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The work included in the thesis is my own work under the supervision of Dr. P. H. Parsania and leads to some contribution in Chemistry subsidized by a number of references.

Date: 18-03-2010
Place: Rajkot

(Mr. Bharat D. Bhuva)

This is to certify that the present work submitted for the Ph. D. Degree of Saurashtra University by Mr. Bharat D. Bhuva is his own work and leads to advancement in the knowledge of Chemistry. The thesis has been prepared under my supervision.

Date : 18-03-2010
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DEDICATED
TO
MY BELOVED
PAPA
ACKNOWLEDGEMENTS

First and foremost, I would like to pay my homage to THE ALMIGHTY GOD “THE WONDERFUL CHEMIST” of this lovely world, whose blessings have made this venture successful. By His grace I am lucky enough to find a real mentor and philosopher Dr. P. H. Parsania - Professor and Head, Department of Chemistry, Saurashtra University, Rajkot. It is my immense pleasure and privilege to express my profound gratitudes to him for his never ending guidance and perseverance. His keen interest, patience and constant encouragement during my research work have enabled me to put my work in the form of the thesis. Association with him has been a lifetime achievement for me.

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Manisha for her continuous support, understanding and loving daughter “Vedi”.

Bharat D. Bhuva
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SYNOPSIS

STUDIES ON SOME POLYURETHANE AND FIBER REINFORCED COMPOSITES

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SYNOPSIS OF THE THESIS TO BE SUBMITTED TO SAURASHTRA UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF SCIENCE - CHEMISTRY

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________________________________________________

PLACE OF THE WORK

DEPARTMENT OF CHEMISTRY
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________________________________________________
GENERAL INTRODUCTION

The use of renewable starting materials in the preparation of polymers has been stimulated over the years by researchers and governmental agencies all over the world as a real result of the real need to replace products of petrochemicals origins. The use of renewable resources in the production of value added polymers for various applications [1,2] is now a days an unquestionable reality that aims to minimize the depletion of the ozone layer and green house effect provoked by the improper use of fossil starting materials [3].

Polyurethanes (PU) are known to be very attractive materials for various applications such as electrical/electronic potting and encapsulation, constructions, water proofing membranes, asphalt extended membranes, highway sealants, sound and vibration damping, automotive and rubber parts, etc [4]. Polyurethanes constitute a class of polymers with great versatility such as excellent abrasion resistance, hardness, enhanced chemicals and solvent resistance, flexibility, high cohesive strength and amenable curing speed [5-7], which permit the manufacturing the products ranging from expanded materials to highly compact materials. Polyurethanes can be tailored made according to their applications as adhesives, additives, a catalyst or a coating material [8].

In plywood industries formaldehyde is used as a main raw material because of generic organic compound. Formaldehyde based adhesives have drawback of formaldehyde emission but due to cost effectiveness formaldehyde is preferable over the use of costly polyols with isocyanates. [9]


The work to be incorporated in the thesis is divided into five chapters:

CHAPTER 1: Introduction

Chapter 2: Synthesis of monomers and resins

CHAPTER 3: Characterization of monomers and resins

CHAPTER 4: Fabrication and physico-chemical studies of Composites

CHAPTER 5: Ultrasonic studies of resins

CHAPTER 6: Summary

CHAPTER 1: Introduction

This chapter of the thesis describes the up to date literature survey on synthesis, applications and characterization of phenolic and epoxy resins, epoxy esters (polyester polyols), polyurethane resins and their composites in various fields of science.

CHAPTER 2: Synthesis of monomers and resins

This chapter is further subdivided into seven sections:

Section-1: Synthesis of 1, 1'-bis (4-hydroxy phenyl) cyclohexane

[Bisphenol–C]

Bisphenol–C was synthesized by Friedel – Crafts condensation of phenol with cyclohexanone by using a mixture of HCl: CH₃COOH (2:1 v/v) as a catalyst at 50-55°C for 4h and was repeatedly recrystallized from methanol-water system prior to their use.
Section-2: Synthesis of 9, 9'-bis (4-hydroxy phenyl) anthrone - 10
(BAN)

BAN was synthesized by condensing anthraquinone with phenol at 120°C for 6h in the presence of stannic chloride (molar ratio 1:7:1.5, respectively) and was isolated from hot acetic acid. BAN was recrystallized repeatedly from dioxane-water system prior to its use.

