

T = Absolute temperature

A = Frequency factor

- **Experimental**

The curing studies of UPUEs were monitored on a Universal V3.0GTA instrument, using benzoyl peroxide as a catalyst. The sample cell of aluminum was used for the DSC scan. Empty cell was used as a reference. Calibration of the DSC instrument was performed by determining the heat of fusion of the standard indium metal supplied by Du Pont [110-116].

0.05 % benzoyl peroxide based on the total weight of the resin sample was added and mixed well in a porcelain disc. The sample weight used for the investigation was in the range of 4-5 mg. and was carefully placed in a sample cell covered with a lid and then it was placed in a DSC cell along with the empty reference cell. The DSC thermograms of all the resin samples were scanned at a constant heating rate of 10°C / min. from 30 °C to 300°C.

3.2.5 Thermogravimetric Study:

The thermal properties of the polymers can be studied by employing different techniques such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and derivatographic analysis (DGA).

Thermogravimetric analysis of a polymer is a very useful technique in assessing the thermal stability of a polymer. For the comparative study of the thermal behavior of a related polymer samples, any one or more of the above methods of analysis under identical experimental conditions can be employed. For example, TGA is carried out in air and in oxygen free nitrogen. It is carried out at different heating rates. It may be noted that the results of the thermal analysis of a given polymer sample by a given method depends on various aspects. The amount and the particle size of the material being examined influence the nature of the thermogram. The speed of the recorder noting the change in the weight and the shape of the sample container also influence the thermogravimetric results. The rates of heating the sample and the ambient atmosphere during the analysis are very important factors to be controlled during thermal analysis. The information furnished by TGA, DTA and DGA are to some extent complimentary. From the results of TGA and DTA, it is possible to note the temperature upto which the material does not lose weight. It is also possible to know the temperature at which the material starts decomposing and pattern of the decomposition [117-118].

Besides the quantitative information derived from the mere inspection of the thermograms, other information such as, the order of the degradation reaction and the activation energy of the degradation reaction can be obtained by analysis of the thermal data furnished by either TGA or DTA.

- **Thermogravimetric analysis:**

The thermal behavior of the UPUEs and UPUEs samples has been studied by TGA. The loss in weight due to pyrolysis of the polymeric material with increase in temperature forms a TG curve. Normally a polymer sample starts losing its weight at a very slow rate up to a particular temperature around 300°C. The loss of weight increases at a faster rate after this temperature. The shape of the TG curve depends upon the nature of the degradation reaction. The analysis of these data by Broido method is often carried out with a view to estimate kinetic parameters like activation energy of the degradation reaction.

The advantages of TGA are enumerated here:

(i) A relatively small set of data is to be treated.

(ii) Continuous recording of weight loss as a function of temperature ensures equal weightage to examination over the whole range of study.

(iii) As single sample is analyzed over the whole range of temperature, the variation in the value of the kinetic parameters, if any, will be indicated.

For the estimation of the kinetic parameters, several methods are employed. All of them involve two assumptions. One, it is assumed that the difference in the thermal and diffusion processes is negligible. Secondly, it is also assumed that the Arrhenius relation is valid over the whole range of temperatures. Since small materials are employed in TG analysis the barriers between the thermal and diffusion processes are quite negligible. Hence, it is reasonable to assume the validity of the Arrhenius relation.

Various methods are proposed to analyze the TGA data depending upon the nature of the experimentation. Out of these, the method proposed by Broido, which is applied to a single set of TGA data is selected for the analysis of the TGA data [119-120].

- **Experimental (TGA):**

The thermogravimetric analysis (TGA) of UPEs samples has been carried out by using a “Universal V3.0G TA Instrument Thermo gravimetric analyzer” in a slow stream of air. The boat prepared from the platinum foil holds the polymer sample that is to be analyzed. It was properly washed and dried. It was suspended on the quartz rod in the TGA balance. The sample (about 5 mg) was placed in the boat. The sample in the boat is covered by quartz tube in which the flow of air was maintained. The weight of the sample was noted on the TGA balance. The whole assembly was brought down in the furnace. It was ascertained that the boat was hanging on quartz rod. The experiment was started by heating the system at a constant rate of 10 ˚C / min. Simultaneous change in the weight was recorded automatically with time (temperature). This will reveal the percentage weight loss of the material as a function of time and also of the temperature. The experiment was stopped at about 800 ˚C.

Chapter 3, Section 3

Fabrication of Composites and steel panel Coating

The section-3 presents:

(A) The fabrication of glass fiber reinforced composites (i.e. laminates) from UPUEs VIa-j, UPUEs VIIa-j and UPUEs VIIIa-j (mentioned in section-1) as matrices and benzoyl peroxide (BPO) was used as a curing agent. The composites were characterized in terms of their chemical resistant, mechanical and electrical properties.

(B) The surface coating on steel panel and characterization.

(A)The fabrication of glass fiber reinforced composites:

The present chapter outlines the fabrication of glass fiber reinforced composites (i.e. laminates) from UPUEs IXa-j, UPUEs Xa-j and UPUEs XIa-j (mentioned in section) as matrix and benzoyl peroxide (BPO) was used as a curing agent. The composites were characterized in terms of their chemical resistant, mechanical and electrical properties.

3.3.1 Introduction to Polymer Composites:

Fiber reinforced polymer (FRP) composites is defined as a polymer matrix, either thermoset or thermoplastic that is reinforced with a fiber or other reinforcing material with sufficient aspect ratio (length to thickness) to provide a discernible reinforcing function in one or more directions. Therefore, fiber reinforced polymer (FRP) composite properties are directional, meaning that the best mechanical properties are in the direction of the fiber placement.

A composite consists of a reinforcing phase embedded in a bulk phase called a matrix, the combination is carried out with the intention of suppressing undesirable properties of the constituents in favor of the desirable ones, and the result is a new and unique material family. Nature excels in employing the composite concept and man has been using fiber reinforced clay bricks since time immemorial. Synthetic composites are at most half a century old. There are several types of composites, but the commercially most important type is fiber reinforced composites with polymer matrix and the structurally most capable form employs continuous fiber reinforcement.

The main advantages of polymer composites lie in excellent specific mechanical properties, corrosion resistance, parts integration possibilities and potentially lower cost. The predominant disadvantages are designers lack of experience, knowledge and material data bases, as well as in low temperature tolerance, arduous manufacturing, and quite often higher cost. While the potential advantages of composites in engineering applications are alluring the complexity they introduce in design and manufacturing demands a lot of skill of both designer and manufacturer. It is therefore imperative that a composite designer has a substantial degree of knowledge of materials and manufacturing issues to be able to do a good job.

Polymer composites are found in all engineering fields where they compete with more traditional construction materials such as wood, steel, aluminum, concrete and plastic. Important applications areas of polymer composites are automobile, boat, aircraft, construction and electrical appliances. In most areas composites are in their infancy in terms of extent of application and the future will prove that polymer composites are worthy of becoming a commodity material.

Composites can be of different types and made up of carbon, graphite, glass, aluminum, boron, aromatic polyamide, jute, sisal, straw, banana-cotton, pineapple leaf, cotton-kapok, coir etc [121-136]. The idea of making composites for engineering use has arisen in recent years from the desire to utilize very stiff and strong fibers. The fibers cannot be used alone, so they require a matrix.

The various types of resins used as matrix binder in fabrication of glass composites are polyester, phenolic (phenol-formalaldehyde), and epoxy resins. However, the epoxy composites offer together compression strength, higher resistance to delimitation and higher moisture resistance than other more conventional thermosetting resins. The most widely known and recognized reinforcing fiber in use is glass.

Glass is amorphous materials drawn into filament from a hot melt. The individual filaments are then processed into yarn roving, or woven fabrics. As the glass fibers issue from their extrusion nozzle, they are coated to protect them during subsequent strand forming and weaving operations. This coating or sizing can also function as coupling agent and promote adhesion between the glass and the resin binder. Epoxy resins bond much more strongly to glass fibers than do polyesters. There are two types of glass used with epoxy resin in a majority of applications, type-E, a lime aluminum borosilicate and type-S, a silicon dioxide aluminum magnesium combination. E-glass is the least expensive and the most widely used in composite structures. S-glass is approximately twice as strong, has a somewhat higher modulus and elongation and is selected when higher performance is the prime consideration.

With glass composites, the strengths of both the glass and the resinous binders are of significance, with the glass contributing the major portion. The resinous binders are selected on the basis of their adhesive strength, their fatigue resistance, their heat resistance, their chemical and moisture resistance, etc. Epoxy resin binders provide perhaps the highest inter-laminar shear strengths obtainable in the present technology. Although the glass fiber has extra ordinary tensile strength, it lacks chemical resistance. Perhaps the most important function of the epoxy resin is to shield the glass fiber from the chemical environment. The low shrinkage of the epoxy resin during cure helps it to remain in contact with the glass surface.

The epoxy glass cloth composites provide mechanical properties superior to the polyesters, electrical properties superior to the phenolic and moisture resistance superior to both. The properties of the laminates can be varied rather widely, as in the case with other epoxy systems, by the selection of modifying agents, and because of this versatility, the epoxy glass cloth laminates are finding increasing use in industry.

Different laminating techniques are used depending on the nature of the products range from liquids to solids. The two basic methods are called wet and dry layup lamination. Wet layup implies the use of liquid resins to impregnate the fiber either before or after it has been laid in place. Dry layup is the conventional technique used for many resin systems. The reinforcement is impregnated with a solvent solution of the resin, the solvent is flashed off, and the result is a dry resin-impregnated sheet known to be prepreg which is used to prepare composite**.** To prepare composites, lamination is normally carried out manually by brush, roller or squeeze application to glass cloth [137-139].

- **The composite concept:**

In load bearing or structural application, composites in most case comprise a bulk phase enclosing a fibrous reinforcing phase; in conventional terminology one talks of matrix and reinforcement. The objective of matrix is to integrally bind the reinforcement together so as to effectively introduce external loads to the reinforcement and to protect from adverse environmental effects. The matrix gives a composite, its shape, surface appearance, environmental tolerance(to high temperature, water, ultra violet light etc.) and overall durability. It is the fibrous reinforcement that carries most of the structural loads and thus largely dictates macroscopic stiffness and strength.

Although numerous examples of the composite concept may be distinguished in everyday life including paper, craft paper, particle (chip) board and reinforced concrete. Practically all successful structural composites have manmade constituents. The matrix may be metallic, ceramic or polymeric origin. While metal and to some degree ceramic matrices are used in structural composite application, polymer matrices are currently by far the most significant matrix category. There are two main polymer families, thermosets and thermoplastics. The vast majorities of current composites application utilize thermosets, which solidify through a chemical reaction called cross-linking or curing. Thermoplastic differ in that they can be melted and therefore solidify through cooling of the melt without any chemical reaction taking place. In polymer matrix composites, the common reinforcement types are (in order of decreasing importance) glass, carbon and polymer. The composite reinforcement may be discontinuous (short fibers) or continuous (endless fibers) and randomly oriented or aligned, see Figure: I.

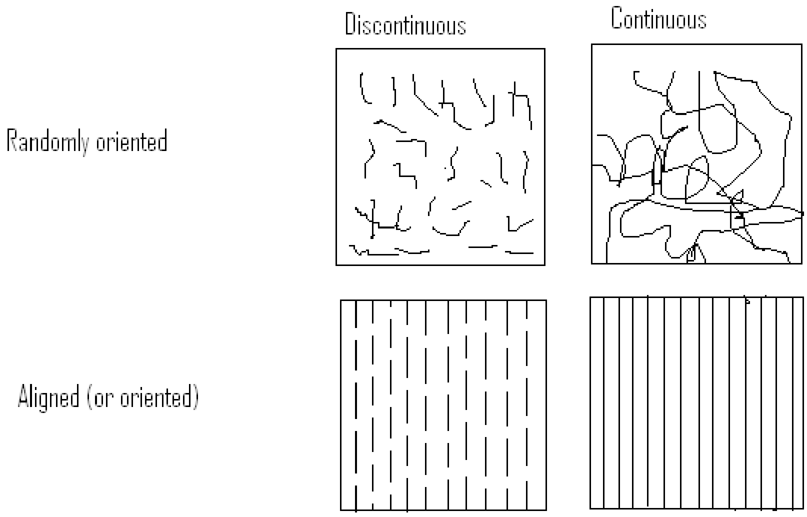


Figure 3.3: Schematic diagram of different reinforcement configuration

Since the reinforcement is the primary load-bearing constituent, its configuration (form and degree of orientation in the matrix) is critical to the macroscopic properties of the composite. It should therefore come as no surprise that the most impressive mechanical properties are found in composites with continuous and aligned reinforcement. While clearly structurally inferior composites with randomly oriented reinforcement are common in both structural and semi structural application, whether the reinforcement in such composites is discontinuous or continuous is of secondary importance from a structural point of view. In many applications different reinforcement configurations are mixed within one and the same component [140-145]

- **Prospects and Limitations**

As materials of construction in automotive and aerospace sectors, plastics are undoubtedly growing in acceptance. Even then, in engineering status, simple plastics still find their place at or near the bottom; but they hold high potential for a much brighter future through material development in the form of glass fiber reinforced polymer (GFRP) composites. In many cases there are clear objections to the use of plastics on consideration of demands on thermal and aging resistance and lack of confidence centering limitations in a desired balance of thermal and mechanical properties. The best way to overcome these limitations and constraints to enable plastics to not only compete with or even overshadow light metals and alloys in stress and safety sensitive engineering applications is to make composites through fiber reinforcement of prospective polymers coupled with judicious cross linking of polymer matrix.

The chemical, thermal and often the electrical performance of composites are controlled by the polymer or the matrix material while the mechanical performance within the polymer’s ultimate temperature capability is dictated by the effectiveness of the reinforcement. Each polymer has basic attributes that no amount of incorporation of reinforcing or other additives of different dose levels and varieties can disguise; no plastic can reliably function even briefly at a temperature above the softening or heat distortion temperature of the base polymer. However, the heat distortion temperature and mechanical (tensile) strength of selected polymers may be substantially enhanced through judicious incorporation of a reinforcing fiber such as glass fiber and by cross-linking with appropriate support and fiber reinforcement; the polymer or the matrix material enables us to partly realize the inherent high strength and stiffness of the reinforcing fiber material.

- **Benefits of Composites Materials:**

Fiber reinforced polymer (FRP) composites have many benefits to their selection and use. The selection of the materials depends on the performance and intended use of the product. It is important for the end user to understand the application environments of the product and convey this information to the composites industry professional. A summary of composite material gives following benefits:

- Light weight
- High strength-to-weight ratio
- Directional strength
- Corrosion resistance
- Weather resistance
- Dimensional stability
- Low thermal conductivity
- Low coefficient of thermal expansion
- Radar transparency
- Non-magnetic
- High impact strength
- High dielectric strength (insulator)
- Low maintenance
- Long term durability
- Part consolidation
- Small to large part geometry possible
- Tailored surface finish

The discovery of light-weight, strong and stiff carbon fibers in the mid 1960s proved to be a turning point in the development of high performance polymer composites offering serious threats to the light alloys in their traditional use as materials of construction in the aerospace sector. A chain of further developments in strong stiff, light weight synthetic fibers, particularly the aromatic polyamides popularly known as aramid fibers and by the trade name

Kevlar, and also developments in aromatic resins and other engineering polymers (as matrix materials) suitable for use in the design of high performance fiber reinforced polymer (FRP) composites followed in the wake of developments of carbon fibers (short fibers and continuous filaments). With the developments in high performance aromatic polymers, the old division between the functional and processing potentials of thermoplastics and thermosets is getting burred progressively. Thermosets, however, commonly exhibit lower shrinkage, improved chemical resistance and thermal performance, while thermoplastics give advantages in higher outputs, better design of parts over and above their recycling potential.

A composite is viewed as a laminate if the reinforcing fibers are arranged in layered fashion such as in the form of webs, fabrics or mats. Mixing of the matrix resin with randomly oriented short fibers, allows the resin fiber mix or the dough to be injection molded or compression molded with or without the presence of a particulate fiber and such dough like short fiber resin mixes are commonly known as dough molding compound. Short fibers are not necessarily randomly arranged. Maximum strength and stiffness are obtained when continuous fibers filaments are aligned parallel to the applied load. Such unidirectional aligned fibers in resin matrix can be most efficiently achieved by such methods as pultrusion.

3.3.2 Fabrication of Glass Fiber Reinforced Composites (GFRC):

The process for making glass fiber reinforced composites (GFRC) comprises of:

(a) Formation of resin and curing agent solution for impregnation of the prepregs.
(b) Wet hand layup of prepregs with the above formulated resin solution.
(c) Laid up prepregs stacks and to cure by heating.

- **Experimental**

The composites were made from woven E-type plain glass cloth by using wet hand layup prepregs technique.

- **Materials**

(a) UPUEs IXa-j, UPUEs Xa-j and UPUEs XIa-j (described in section-1) were used as resin matrices for the fabrication of glass fiber reinforced composites (GFRC).

(b) Woven E-type plain glass cloth was obtained from Unnati Corporation, Ahmedabad.

(c) Benzoyl peroxide (BPO) and solvent Tetrahydrofuran (THF) used were of laboratory grade.

- **Composite Fabrication**

The glass fiber to the resin ratio for the fabrication of the composite was 60: 40 (30 % UPUEs IXa-j, UPUEs Xa-j and UPUEs XIa-j + 10 % Epoxy resins, i.e. DGEBA, DGEBC and DGEBF). A typical method for the fabrication of the glass fiber reinforced composites (GFRC) is given below.

A suspension of the resins was prepared in tetrahydrofuran (THF). To this 0.05 % of the resin, benzoyl peroxide was added as a catalyst. This mixture was stirred for about five minutes. The suspension mixture was then applied to a 150 mm × 150 mm glass fiber ply with the help of a brush. The solvent was then allowed to evaporate. The dried prepreg plies were then stacked on top of one another between the steel plates coated with a Teflon film release sheet, and compressed in a flat plates under 70 psi pressure. Keeping it in an autoclave oven maintained at their respective curing temperature for about six hours cured this prepregs stack. The composites so obtained were cooled to 50 °C before the pressure was released. These composites were designated same as resin with a superscript C. the test specimens were made by cutting the composite and machining them to final dimensions according to ASTM standards [146-151]. The processing parameters for the composite fabrication are furnished in Table 3.3.1.

Table 3.3.1

Process Parameters for Composite Fabrication

Glass fiber cloth : Resin mixture ratio = 60 : 40 W/W	
Reinforcing material	E-glass cloth, 15mile, 10 layers
Resin content	40 ± 2 %
Composite size	150 mm × 150 mm
Curing agent	Benzoyl peroxide (0.05 % based on weight of resin)
Curing temperature	Depending on the resin employed
Curing time	6 hours
Pressure	70 psi

3.3.3 Characterization of Composites:

The use of the composites for different applications depends upon the properties of that particular composite fabricated by employing a particular resin. Hence here, the fabricated glass fiber reinforced composites from UPUEs VI – VIIIa-j were characterized for their physical, mechanical, electrical and chemical properties.

- **Physical Properties**

The glass fiber reinforced composites of UPUEs VI – VIIIa-j were evaluated for their physical properties such as density and color. They were also evaluated for the properties such as resin content, water absorption and boiling water absorption.

- **Resin content**

The resin contents of the composites were determined according to the following method. The dry weighed sample of the composite (1 cm × 1 cm) was heated at around 600°C for about 2.5 hours till a constant weight is obtained in electric furnace and weighing the residue. The resin content was calculated as follows,

$$\text{Resin content } (\%) = 100 \times \frac{\text{Weight of Sample } - \text{ Weight of Residue}}{\text{Weight of Sample}}$$

- **Water absorption**

The dry weighed sample piece of the composite (2 cm × 2 cm) was immersed in water for 24 hours at room temperature. The sample was then wiped out with the filter paper and weighed. The water absorption was calculated from the following equation.

$$\% \text{ of water absorption} = 100 \times \frac{\text{Increase in weight of sample}}{\text{Weight of Sample}}$$

- **Boiling water absorption**

It was determined by immersing the dry weighed sample of the composite (2 cm × 2 cm) in the boiling water for one hour. The boiling water absorption was calculated using the same above equation.

The color, resin content, water absorption and boiling water absorption of all the UPUEs VI – VIIIa-jcomposites are furnished in Tables 4.2, 4.3 and 4.4 respectively.

3.3.4 Mechanical Properties:

The mechanical properties are the most important properties of the composites used in engineering materials because virtually all the service conditions and majority of the end user applications involve some degree of mechanical stress and thus are considered as relevant properties of the composites. Numbers of testing methods have been developed to characterize mechanical properties of the composites such as tensile strength, flexural strength, impact strength, compressive strength, inter laminar strength and hardness. The following discussion is limited to the testing methods like flexural strength, compressive strength, notched izod impact strength and Rockwell hardness.

All the above tests were performed according to the ASTM methods.

(1) Flexural Strength Test

The flexural strength of the composites was measured on the universal instrontesting machine of the model number A- 7437. The tests were performed according to ASTM D-790 method at room temperature. The specimen size was 8 cm × 1.25 cm × 0.3 cm. The flexural strength was calculated by using the following equation,

$$\text{Flexural strength}\left(\text{Kg/cm2}\right)=\frac{3PL}{2bd2}$$

Where,

P = Load in KgF

L = Distance between two span in cm

d = Thickness of the specimen in cm

b = Width of the specimen in cm

(2) Compressive Strength

The compressive strength of the composites was measured on a universal instron testing machine of the model number A- 7437. The tests were performed according to ASTM D-695 method at room temperature. The specimen size for the test was 1.25 cm × 1.25 cm × 0.3 cm. The compressive strength was calculated by using the following equation,

$$\text{Compressive strength (Kg/cm2)} = \frac{\text{Maximum compressive load carried by specimen (Kg)}}{\text{Cross sectional area of the specimen (cm2)}}$$

(3) Notch IzodImpact Test

The izod impact strength of the composites was measured on a ZWICK model number 8900 impact machine. The tests were performed according to ASTM D-256 method at room temperature. The specimen size for the test was 6.5 cm × 1.3 cm × 0.3 cm. The notch izod impact strength was calculated by using the following equation,

$$\text{Izod impact strength (J/cm)} = \frac{\text{Energy absorbed}}{\text{Thickness of specimen}}$$

(4) Rockwell Hardness

The Rockwell hardness test of the composites was performed on a rockwell hardness tester model RAS / Saro Eng. Pvt. Ltd., India. The test was performed at the room temperature and the specimen size was 2.5 cm × 2.5 cm × 0.3 cm. The rockwell hardness is obtained directly from the M scale dial reading.

(5) Electrical properties

The composites prepared from APEs VI - VIIIa-j were also analyzed for their electrical strength. The measurements were carried out on a high voltage tester oil machine.

All the above tests were performed on three individual specimens and the average results have been furnished in resultsand discussion.

(B) Surface Coatings:

3.3.5 Introduction to surface Coatings:

The word "coating” is used to describe the material that is applied to a substrate , the resultant dry film , and the process of application .The coating may be distinguished as organic , inorganic or blend of both [152]. Surface coatings have been used for thousands of years in gradually increasing quantities as civilization developed .In the prehistoric period painting was limited almost entirely to the decoration of caves and other dwellings .The ancients applied coatings to their ships ,utensils , musical instruments , weapons , mummies, temples and palaces. For centuries Surface coatings were used only for decorative purposes and their preparation and applications remained more of an art than a science .

The materials used were derived from nature. After the industrial revolution, the need for protection of metal objects arose. This in turn slowly transformed the art of paint-making and its application, into science which gave an impetus to scientists for making efforts for better understanding of coating compositions, their constituents, applications , and testing . Besides, the discoveries of new materials and their various applications constantly pose a challenge for surface coating research in terms of satisfying increasingly stringent requirements of protection coupled with decoration in certain instances under diverse service conditions [153-155].

3.3.6 Resins (i.e. Binders) for Coating Industries :

A wide range of binders is commercially available for coating industries nowadays but earlier chemists had to depend on natural products like natural resins or oils until the attempts were made to modify the natural resins to produce synthetic natural products and led to availability of synthetic polymers used in recent age. Very first synthetic plastic suitable for coating material and which is still in use today was phenolic resin, developed by Leo Backeland in early 1900s [156]. After this, there came the new resin called alkyd in 1923, which is used till date. After the industrial revolution, extensive research in the field of polymer chemistry resulted in the availability of numbers of different resins suitable for surface coating industries. Resins are the continuous phase in a paint film and are largely responsible for the protective and general mechanical properties of the film. A large number of resins with different chemical composition, solubility, nature of film formation, application characteristics and performance properties of their films are available for surface coating industries. It is generally found that the performance properties of a coating system are best at higher molecular weight of resin but it will be difficult to process high molecular weight polymer during paint manufacturing or even at the time of paint application were as at low molecular weight polymer will facilitate ease of processing during manufacturing of a coating system but at the loss of performance properties.

To achieve the optimum balance between ease of processing and performance properties two distinct methods are used to arrive at final films. In the first approach film formation takes place solely due to evaporation of solvents from the film and no chemical reaction of any sort is involved in film formation. The resin used is of sufficiently high molecular weight to provide better performance properties but the dried paint film remains sensitive to parent solvent / solvents. Such types of resins are known as non-convertible resins. In the second method initially a low molecular weight precursor or a prepolymer is used to provide ease of processing and ease of application which is then converted to a high molecular weight polymer to provide better performance properties through chemical reaction known as curing. Curing reaction involves use of either simple chemicals called curing agents or another resin with some special functional groups. Such resins are referred as convertible resins. The most commonly used convertible resins in surface coating industries are briefly discussed below:

- **Alkyd Resins**

Alkyd resins have been used as coatings binders for almost a century. This special class of polyesters is derived from naturally occurring oils, including soybean, sunflower, and linseed oils, polyols, and dibasicacids. It is widely used for surface coating as binders, adhesives and plasticizer Alkyd of interest since it tends to be the lowest in cost among the coating materials and tends to give a coating that exhibits fewer film defects during applications.

Alkyds are formed by polycondensation of a dibasic acid and a polyhydric alcohol in the presence of glyceride oil or oil derived fatty acid. Most commonly used dibasic acid in alkyd synthesis is phthalic anhydride while glycerol, pentaerythritol, trimethylol propane, glycols etc. are used as polyhydric alcohols. The nature and amount of oil / oil derived fatty acid determines the drying characteristics of the alkyd resin. Saturated fatty acid yields non-drying or plasticizing resin while drying properties are conferred by unsaturated acids [157-159].

- **Phenolic Resins**

The formation of resinous materials by the reaction of phenol and formaldehyde has been known for many years. Phenolic resin finds application in protective coatings [160]. The reaction of phenol and formaldehyde alone is slow but in presence of acid or alkali catalysts they react rapidly and produce different products: Novolacs and Resoles. Novolacs are produced when molar ratio of formaldehyde to phenol is less than one and acid catalyst is used. Since they are insoluble in oils and hydrocarbon solvents, they are not used in surface coating industries but widely used in plastic industries as a thermoplastic material. Resoles are produced when the molar ratio of formaldehyde to phenol is greater than one and alkali catalyst like sodium hydroxide or lime is used. Resoles are thermo-setting and soluble in oils so they are used widely in varnish making but if they are further heated, they react to produce insoluble and infusible products and result in little application in surface coating industries. It is found that resoles react with rosin to give products which could be esterified with polyhydric alcohols and the resulting resins are soluble in oils and these resins are known as rosin modified phenolics which find extensive application in decorative undercoats, primers, marine paints and in certain types of printings inks.

- **Polyester Resins**

The product obtained from the condensation polymerization of a polyhydric alcohol and polyfunctional acid is known as polyester resin and widely used in surface coating industries. The most commonly used polyfunctional acids are maleic anhydride, phthalic anhydride, adipic acid, sebacic acid, etc. whereas ethylene glycol, propylene glycol, diethylene glycols are used as polyhydric alcohols. Depending upon the raw material used, polyester can be either saturated polyester or unsaturated polyester. Both find extensive use in surface coating [161-165]. Unsaturated polyesters are cured by many different ways but the basic reaction of curing is free radical initiated addition reaction. Free radical initiation can be achieved either at elevated temperature by use of an electron beam or UV beam or certain metal ions as a catalyst by decomposition of peroxides. Unsaturated polyesters are generally dissolved in reactive solvent such as styrene to produce final resin and then curing is carried out. Saturated polyesters are such formulated so that they produce high hydroxyl contents as they are mainly used in production of polyurethanes. They also react with some amino resins.

- **Epoxy Resins**

Epoxy resins are the products of condensation of epichlorohydrin and diphenylol propane derivatives. The most commonly used diphenylol derivative is 2, 2’ – bis (4 – hydroxyphenyl) propane also known as its trivial name bisphenol – A. They are formed by condensing the reactants in presence of alkali and resulting product is known as diglycidyl ether of bisphenol – A (DGEBA). Epoxy resins contain hydroxyl and epoxy groups. They can be cured by cold curing or stoving with a wide range of materials which includes amino and phenolic resin, amines, anhydrides, polyamides and isocyanates etc. The resulting films of epoxy resins are very abrasion resistant, resistant to chemical attach and show a high degree of adhesion to metal and other surfaces and thus widely used in industrial maintenance field [166].

- **Amino Resins**

These are derived by reaction between formaldehyde and either urea or melamine to produce urea-formaldehyde or melamine-formaldehyde resins respectively [167]. They are not used on their own as a coating material as they give very brittle films but widely used in combination with alkyd resins mainly and also with other resins in co-cure systems. Amino resins used in surface coating industries are generally modified with butanol. The modification of amino resins with butanol provides solubility in normal coating solvents and better compatibility with other resins in co-cure systems. Melamine formaldehyde shows better properties than ureaformaldehyde in terms of color retention and exterior durability.

Amino-alkyd systems are widely used in stoving finishes of all types. Amino resins are also used with many other resins like saturated polyester, epoxies, acrylics etc.

- **Polyurethane Resins**

The basis of formation of these polymers is reaction of a diisocyanate with compounds containing an active hydrogen atom to produce urethane linkages. There are many compounds that contain active hydrogen like water, alcohol, amines hydroxyl group etc. thus a polyurethane film may contain ester, ether, amide, urea or other groups. The hydroxyl component may be polymeric polyols like polyesters, polyether etc. diisocyanates generally used are toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HMDI) etc. polyurethanes can be either single pack or two pack system. Polyurethane coating facilitate low temperature curing. They provide wide range of flexibility and hardness. They also possess good adhesion and exhibit excellent weather resistance. Other film properties are good resistance to moisture, chemical attack and many solvents [168-171].

3.3.7 Application of Coating Materials:

Several property demands of a coating material can be fulfilled only if the coating material forms films with considerable physical integrity. The process of film formation, the conversion of liquid composition into an adherent and durable film, comprises three main steps: application, fixation and curing. Coatings can be applied on a substrate by various methods like brushing, spraying, electrode position, dipping etc. the method of application of coating depends upon nature of composition and nature of substrate on which coating has to be applied. After application of coating material, there comes the fixation step in which coating is stabilized on substrate against any tendency of run off or to form an uneven film. This depends upon many factors like film thickness, rate of solvent evaporation and rheological properties of coating material. Rate of solvent evaporation should be controlled carefully as it causes rapid film viscosity build up resulting in fixation. Thus, fixation is controlled mainly by rheological properties of coating material.

The final stage of film formation process is drying or curing in which film is converted into a durable coating. Depending upon nature of resin, drying process can be either physical drying or chemical drying. Physical drying mainly takes place due to solvent evaporation and film integrity is generally obtained by chain entanglements. Very high molecular weight polymers provide more chain entanglements which in turn result in better film integrity and finally a durable coating. In case of chemical drying, some types of chemical reactions at room temperature or at elevated temperature are always encountered. These chemical reactions yield high molecular weight polymer with three–dimensional network to obtain a durable film. These reactions are generally termed as cross linking reactions. Cross linking reactions can occur either due to auto oxidation of unsaturation present in resin structure or due to condensation reaction between the functional groups present in same resin or other resin or even between the functional groups present in an additive and the resin. In later case, the additive is termed as curing or cross linking agent.

- **Auto Oxidative Drying and Its Mechanism**

Film formation in case of drying oils or oil modified resins containing unsaturated fatty acids takes place due to oxidative drying. Several workers have reported their work in this area. During drying, the most important reaction of drying oil involved is with atmospheric oxygen which results in isomerization, polymerization and degradation of C – C bond and formation of oxidation products. A number of structural features of oils affect the oxidation of oils, the most important being [172].

(a) Number of unsaturation / double bonds

(b) Either conjugated or non-conjugated double bonds

(c) Geometric arrangement of substituent groups around double bonds.

3.3.8 Preparation of Coating Composition:

- **Panel Preparation**

The mild steel panels were first degreased in alkali solution and subsequently swabbed with xylene to remove any type of oily material or contaminant. After the xylene has evaporated, panels were burnished with emery paper as per Indian Standards [173]. Panels were again washed with xylene after burnishing to remove any trace of emery paper particles or metal particles. As soon as the panels were dry, coatings were applied on them without any delay.

- **Application of Coating**

The coating compositions of various blends prepared as above were applied on mild steel panels with a synthetic fiber brush having 2.5 inch width. The brush was dipped in the composition and excess material was removed from it. The coating was applied by pulling down the brush on panel applying sufficient and uniform pressure to have a continuous and uniform film. After the application, the panels were kept horizontal in a clean atmosphere, free from dust and allowed to dry naturally under diffused daylight [174].

3.3.9 Film Characterization:

The coated panels were examined for drying time, adhesion test, flexibility test, scratch hardness, pencil hardness, impact resistance and chemical resistance by standard methods.

- **Determination of Drying Time**

Mild steel panels were used to determine the air-drying time of films of various coats [175-183]. The panels were prepared in the above manner and coating compositions were applied. The films were checked for ‘‘surface dry’’ and ‘‘tackfree dry’’ stages at regular intervals of time. While moving the finger on the film without applying any pressure if impression of fingerprint is not observed on the film, it was said to be ‘‘surface dry’’ .If the thumb is pressed on the film and twisted with applying some pressure and yet no thumb impression or detachment of film is observed then it was said to be ‘‘tack – free dry’’. The results are given in Tables 5.5 and 5.6.

- **Determination of Adhesion**

Adhesion of films to substrate was determined by employing crosshatch adhesion test according to ASTM D-3359 and panels for the test were prepared in the manner described above. Cross-hatch adhesion test was carried out after 168 hours of coating application. By using a sharp - edged knife, 10 parallel lines 1mm apart from each other were drawn on the film. Another set of such lines at right angles of 90 o to previous lines was superimposed to give a pattern of squares consisting of 100 squares with each square having 1 mm side length. A self - adhesive tape was stuck over the square pattern in such a way that no air is present between tape and film. Intimate contact between tape and film was ensured by pressing the tape over the length with fingers. The tape was kept in contact for 10 seconds and then the tape was rapidly pulled off in a single stroke at an angle of 120 o approximately. The test was rated ‘‘passed’’ if not more than 5% of squares were removed.

Determination of Flexibility

For the determination of flexibility, tinned mild steel panels were used. The coating compositions were applied and cured in the manner mentioned above. Flexibility test were carried out using mandrels having specific rod diameter. A test panel was inserted between the hinges and rod in such a way that the coated side was kept outside to the direction of bending. The hinge was closed at a single stretch without jerking in about a second causing the test panel to bend through an angle of 180o. The panel was examined for presence of cracks or loss of adhesion without removing the panel from the mandrill. Generally 1/4 inch rod diameter mandrel was used and if film passed through 1/4 inch mandrel then it was said to pass the flexibility test.

- **Determination of Hardness**

Hardness of films of various UPUEs were determined using tinned mild steel panels after 168 hours of coating application. Two different methods were used to determine the hardness.

- **Scratch Hardness**

In first method, a hand operated instrument was used in which test panel was kept on a sliding base with coated side upward and scratched under specific load with a needle which was in contact with film on test panel. The load was kept increasing till the film was scratched which was indicated by a light bulb that glows when film is scratched. The results were expressed in (Kg) corresponding to the load at which film is scratched.

- **Pencil Hardness**

In this method, pencils having different hardness were used. Sharp tipped pencils having hardness 4B (soft) and 6H (hard) were used to scratch the film. The pencil was held approximately at an angle of 45o to the film and with uniform pressure pulled down over the length of the film. The test was repeated till a pencil with specific hardness was able to scratch the film. The hardness of that pencil was reported as the pencil hardness test.

Determination of Impact Resistance

The coated test panels for the impact resistance test were prepared in the manner described above. The test was carried out after 168 hours of coating application. The coated panel was kept on a platform with the coated side upward. The panel was then indented with an object of specific weight from varying heights. The test was repeated by increasing the height from which the object falls till the film was cracked or detached. The results are generally expressed in (in. Ib) i.e. the number of inches the weight falls times its weight.

Determination of Chemical Resistance Properties

For the assessment of chemical resistance of the films to various chemicals, tinned mild steel panels were used which were prepared, coated and cured as mentioned above. Before subjecting the test panels to chemical resistance test, the backside of coated panel (i.e. the non coated side) was coated with epoxy resin and cured at room temperature for 48 hours. Subsequently all the four edges of the panel were sealed with paraffin wax by dipping approximately 1 cm of each side in molten wax and cooling at room temperature to form a 1 cm thick impervious and continuous layer of wax. When the panels were subjected to solvent resistance test particularly, the edges of the panel were sealed with epoxy resin cured at room temperature for (48 hrs.) instead of wax. The immersion method was utilized to assess the chemical resistance of films in which the panels were immersed vertically in the baths containing

Solutions of different chemicals in specific concentration were used at room temperature for the specific time period. Upon completion of the specified time period the panels were removed from the baths and allowed to dry before visual examination. The following solutions with their respective concentrations were used for chemical resistance test:

(1) For acid resistance: 5% HCl solution
(2) For alkali resistance: 3% NaOH solution
(3) For water resistance: Distilled water
(4) For solvent resistance: xylene

Chapter-4

Results and Discussion

Chapter-4 represents the results of analytical measurements.

4.1 IR Spectral Characteristics of unsaturated Polyesters Resins (UPEs):

IR spectral feature of all unsaturated Polyesters Resins VIa-j, VIIa-j and VIIIa-j are discussed profoundly. The unsaturated Polyesters Resins are not studied by polymer scientists so far. So it will be challenging task in the present study to interpret the IR spectra of our samples. Does the IR spectrum of UPEs contain the characteristic bands of the unsaturated polyesters? Does it exhibit all the vibrations like unsaturated polyesters? By taking the IR spectra of our samples - we conclude that the IR spectra of polyesters are mainly consist the following bands:

1. The IR spectra of all the UPEs show a strong band around 1730 cm^{-1} which is the characteristic band for >C=O stretching of the A,B –unsaturated esters.

2. The spectra of all the resins show the characteristic >C=O stretching band of amide group around 1690 cm^{-1} and characteristic –NH band of amide group between 1550-1510 cm^{-1}.

3. The spectra of all the resins show the characteristic band of the secondary hydroxyl group between 3600-3200 cm^{-1} for O-H stretching.

4. The spectra of all the resins show a characteristic band for the ether group around 1260 cm^{-1}.

5. The spectra of all the resins show a band around 1655cm^{-1} which may arise from cis C=C stretching vibration.

Thus, the IR spectral analysis of the resins confirms the formation of the unsaturated Polyesters Resins.

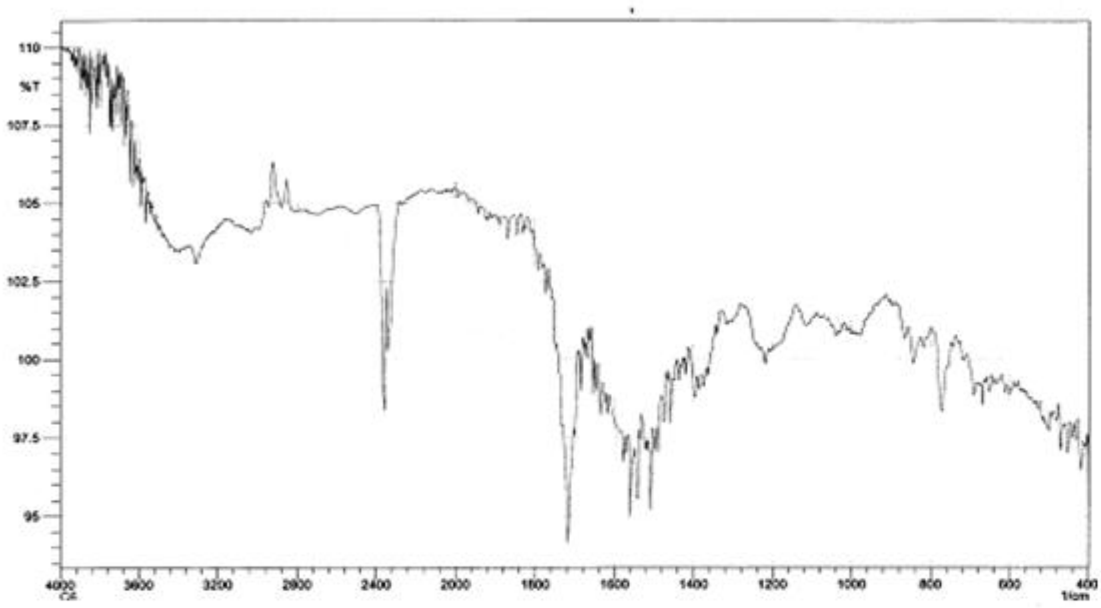


Figure 4.1 IR Spectrum of IIIa

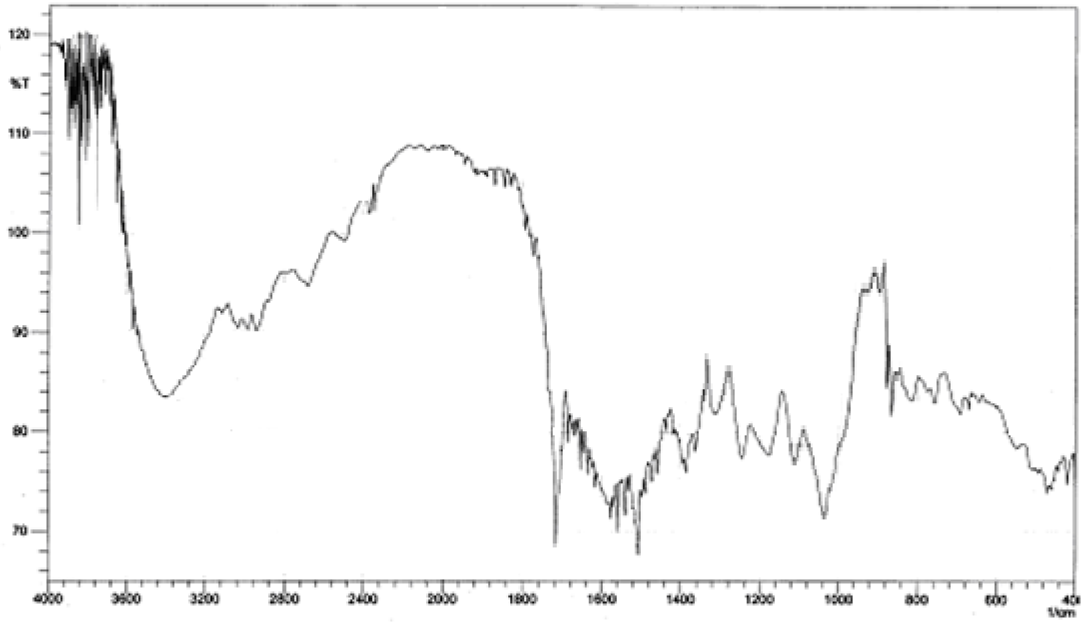


Figure 4.2 IR Spectrum of IIIb

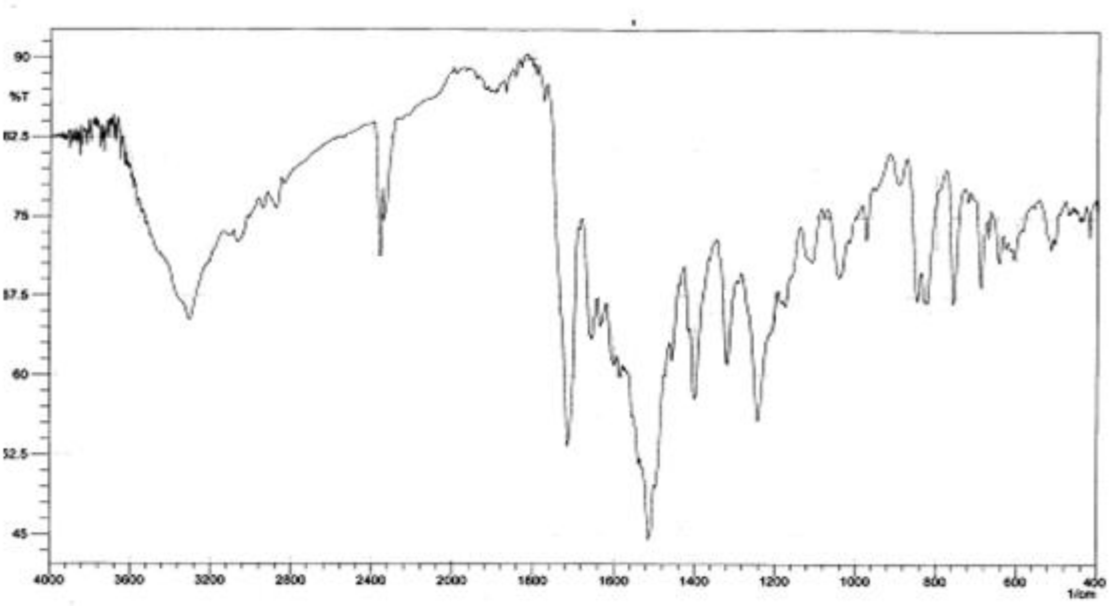


Figure 4.3 IR Spectrum of IIIc

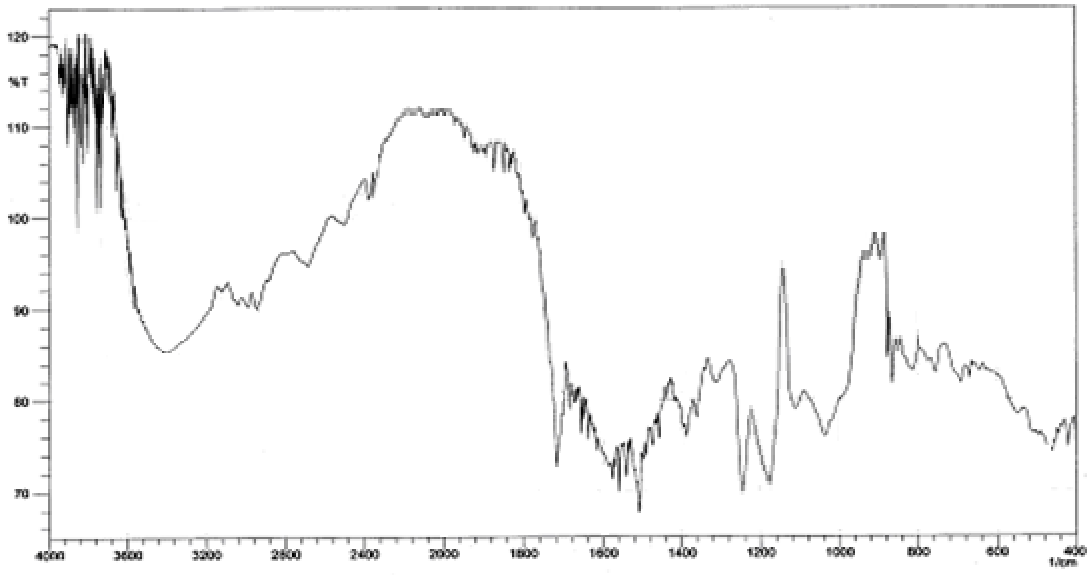


Figure 4.4 IR Spectrum of IIId

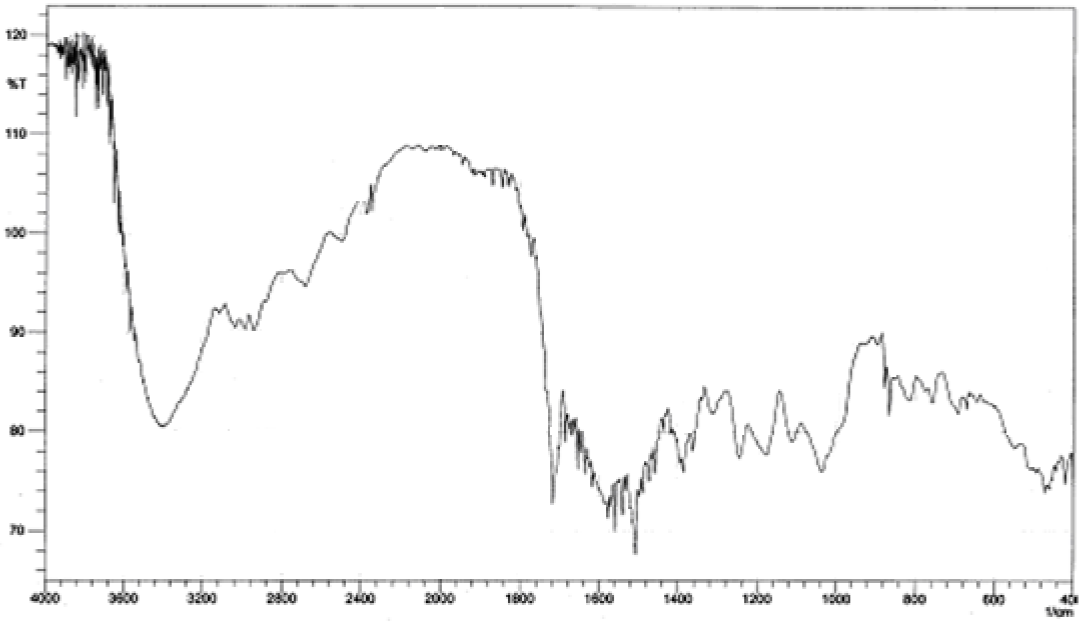


Figure 4.5 IR Spectrum of IIIe

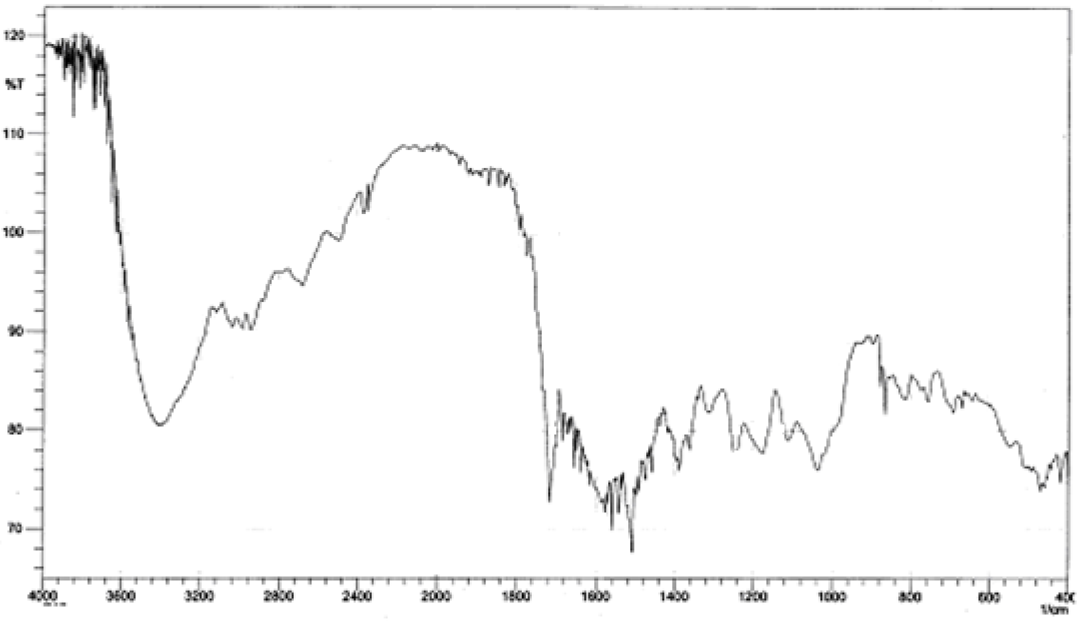


Figure 4.6 IR Spectrum of IIIf

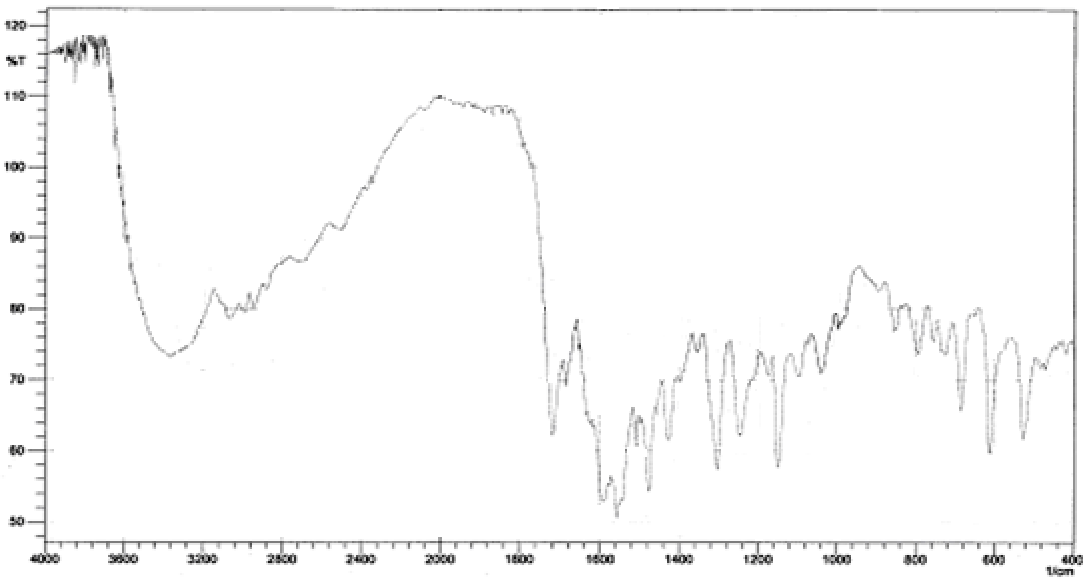


Figure 4.7 IR Spectrum of IIIg

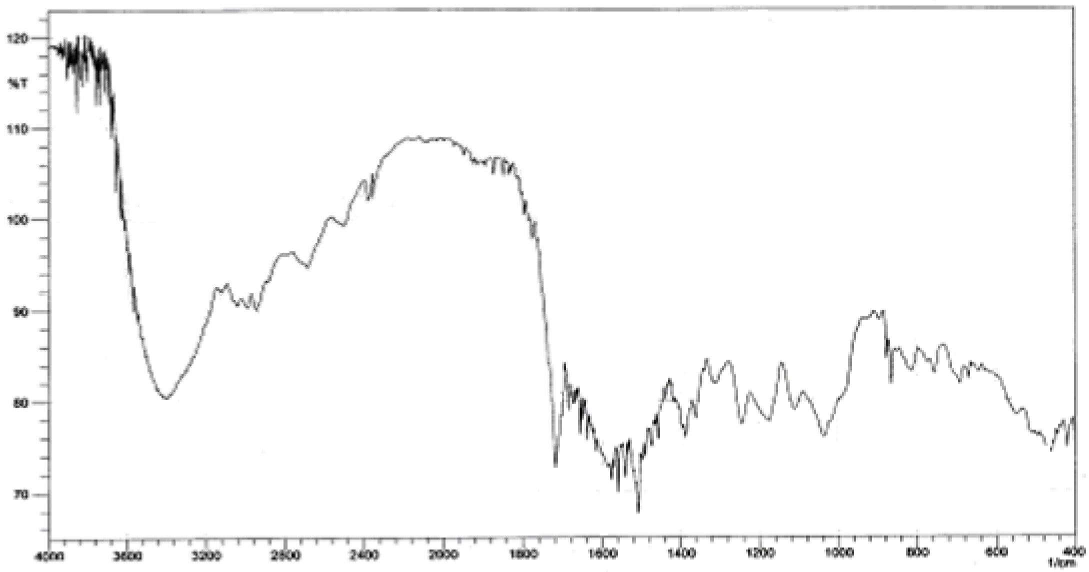


Figure 4.8 IR Spectrum of IIIh

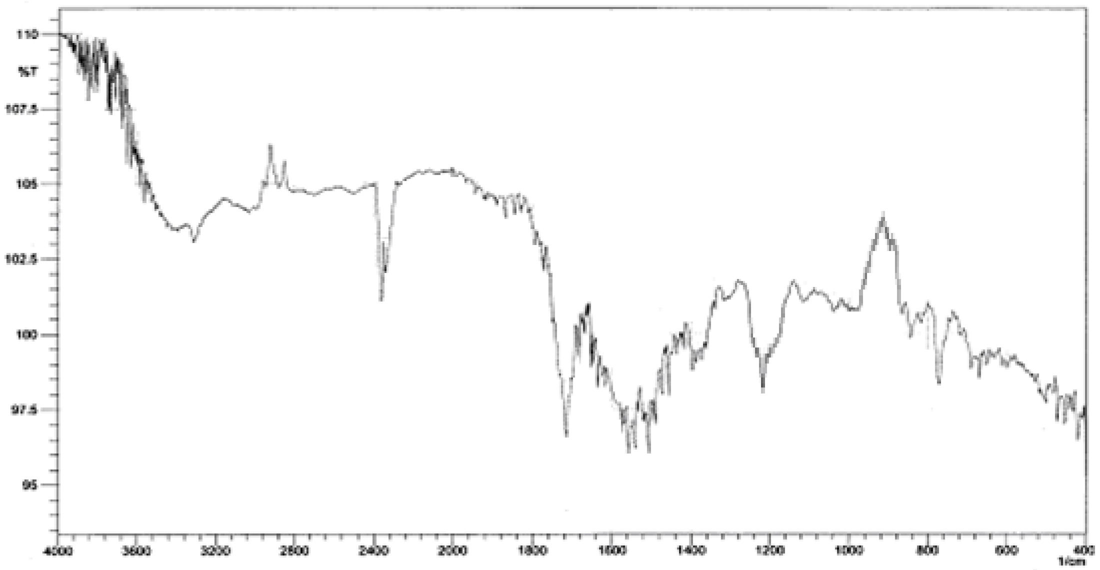


Figure 4.9 IR Spectrum of IIIi

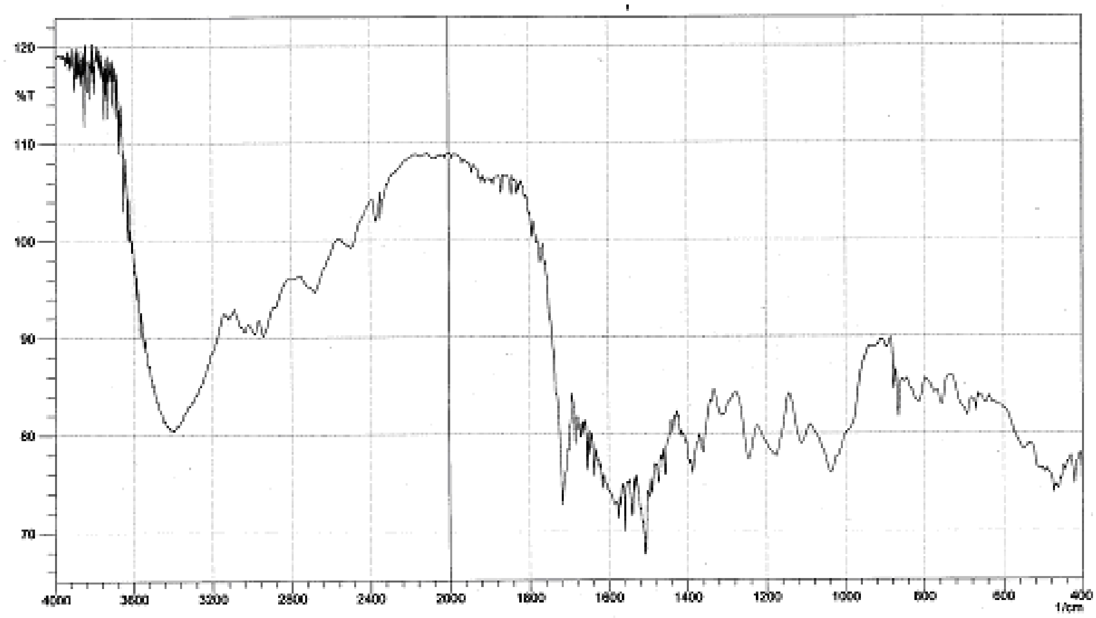


Figure 4.10 IR Spectrum of IIIj

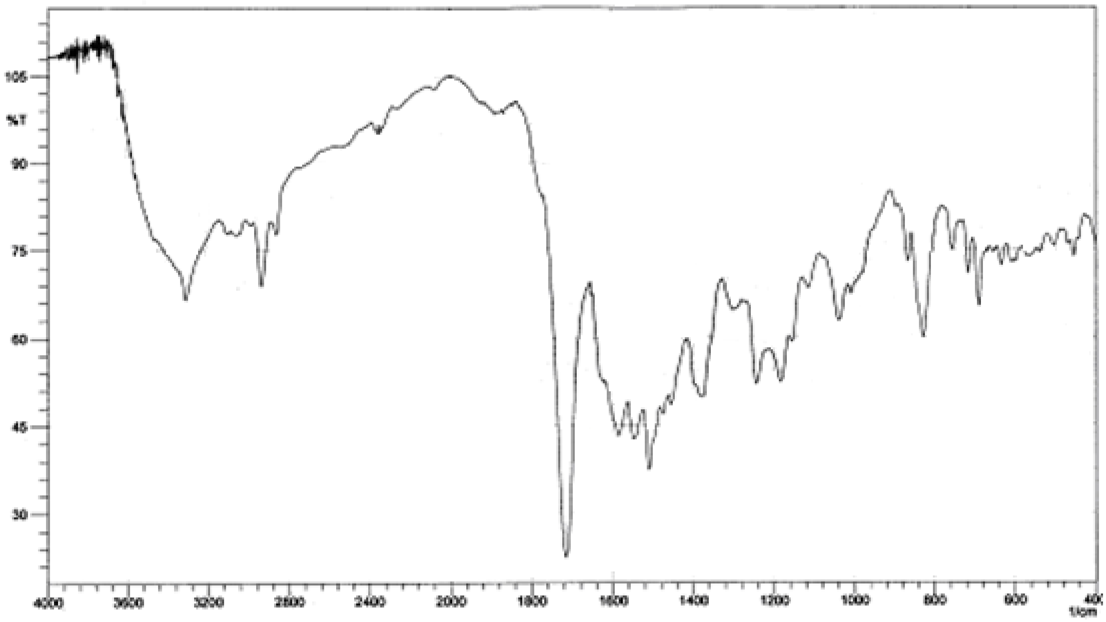


Figure 4.11 IR Spectrum of Va

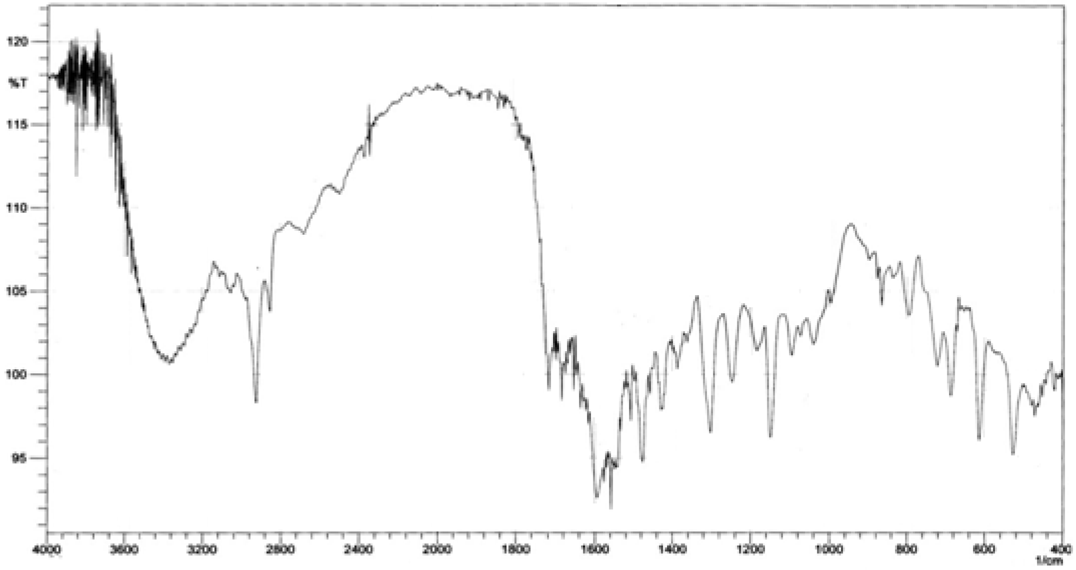


Figure 4.12 IR Spectrum of Vb

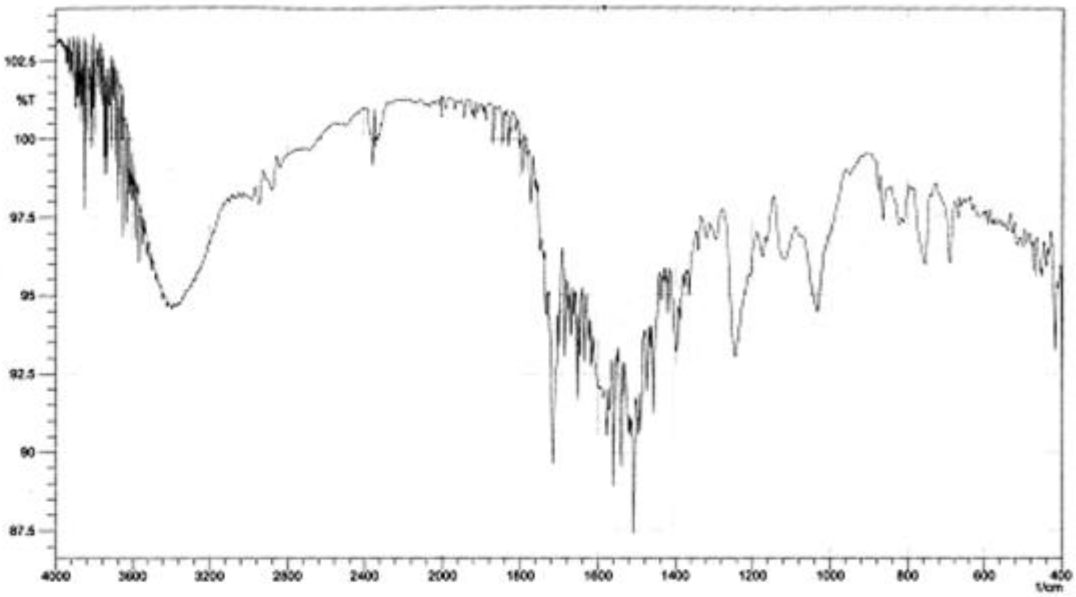


Figure 4.13 IR Spectrum of Vc

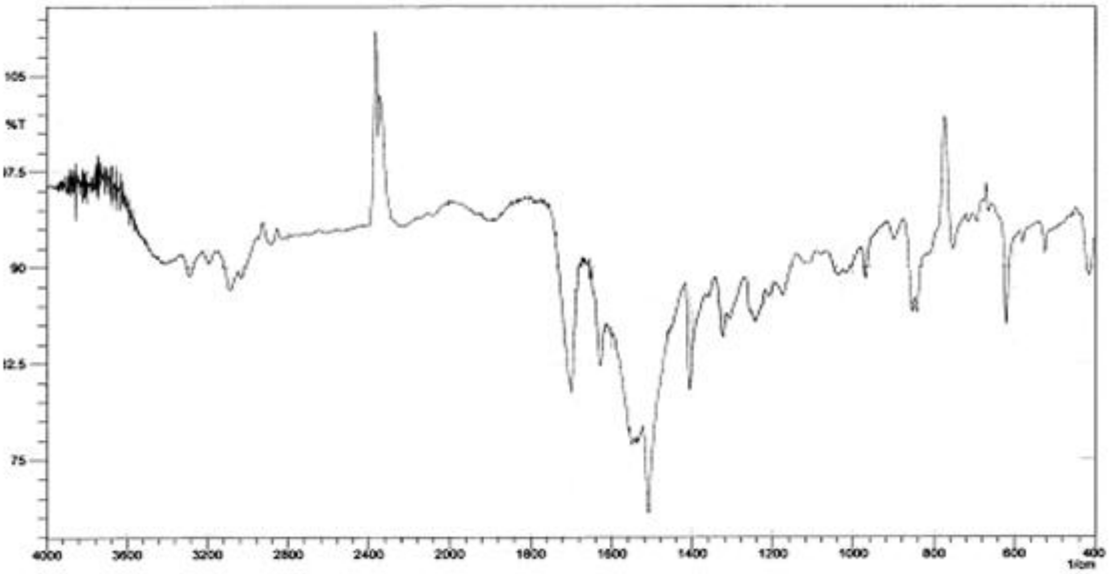


Figure 4.14 IR Spectrum of Vd

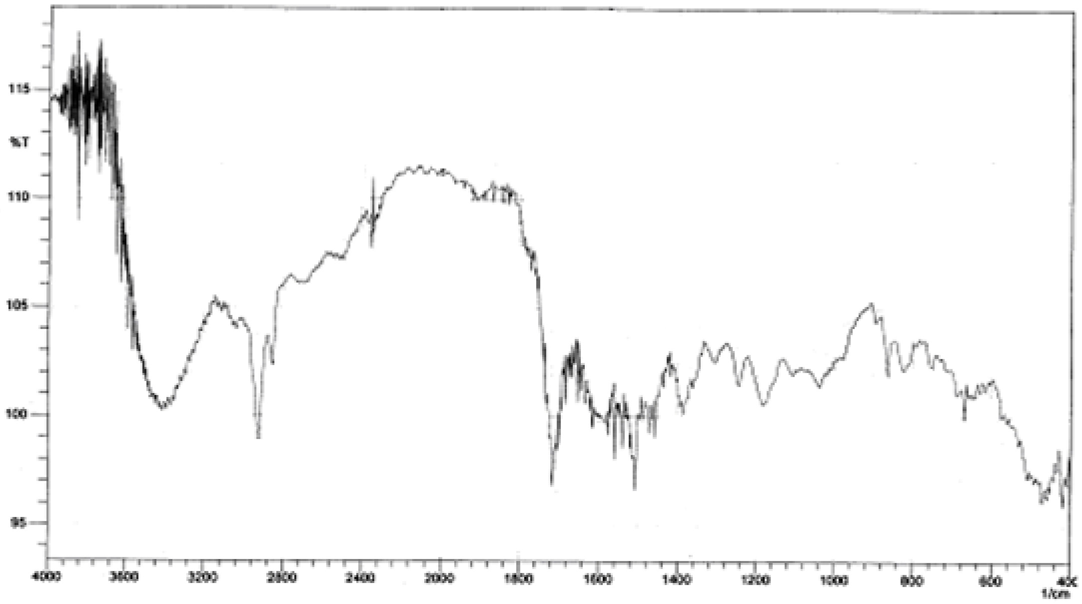


Figure 4.15 IR Spectrum of Ve

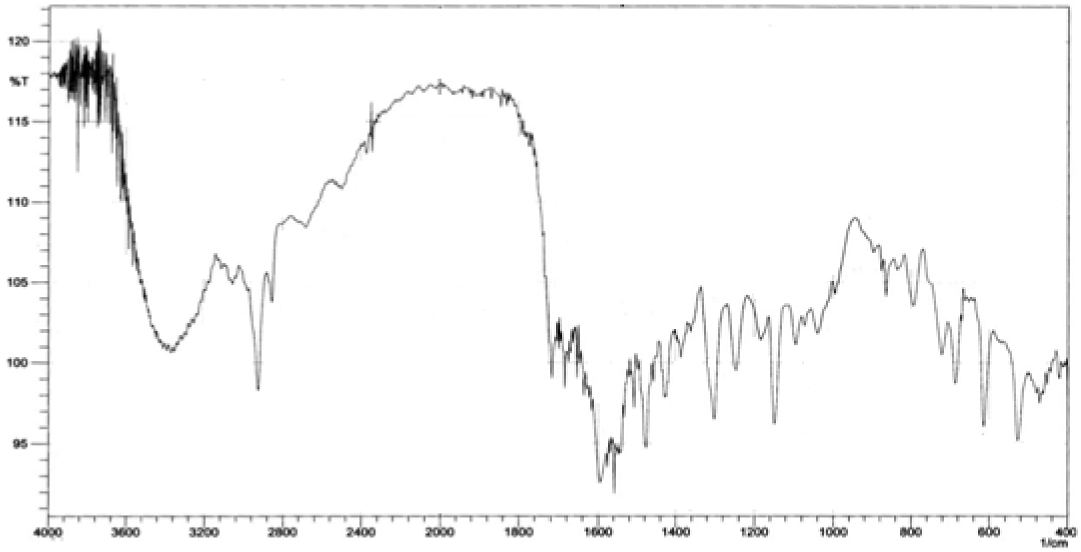


Figure 4.16 IR Spectrum of Vf

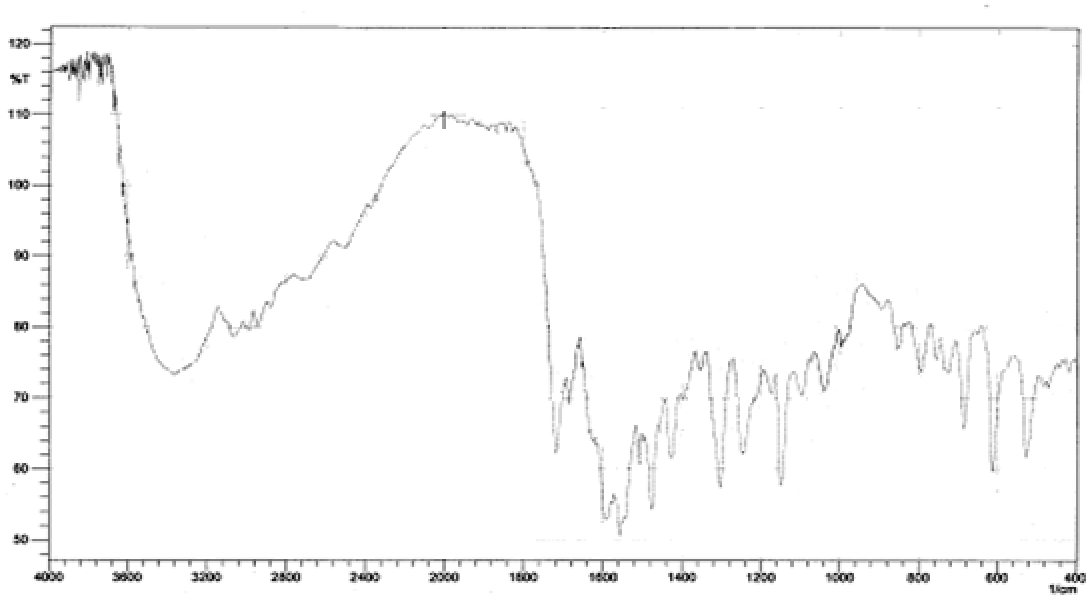


Figure 4.17 IR Spectrum of Vg

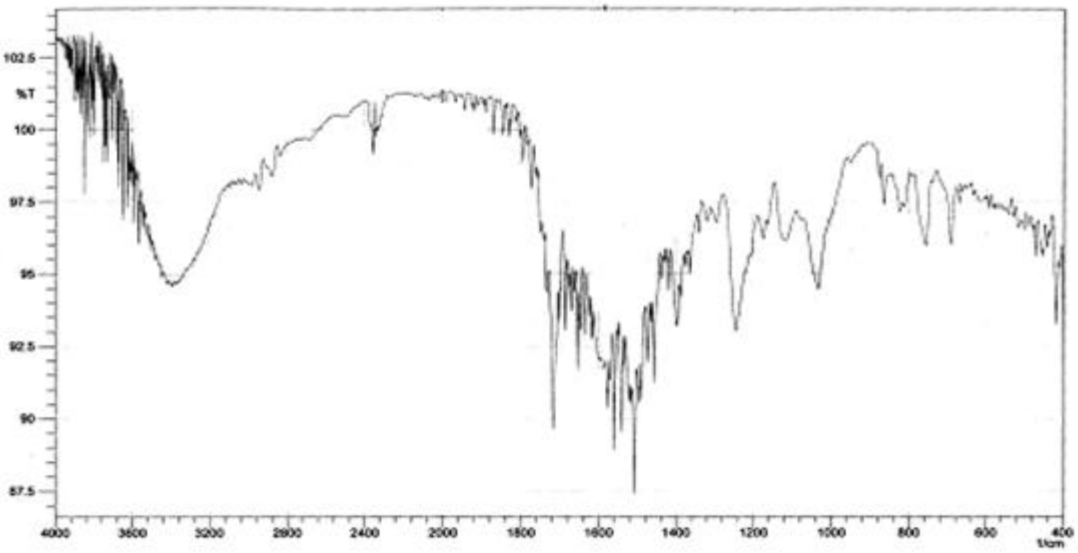


Figure 4.18 IR Spectrum of Vh

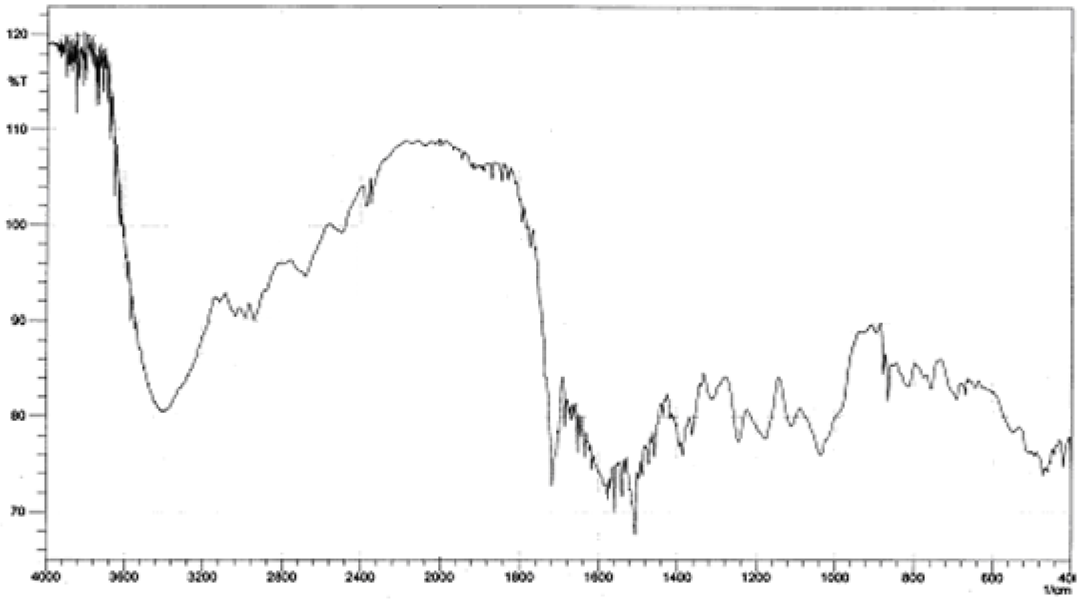


Figure 4.19 IR Spectrum of Vi

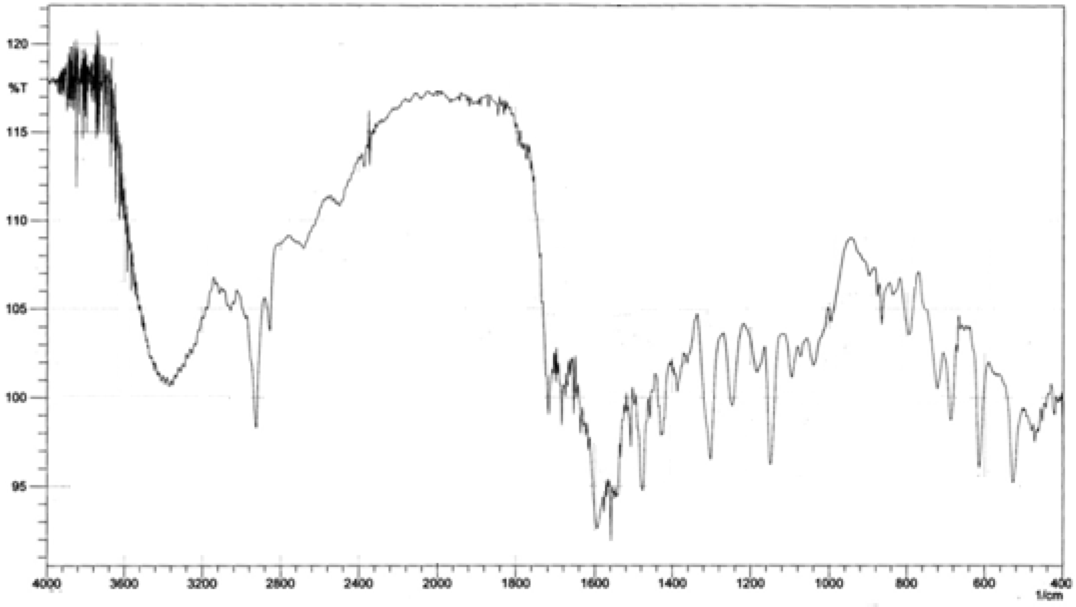


Figure 4.20 IR Spectrum of Vj

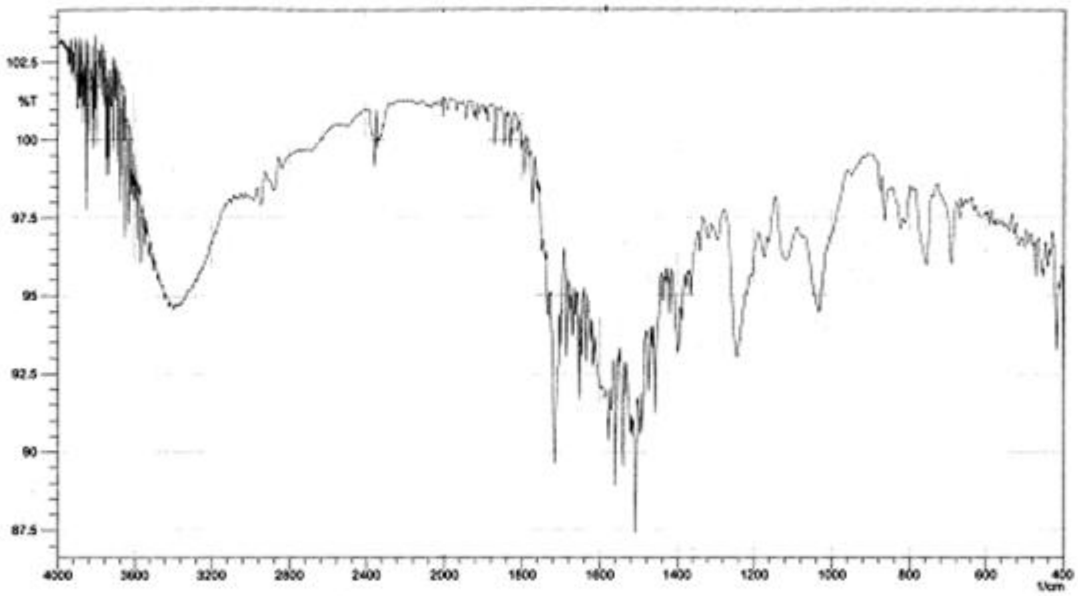


Figure 4.21 IR Spectrum of VIa

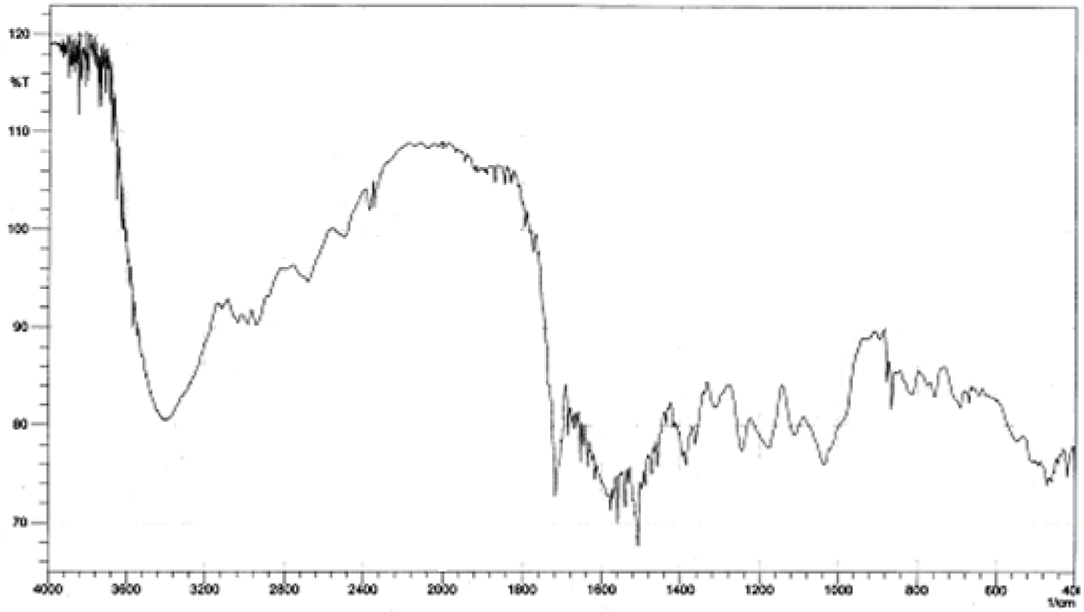


Figure 4.22 IR Spectrum of VIb

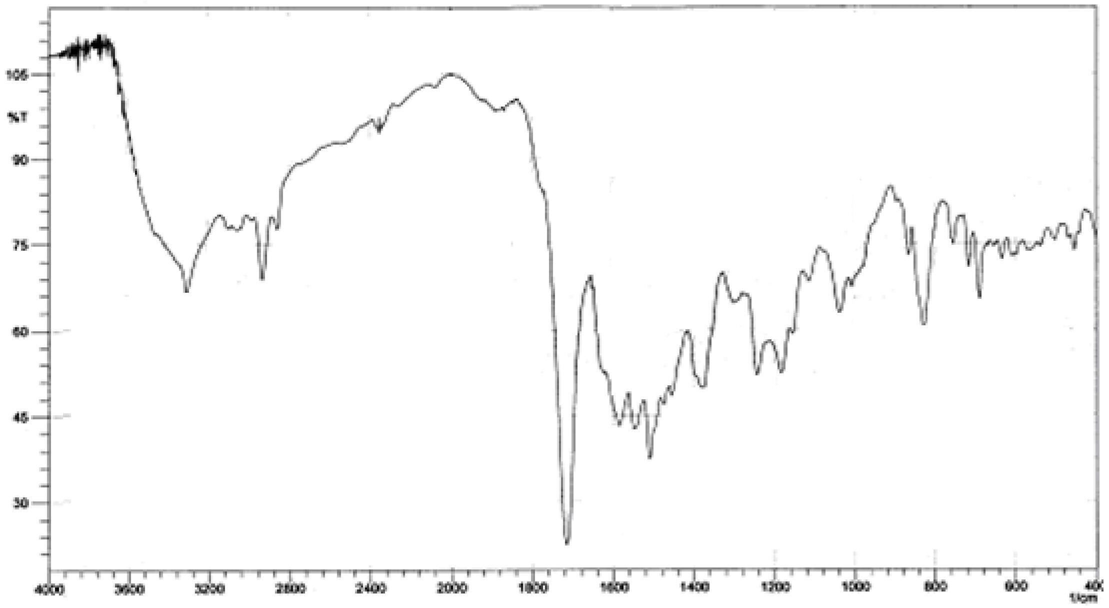


Figure 4.23 IR Spectrum of VIc

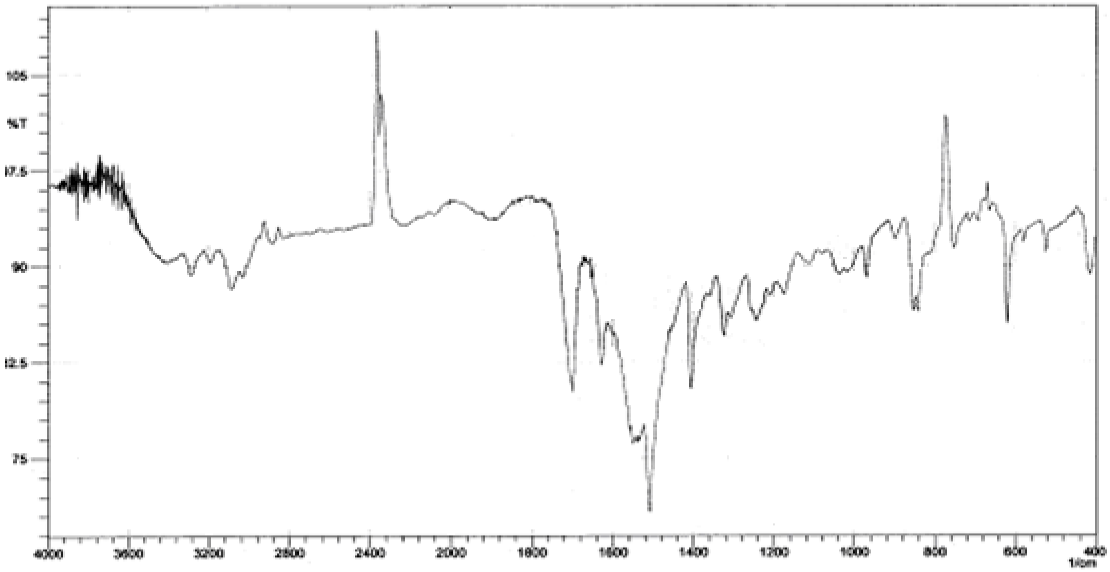


Figure 4.24 IR Spectrum of VId

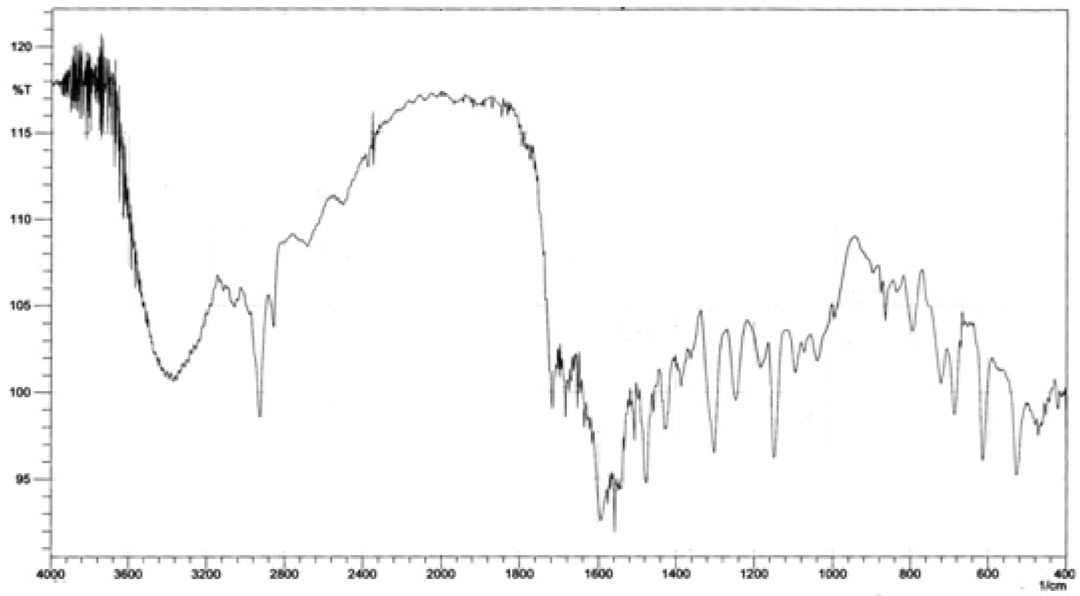


Figure 4.25 IR Spectrum of VIe

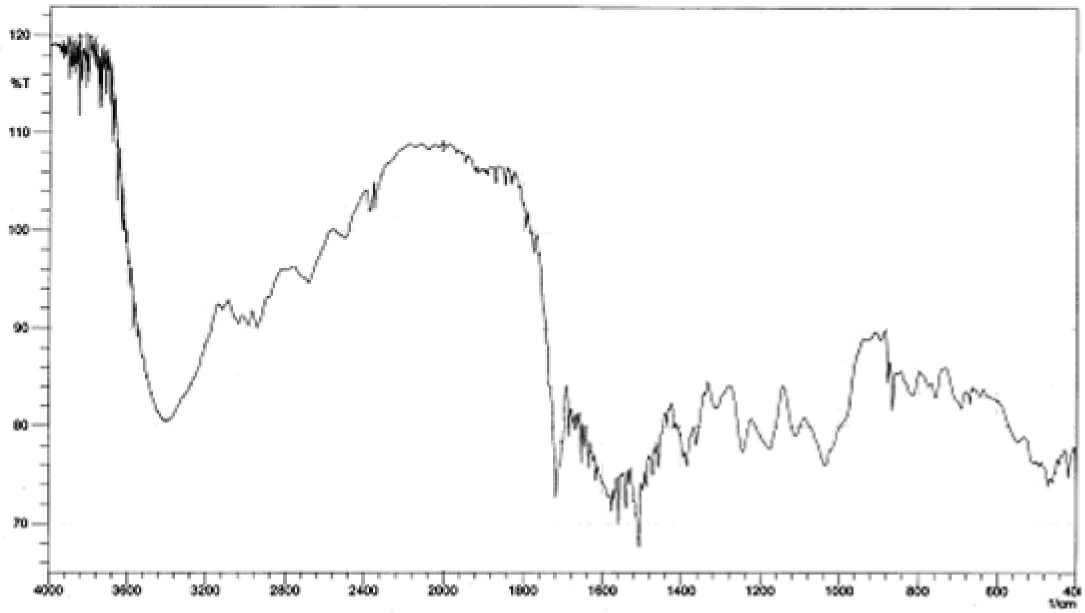


Figure 4.26 IR Spectrum of VIf

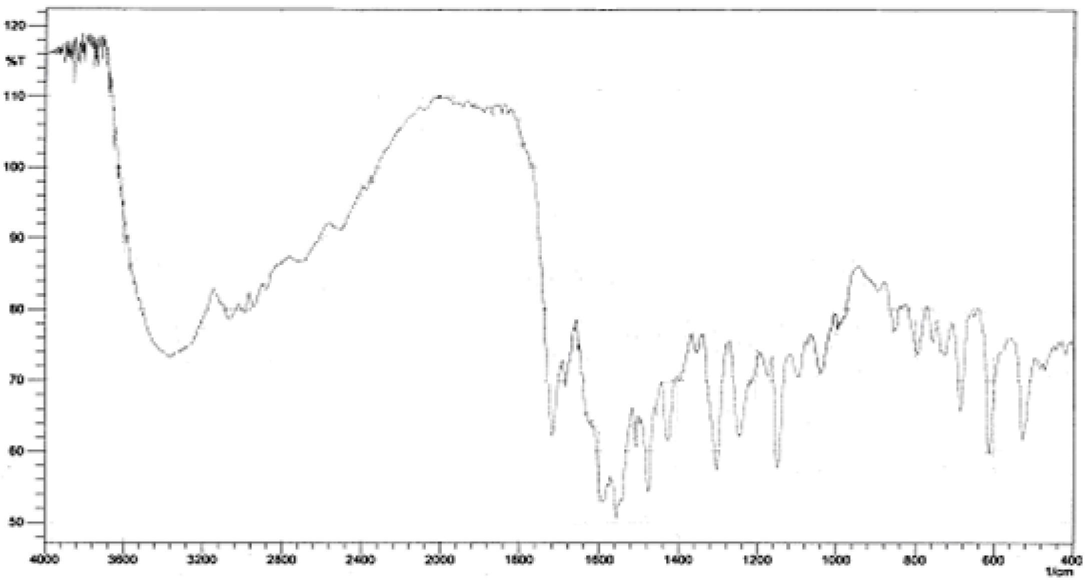


Figure 4.27 IR Spectrum of VIg

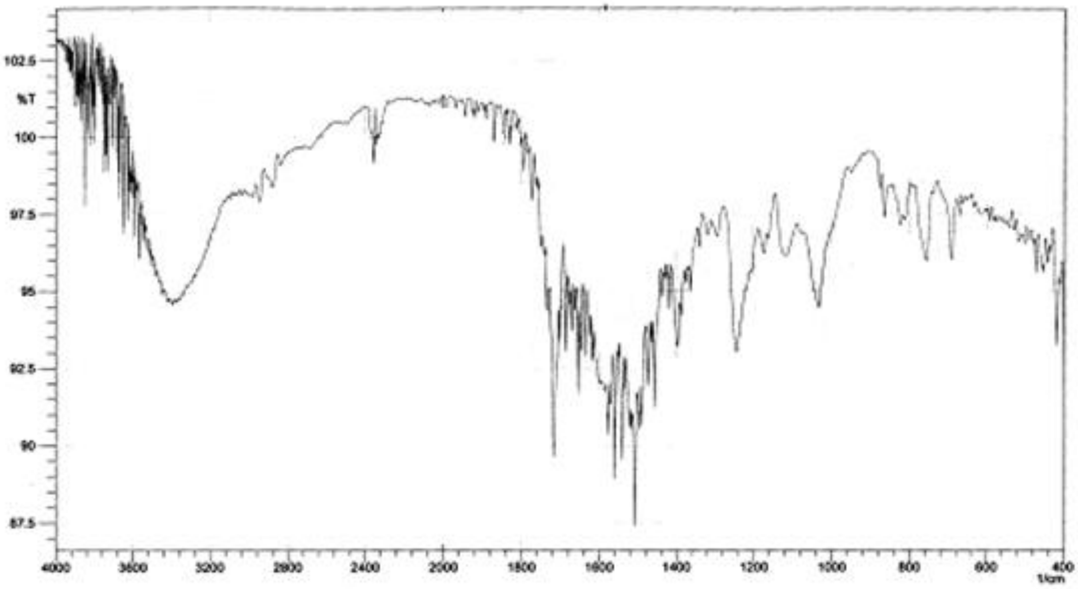


Figure 4.28 IR Spectrum of VIh

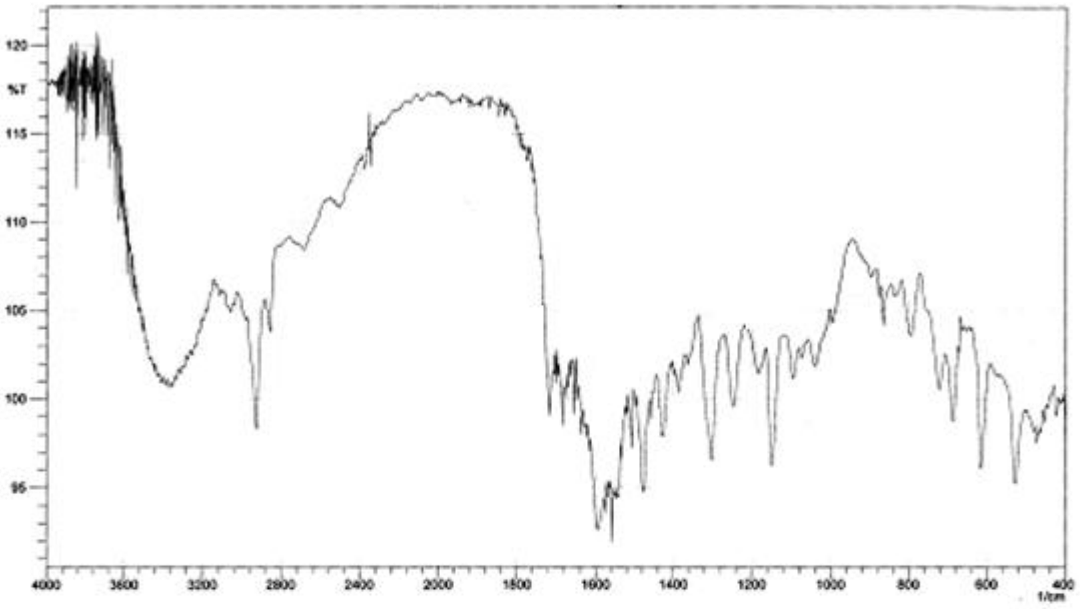


Figure 4.29 IR Spectrum of VIi

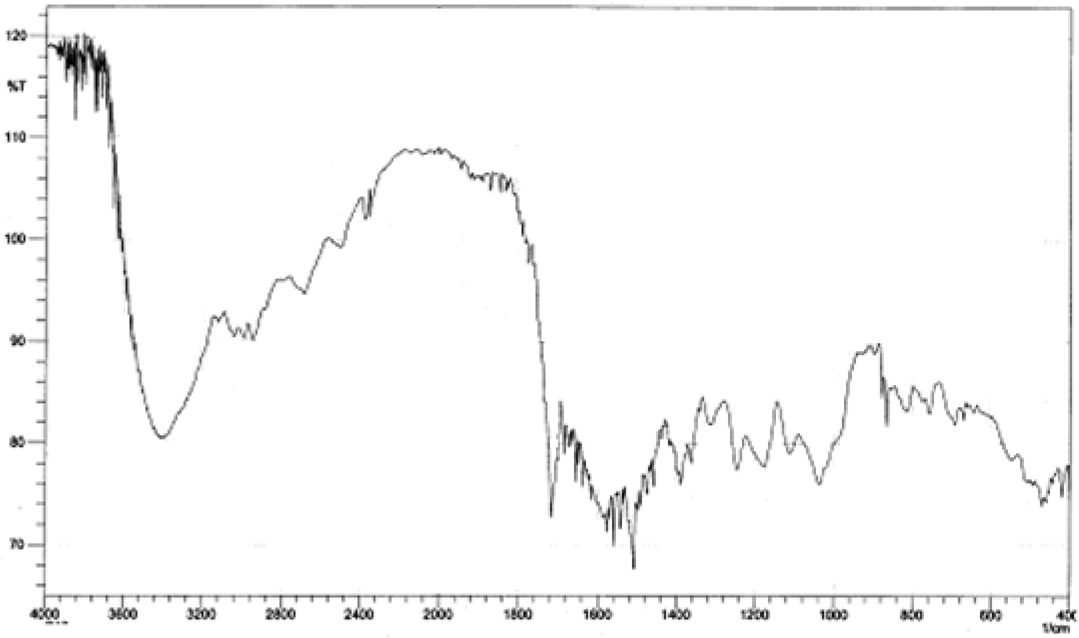


Figure 4.30 IR Spectrum of VIj

• IR Spectral Characteristics of poly(urethane-ester)s (PUEs):

The bands around 1541–1551cm^{-1} and 1600–1635cm^{-1} confirm the formation of urethane linkage. These spectra do not show hydroxyl group frequency due to the formation of urethane linkage, which gives evidence of the structure of poly(urethane-ester)s. The IR spectra of PUEs not much resolve due to interactive blending with vinyl ester some of them are shown below.

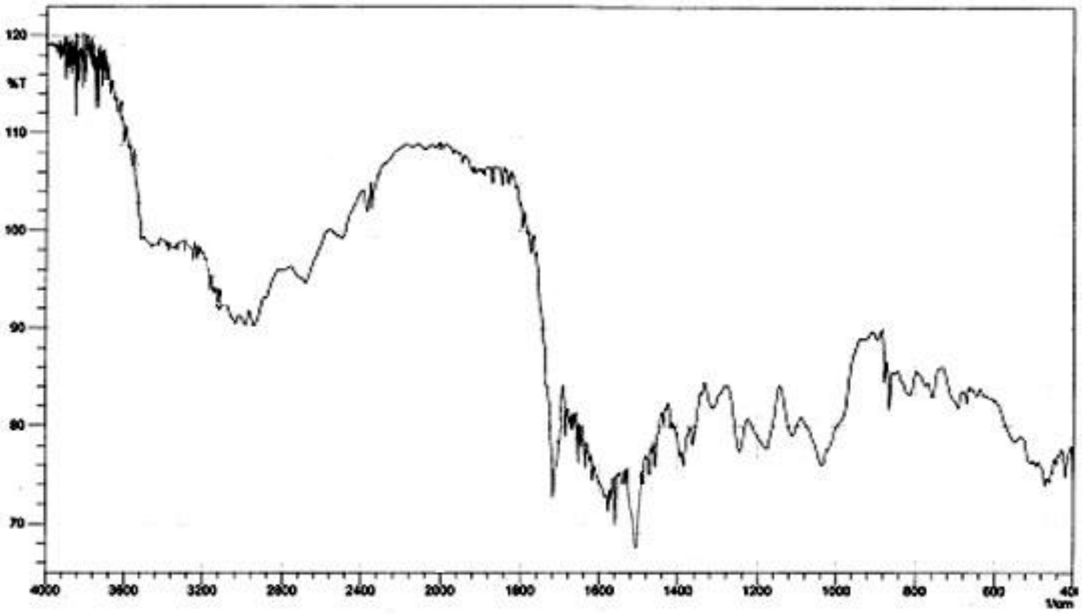


Figure 4.31 : IR Spectra of PUEs IXa

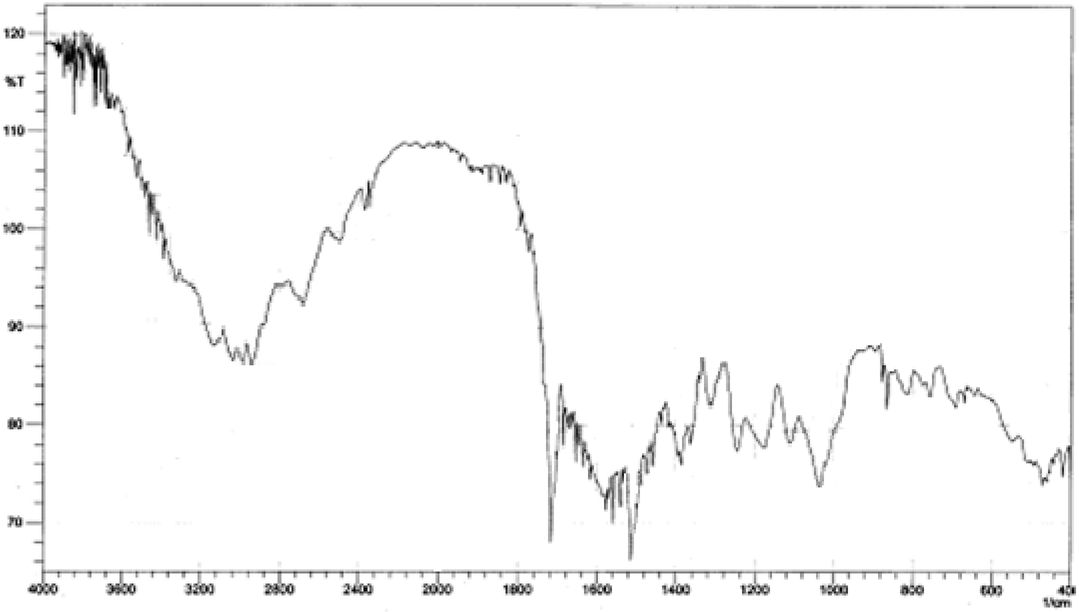


Figure 4.32: IR Spectra of PUEs IXb

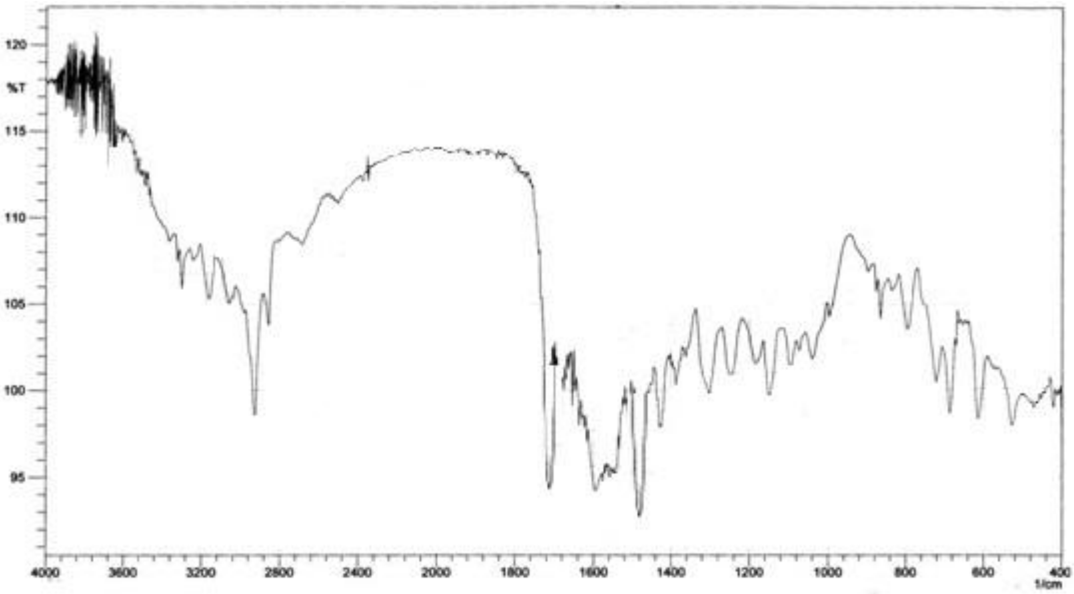


Figure 4.33: IR Spectra of PUEs IXd

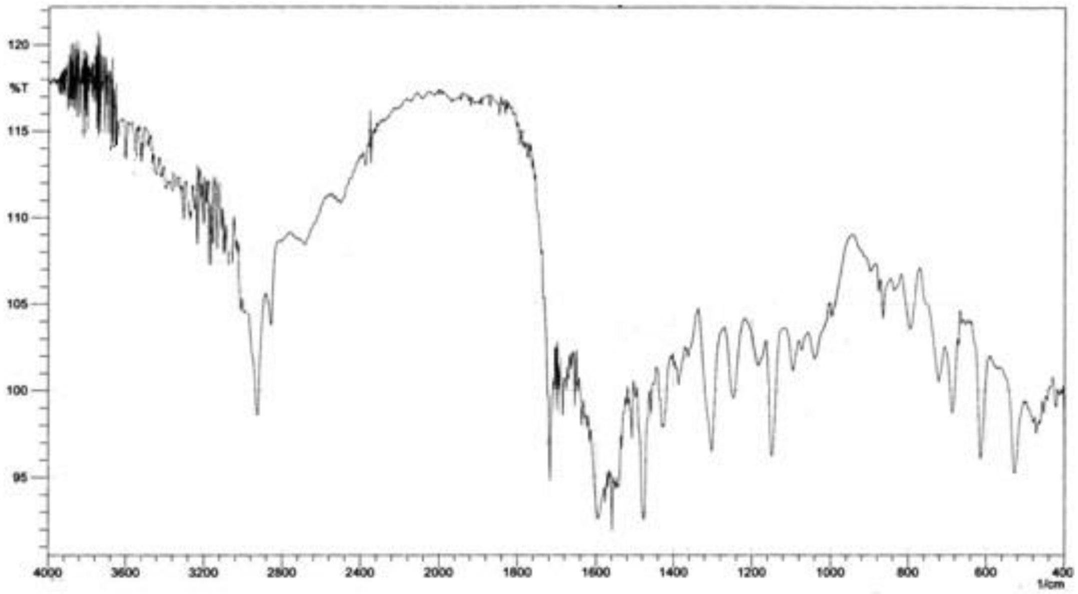


Figure 4.34 : IR Spectra of PUEs IXg

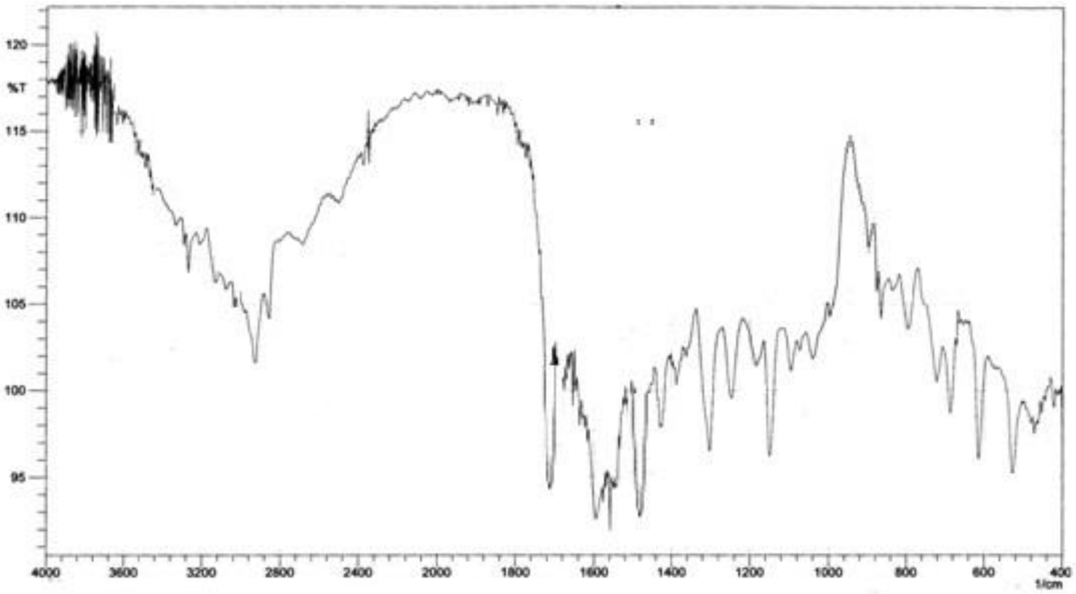


Figure 4.35: IR Spectra of PUEs IXi

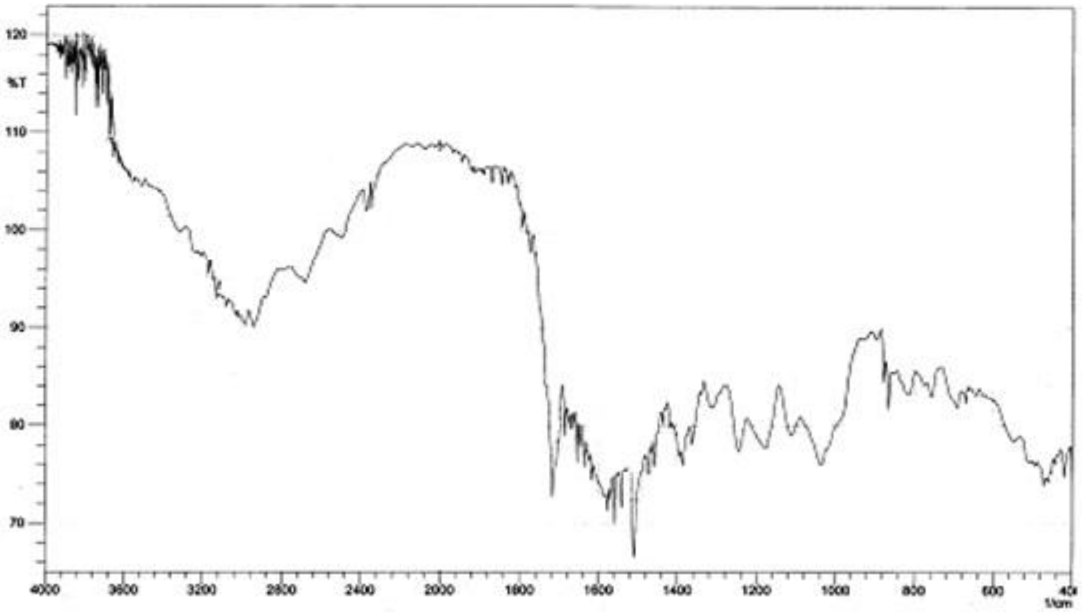


Figure 4.36: IR Spectra of PUEs IXj

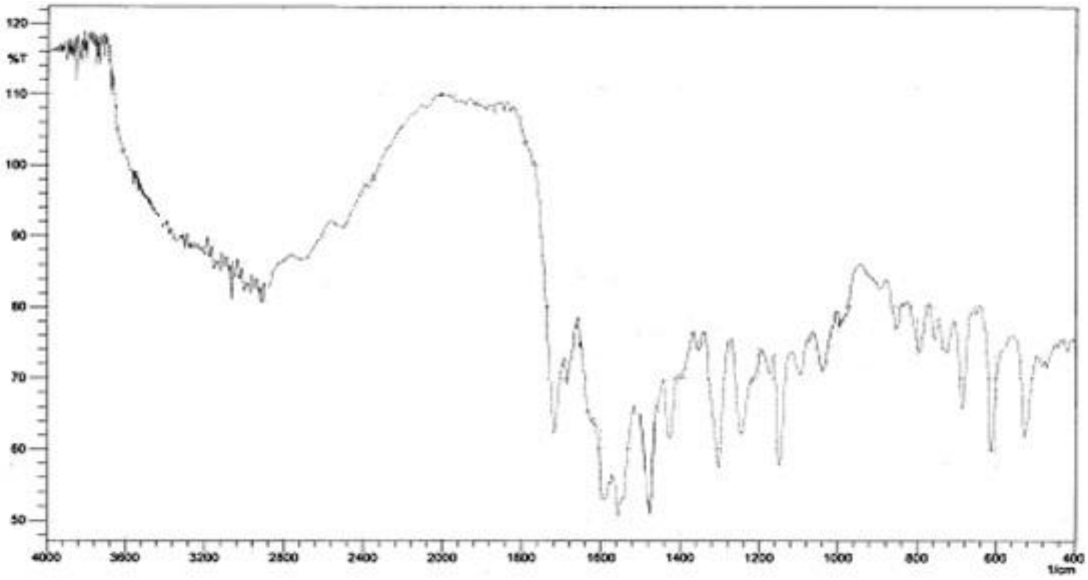


Figure 4.37 : IR Spectra of PUEs Xa

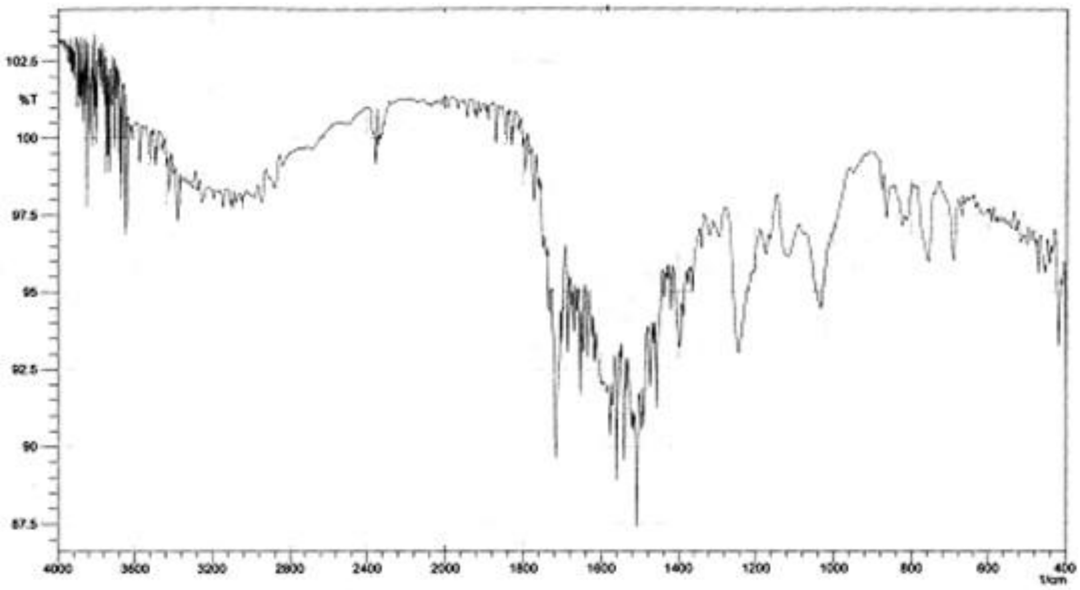


Figure 4.38 : IR Spectra of PUEs Xb

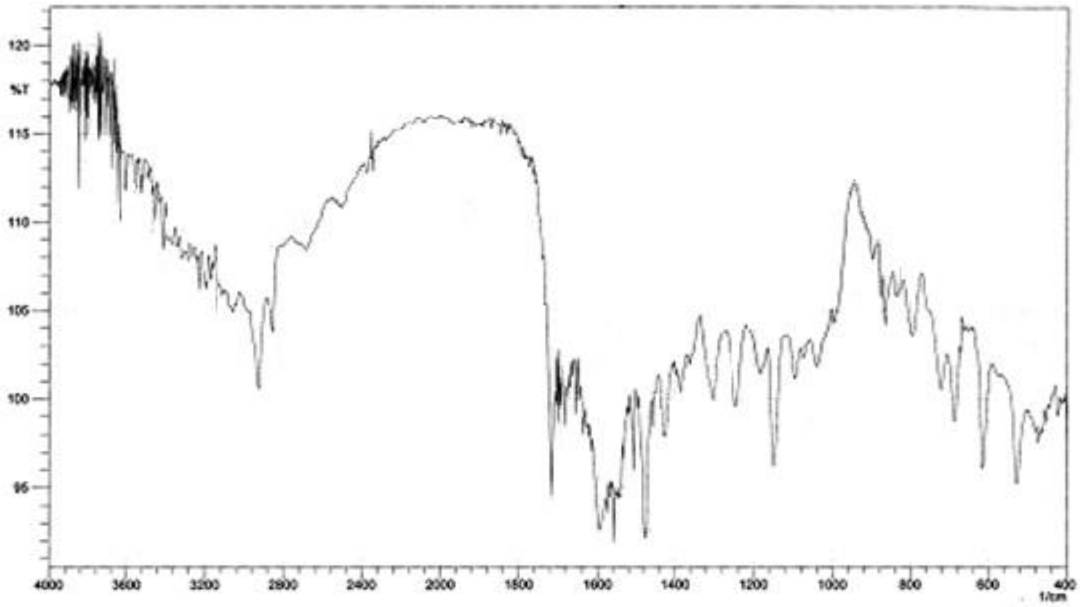


Figure 4.39: IR Spectra of PUEs Xd

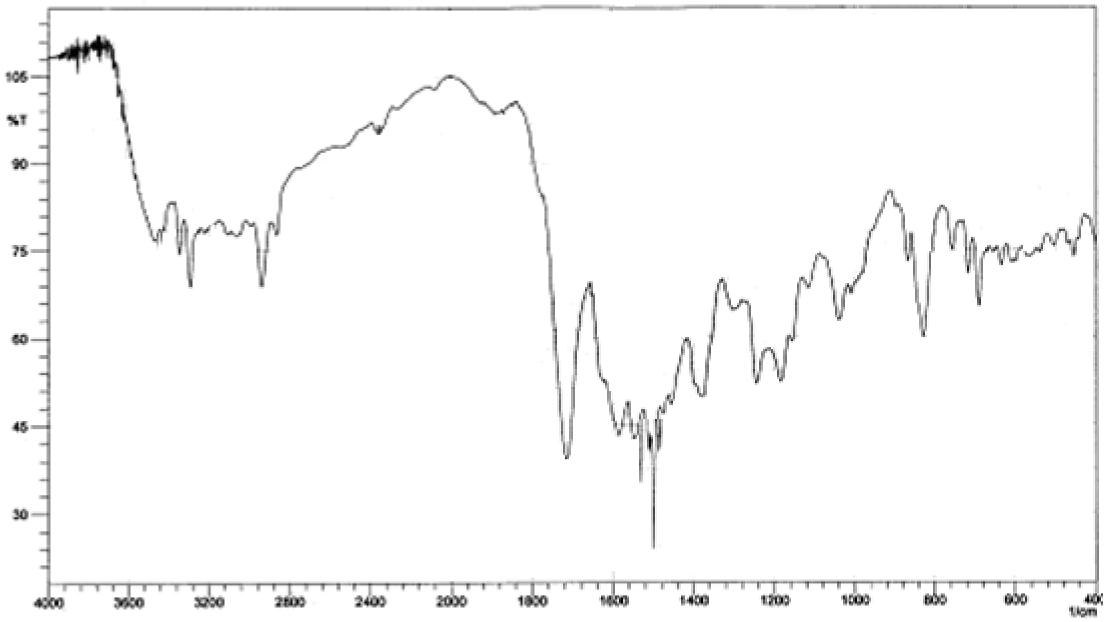


Figure 4.40: IR Spectra of PUEs Xd

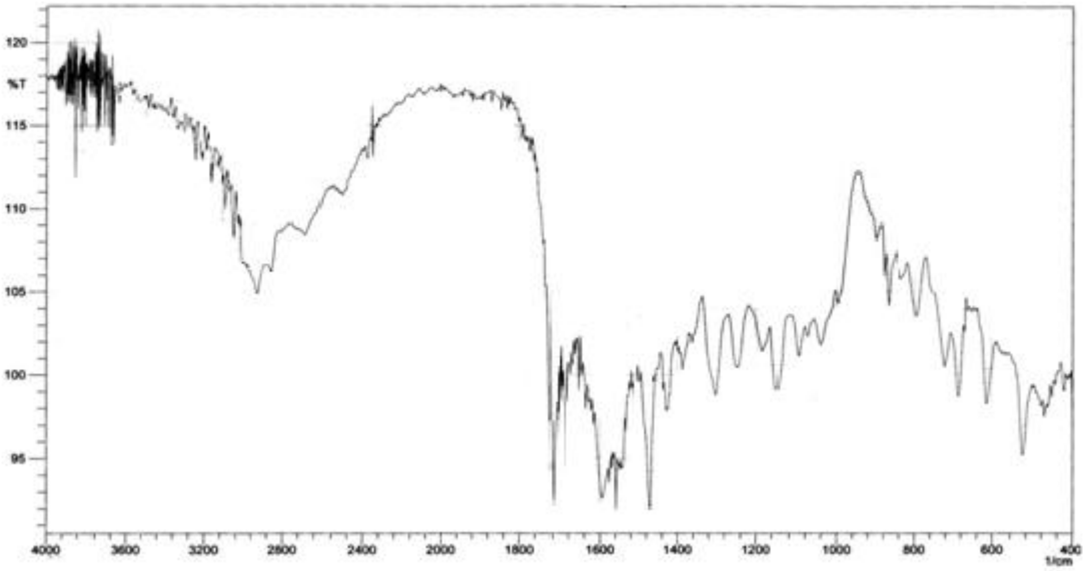


Figure 4.41: IR Spectra of PUEs Xg

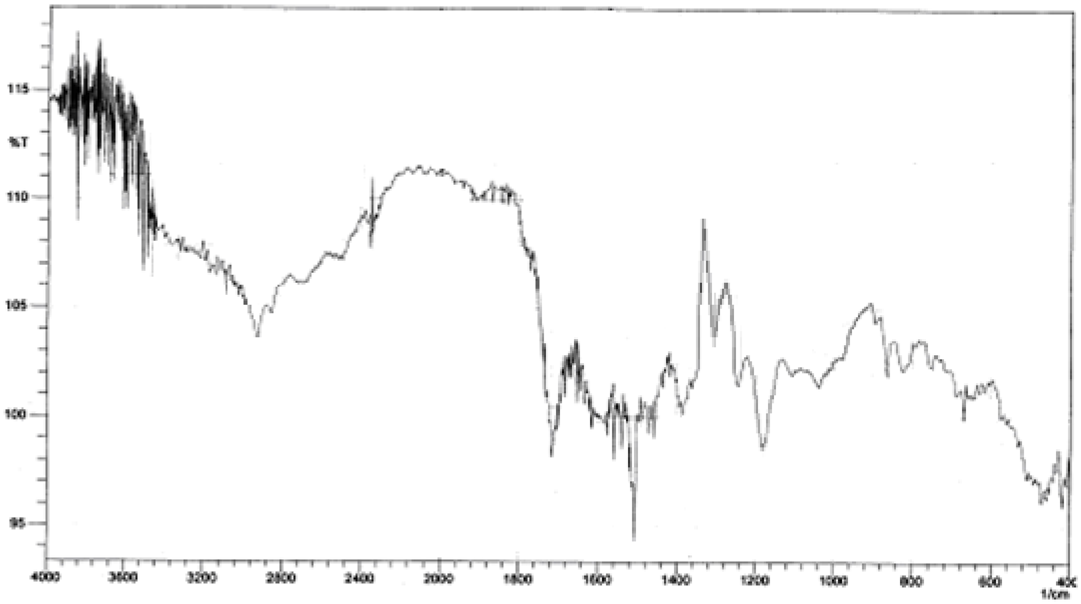


Figure 4.42: IR Spectra of PUEs Xj

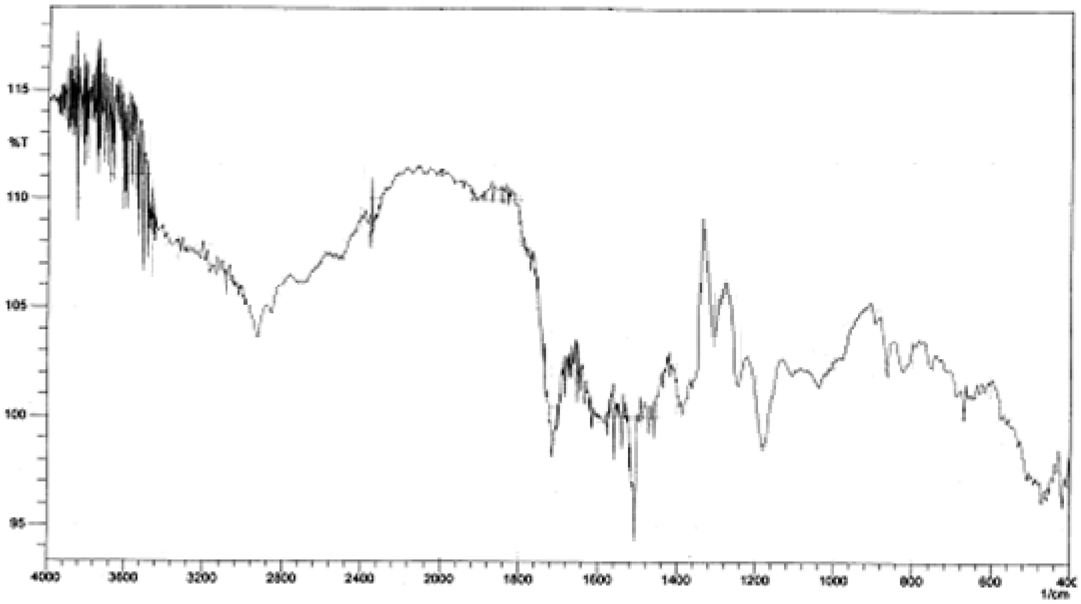


Figure 4.43: IR Spectra of PUEs Xia

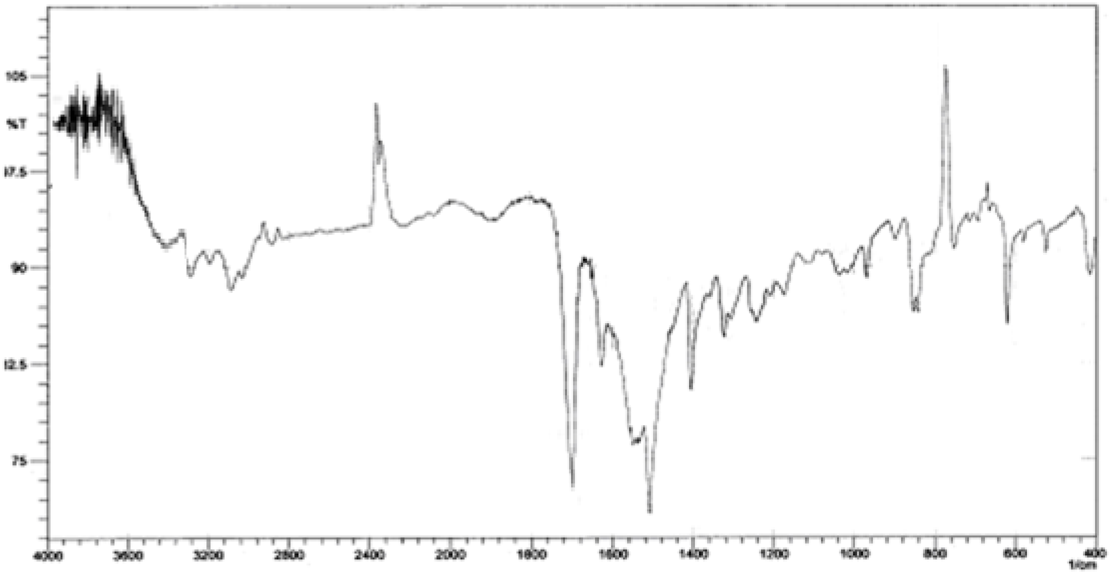


Figure 4.44: IR Spectra of PUEs XId

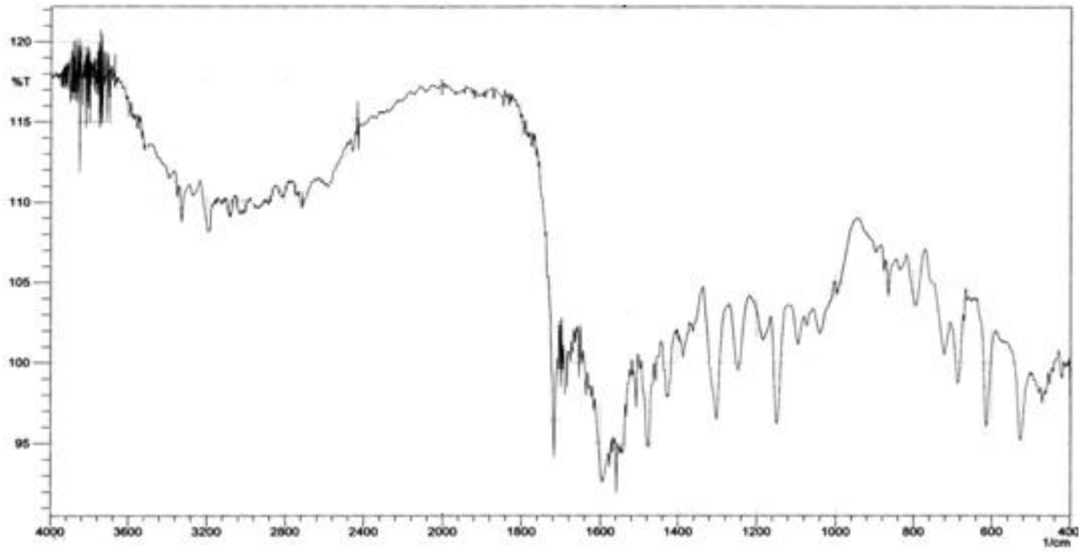


Figure 4.45: IR Spectra of PUEs XIg

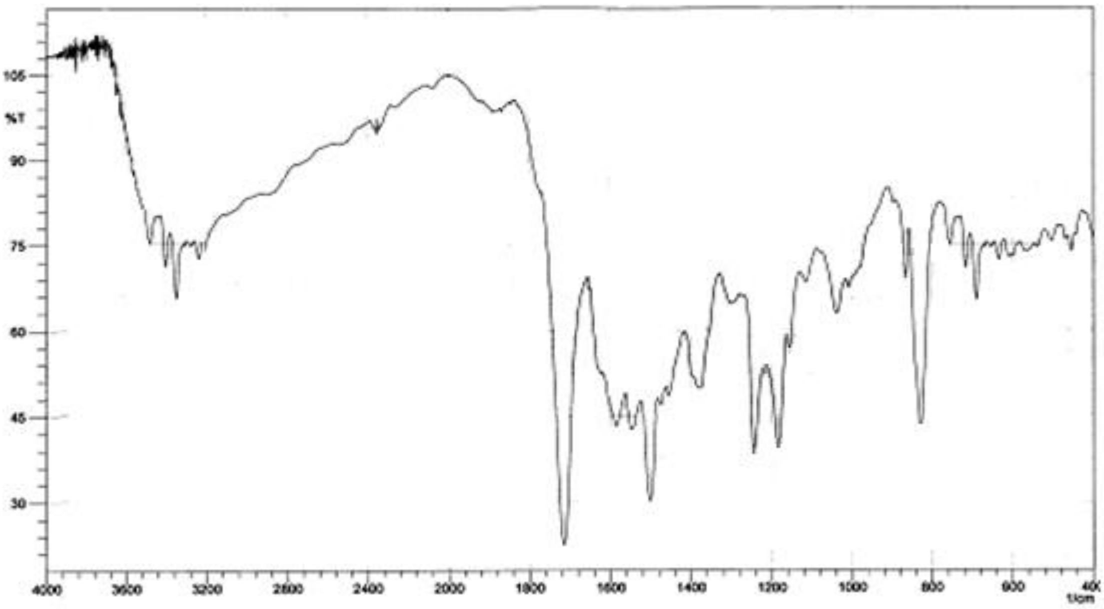


Figure 4.46: IR Spectra of PUEs XIh

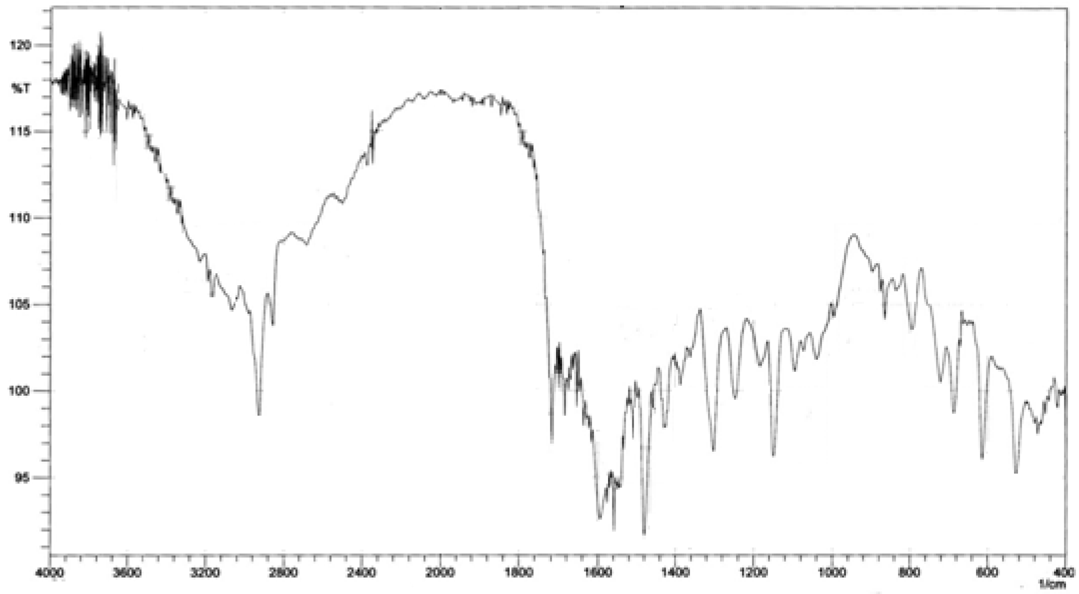


Figure 4.47: IR Spectra of PUEs XIi

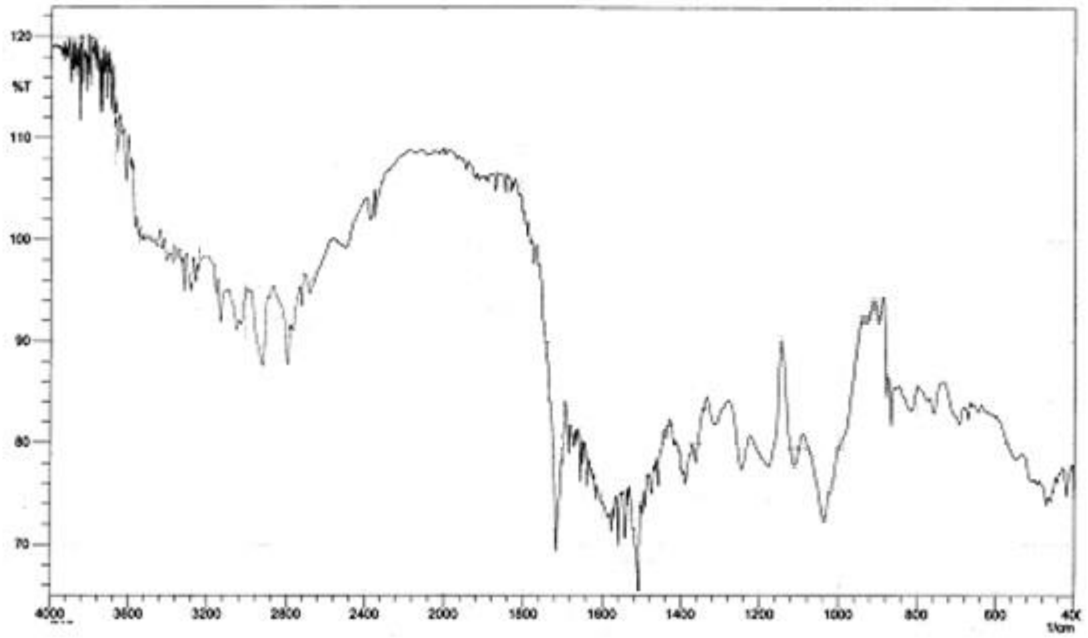


Figure 4.48: IR Spectra of PUEs XIj

4.2 Molecular weight determination:

Non-aqueous Conductometric Titration of AUPEs

As mentioned above the number average molecular weight ($\overline{Mn}$) determination of acrylated unsaturated Polyesters Resins VIa-j and VIIa-j were carried out by non-aqueous conductometric titration in pyridine against sodium methoxide as a titrant base as method discussed in section-2 of chapter-3.

The results of such titrations of AUPEs VI-VIIa-j are furnished in Tables 4.1 to 4.2 and typical plot are shown in Figures 4.49 to 4.50.

Table 4.1

Non-Aqueous Conductometric Titration of AUPEs VIa-j

Solvent : Anhydrous pyridine Titrant : 0.11 N Sodium methoxide		
Resin Sample	**m. moles of NaOMe / 100 gm resin at break X**	**Mn = 10^5 / X**
VIa	22.07	4531
VIb	22.03	4539
VIc	18.71	5344
VId	19.64	5091
VIe	18.88	5294
VIf	18.91	5287
VIg	20.10	4975
VIh	20.07	4981
VIi	21.03	4754
VIj	21.70	4608

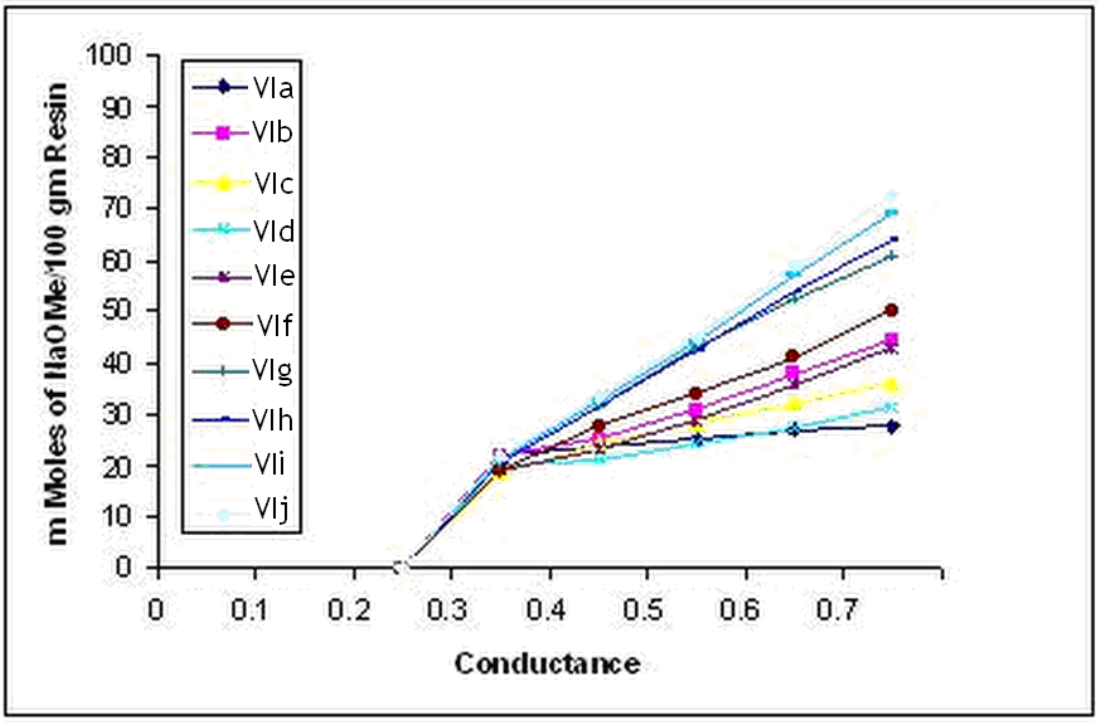


Figure 4.49 Titration Plots of AUPEs VIa-j

Table 4.2

Non-Aqueous Conductometric Titration of AUPEs VIIa-j

Solvent : Anhydrous pyridine

Titrant : 0.11 N Sodium methoxide

Resin Sample	**m. moles of NaOMe / 100 gm resin at break X**	**Mn = 10^5 / X**
VIIa	21.00	4761
VIIb	20.97	4767
VIIc	18.21	5490
VIId	18.12	5517
VIIe	18.14	5512
VIIf	18.86	5302
VIIg	19.14	5222
VIIh	18.92	5284
VIIi	19.79	5052
VIIj	20.52	4872

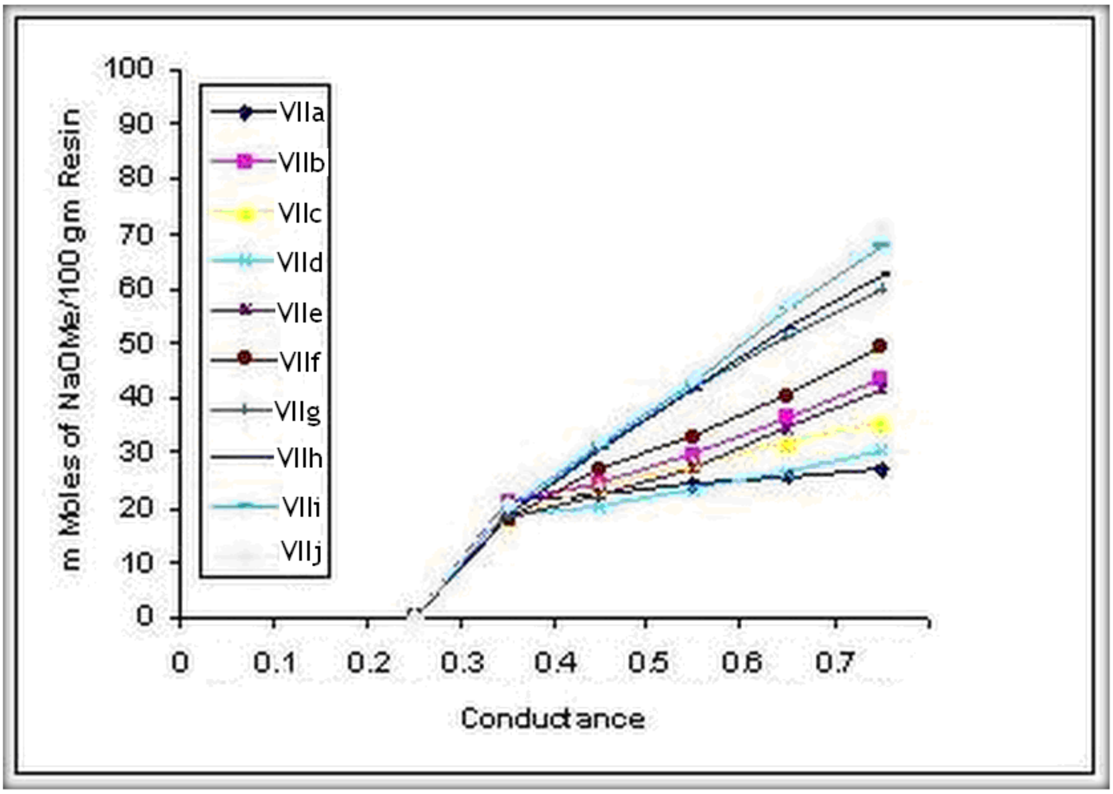


Figure 4.50 Titration Plots of AUPEs VIIa-j

Table 4.3

Molecular weight determination of AUPEs VIIIa-j samples by VPO method

Resin Sample	Slop	*Mn* = K / Slop
VIIIa	0.587	4369
VIIIb	0.588	4363
VIIIc	0.571	5079
VIIId	0.568	4907
VIIIe	0.557	5106
VIIIf	0.560	5116
VIIIg	0.572	4885
VIIIh	0.567	4836
VIIIi	0.556	4676
VIIIj	0.551	4462

Solvent: DMF;

Temperature: 90 °C;

Calibrant: Polystyrene

Time interval for steady state: 10 minutes

Concentration **:** 2.82, 5.64, 8.46. 11.28

- **Results and Discussion**

The typical non-aqueous conductometric titration curves of the AUPEs VI-VIIa-j are shown in Figures 4.1 to 4.2.

Inspection of the titration curves of the AUPEs indicates that there is only one break. This break indicates the neutralization of – COOH end group. Beyond this break, a continuous increase in conductance was observed on further addition of the titrant. In the plot, the milimoles of base titrant / 100 gm. of resin (X) corresponding to the break in each of the APEAs was divided to 1,00,000 gave the $\overline{Mn}$. The estimated values of $\overline{Mn}$ are furnished in Tables respectively.

Examination of the results reveals that,

1. The number average molecular weight of AUPEs VIa-j is in the range of 4531-5344 gm. / mole.

2. The number average molecular weight of AUPEs VIIa-j is in the range of 4761-5517 gm. / mole.

3. The number average molecular weight of AUPEs VIIIa-j is in the range of 4363-5116 gm. / mole which is calculated by vapor pressure osmometry.

4. Result of $\overline{Mn}$ of all the AUPEs VI-VIIIa-j reveals that the degree of polymerization is around six for all the polymers.

4.3 Curing Study of polymers by differential scanning calorimetry:

The curing study of UPUEs IX-XI a-j was monitored on a Universal V3.0GTA instrument using benzoyl peroxide as a catalyst. The sample cell of aluminum was used for the DSC scan. Empty cell was used as a reference calibration of the DSC instrument was performed by determining the heat of fusion of the standard indium metal supplied by Du Pont.

0.05 % benzoyl peroxide based on the total weight of the resin sample was added and mixed well in a porcelain disc. The sample weight used for the investigation was in the range of 4-5 mg. and carefully placed in a sample cell covered with a lid and then it was placed in DSC cell along with the empty reference cell. The DSC thermograms of all the resin samples were scanned at a constant heating rate of 10°C / min. from 30°C to 300°C.

The values of the activation energy (E_a), order of reaction (*n*) and the DSC data of all the UPUEs IX-XIa-j samples obtained from the DSC thermograms are provided in Tables 4.4 to 4.6 respectively. The DSC thermograms of all the UPUEs IX-XIa-j are shown in Figures 4.52 to 4.71.

Table 4.4

DSC Curing Data of UPUEs IXa-j

UPUEs IXa-j	Initial Temp. (°C)	Peak Temp. (°C)	Final Temp. (°C)	Activation Energy (Ea) KJ/mol	Order of Reaction (*n*)
IXa	133	163	197	234.7	**1.87**
IXb	135	162	200	236.2	**1.86**
IXc	117	150	165	240.1	**1.82**
IXd	126	155	171	246.3	**1.79**
IXe	140	155	168	210.6	**1.92**
IXf	139	160	182	184.4	**1.94**
IXg	123	153	168	224.4	**1.90**
IXh	120	149	176	249.6	**1.76**
IXi	118	150	172	248.7	**1.77**
IXj	117	148	160	176.6	**1.95**

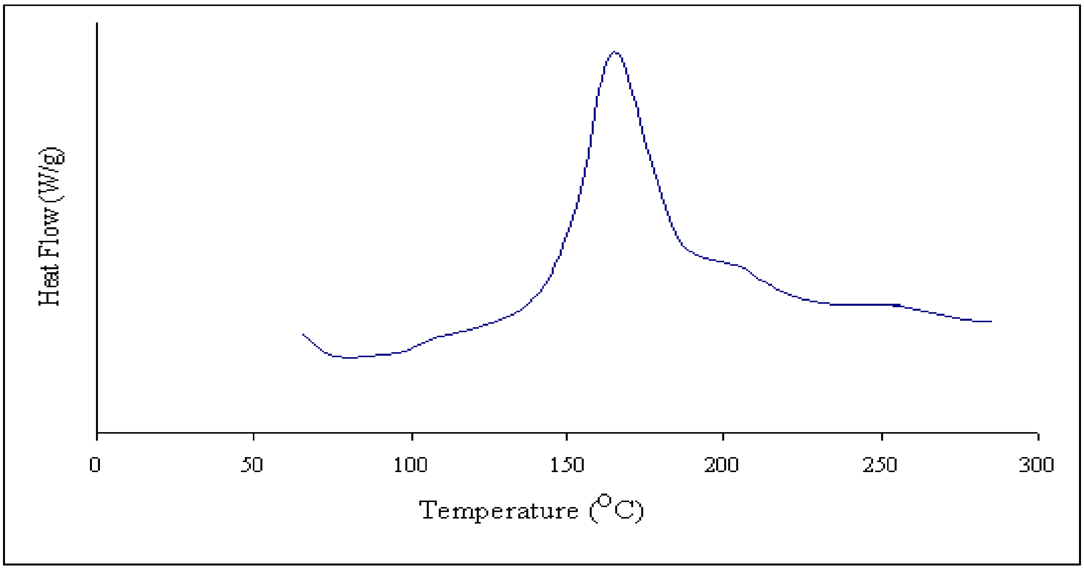


Figure 4.52 DSC of IXa

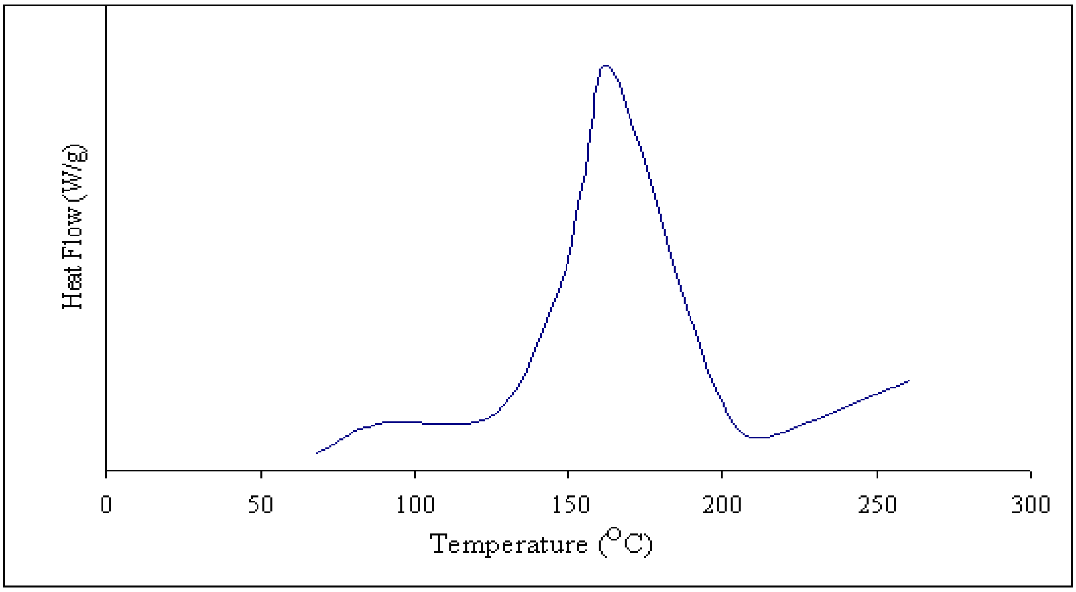


Figure 4.53 DSC of IXb

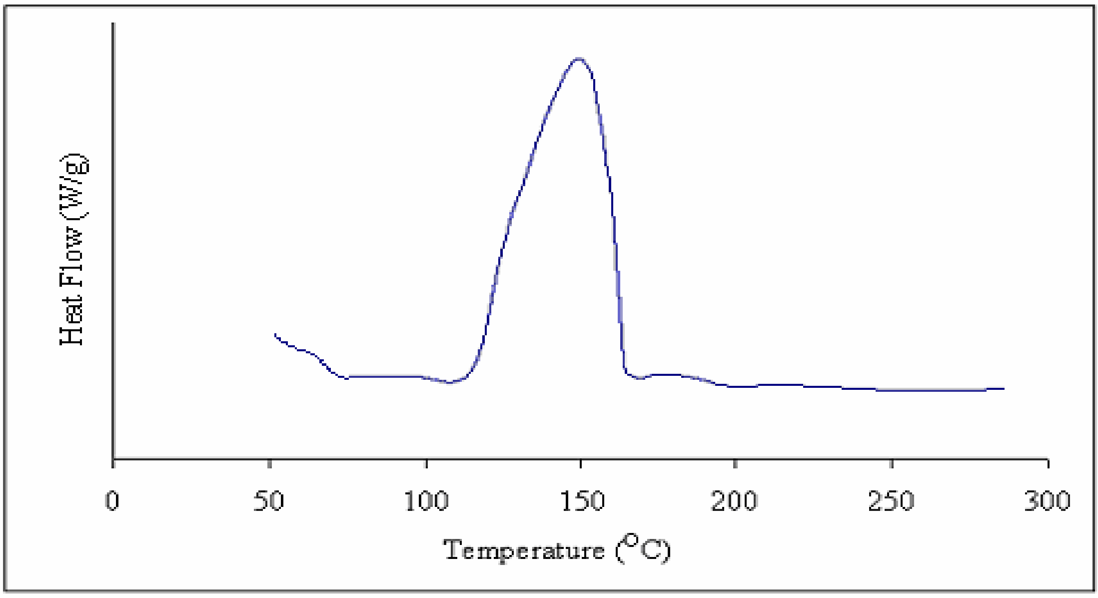


Figure 4.54 DSC of IXc

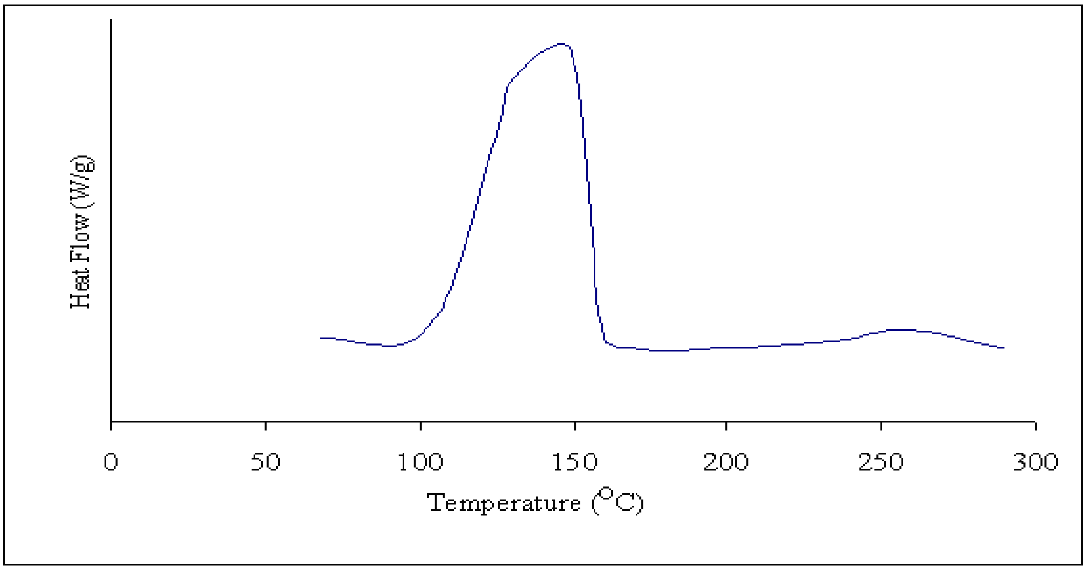


Figure 4.55 DSC of IXd

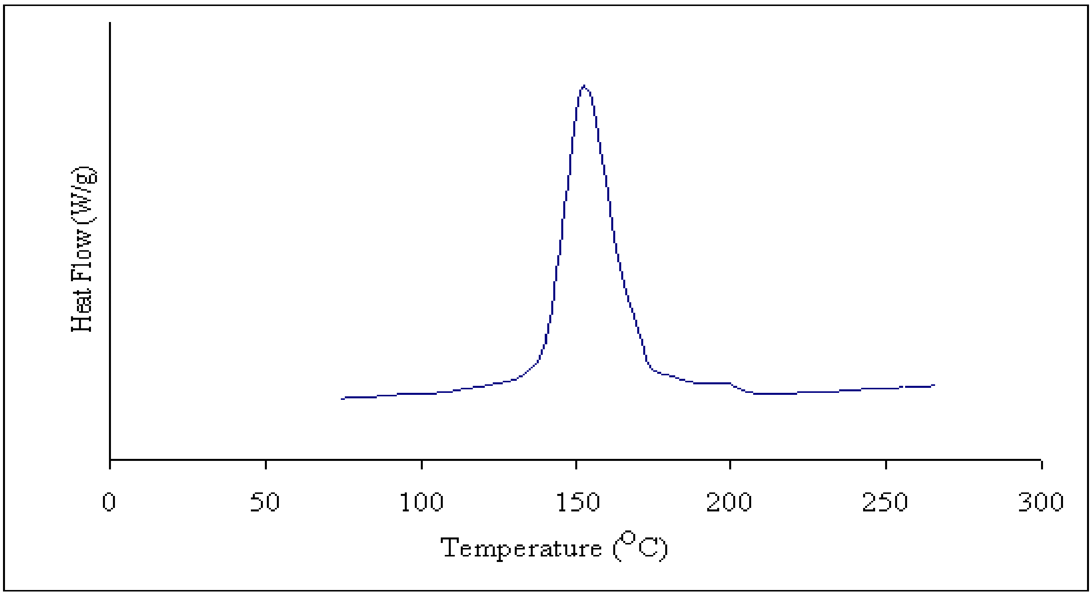


Figure 4.55 DSC of IXe

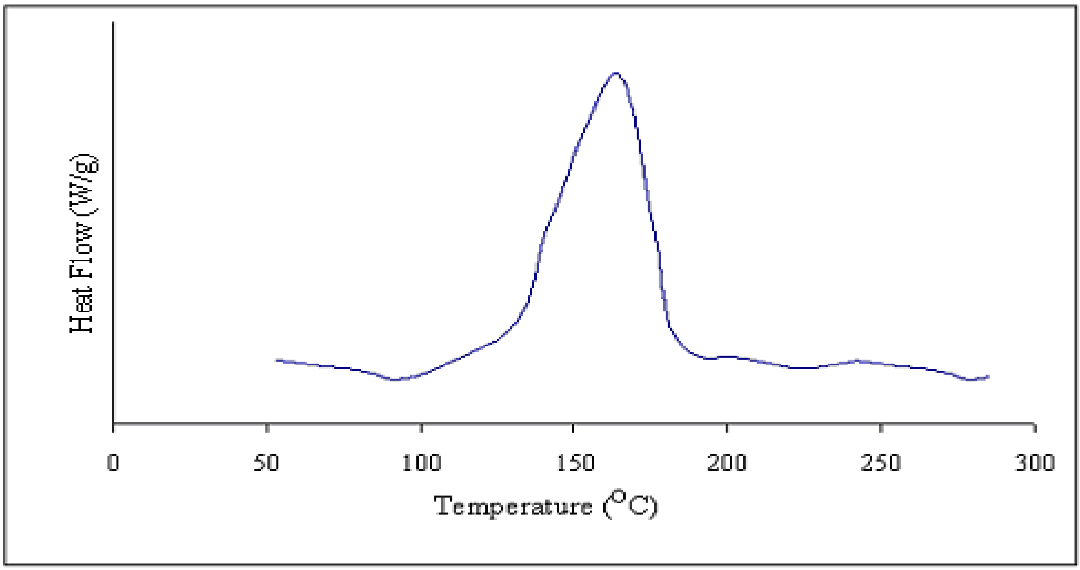


Figure 4.57 DSC of IXf

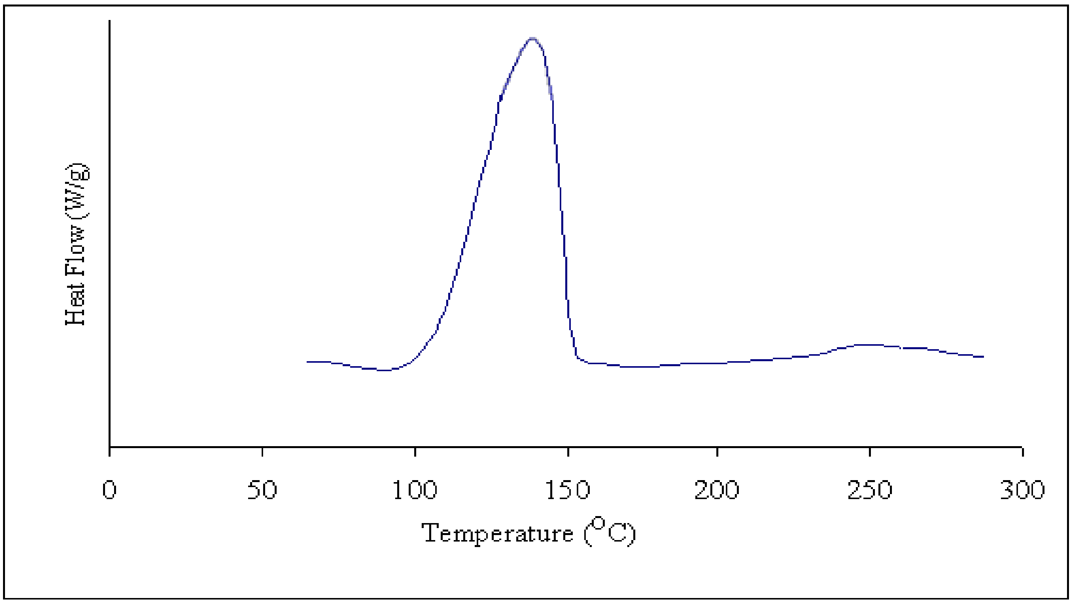


Figure 4.58 DSC of IXg

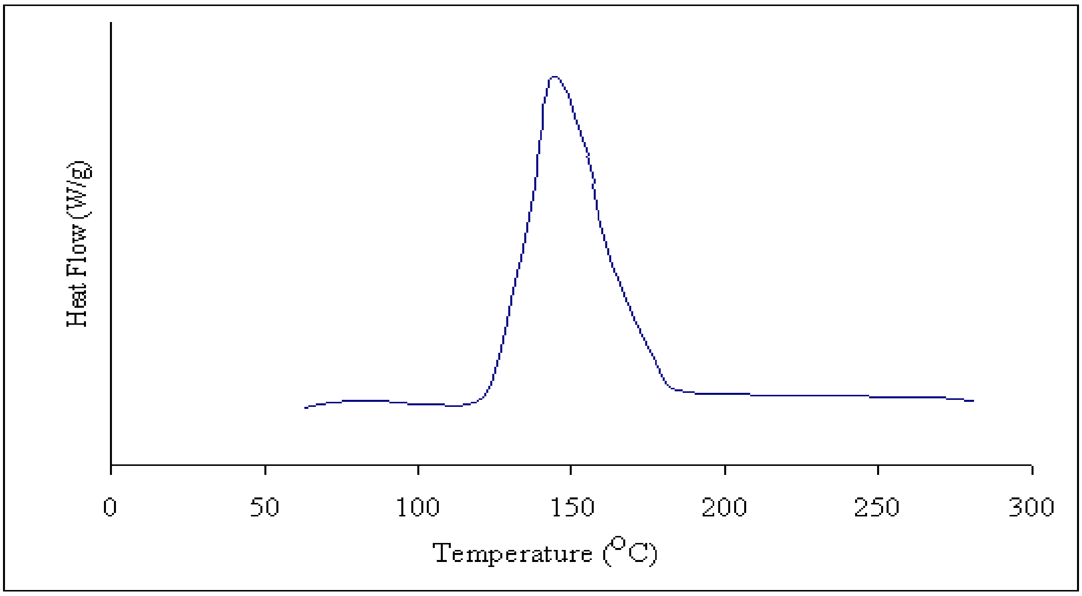


Figure 4.59 DSC of IXh

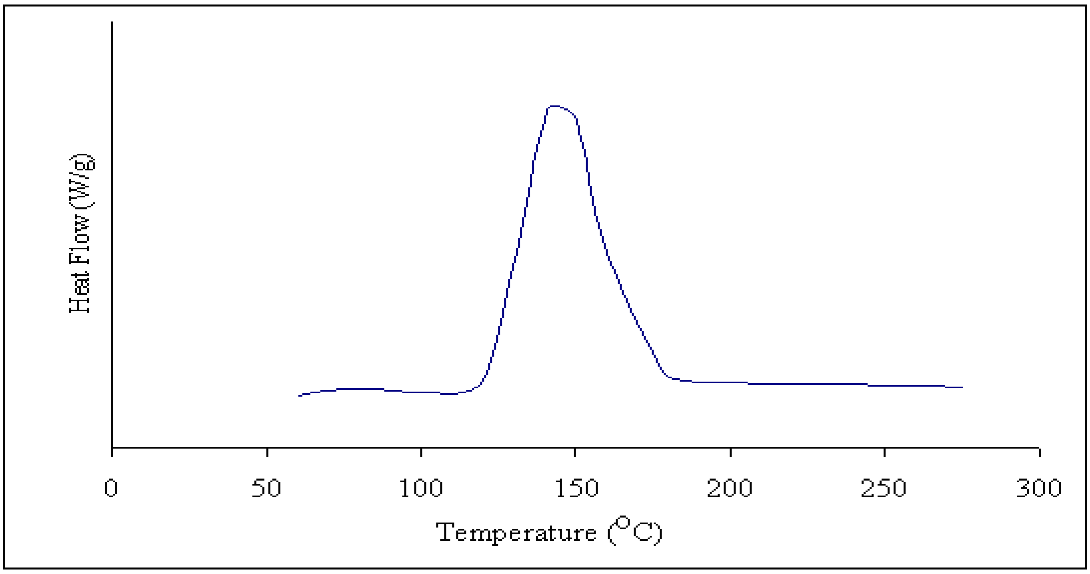


Figure 4.60 DSC of IXi

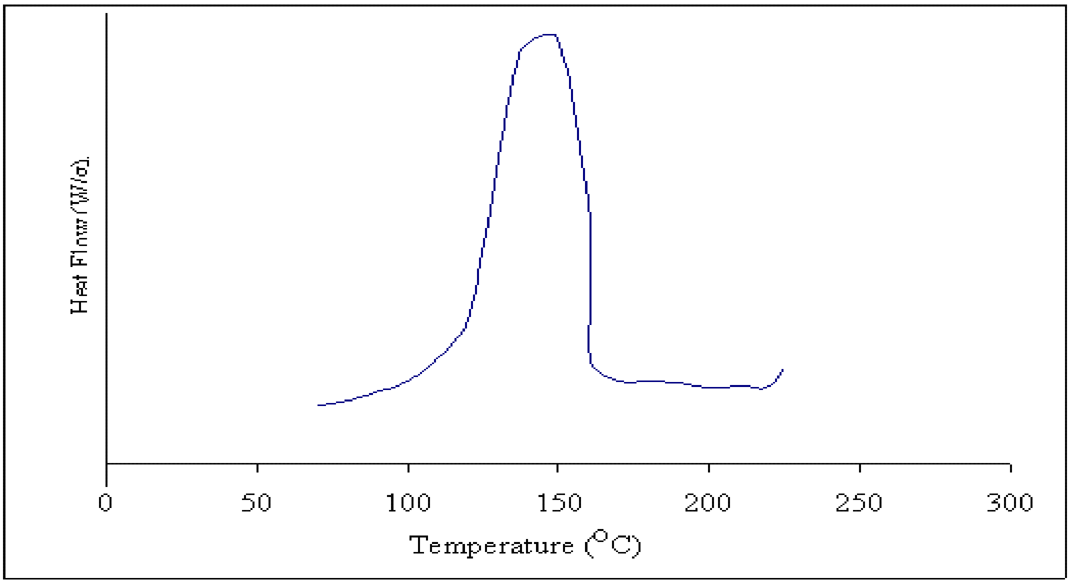


Figure 4.61 DSC of IXj

Table 4.5

DSC Curing Data of UPUEs Xa-j

UPUEs Xa-j	Initial Temp. (˚C)	Peak Temp. (˚C)	Final Temp. (˚C)	Activation Energy (Ea) KJ/mol	Order of Reaction (*n*)
Xa	120	146	167	180.3	**1.93**
Xb	110	133	150	181.4	**1.93**
Xc	128	166	181	192.3	**1.91**
Xd	124	140	156	200.6	**1.89**
Xe	114	137	151	210.7	**1.92**
Xf	112	150	163	190.3	**1.90**
Xg	110	132	149	214.6	**1.91**
Xh	111	130	150	234.6	**1.86**
Xi	120	150	164	236.3	**1.86**
Xj	121	154	172	186.6	**1.91**

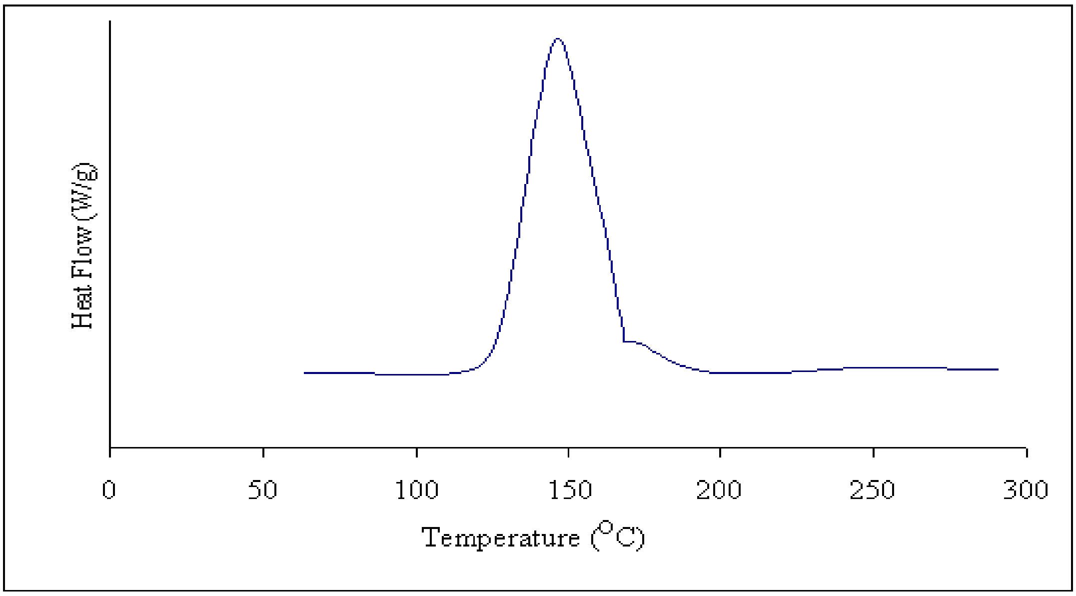


Figure 4.62 DSC of Xa

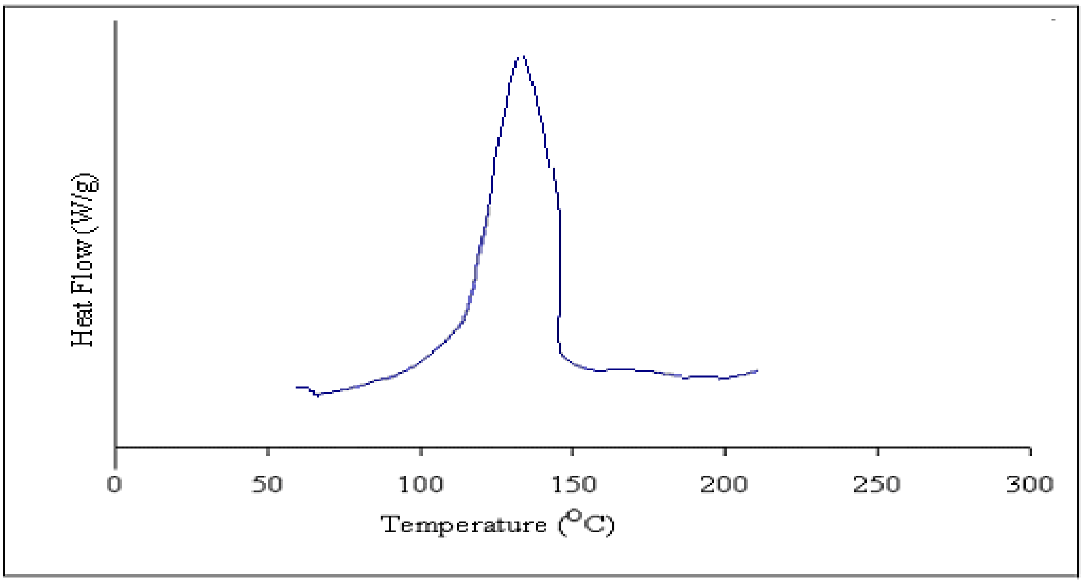


Figure 4.63 DSC of Xb

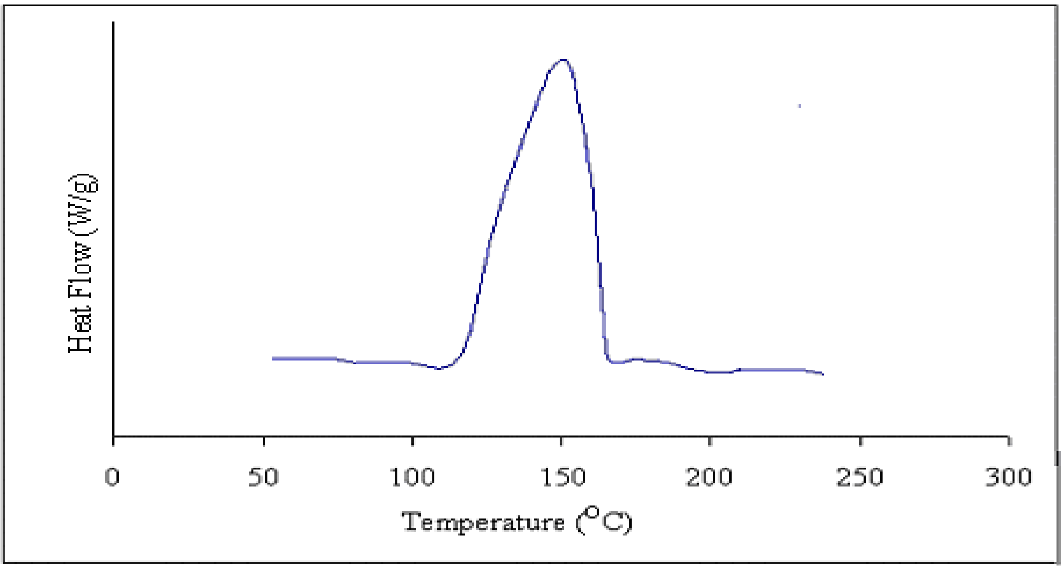


Figure 4.64 DSC of Xc

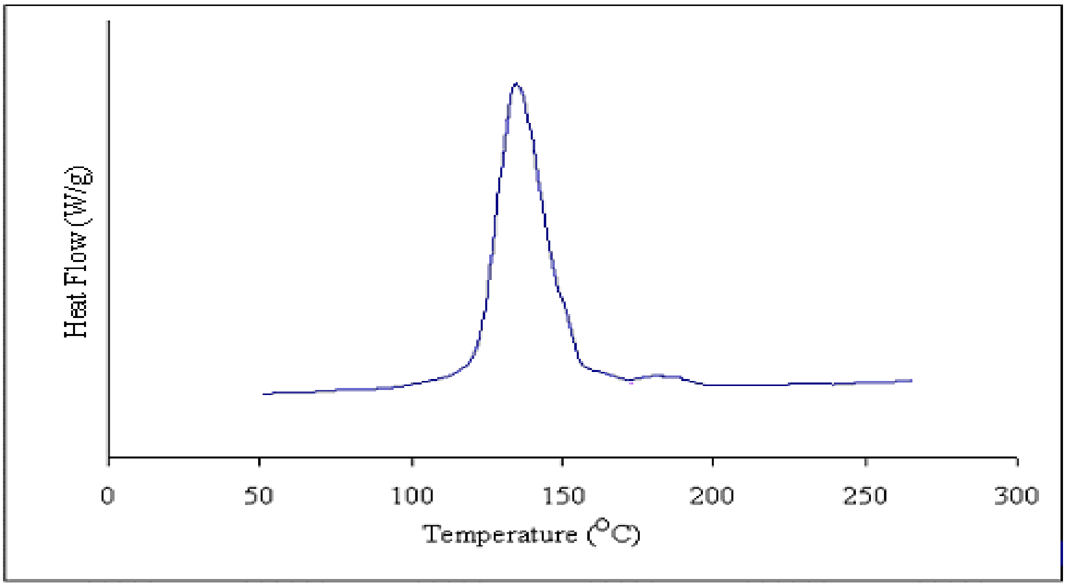


Figure 4.65 DSC of Xd

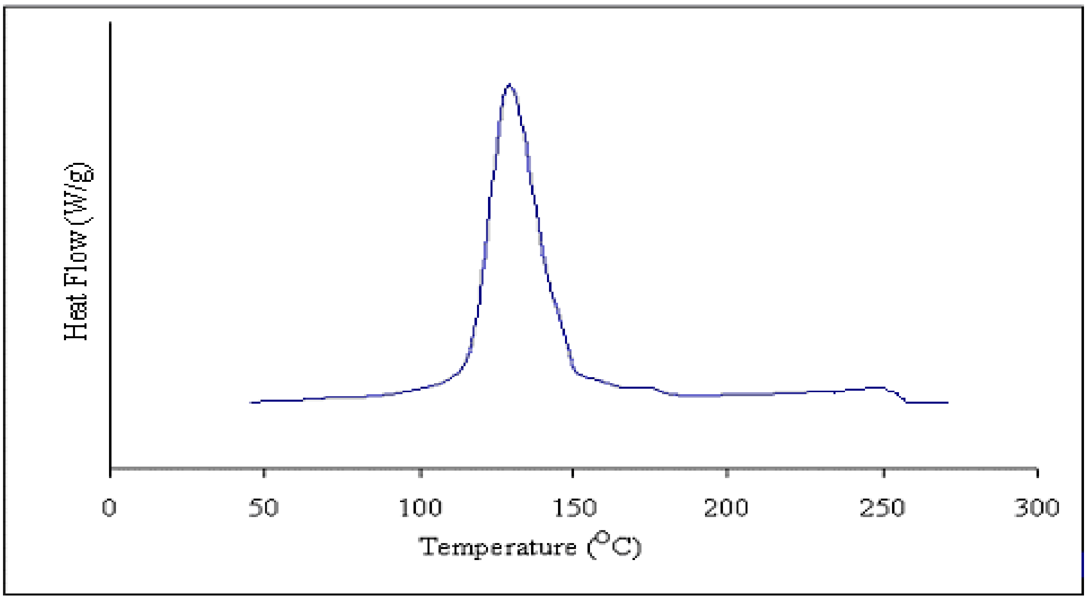


Figure 4.66 DSC of Xe

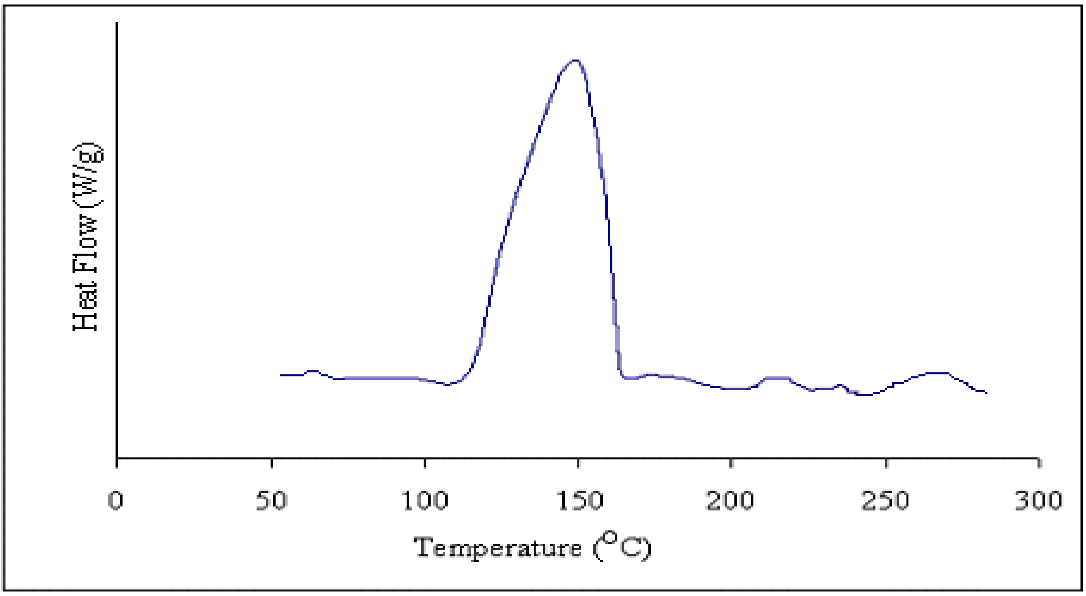


Figure 4.67 DSC of Xf

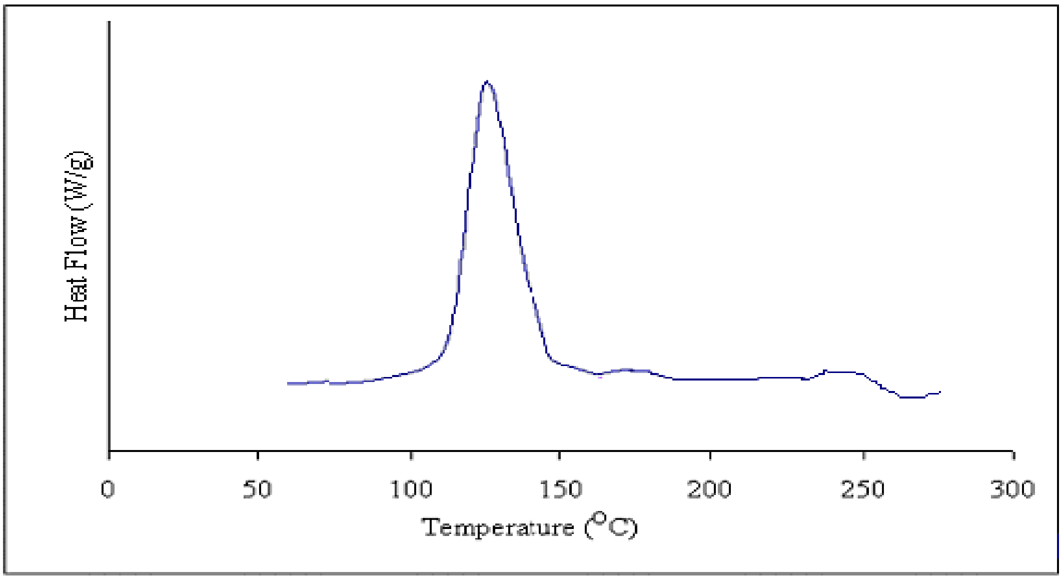


Figure 4.68 DSC of Xg

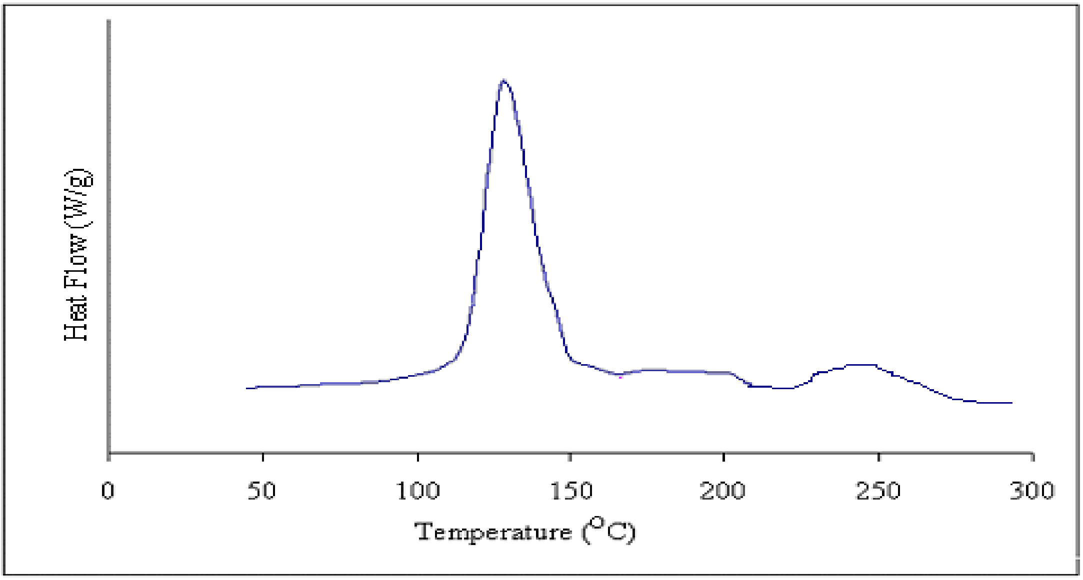


Figure 4.69 DSC of Xh

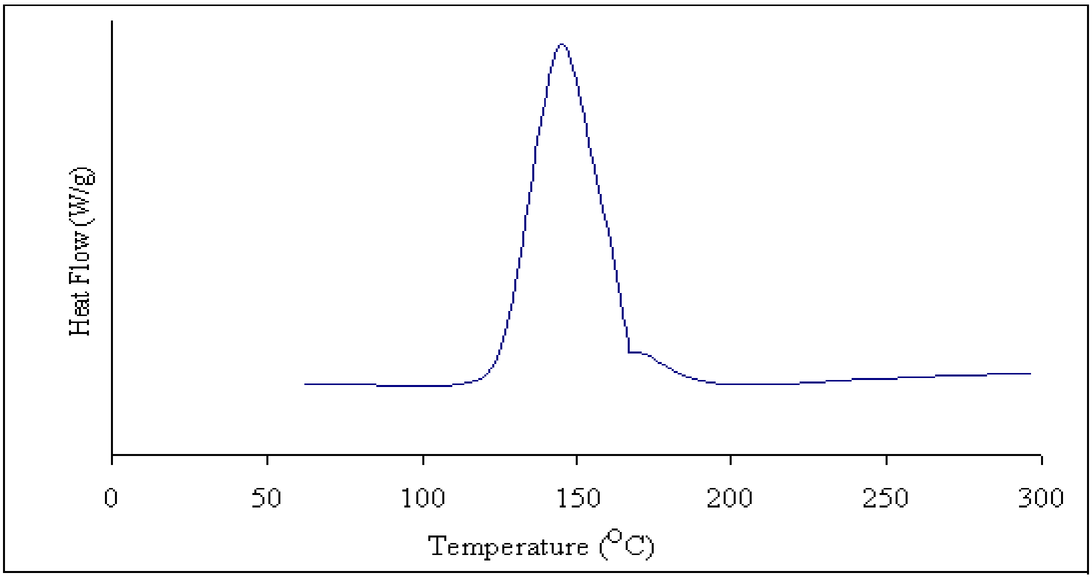


Figure 4.70 DSC of Xi

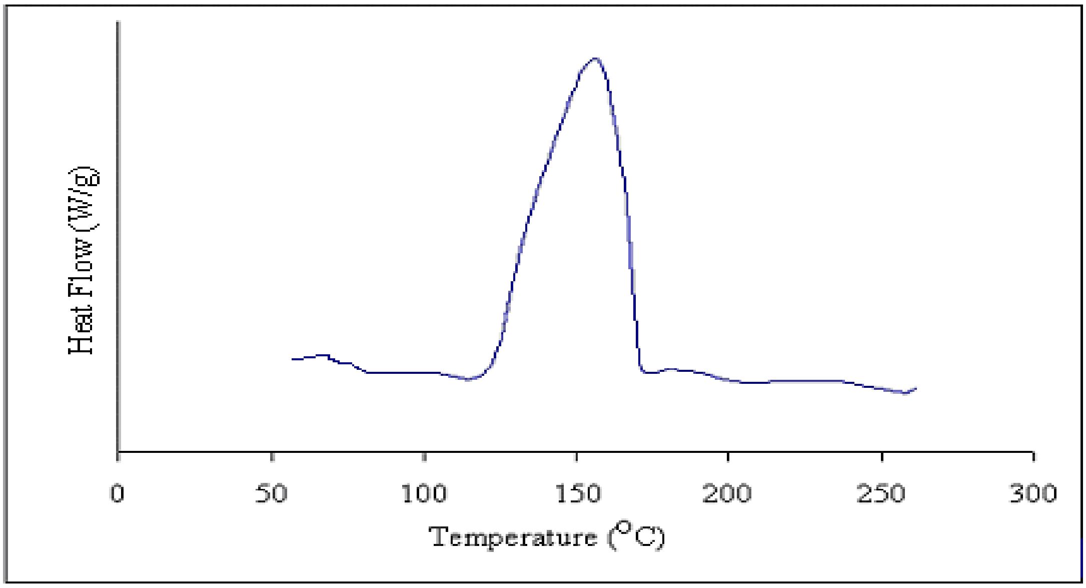


Figure 4.71 DSC of Xj

Table 4.6

DSC Curing Data of UPUEs XIa-j

UPUEs XIa-j	Initial Temp. (°C)	Peak Temp. (°C)	Final Temp. (°C)	Activation Energy (Ea) KJ/mol	Order of Reaction (*n*)
XIa	110	146	160	176.4	**1.94**
XIb	116	150	180	180.3	**1.95**
XIc	102	140	150	202.6	**1.88**
XId	120	140	160	213.4	**1.91**
XIe	137	146	162	202.9	**1.85**
XIf	122	154	174	188.7	**1.91**
XIg	106	123	146	220.3	**1.90**
XIh	117	144	163	240.6	**1.83**
XIi	110	143	159	235.8	**1.86**
XIj	112	148	161	190.3	**1.89**

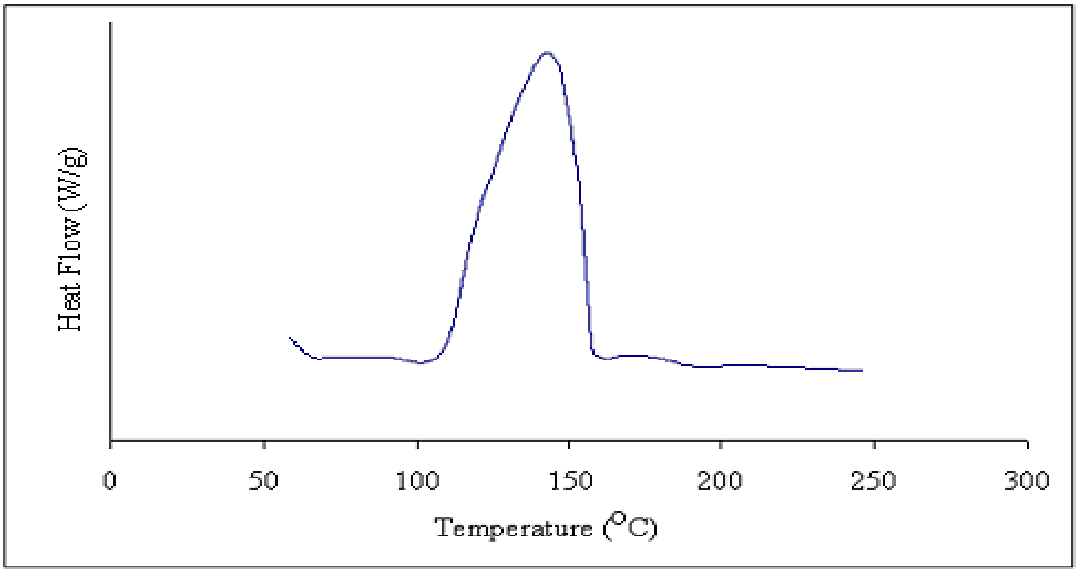


Figure 4.72 DSC of XIa

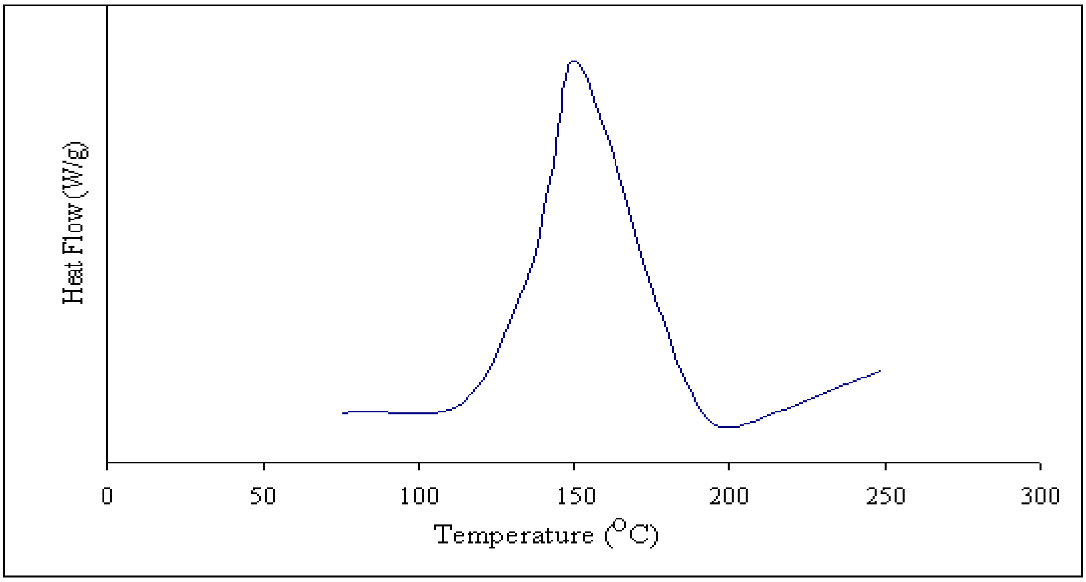


Figure 4.73 DSC of XIb

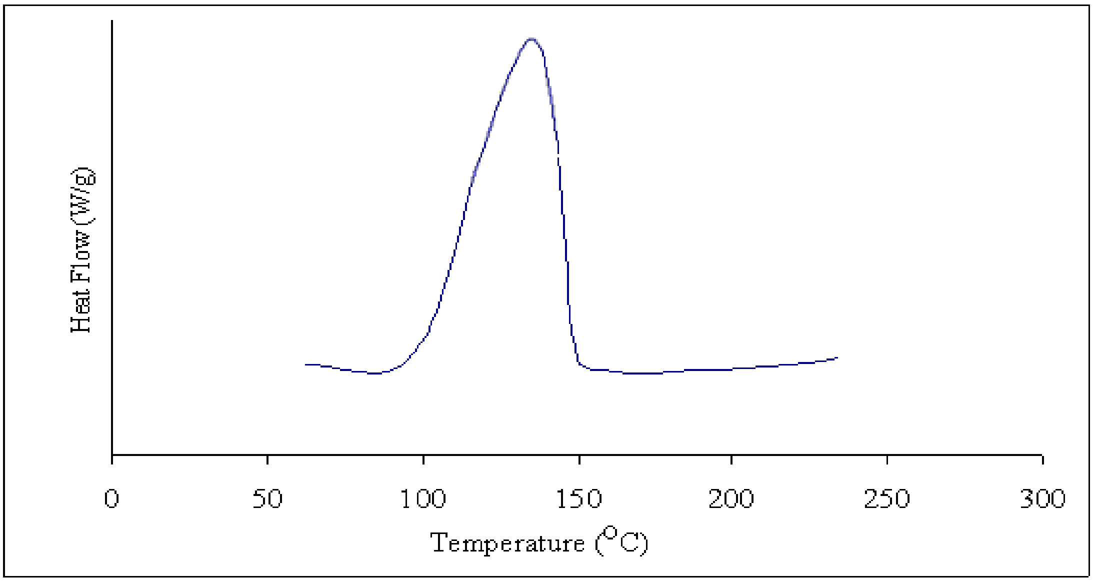


Figure 4.74 DSC of XIc

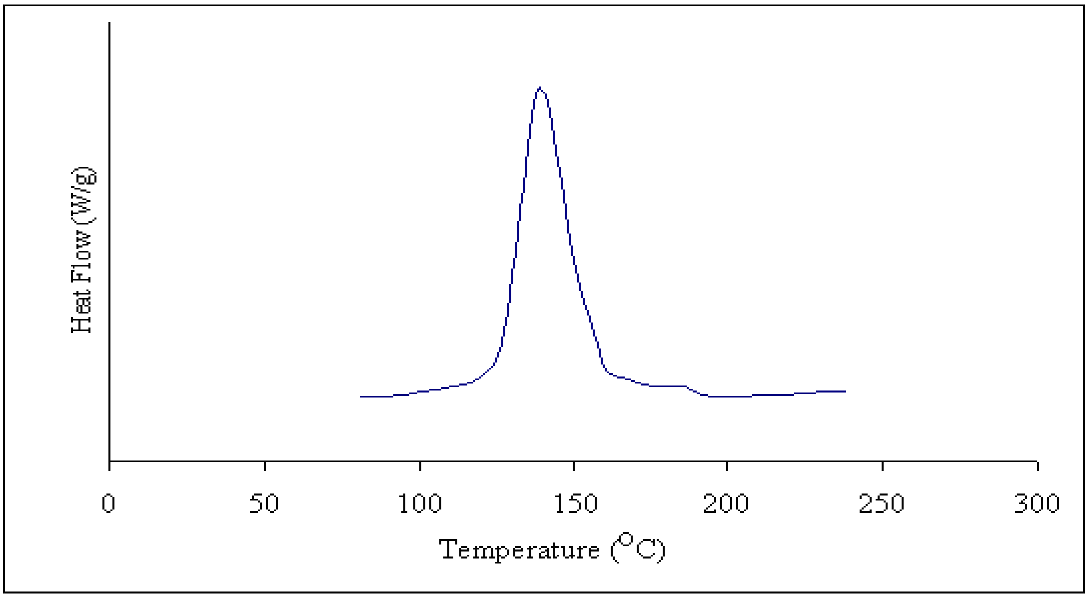


Figure 4.75 DSC of XId

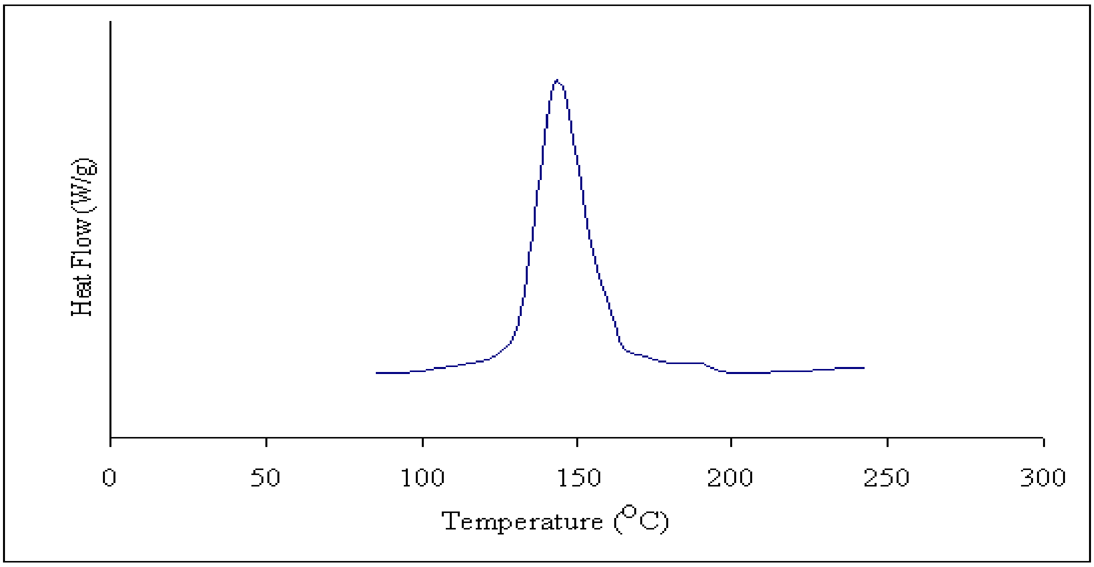


Figure 4.76 DSC of XIe

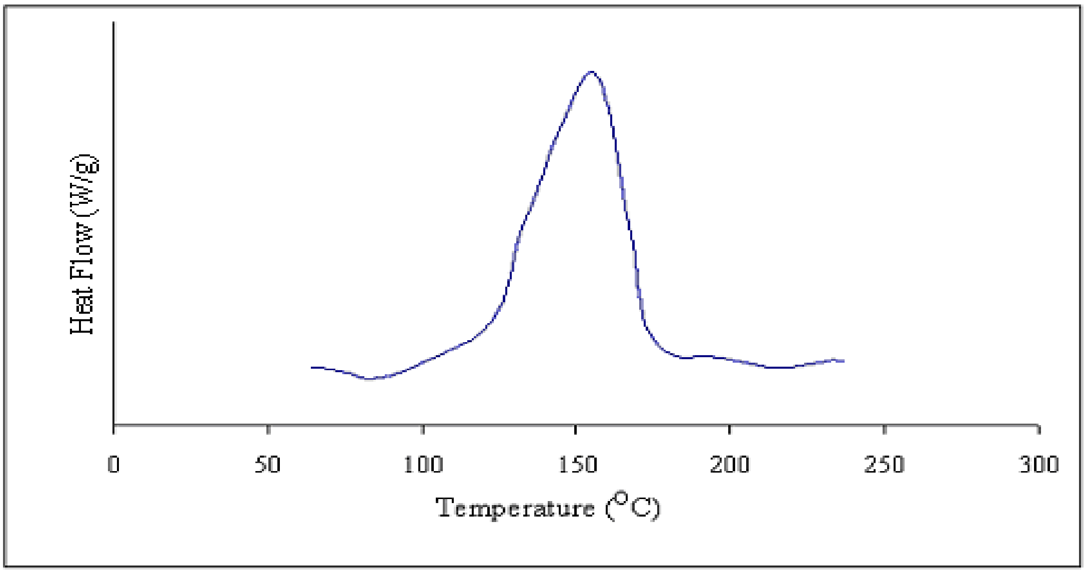


Figure 4.77 DSC of XIf

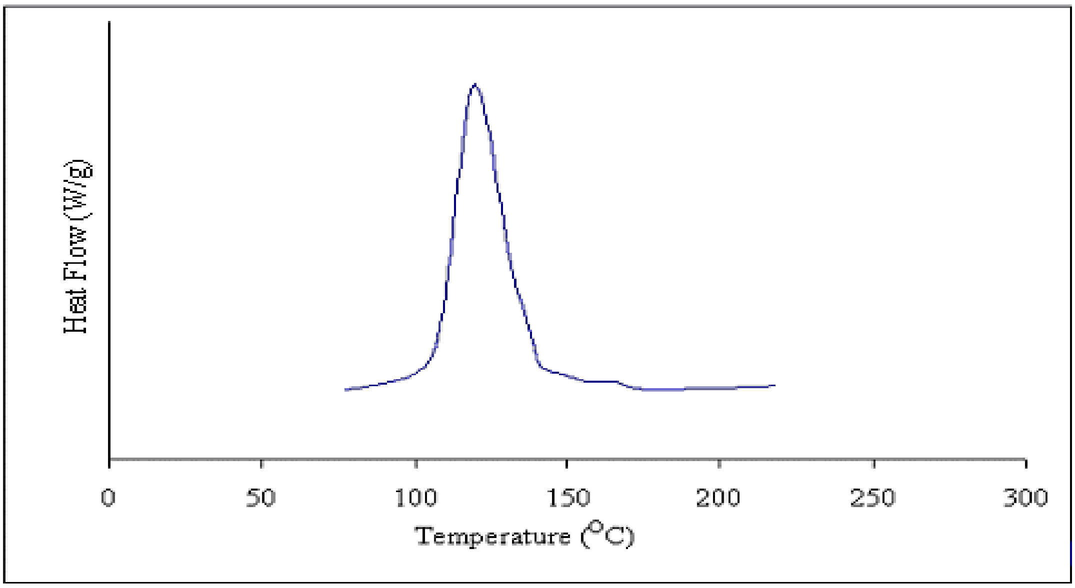


Figure 4.78 DSC of XIg

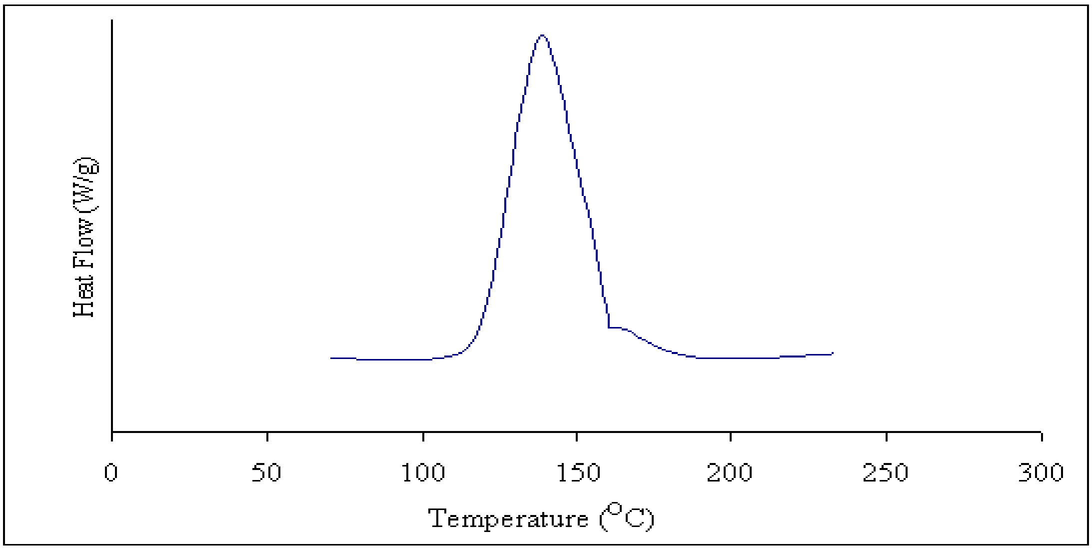


Figure 4.79 DSC of XIh

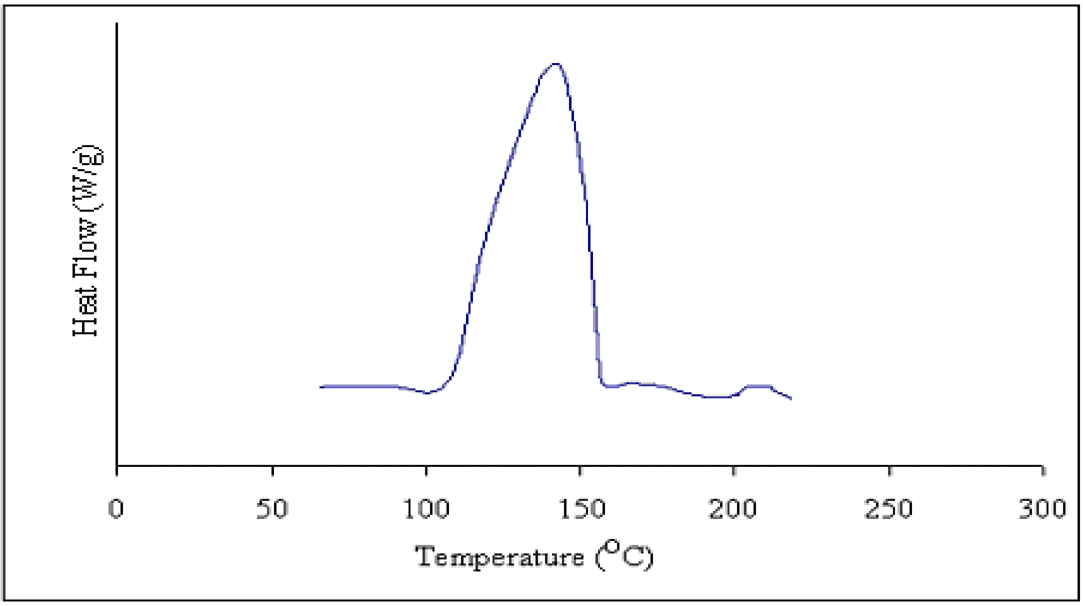


Figure 4.80 DSC of XIi

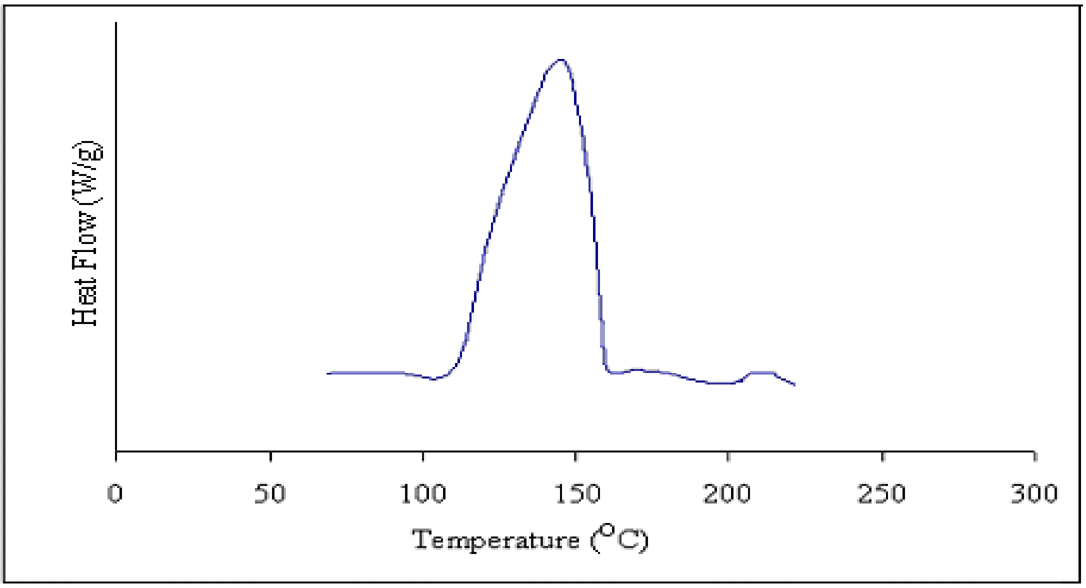


Figure 4.81 DSC of XIj

Results and Discussion

The curing studies of all the UPUEs IX-XIa-j samples were carried out by using benzoyl peroxide (BPO) as a catalyst. 0.05 % Benzoyl peroxide based on the total weight of the resin sample was added. The results obtained from the DSC scan are provided in Tables 3.1 to 3.3 respectively. Examination of the DSC thermograms of all the UPUEs IX-XIa-j reveals that:

1. From the DSC thermograms, the cure onset temperature (T_i), peak exotherm temperature (T_p) and the temperature of completion (T_f) for each of the UPUEs IX-XIa-j samples were obtained.

2. All the UPUEs IXa-j resins with BPO (as a catalyst) gave a single exothermic peak in the range of 117 to 200 °C.

3. All the UPUEs Xa-j resins with BPO (as a catalyst) gave a single exothermic peak in the range of 110 to 181 °C.

4. All the UPUEs XIa-j resins with BPO (as a catalyst) gave a single exothermic peak in the range of 102 to 180 °C.

5. From the DSC thermograms the values of kinetic parameters such as activation energy (E_a) and the order of reaction (n) were also obtained. This suggests that it is a second order reaction.

6. The results also show that the curing temperature of reaction is up to 150 °C thus they can be processed (i.e. making article) easily.

DSC thermograms UPUEs are presented in Figs. DSC transition temperature and the characteristic temperatures for the assessment of the relative thermal stability of polymers are initial decomposition temperature (T_o), temperature of maximum weight loss (T_{max}) and temperature of final decomposition (T_f) are presented in respective Tables. The glass transition temperature was measured at the half width of the transition after plotting tangents on the curve, while melting temperature was recorded as the peak temperatures of observed endotherms.

DSC studies on polyurethanes often report the presence of two *T*gs, one associated with the amorphous soft phase, and the other with the hard phase. Stronger segregation of segments can reduce the soft segment *T*g, while segmental mixing is expected to lead to an increment in the soft segment *T*g. In case of strong segmental mixing, one can expect the copolymer *T*g to have a value that is in between the *T*gs of the hard and soft segments.

4.4 Thermogravimetric analysis(TGA):

The thermogravimetric analyses (TGA) of UPUEs IX-XIa-j samples have been carried out by using a "Universal V3.0G TA Instrument Thermo gravimetric analyzer" in a slow stream of air. The boat prepared from the platinum foil holds the polymer sample that is to be analyzed. It was properly washed and dried. It was suspended on the quartz rod in the TGA balance. The sample (about 5 mg) was placed in the boat. The sample in the boat was covered by quartz tube in which the flow of air was maintained. The weight of the sample was noted on the TGA balance. The whole assembly was brought down in the furnace. It was ascertained that the boat was hanging on quartz rod. The experiment was started by heating the system at a constant rate of 10 $^{\circ}$C / min. Simultaneous change in the weight was recorded automatically with time (temperature). This will reveal the percentage weight loss of the material as a function of time and also of the temperature. The experiment was stopped at about 800 $^{\circ}$C.

The thermograms were analyzed to obtain the information about the percentage weight loss at different temperatures. The results of these analyses are furnished in Tables 4.7 to 4.9 respectively. The typical TGA thermograms of the UPUEs IX-XIa-j are shown in Figures 4.82 to 4.111.

Table 4.7

TGA Data of UPUEs IXa-j

UPUEs IXa-j	% Weight loss at various Temperature (°C) from TGA			
	150	**300**	**450**	**600**
IXa	1.72	10.02	49.78	**77.81**
IXb	1.74	10.04	49.81	**77.82**
IXc	1.95	12.15	58.28	**78.15**
IXd	1.37	11.03	50.38	**78.77**
IXe	1.43	11.29	60.06	**73.80**
IXf	1.42	11.26	60.04	**73.92**
IXg	1.36	11.04	50.36	**78.76**
IXh	1.34	11.03	50.39	**78.79**
IXi	1.97	10.46	47.16	**74.70**
IXj	1.96	11.20	45.25	**80.05**

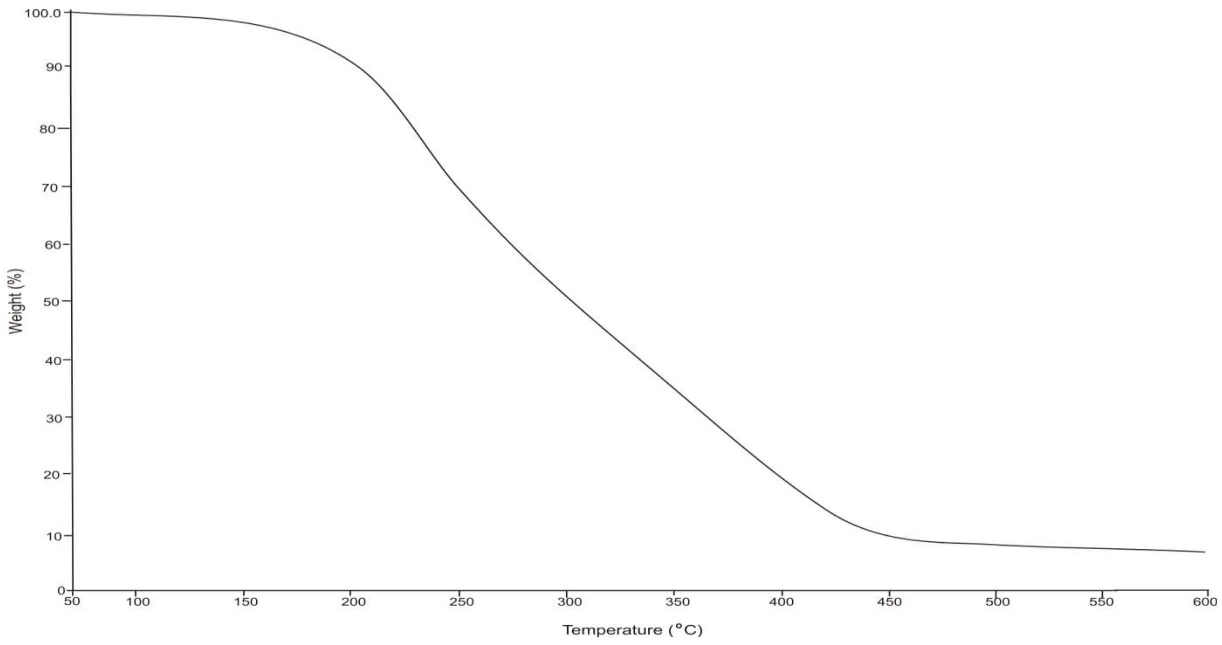


Figure 4.82: TGA of IXa

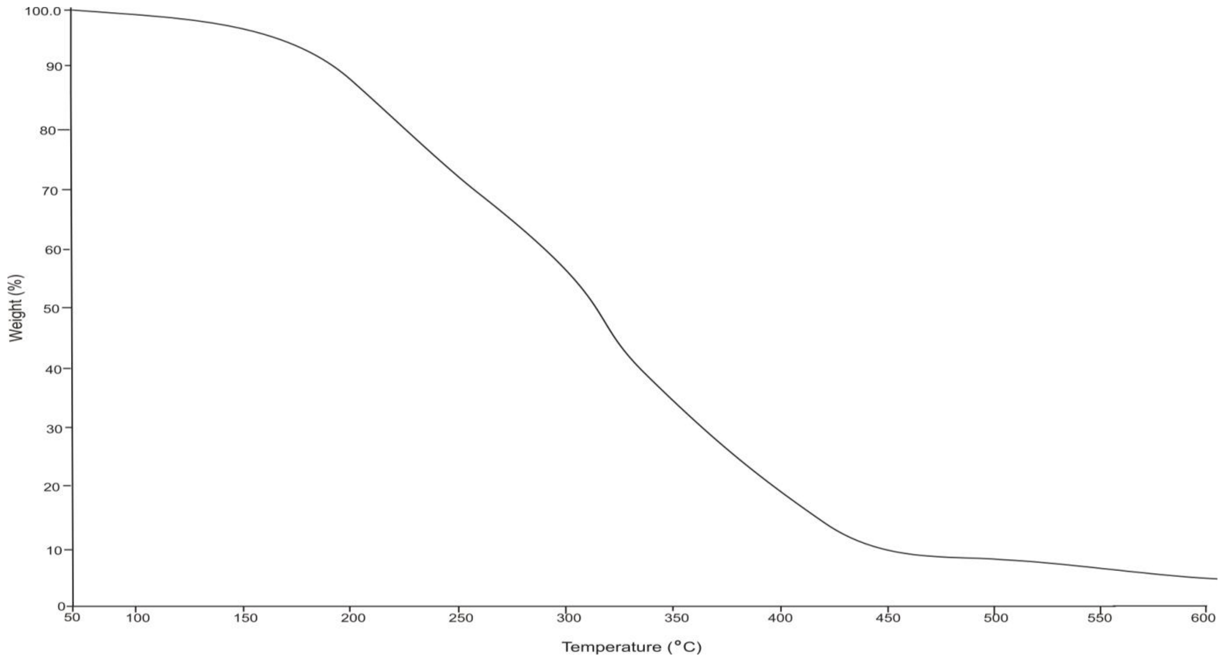


Figure 4.83: TGA of IXb

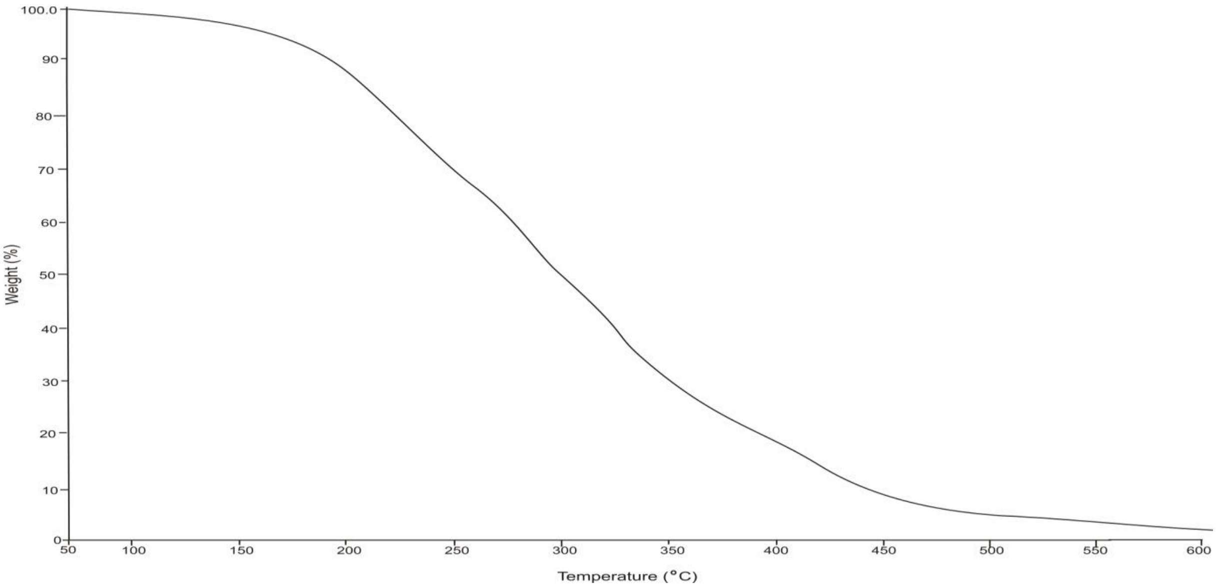


Figure 4.84: TGA of IXc

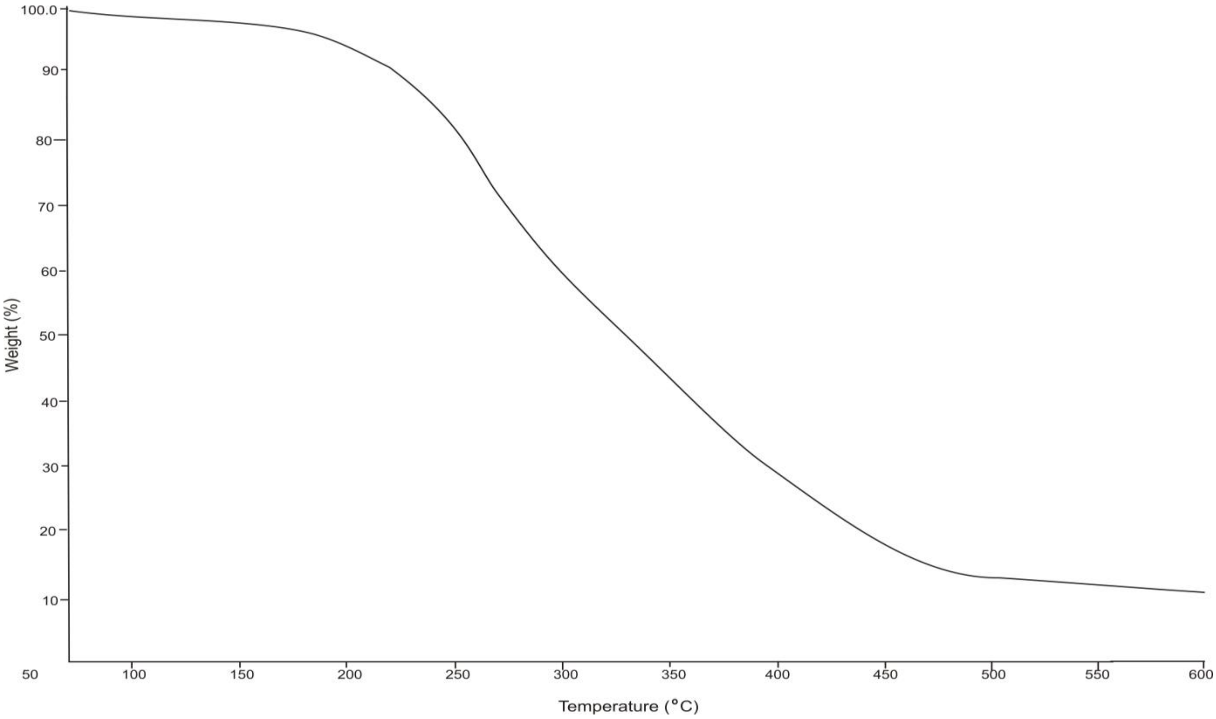


Figure 4.85: TGA of IXd

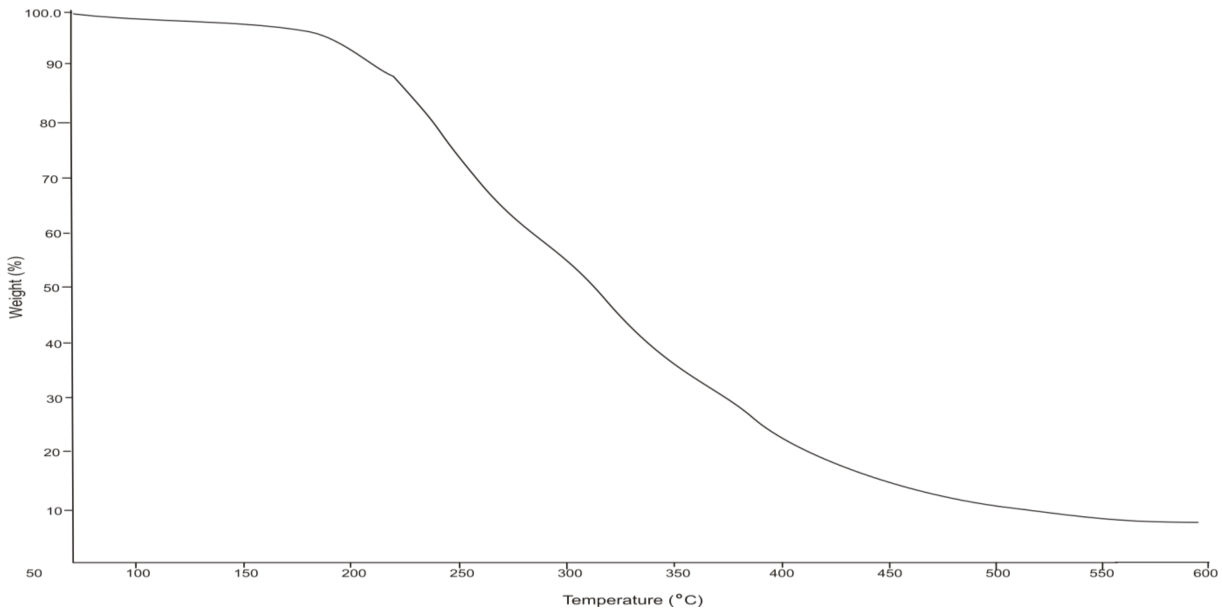


Figure 4.86: TGA of IXe

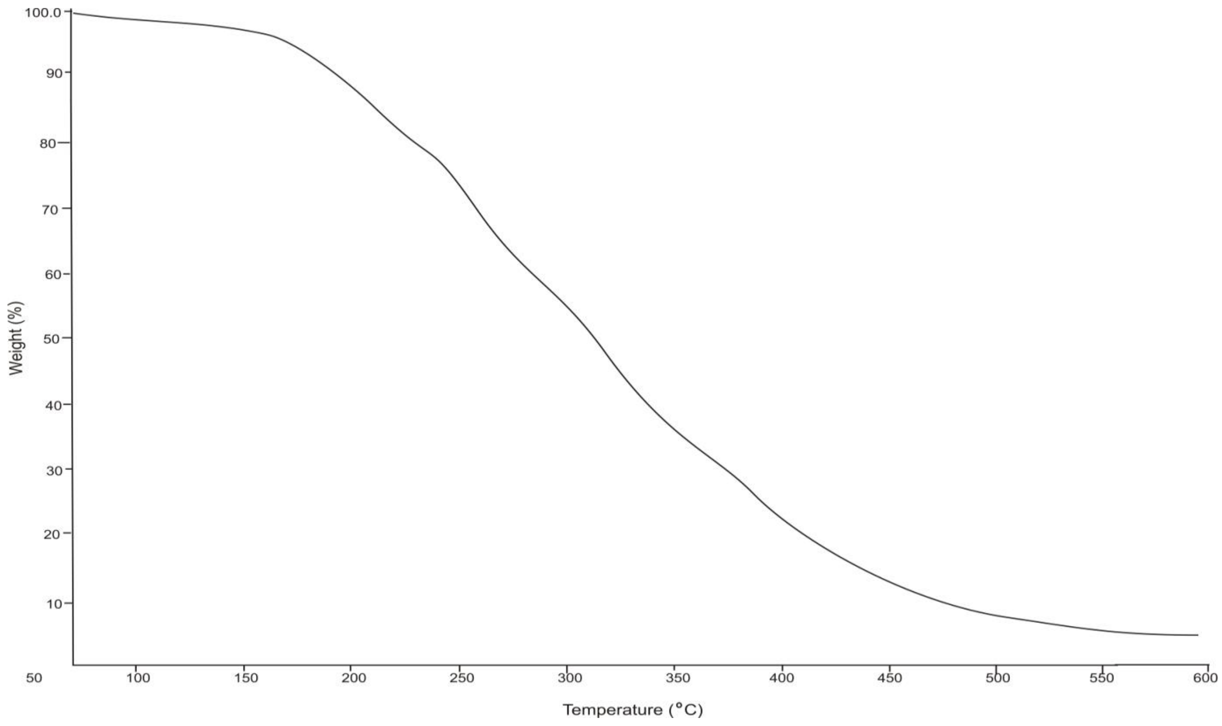


Figure 4.87: TGA of IXf

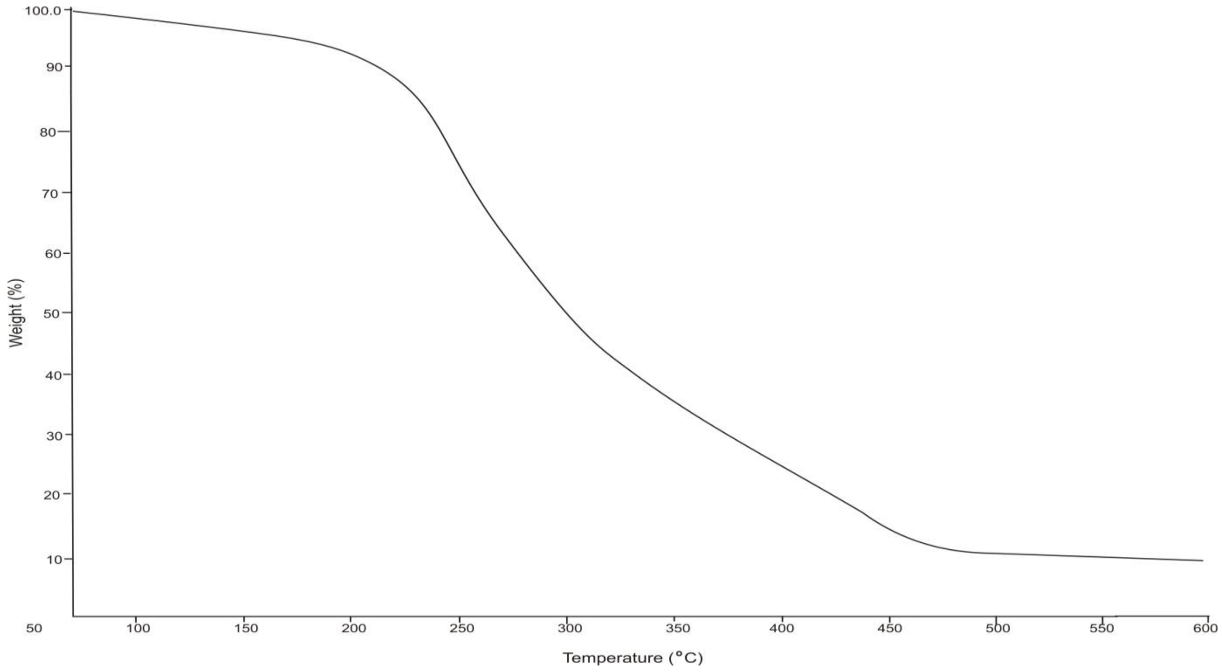


Figure 4.88: TGA of IXg

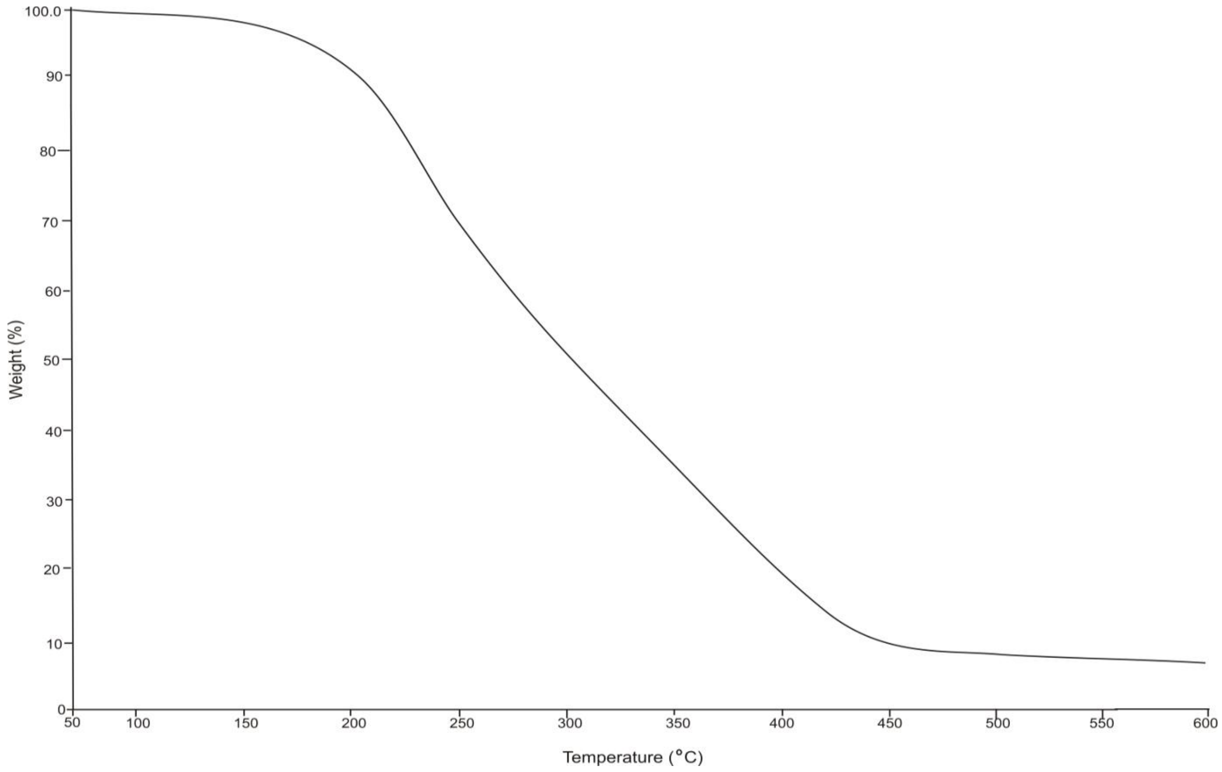


Figure 4.89: TGA of IXh

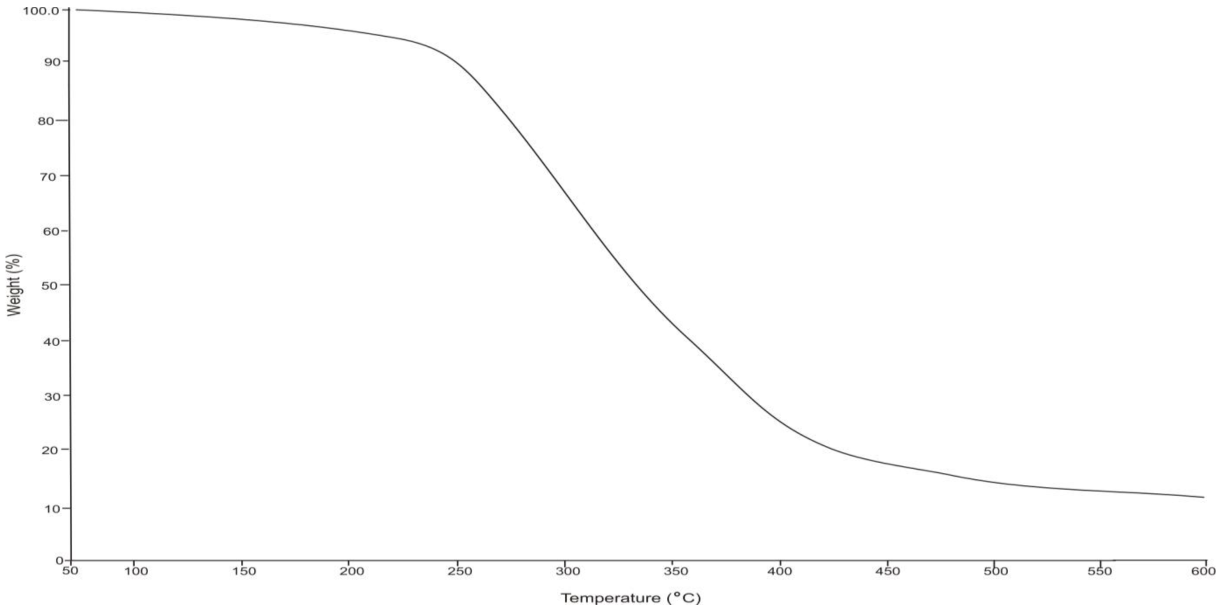


Figure 4.90: TGA of IXi

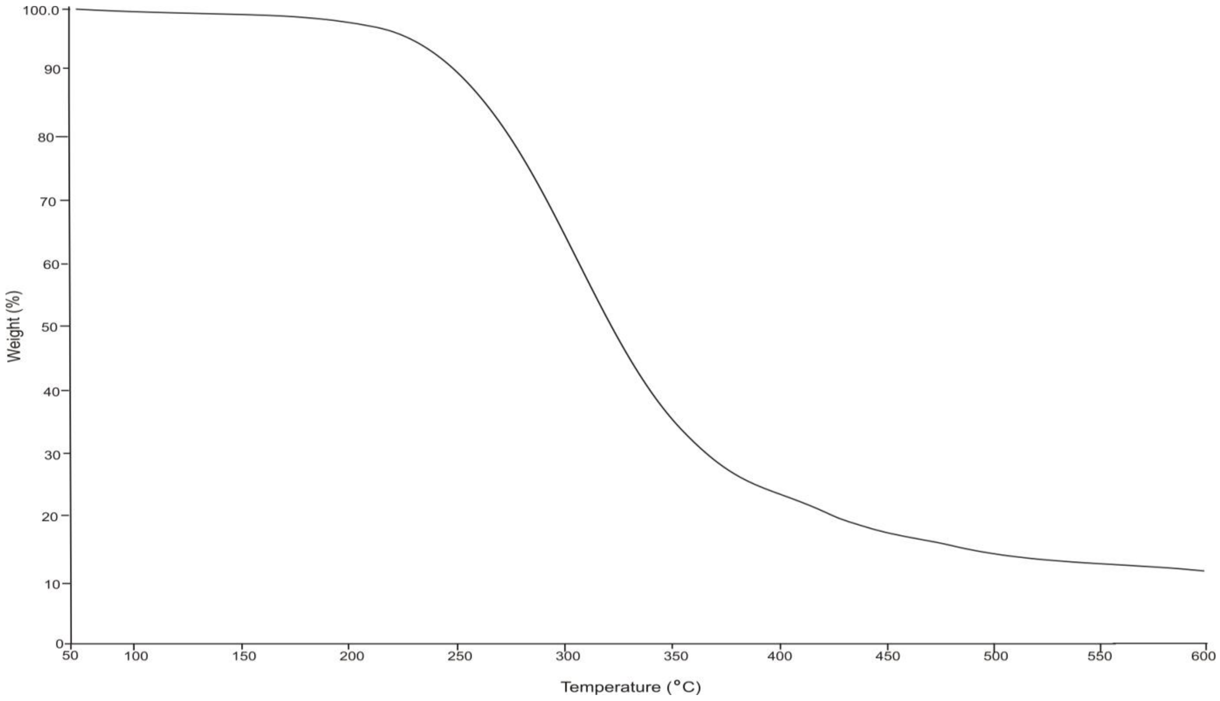


Figure 4.91: TGA of IXj

Table 4.8

TGA Data of UPUEs Xa-j

UPUEs Xa-j	% Weight loss at various Temperature (°C) from TGA			
	150	**300**	**450**	**600**
Xa	1.76	12.43	45.40	**77.12**
Xb	1.75	12.41	45.39	**77.10**
Xc	1.74	12.40	43.19	**70.50**
Xd	1.55	11.57	41.09	**72.62**
Xe	1.01	11.33	41.20	**70.31**
Xf	1.02	11.31	41.18	**70.28**
Xg	1.54	11.55	41.06	**72.58**
Xh	1.57	11.59	41.13	**72.66**
Xi	1.54	11.23	48.11	**77.00**
Xj	1.25	10.13	40.11	**79.89**

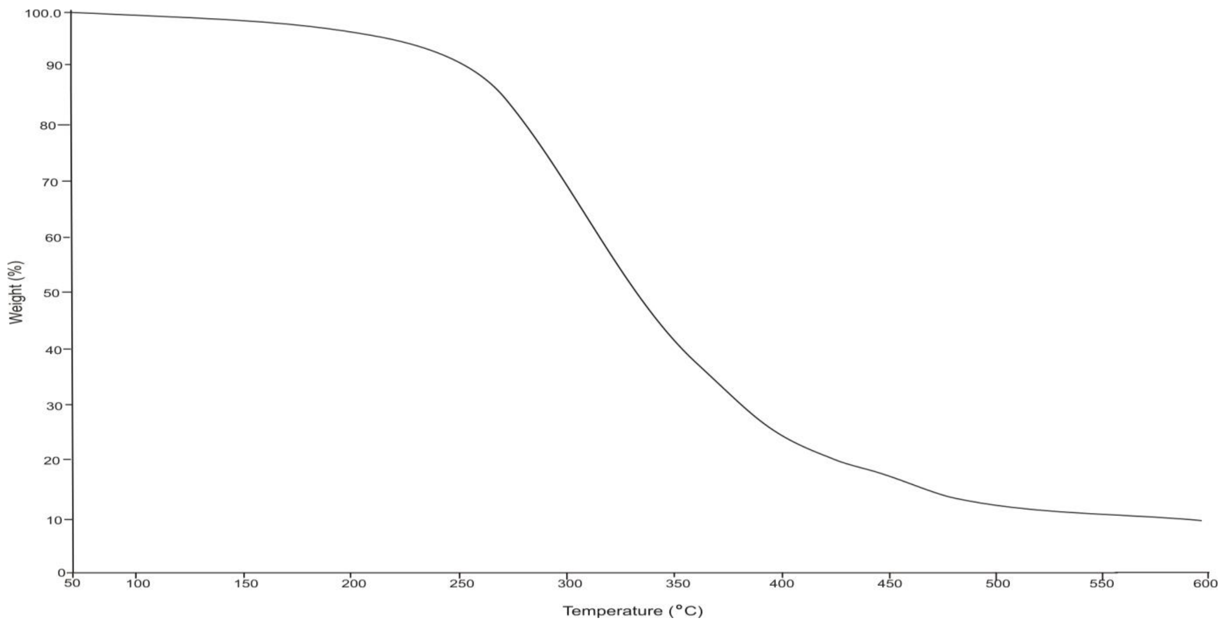


Figure 4.92: TGA of Xa

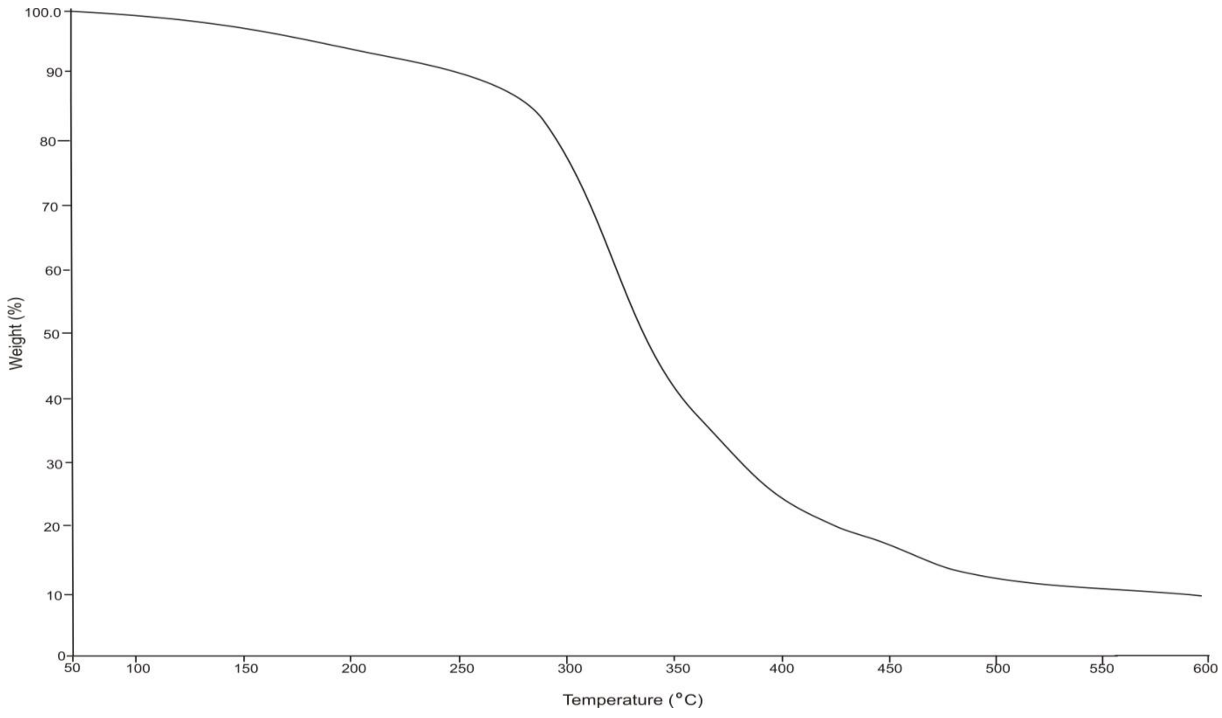


Figure 4.93: TGA of Xb

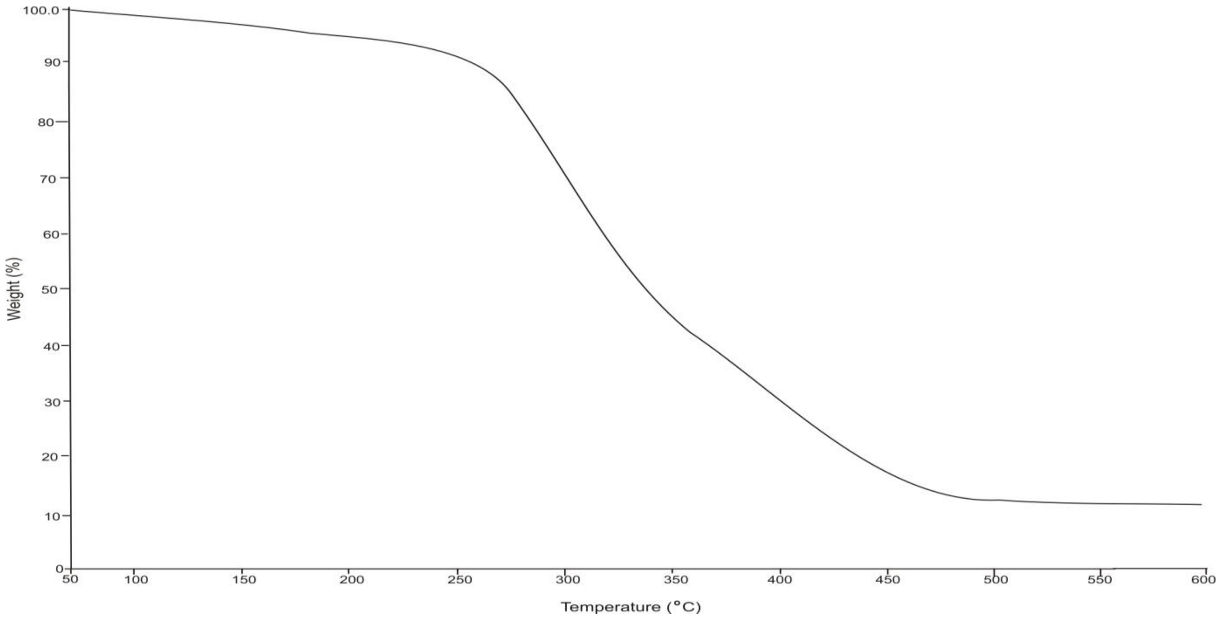


Figure 4.94: TGA of Xc

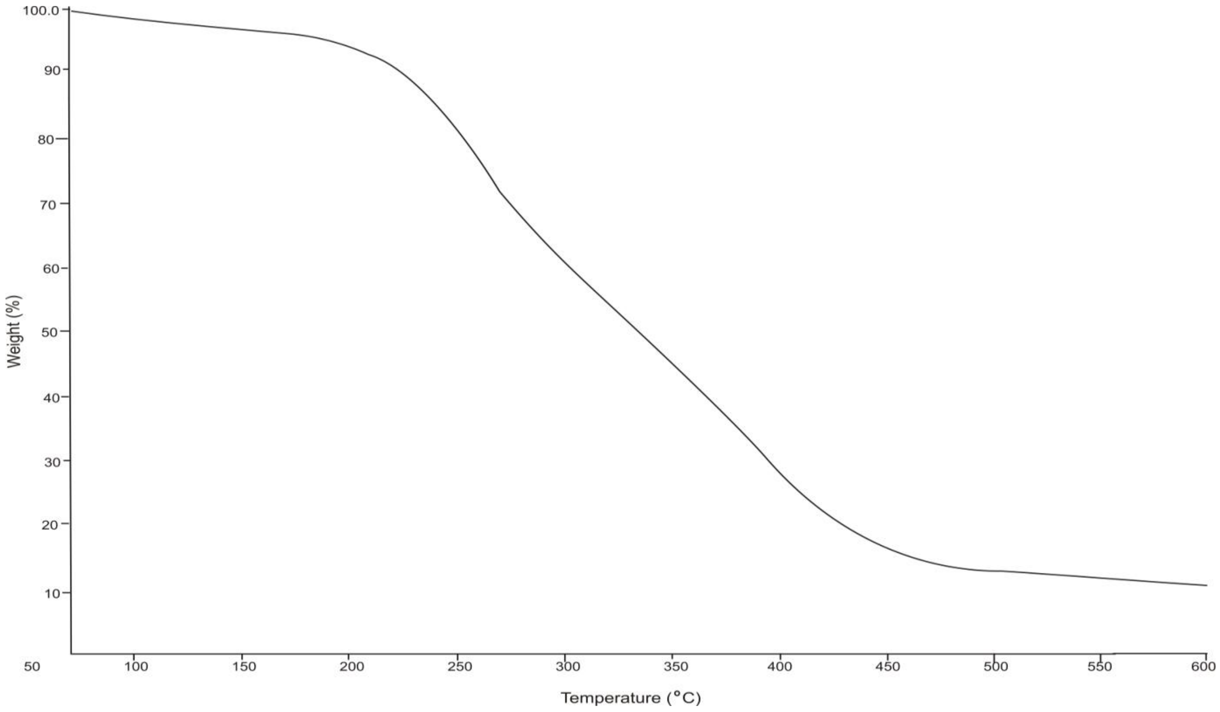


Figure 4.95: TGA of Xd

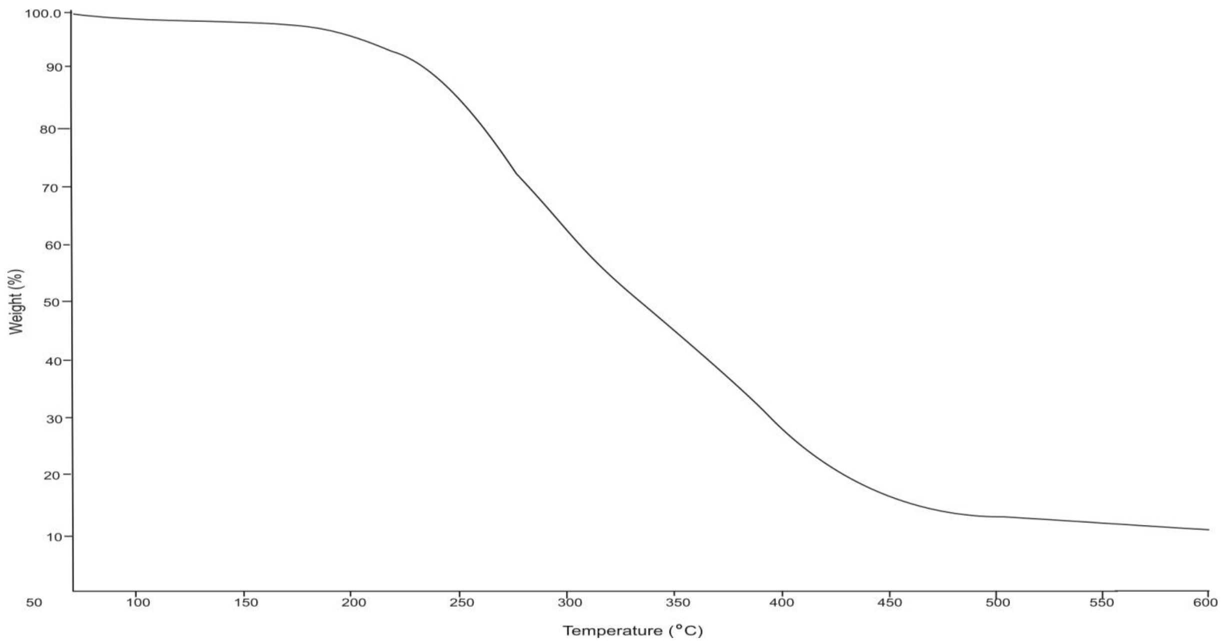


Figure 4.96: TGA of Xe

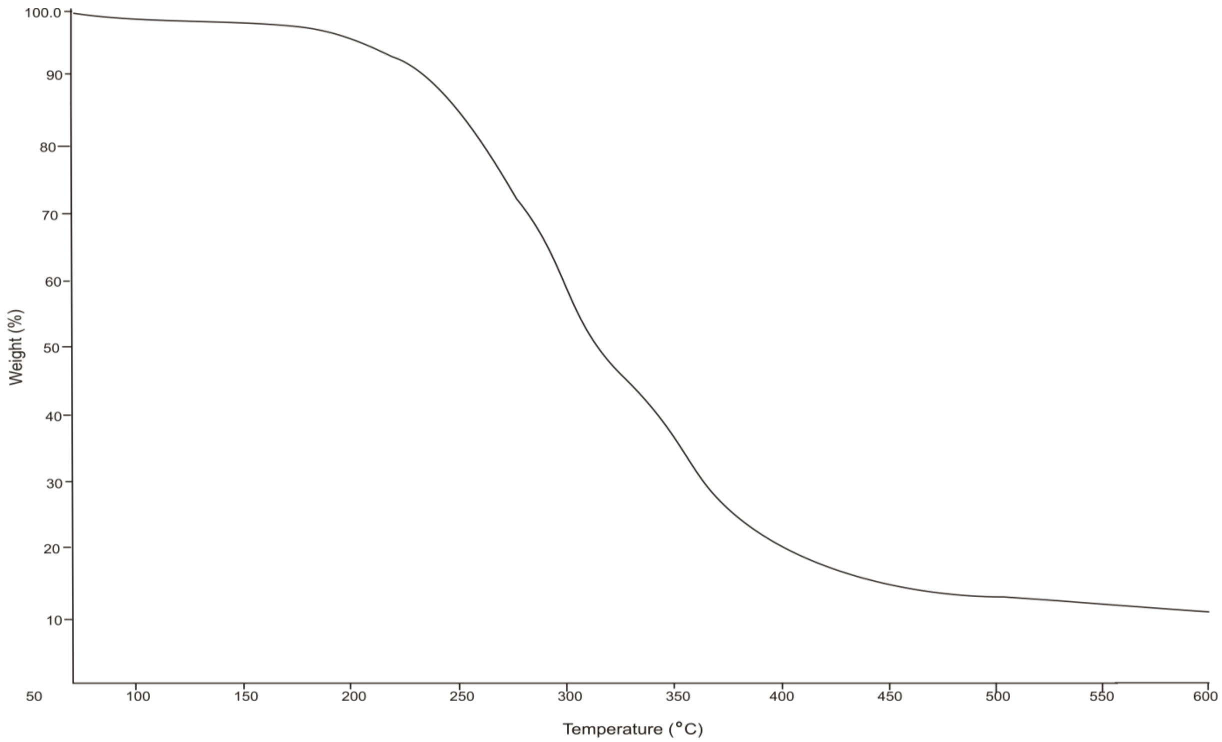


Figure 4.97: TGA of Xf

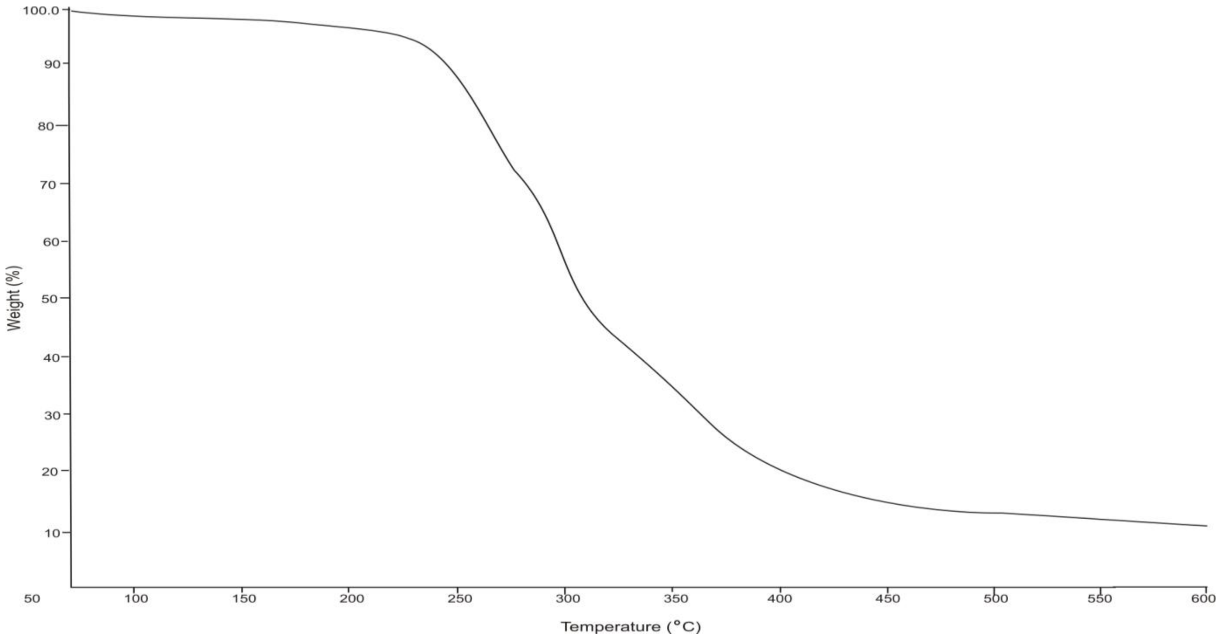


Figure 4.98: TGA of Xg

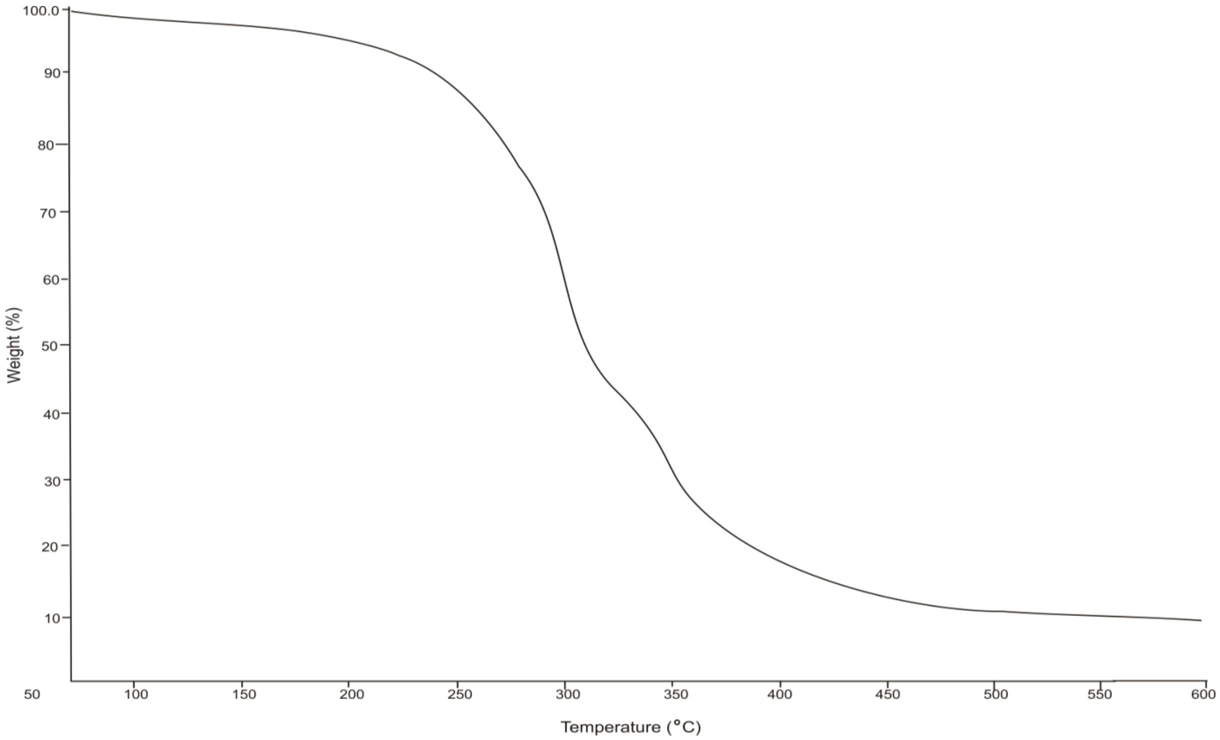


Figure 4.99: TGA of Xh

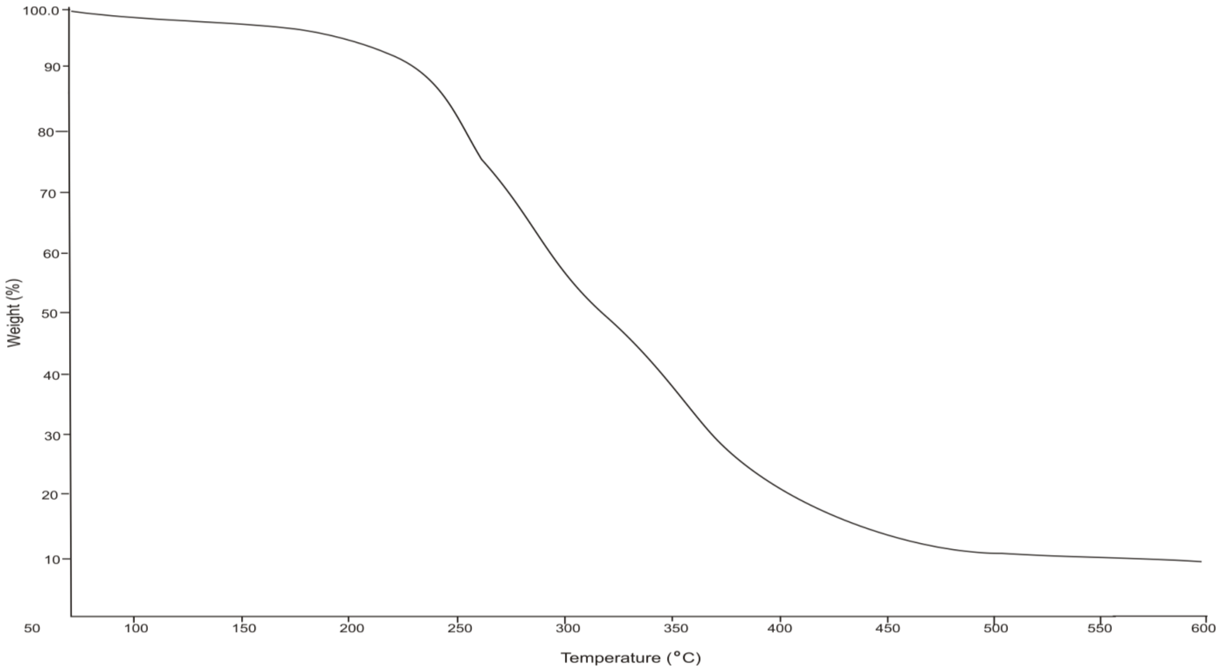


Figure 4.100: TGA of Xi

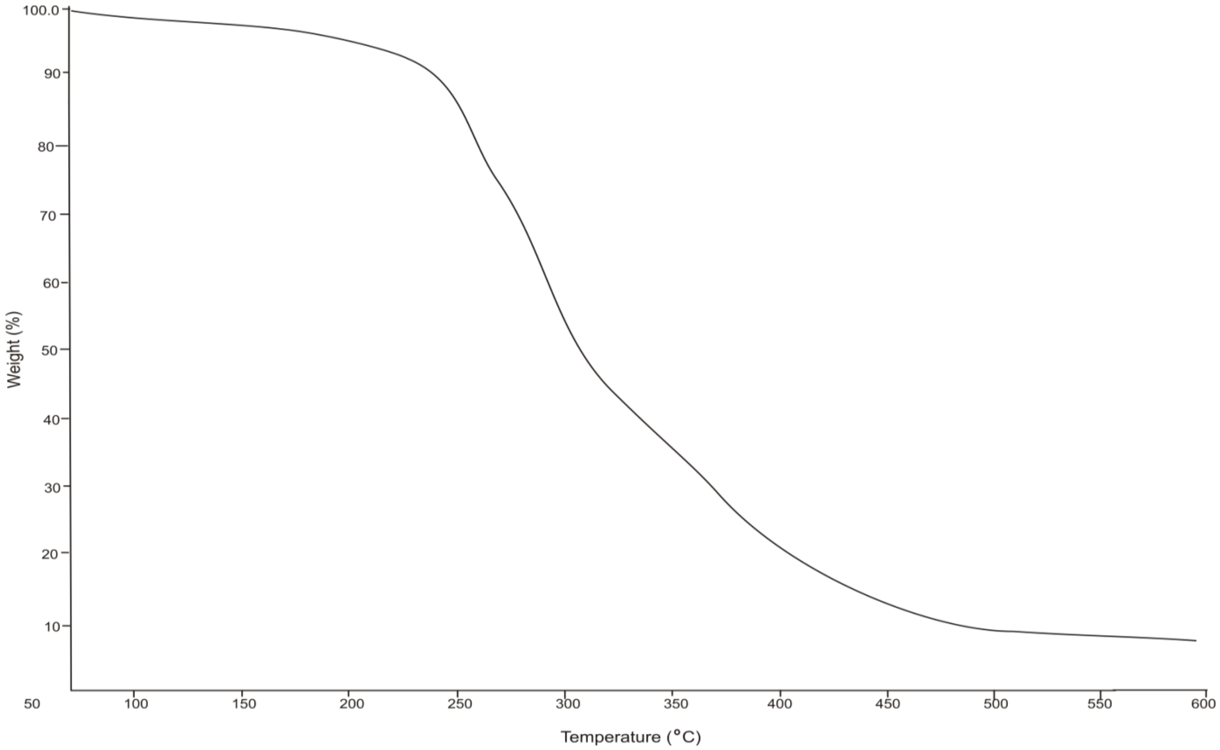


Figure 4.101: TGA of Xj

Table 4.9

TGA Data of UPUEs XIa-j

UPUEs XIa-j	% Weight loss at various Temperature (°C) from TGA			
	150	**300**	**450**	**600**
XIa	1.68	12.47	45.45	**77.16**
XIb	1.64	12.49	45.47	**77.18**
XIc	1.79	12.45	43.23	**70.18**
XId	1.60	11.62	41.13	**72.68**
XIe	1.06	11.36	41.25	**70.35**
XIf	1.09	11.39	41.27	**70.39**
XIg	1.40	11.08	41.42	**78.81**
XIh	1.43	11.10	41.45	**74.84**
XIi	1.98	10.51	48.20	**74.76**
XIj	1.81	11.25	40.30	**80.10**

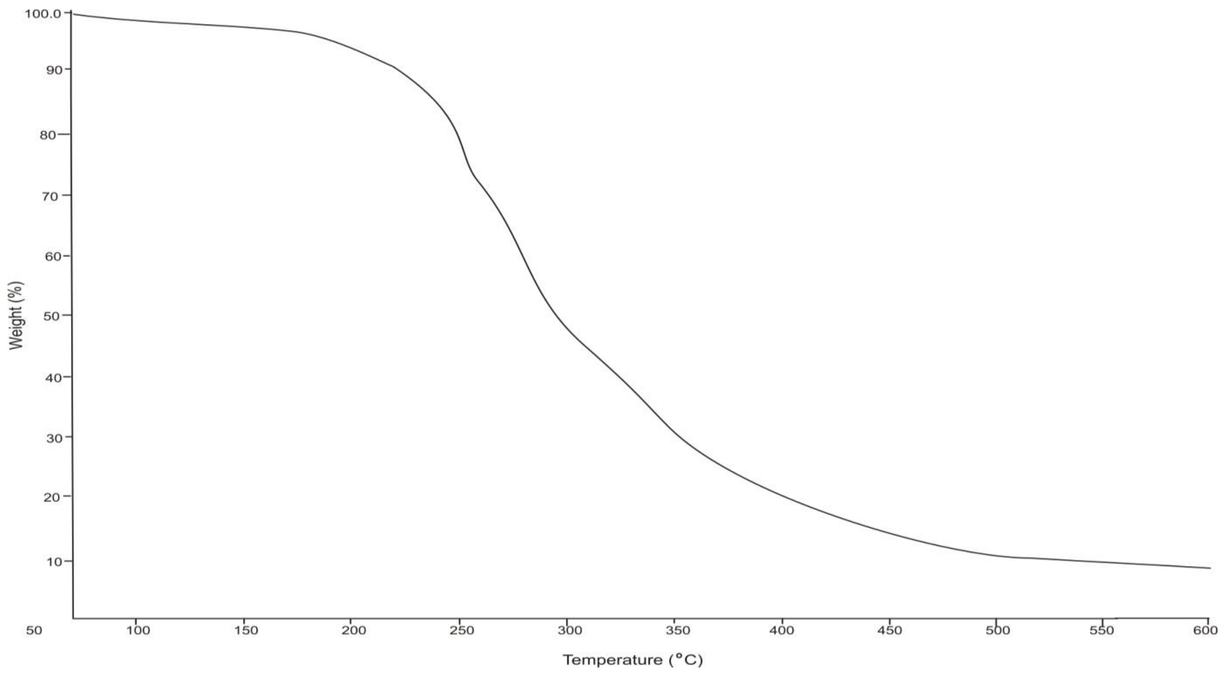


Figure 4.102: TGA of XIa

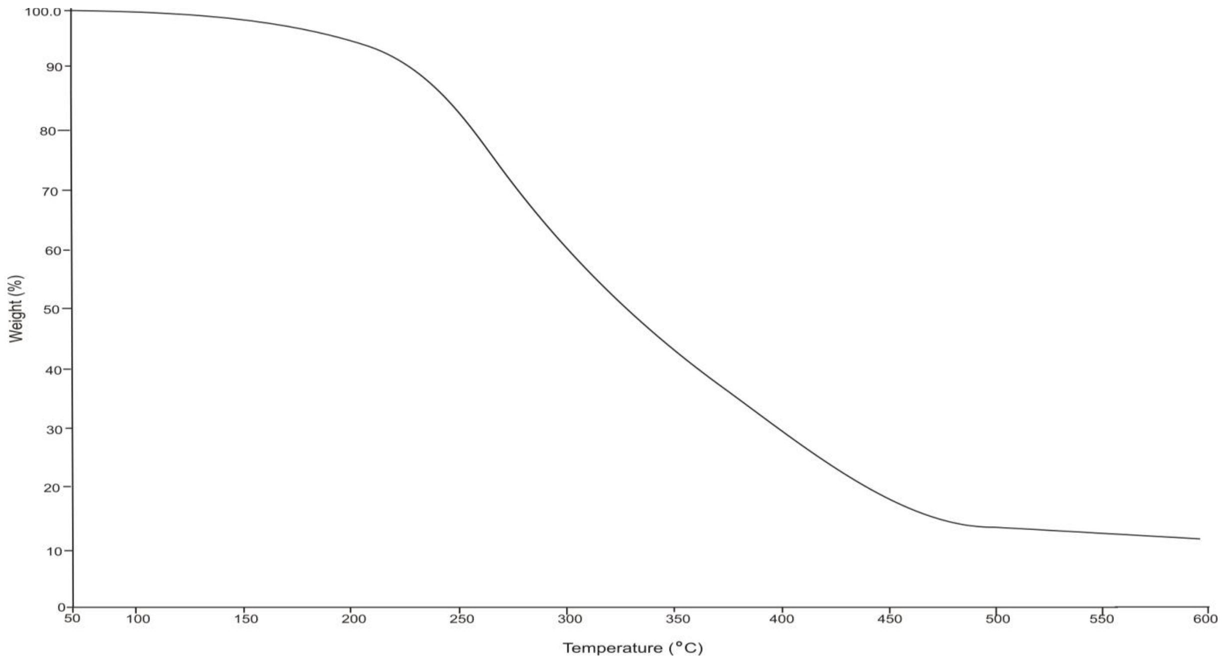


Figure 4.103: TGA of XIb

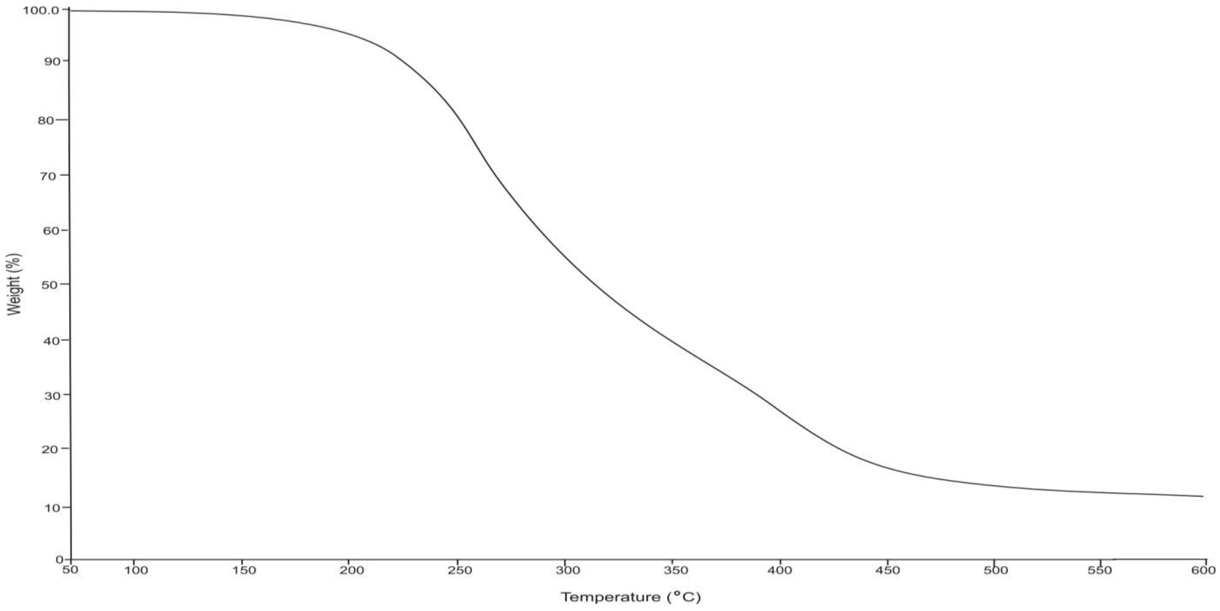


Figure 4.104: TGA of XIc

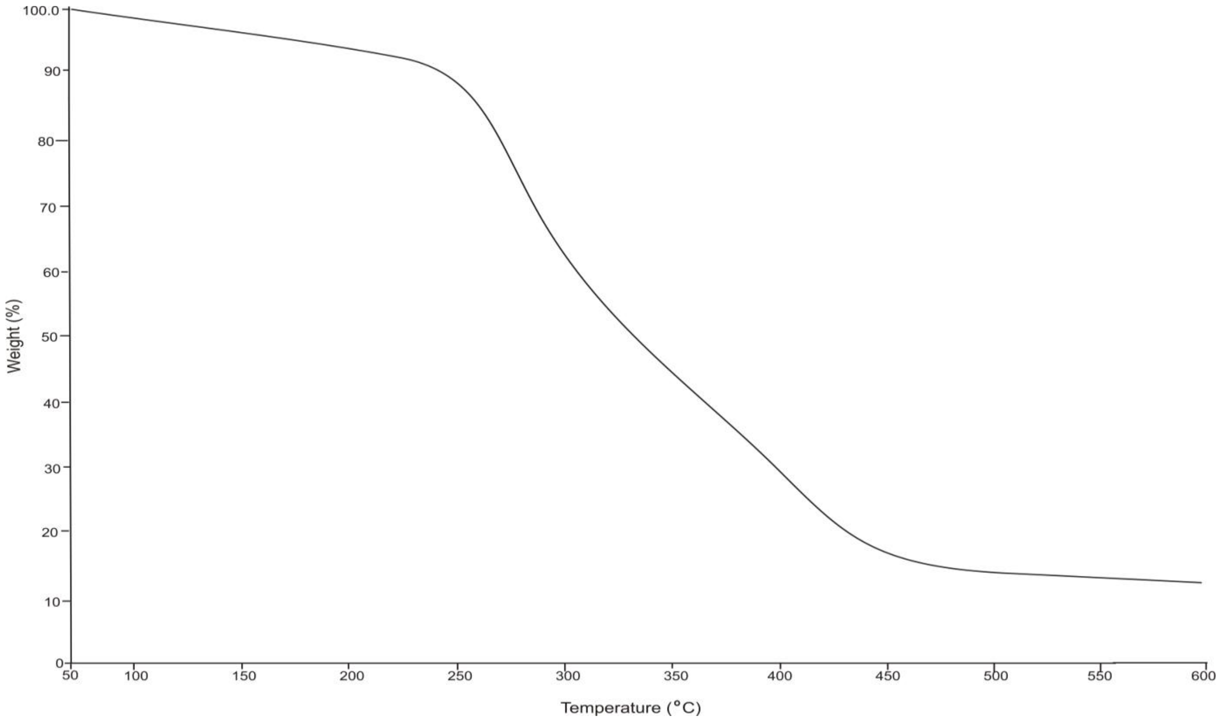


Figure 4.105: TGA of XId

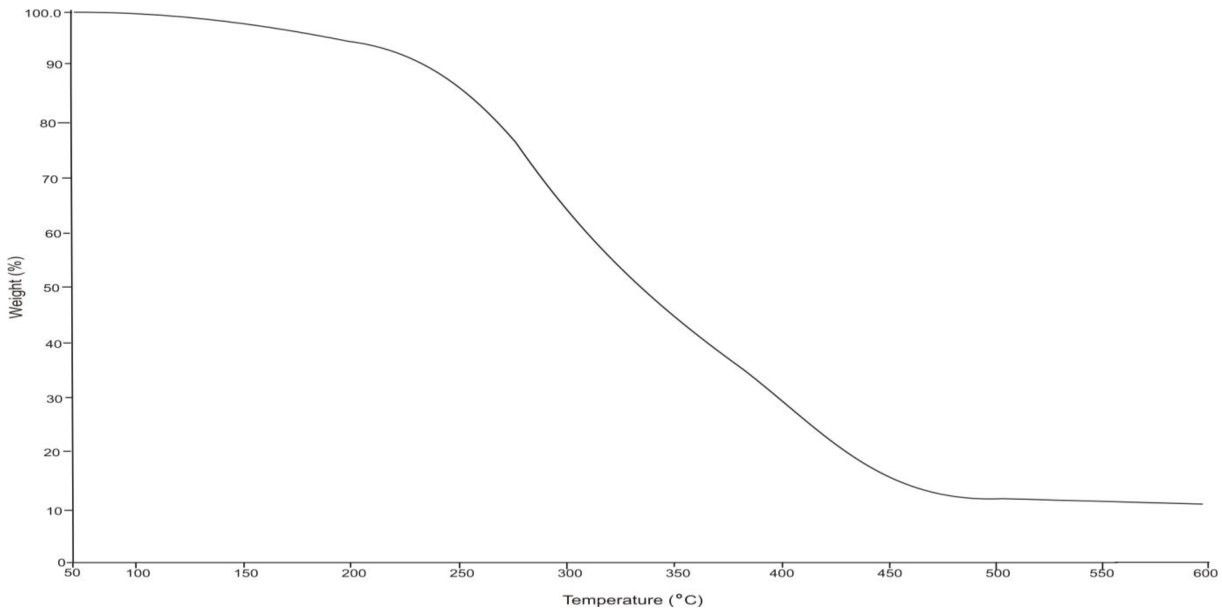


Figure 4.106: TGA of XIe

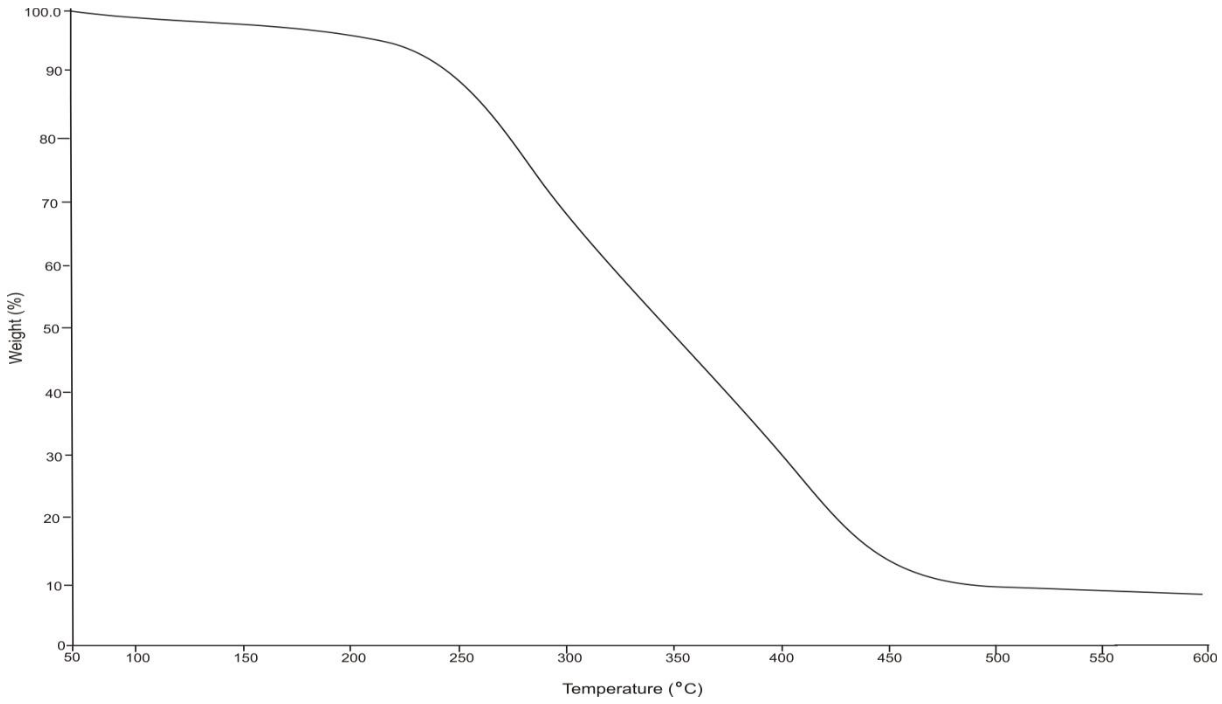


Figure 4.107: TGA of XIf

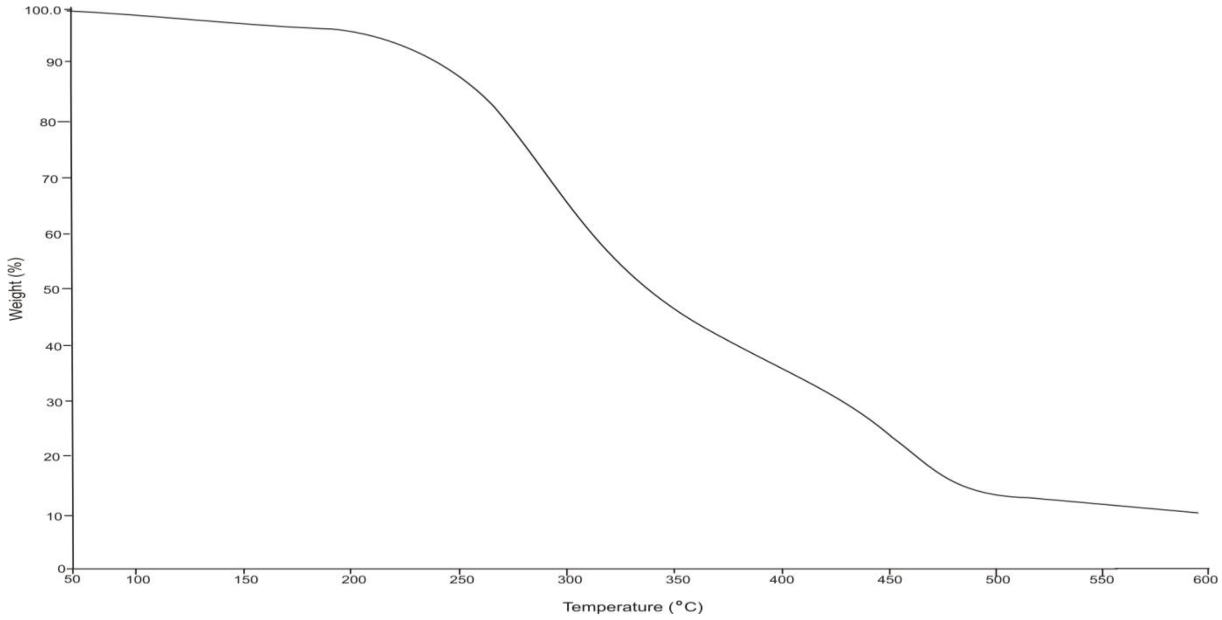


Figure 4.108: TGA of XIg

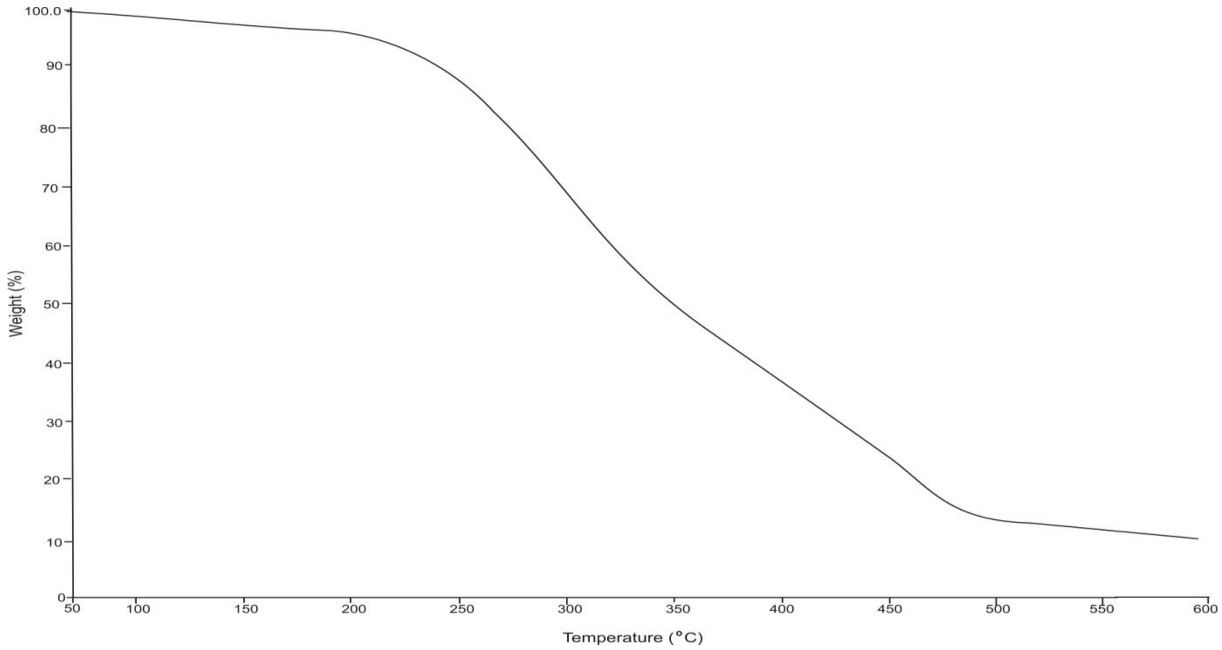


Figure 4.109: TGA of XIh

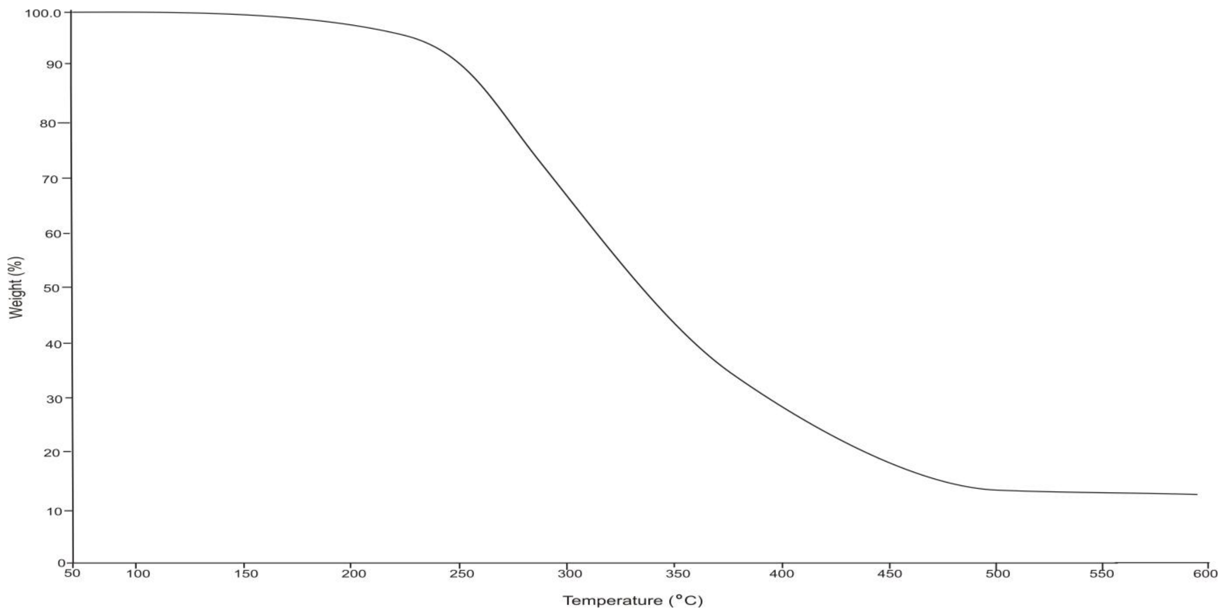


Figure 4.110: TGA of XIi

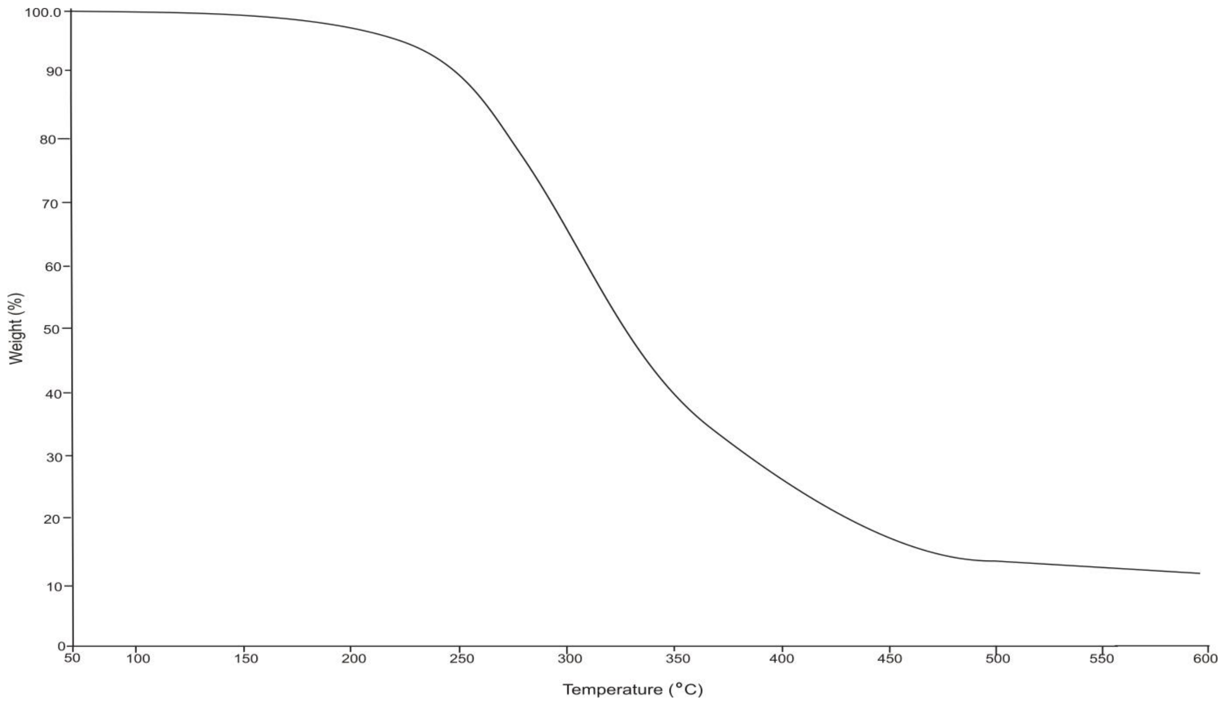


Figure 4.111: TGA of XIj

Results and Discussion (TGA)

Examination of the TGA thermograms data of all the UPUEs IX-XIa-j samples reveals that:

1. Most of the polymer samples degrade in a single step.

2. All the UPUEs IXa-j samples start their degradation at around 150 °C and weight loss of about 1.34 to 1.97% was observed. The rate of degradation of all the UPUEs IXa-j samples increase rapidly between 300 to 450 °C and weight loss of about 50 to 60% was observed. The products lost upto 74 to 80% at 600 °C.

3. All the UPUEs Xa-j samples start their degradation at around 150 °C and weight loss of about 1.01 to 1.76% was observed. The rate of degradation of all the AUPEs Xa-j samples increase rapidly between 300 to 450 °C and weight loss of about 40 to 48% was observed. The products lost upto 70 to 80% at 600 °C.

4. All the UPUEs XIa-j samples start their degradation at around 150 °C and weight loss of about 1.06 to 1.98% was observed. The rate of degradation of all the UPUEs XIa-j samples increases rapidly between 300 to 450 °C and weight loss of Nearly 40 to 48% was observed. The products lost upto 70 to 80% at 600 °C.

4.5 Characterization of Composites:

The use of the composites for different applications depends upon the properties of that particular composite fabricated by employing a particular resin. Hence here, the fabricated glass fiber reinforced composites from UPUEs IX-XIa-j were characterized for their physical, mechanical, electrical and chemical properties.

Table 4.10

Physical Properties of Glass Fiber Reinforced Composites

Based on UPUEs IXa-j

CompositesIX a-j	Color	Resin Content (%)	Water Absorption (%)	Boiling Water Absorption (%)
(IXa)	Brown	37.0	2.68	**3.50**
(IXb)	Brown	37.80	2.63	**3.55**
(IXc)	Reddish Brown	39.0	2.30	**3.66**
(IXd)	Reddish Brown	38.85	2.20	**3.78**
(IXe)	Reddish Brown	38.0	2.13	**3.76**
(IXf)	Reddish Brown	38.50	2.10	**3.74**
(IXg)	Reddish Brown	39.0	2.25	**3.75**
(IXh)	Reddish Brown	38.50	2.35	**3.70**
(IXi)	Reddish Brown	38.60	2.12	**3.68**
(IXj)	Black	37.50	2.88	**3.82**

Table 4.11

Physical Properties of Glass Fiber Reinforced Composites

Based on UPUEs Xa-j

Composites Xa-j	Color	Resin Content (%)	Water Absorption (%)	Boiling Water Absorption (%)
(Xa)	Brown	37.50	2.78	**3.62**
(Xb)	Brown	37.00	2.70	**3.66**
(Xc)	Reddish Brown	37.65	2.25	**3.70**
(Xd)	Reddish Brown	37.75	2.30	**3.72**
(Xe)	Reddish Brown	39.0	2.33	**3.76**
(Xf)	Reddish Brown	38.80	2.13	**3.70**
(Xg)	Reddish Brown	38.0	2.17	**3.80**
(Xh)	Reddish Brown	37.0	2.45	**3.62**
(Xi)	Reddish Brown	38.0	2.20	**3.58**
(Xj)	Black	37.50	2.70	**3.88**

Table 4.12

Physical Properties of Glass Fiber Reinforced Composites

Based on UPUEs XIa-j

Composite XI a-j	Color	Resin Content (%)	Water Absorption (%)	Boiling Water Absorption (%)
(XIa)	Brown	37.40	2.66	**3.58**
(XIb)	Brown	37.0	2.70	**3.55**
(XIc)	Reddish Brown	38.0	2.27	**3.70**
(XId)	Reddish Brown	38.60	2.20	**3.70**
(XIe)	Reddish Brown	38.55	2.25	**3.80**
(XIf)	Reddish Brown	38.85	2.28	**3.73**
(XIg)	Reddish Brown	39.0	2.20	**3.80**
(XIh)	Reddish Brown	37.80	2.30	**3.65**
(XIi)	Reddish Brown	38.0	2.15	**3.66**
(XIj)	Black	38.45	2.78	**3.80**

- **Mechanical Properties:**

The mechanical properties are the most important properties of the composites used in engineering materials because virtually all the service conditions and majority of the end user applications involve some degree of mechanical stress and thus are considered as relevant properties of the composites **[46, 47]**. Numbers of testing methods have been developed to characterize mechanical properties of the composites such as tensile strength, flexural strength, impact strength, compressive strength, inter laminar strength and hardness. The following discussion is limited to the testing methods like flexural strength, compressive strength, notched izod impact strength and Rockwell hardness.

All tests were performed according to the ASTM methods.

The unsaturation provides extra cross-linking sites to the polyesters and yield with the thermally stable aromatic rings in the poly(urethane-ester) network. Significant improvements of composites were observed in terms of mechanical properties and thermal characteristics. The dimensional stable rigid composites with low thermal conductivity have the potential to be used in the various applications from aerospace to microelectronics.

The mechanical and electrical properties of all the composites fabricated from UPUEs (IX-XI)a-j are furnished in Tables respectively. All the composites have better mechanical properties. There is not much variation in the mechanical properties in all the series but among them UPUEs (IX-XI)d,e,f,h shows slightly improvement in various mechanical strength than others because of presence of sulfone and ether groups.

The results show that composites have good chemical resistant property, good mechanical and electrical strength. The results of these novel UPUEs suggest that these resins can be competitors to commercial unsaturated polyester resins.

Table 4.13

Mechanical and Electrical Properties of Glass Fiber Reinforced Composites

Based on UPUEs IXa-j

Composites IXa-j	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell Hardness (R)	Electrical strength in air (KV/mm)
(IXa)	385	383	431	96	**22.1**
(IXb)	389	390	437	98	**22.4**
(IXc)	390	396	450	108	**22.9**
(IXd)	398	400	448	99	**23.8**
(IXe)	390	392	440	101	**22.1**
(IXf)	393	399	448	107	**22.6**
(IXg)	395	397	442	101	**23.6**
(IXh)	399	393	448	104	**23.1**
(IXi)	380	384	455	102	**22.3**
(IXj)	384	408	452	106	**24.0**

Table 4.14

Mechanical and Electrical Properties of Glass Fiber Reinforced Composites Based on UPUEs Xa-j

Composites Xa-j	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell Hardness (R)	Electrical strength in air (KV/mm)
(Xa)	378	380	434	98	**22.0**
(Xb)	383	384	442	102	**22.3**
(Xc)	392	391	451	110	**22.8**
(Xd)	393	398	446	104	**23.6**
(Xe)	383	391	442	103	**22.4**
(Xf)	388	397	450	108	**22.7**
(Xg)	392	395	446	105	**23.4**
(Xh)	395	390	448	101	**23.2**
(Xi)	384	386	454	103	**22.5**
(Xj)	386	390	453	107	**24.3**

Table 4.15

Mechanical and Electrical Properties of Glass Fiber Reinforced Composites

Based on UPUEs XIa-j

Composites XIa-j	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell Hardness (R)	Electrical strength in air (KV/mm)
(XIa)	382	388	436	100	**21.9**
(XIb)	386	381	440	103	**21.6**
(XIc)	394	395	446	103	**22.6**
(XId)	395	402	443	98	**23.5**
(XIe)	392	400	440	101	**22.3**
(XIf)	385	393	442	102	**22.6**
(XIg)	395	389	441	100	**23.2**
(XIh)	399	398	446	98	**23.5**
(XIi)	388	390	445	99	**22.1**
(XIj)	390	395	448	103	**24.2**

- **Chemical Properties**

The chemical resistance of the polymer composites is the prime consideration in selecting the proper material. Most polymers will undergo cracking due to the effect of solvent, which may be due to the replacement of a polymer-polymer to polymer-solvent bonds by lowering the cohesive bond energies of the surface layers of the affected materials. These new bonds may not contribute to the overall strength of the material and reduce strength of the material. However it is extremely difficult to generalize resistance of polymer to solvents and chemicals. Poor chemical resistance of the polymers limits their application.

Hence, the chemical resistance of the composites prepared from UPUEs IX-XI a-j has been studied according to ASTM D-543 method. The chemicals used for the study were H_2SO_4 (25 % V/V), HCl (25 % V/V), NaOH (25 % W/V), ethanol, acetone, THF and DMF. For this purpose, the specimen of each composite (2 cm × 2 cm) was placed in the reagents for seven days at room temperature. After seven days the specimen were removed and were dried. They were then examined for the percentage change in the thickness and weight of the specimen. Their results are furnished in Tables 4.16 to 4.18 respectively.

Table 4.16

Chemical Properties of Glass Fiber Reinforced Composites of UPUEs IXa-j

Composites	(%) Change	Reagents						
		25% H$^-$$_2SO_4$	**25% HCl**	**25% NaOH**	**Ethanol**	**Acetone**	**THF**	DMF
(IXa) [c]	Thick. / (Wt.)	4.12 / (3.51)	3.03 / (2.39)	3.38 / (2.49)	0.84 / (0.49)	0.89 / (0.59)	2.23 / (1.85)	**4.43 / (4.12)**
(IXb) [c]	Thick. / (Wt.)	4.10 / (3.50)	3.01 / (2.38)	3.40 / (2.51)	0.85 / (0.48)	0.90 / (0.59)	2.21 / (1.84)	**4.44 / (4.12)**
(IXc) [c]	Thick. / (Wt.)	4.60 / (3.84)	2.87 / (2.36)	3.45 / (2.21)	0.68 / (0.46)	0.81 / (0.56)	2.38 / (1.85)	**4.16 / (3.96)**
(IXd) [c]	Thick. / (Wt.)	4.71 / (3.89)	2.92 / (2.37)	3.48 / (2.23)	0.78 / (0.53)	0.86 / (0.63)	2.39 / (1.84)	**4.18 / (3.98)**
(IXe) [c]	Thick. / (Wt.)	4.84 / (4.11)	3.06 / (2.41)	2.37 / (2.19)	0.63 / (0.43)	0.78 / (0.58)	2.41 / (1.90)	**4.23 / (3.99)**
(IXf) [c]	Thick. / (Wt.)	4.87 / (4.13)	3.03 / (2.39)	2.35 / (2.17)	0.61 / (0.41)	0.76 / (0.57)	2.42 / (1.91)	**4.21 / (3.98)**
(IXg) [c]	Thick. / (Wt.)	4.79 / (4.05)	2.98 / (2.34)	3.41 / (2.16)	0.79 / (0.62)	0.82 / (0.63)	2.38 / (1.85)	**4.13 / (3.93)**
(IXh) [c]	Thick. / (Wt.)	4.75 / (4.03)	2.91 / (2.32)	3.53 / (2.26)	0.72 / (0.51)	0.81 / (0.60)	2.41 / (1.87)	**4.17 / (4.00)**
(IXi) [c]	Thick. / (Wt.)	4.03 / (3.43)	2.27 / (2.08)	2.38 / (2.20)	0.53 / (0.40)	0.53 / (0.42)	2.11 / (1.68)	**4.19 / (3.98)**
(IXj) [c]	**Thick. / (Wt.)**	**4.72 / (3.88)**	**2.68 / (2.28)**	**3.33 / (2.41)**	**0.56 / (0.39)**	**0.56 / (0.38)**	**1.93 / (1.52)**	4.13 / (3.94)

Table 4.17

Chemical Properties of Glass Fiber Reinforced Composites of UPUEs Xa-j

Composites	(%) Change	Reagents						
		25% H$^-$ $_2$SO$_4$	**25% HCl**	**25% NaOH**	**Ethanol**	**Acetone**	**THF**	DMF
(Xa) ^{c}	Thick. / (Wt.)	4.08 / (3.49)	3.00 / (2.37)	3.35 / (2.46)	0.82 / (0.48)	0.86 / (0.56)	2.22 / (1.83)	**4.40 / (4.10)**
(Xb) ^{c}	Thick. / (Wt.)	4.07 / (3.49)	3.01 / (2.37)	3.37 / (2.47)	0.83 / (0.48)	0.87 / (0.56)	2.21 / (1.83)	**4.41 / (4.10)**
(Xc) ^{c}	Thick. / (Wt.)	4.57 / (3.82)	2.85 / (2.34)	3.40 / (2.19)	0.65 / (0.44)	0.79 / (0.54)	2.36 / (1.84)	**4.14 / (3.98)**
(Xd) ^{c}	Thick. / (Wt.)	4.68 / (3.87)	2.90 / (2.35)	3.45 / (2.20)	0.75 / (0.50)	0.83 / (0.60)	2.37 / (1.83)	**4.15 / (3.95)**
(Xe) ^{c}	Thick. / (Wt.)	4.82 / (4.10)	3.02 / (2.39)	2.34 / (2.17)	0.60 / (0.41)	0.80 / (0.60)	2.40 / (1.89)	**4.20 / (3.96)**
(Xf) ^{c}	Thick. / (Wt.)	4.85 / (4.12)	3.00 / (2.38)	2.33 / (2.17)	0.60 / (0.41)	0.74 / (0.56)	2.40 / (1.88)	**4.20 / (3.97)**
(Xg) ^{c}	Thick. / (Wt.)	4.76 / (4.02)	2.95 / (2.31)	3.39 / (2.15)	0.76 / (0.60)	0.80 / (0.62)	2.35 / (1.84)	**4.13 / (3.93)**
(Xh) ^{c}	Thick. / (Wt.)	4.73 / (4.00)	2.89 / (2.30)	3.50 / (2.24)	0.70 / (0.49)	0.78 / (0.58)	2.40 / (1.87)	**4.15 / (3.98)**
(Xi) ^{c}	Thick. / (Wt.)	4.01 / (3.41)	2.23 / (2.05)	2.35 / (2.19)	0.52 / (0.40)	0.52 / (0.41)	2.08 / (1.66)	**4.16 / (3.96)**
(Xj) ^{c}	**Thick. / (Wt.)**	**4.70 / (3.87)**	**2.64 / (2.26)**	**3.30 / (2.40)**	**0.55 / (0.38)**	**0.55 / (0.37)**	**1.90 / (1.51)**	4.10 / (3.91)

Table 4.18

Chemical Properties of Glass Fiber Reinforced Composites of UPUEs XIa-j

Composites	(%) Change	Reagents						
		25% H^{-} $_{2}SO_{4}$	**25% HCl**	**25% NaOH**	**Ethanol**	**Acetone**	**THF**	DMF
(XIa) ^{c}	Thick. / (Wt.)	4.16 / (3.53)	3.05 / (2.40)	3.41 / (2.50)	0.86 / (0.51)	0.91 / (0.60)	2.27 / (1.88)	**4.45 / (4.14)**
(XIb) ^{c}	Thick. / (Wt.)	4.14 / (3.53)	3.04 / (2.39)	3.40 / (2.51)	0.85 / (0.50)	0.91 / (0.60)	2.26 / (1.88)	**4.45 / (4.14)**
(XIc) ^{c}	Thick. / (Wt.)	4.64 / (3.86)	2.89 / (2.38)	3.47 / (2.23)	0.71 / (0.49)	0.84 / (0.59)	2.41 / (1.87)	**4.18 / (3.98)**
(XId) ^{c}	Thick. / (Wt.)	4.73 / (3.91)	2.94 / (2.39)	3.50 / (2.25)	0.80 / (0.55)	0.88 / (0.64)	2.42 / (1.86)	**4.19 / (3.98)**
(XIe) ^{c}	Thick. / (Wt.)	4.86 / (4.13)	3.08 / (2.42)	2.39 / (2.21)	0.65 / (0.45)	0.79 / (0.58)	2.45 / (1.94)	**4.26 / (4.01)**
(XIf) ^{c}	Thick. / (Wt.)	4.89 / (4.15)	3.06 / (2.42)	2.37 / (2.20)	0.63 / (0.43)	0.78 / (0.57)	2.43 / (1.92)	**4.22 / (3.99)**
(XIg) ^{c}	Thick. / (Wt.)	4.80 / (4.05)	3.00 / (2.36)	3.44 / (2.19)	0.82 / (0.65)	0.85 / (0.64)	2.40 / (1.86)	**4.16 / (3.95)**
(XIh) ^{c}	Thick. / (Wt.)	4.76 / (4.04)	2.93 / (2.35)	3.56 / (2.27)	0.76 / (0.54)	0.83 / (0.61)	2.43 / (1.88)	**4.19 / (4.03)**
(XIi) ^{c}	Thick. / (Wt.)	4.06 / (3.45)	2.30 / (2.11)	2.40 / (2.22)	0.55 / (0.44)	0.55 / (0.45)	2.13 / (1.70)	**4.22 / (4.00)**
(XIj) ^{c}	**Thick. / (Wt.)**	**4.73 / (3.89)**	**2.41 / (2.30)**	**3.36 / (2.42)**	**0.58 / (0.41)**	**0.58 / (0.40)**	**1.95 / (1.55)**	4.16 / (3.97)

- **Results and Discussion (GFRC)**

The structure of the glass cloth core fibers in the direction of the core plane is almost random. There are relatively very few fibers oriented in the direction perpendicular to the plane. During compression, the fiber structure oriented perpendicular to the plane is diminished during compression.

The composites were fabricated from UPUEs IX-XI a-j j using benzoyl peroxide as a curing agent of the resins.

Resin content of the fabricated composites was determined by a reported method for all the composites and was found in the range of 37.0 to 39 %. From the results, it is observed that around 1-4 % loss of the matrix system took place during the workup of composite fabrication. Examination of the result reveals that for all UPUEs IX-XI a-j based composites absorb about 2.10 to 2.88 % of water.Examination of boiling water absorption test reveals that, for all UPUEs IX-XI a-j based composites absorbs 3.50 to 3.88% of boiling water.

The mechanical and electrical properties of all the composites fabricated from UPUEs IX-XI a-j are furnished in Tables respectively. All the UPUEs IX-XI a-j jcomposites have better mechanical properties. There is not much variation in the mechanical properties in all the series.

The electrical strength of the UPUEs IX-XI a-j based composites is in the range of 21.6 to 24.3KV/mm respectively. As there is no appreciable change in the electrical strength, no attempt was made to interpret this data. However, the values of the electrical strength of the composites of both the type of resins are rather low. This could result in a charred path, over which subsequent discharge could take place a minute leakage of current may arise from surface contamination.

The results of the chemical resistance test of the composites fabricated from UPUEs IX-XI a-j are furnished in Tables 4.16 to 4.18 respectively. Results reveals that all the composites are very negligibly affected by the common organic solvents like ethanol, acetone etc. However, considerable percentage change in thickness and weight is observed in DMF, H_2SO_4 and NaOH for all the composites.

Hence, the chemical resistance of the composites prepared from UPUEs IX-XI a-j j has been studied according to ASTM D-543 method. The chemicals used for the study were H_2SO_4 (25 % V/V), HCl (25 % V/V), NaOH (25 % W/V), ethanol, acetone, THF and DMF. For this purpose, the specimen of each composite (2 cm × 2 cm) was placed in the reagents for seven days at room temperature. After seven days the specimen were removed and were dried. They were then examined for the percentage change in the thickness and weight of the specimen. Their results are furnished in Tables 4.16 to 4.18 respectively.

4.6 characterization of steel panel coating:

The details about the steel panel coating mentioned below.

Characterization of coating film:

Table 4.19 Properties of films prepared from UPUEs IXa-j

Designation	Drying time in minutes		Adhesion	Flexibility
	Surface dry	Tack-free dry		
(IXa)	84	245	P	P
(IXb)	75	230	P	P
(IXc)	73	232	P	P
(IXd)	81	241	P	P
(IXe)	69	240	P	P
(IXf)	82	243	P	P
(IXg)	76	231	P	P
(IXh)	72	237	P	P
(IXi)	77	238	P	P
(IXj)	86	240	P	P

Table 4.20 Properties of films prepared from UPUEs Xa-j

Designation	Drying time in minutes		Adhesion	Flexibility
	Surface dry	Tack-free dry		
(Xa)	80	238	P	P
(Xb)	73	241	P	P
(Xc)	74	238	P	P
(Xd)	78	228	P	P
(Xe)	73	234	P	P
(Xf)	77	251	P	P
(Xg)	81	247	P	P
(Xh)	77	256	P	P
(Xi)	61	242	P	P
(Xj)	78	237	P	P

Table 4.21 Properties of films prepared from UPUEs XIa-j

Designation	Drying time in minutes		Adhesion	Flexibility
	Surface dry	Tack-free dry		
(XIa)	71	244	P	P
(XIb)	78	262	P	P
(XIc)	84	244	P	P
(XId)	67	257	P	P
(XIe)	83	288	P	P
(XIf)	81	235	P	P
(XIg)	68	264	P	P
(XIh)	81	273	P	P
(XIi)	89	236	P	P
(XIj)	69	257	P	P

The drying time data shown in Tables suggest that these films give good surface dry and good tack-free dry properties as well as good adhesion and flexibility. The drying time reduces on increasing the amount of UPE resin added. Presence of suitable driers, the oxygen activation of the methylene group is further accelerated, which results in faster drying time. The drying time is further improved as the concentration of epoxy resin increases.

Table 4.22 Mechanical properties of films prepared from UPUEs IXa-j

Designation	Scratch hardness Kg	Pencil hardness	Impact resistance Direct in.lb
(IXa)	**2.20**	**3H**	**175**
(IXb)	**2.43**	**4H**	**169**
(IXc)	**2.21**	**2H**	**158**
(IXd)	**2.56**	**4H**	**180**
(IXe)	**2.48**	**4H**	**176**
(IXf)	**2.41**	**4H**	**157**
(IXg)	**2.56**	**3H**	**173**
(IXh)	**2.67**	**5H**	**156**
(IXi)	**2.31**	**3H**	**176**
(IXj)	**2.36**	**4H**	**158**

Table 4.23 Mechanical properties of films prepared from UPUEs Xa-j

Designation	Scratch hardness Kg	Pencil hardness	Impact resistance Direct in.lb
(Xa)	**2.34**	**3H**	**175**
(Xb)	**2.23**	**4H**	**169**
(Xc)	**2.56**	**5H**	**158**
(Xd)	**2.46**	**3H**	**180**
(Xe)	**2.27**	**4H**	**176**
(Xf)	**2.44**	**4H**	**157**
(Xg)	**2.36**	**5H**	**173**
(Xh)	**2.53**	**5H**	**156**
(Xi)	**2.62**	**3H**	**176**
(Xj)	**2.63**	**6H**	**158**

Table 4.24 Mechanical properties of films prepared from UPUEs XIa-j

Designation	Scratch hardness Kg	Pencil hardness	Impact resistance Direct in.lb
(XIa)	**2.23**	**3H**	**145**
(XIb)	**2.34**	**5H**	**173**
(XIc)	**2.52**	**3H**	**136**
(XId)	**2.43**	**4H**	**193**
(XIe)	**2.44**	**5H**	**143**
(XIf)	**2.36**	**3H**	**158**
(XIg)	**2.58**	**5H**	**198**
(XIh)	**2.75**	**5H**	**173**
(XIi)	**2.85**	**3H**	**145**
(XIj)	**2.46**	**5H**	**163**

Excellent scratch hardness was obtained from the films prepared from these blends. As the use of aromatic monomers, gradual increase in hardness is observed. Also the films show significant improvement in hardness. This improvement can be attributed to excellent structural compatibility of components in the blend which form a crosslinked polymer. Pencil hardness and impact resistance were also good. All the UPUEs (IX-XI)a-j have better mechanical properties. There is not much variation in the mechanical properties in all the series.

Table: 4.25 Chemical resistances properties of films prepared from UPUEs IXa-j

Designation	Acid resistance 5% HCl 24 h	Alkali resistance 3% NaOH 2h	Water resistance (Dist. Water) 168 h	Solvent resistance Xylene 168 h
(IXa)	**2**	**4**	**4**	**3**
(IXb)	**2**	**3**	**4**	**3**
(IXc)	**3**	**2**	**4**	**3**
(IXd)	**3**	**2**	**5**	**2**
(IXe)	**2**	**3**	**5**	**3**
(IXf)	**4**	**2**	**3**	**2**
(IXg)	**2**	**3**	**4**	**2**
(IXh)	**3**	**3**	**4**	**3**
(IXi)	**3**	**4**	**4**	**3**
(IXj)	**2**	**2**	**3**	**4**

*0 = film completely removed.

*1 = film removed and particularly cracked.

*2 = film partially cracked.

*3 = loss in gloss.

*4 = slight loss in gloss.

*5 = film largely unaffected.

Table 4.26 Chemical resistances properties of films prepared from UPUEs Xa-j

Designation	Acid resistance 5% HCl 24 h	Alkali resistance 3% NaOH 2h	Water resistance (Dist. Water) 168 h	Solvent resistance Xylene 168 h
(Xa)	**2**	**4**	**4**	**2**
(Xb)	**3**	**3**	**4**	**2**
(Xc)	**4**	**2**	**5**	**4**
(Xd)	**3**	**2**	**5**	**3**
(Xe)	**3**	**4**	**5**	**2**
(Xf)	**3**	**3**	**3**	**3**
(Xg)	**3**	**3**	**4**	**2**
(Xh)	**2**	**2**	**4**	**3**
(Xi)	**4**	**3**	**4**	**4**
(Xj)	**3**	**2**	**4**	**3**

Table 4.27 Chemical resistances properties of films prepared from UPUEs XIa-j

Designation	Acid resistance 5% HCl 24 h	Alkali resistance 3% NaOH 2h	Water resistance (Dist. Water) 168 h	Solvent resistance Xylene 168 h
(XIa)	**3**	**3**	**4**	**2**
(XIb)	**2**	**4**	**4**	**2**
(XIc)	**4**	**2**	**4**	**4**
(XId)	**3**	**2**	**3**	**3**
(XIe)	**3**	**3**	**5**	**3**
(XIf)	**3**	**2**	**2**	**2**
(XIg)	**4**	**2**	**4**	**2**
(XIh)	**2**	**3**	**4**	**2**
(XIi)	**2**	**3**	**5**	**3**
(XIj)	**3**	**2**	**4**	**2**

Chemical resistance tests of the films gave satisfactory results as shown in Tables, due to combination of individual properties of components. Each individual components of the blend shows good acid, alkali, solvent and water resistance and so the resistance of resultant blend is also improved. It was observed that films of resins having more aromatic ring system this can be attributed to rigidity and hence chemical resistance.

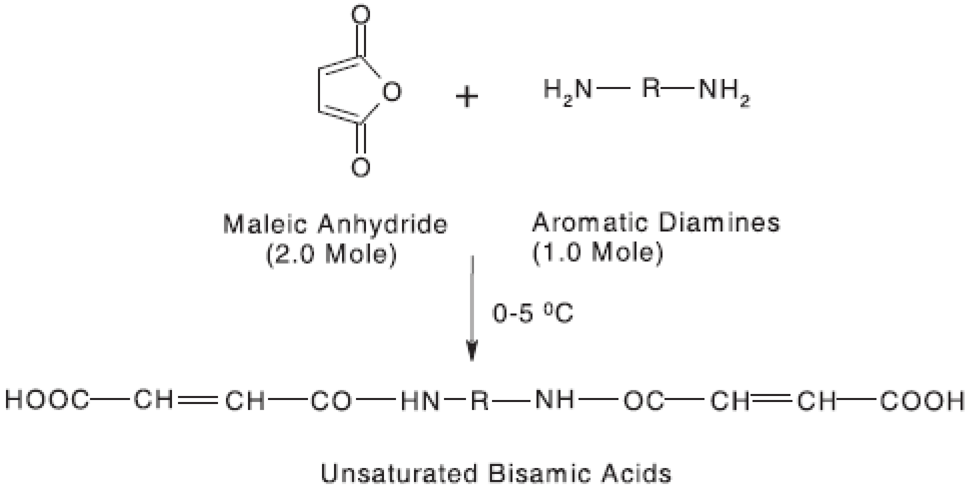
Chapter-5

Summary and Conclusion

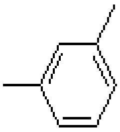
The epoxy resins are used in a large number of fields, including surface coatings, in adhesives, reinforced with carbon fiber. The polyesters are most widely versatile materials and have broad spectrum of characteristics and wide applications ranging from aerospace to micro electronics. They are also important as laminating resins, molding composites, fibers, films, surface coating resins, fiber cushion. Polyurethanes are widely used in high resiliency flexible foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives and sealants, Spandex fibers, seals, gaskets, carpet underlay, and hard plastic parts (such as for electronic instruments).

Merging of all the four unsaturation, epoxy, ester and urethane segments into one polymer chain has not received attention academically and technically. Certain properties of thermoplastics may also be improved via blending or addition to an unsaturated resin is another possibility. In order to improve certain properties of such reported polymers their blending with commercial vinyl esters (epoxy resin) such as vinyl ester epoxy resin may afford a commercially important material for wide industrial applications. Hence the present report comprises synthesis of poly (urethane-ester) having epoxy residues. Also, glass fiber reinforced composites of these polymers have been laminated and characterized by chemical, mechanical and electrical properties. The whole work is shown in Scheme

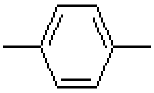
i. Various bisamic acids were prepared by reported method. The scanned procedure is as follows.



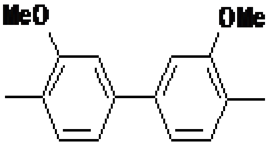
Where, R =



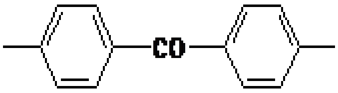
(Ia)



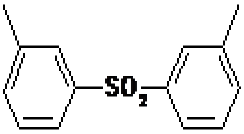
(Ib)



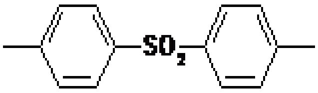
(Ic)



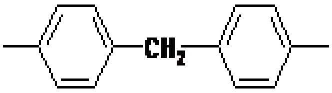
(Id)



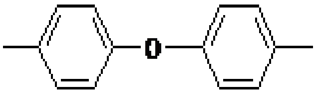
(Ie)



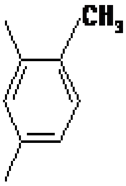
(If)



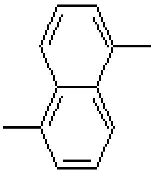
(Ig)



(Ih)

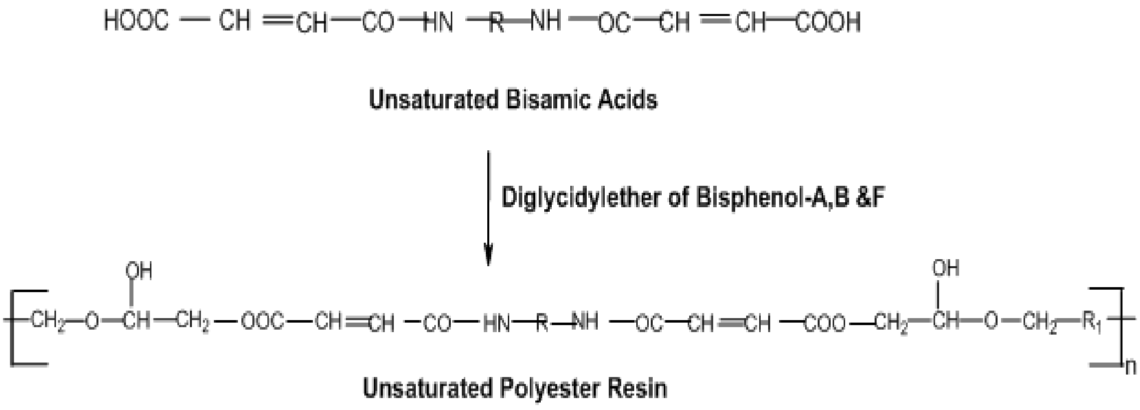


(Ii)

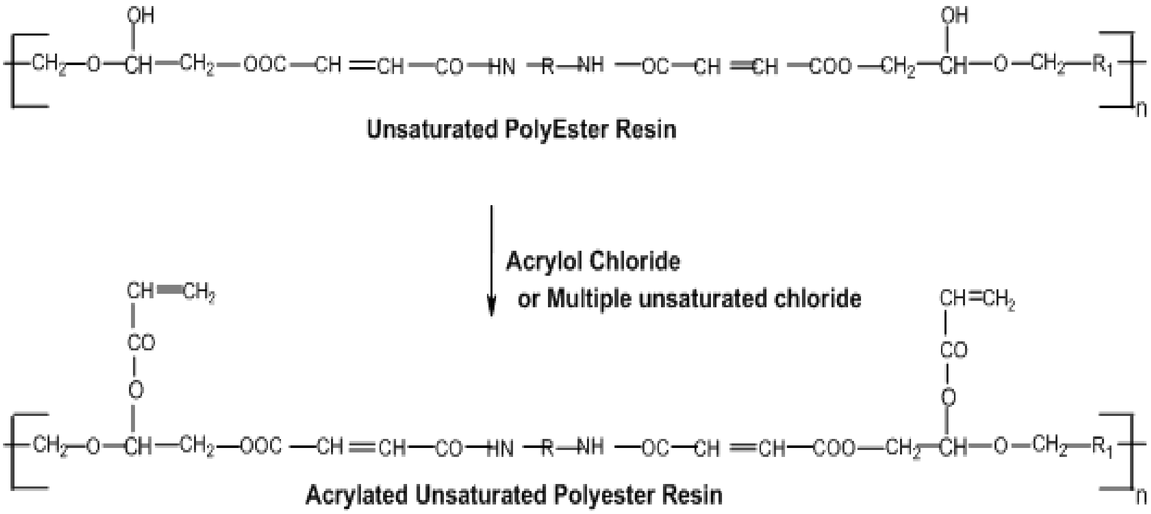


(Ij)

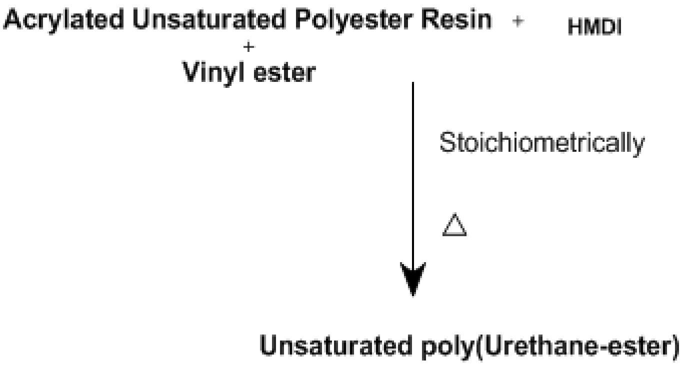
ii. All the bisamic acids were purified for next step, reaction as follows:



iii. All the unsaturated polyesters were then acrylated by multiple unsaturated chloride.



iv. All acrylated Unsaturated polyester, vinyl ester and Hexa methylene diisocyanate were blended stoichiometrically to form urethane linkage.



In this regards following polymer systems have been prepared, characterized and fabricated for GRC and surface coating.

Unsaturated polyesters were successfully synthesized using different aromatic diamines and diglycidyether of bisphenols. Unsaturated polyesters, vinyl ester and hexamethylene diisocyanates used for the production of unsaturated poly(urethane-ester).

All the produced polymer systems have been characterized by following techniques:

- The C, H, and N contents were estimated by means of Thermofinagan 1101 flash elemental analyzer (Italy).
- The IR spectra were recorded in KBr pellets on a Nicollet 760 D spectrometer.
- The number average weights were estimated by non-aqueous conductometric titration followed by the method reported in the literature. Pyridine was used as a solvent and tetra-n-butyl ammonium hydroxide was used as a titrant.
- Curing of all blends was carried out on a differential scanning calorimeter (DSC) by using benzoyl peroxide as a catalyst. A universal V3 gTA DSC was used for this study.
- Unreinforced cured samples of blends were subjected to thermogravimetric analysis (TGA) on Du Pont 950 thermo gravimetric analyzer.
- The Flexural strength was measured according to ASTM D 790.
- The Compressive strength was measured according to ASTM D 695.
- The Impact strength was measured according to ASTM D 256.
- The Rockwell hardness was measured according to ASTM D 785.
- The Electrical strength was measured according to ASTM D 149.

The values of C, H, N of each of the unsaturated polyesters and acrylated unsaturated polyesters were consistent with their predicted structures. The number average molecular weight of both unsaturated polyesters and acrylated unsaturated polyesters were estimated by nonaqueous conductometric titration method and vapor pressure osmometric method. The results indicate that the degree of polymerization is about 6. The IR spectra were consistent with the ones expected from the structures of the unsaturated polyesters and poly(urethane-ester)s.

The TGA data of all UPUEs reveals that decomposition starts around 290°C, depending on the nature of the polymers. The rate of decomposition increases by increasing the temperature and it is the fastest between 400 °C and 550° C. It was observed that the weight loss is completed beyond 760 °C.

The unsaturation provides extra cross-linking sites to the polyesters and yield with the thermally stable aromatic rings in the poly(urethane-ester) network. Significant improvements of composites were observed in terms of mechanical properties and thermal characteristics. The dimensional stable rigid composites with low thermal conductivity have the potential to be used in the various applications from aerospace to microelectronics

The results show that composites have good chemical resistant property, good mechanical and electrical strength. The results of these novel unsaturated polyester resins suggest that these resins can be competitors to commercial unsaturated polyester resins.

Suggestion for further study:

- The produced polymer systems can be blends with following commercial materials.
    - Unsaturated polyester resins based on methyl acrylate + phthelicanhydride + propylene glycol.
    - Unsaturated polyester resins based on methyl acrylate + iso-phthelicanhydride + propylene glycol.
    - Acrylated terminated polyimides.

- Different types of Diamines can be used according to the properties we need. i.e aliphatic Diamines

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