Section-3: Synthesis of bisphenol formaldehyde resin (BCF/BANF)

Bisphenol-C-formaldehyde resin and BAN-formaldehyde were synthesized by condensing bisphenols with formaldehyde by using alkali as a catalyst at 70°C for 2h. White crystalline resins were repeatedly purified from methanol-water system prior to their use.

Where, BCF:  \[ Z = \quad \]  
BANF:  \[ Z = \quad \]
Section-4: Synthesis of BC-formaldehyde maleate resin

BC-formaldehyde-maleate resin was synthesized by condensing BCF and maleic anhydride by using 1, 4-dioxane as a solvent and phenothiazine as a catalyst at 80°C for 6 h. The solid creamish product was purified repeatedly from MEK-water system prior to its use.

[Chemical structure of BCFM]

BCFM: \( Z = \overset{\text{O}}{\text{C}}\overset{\text{C}}{\text{H}}\overset{\text{C}}{\text{H}}\overset{\text{C}}{\text{CH}}\overset{\text{O}}{\text{Z}}\)

Section-5: Synthesis of epoxy resin of BAN

Epoxy resin of BAN was synthesized by condensing BAN with epichlorohydrin by using isopropanol as a solvent and alkali as a catalyst at reflux temperature for 3 h. The resin was isolated from chloroform.

[Chemical structure of EBAN]

EBAN: \( Z = \overset{\text{O}}{\text{C}}\overset{\text{C}}{\text{H}}\overset{\text{C}}{\text{CH}}\overset{\text{C}}{\text{H}}\overset{\text{O}}{\text{Z}}\)

Section-6: Synthesis of polyester polyols

The polyester polyols were synthesized by condensing EBAN with ricinoleic acid/ oleic acid/ acrylic acid (1:2 mole ratio) by using 1, 4-dioxane as a solvent and triethyl amine as a catalyst at reflux temperature for 4-6 h. The general structure of the polyester polyols is as under
Section-7: Synthesis of polyurethane resins

[A] Synthesis of polyurethanes of EBANRA, EBANOA and EBANAA

Polyurethanes of EBANRA, EBANOA and EBANAA were prepared by reacting polyester polyols with 2, 4-toluene diisocyanate by using CHCl₃ as a solvent at room temperature for 15 min.

[B] Synthesis of copolyurethane resin

Copolyurethane resins of PU were synthesized by reacting corresponding polyols, TDI and PEG-200 (30% of polyester polyols) at room temperature.

[C] Synthesis of polyurethanes of BCFM and EBAN

Polyurethane resins of BCFM/EBAN were synthesized by reacting BCFM/EBAN with toluene diisocyanate (1:3 mole ratio) using MEK/CHCl₃ as a solvent at room temperature for 15-30 min.

CHAPTER 3: Characterization of monomers and resins

This chapter is further subdivided into eight sections:
Section-1: Spectral characterization of the resins

Formation of different linkages in the resins and monomers are supported by IR and NMR spectral data.

Section-2: Determination of epoxy equivalent of the epoxy resins

The epoxy equivalent of the resins was determined by pyridine-pyridinium chloride method.

Section-3: Determination of acid value of the polyester polyols

The acid values of polyester polyols were determined titrimetrically by using alcoholic KOH as a titrant, acetone as a solvent and phenolphthalein as an indicator.

Section-4: Determination of hydroxyl value of polyester polyols

The hydroxyl values of the polyester polyols were determined according to acetic anhydride-pyridine method using aqueous NaOH as a titrant and phenolphthalein as an indicator.

Section-5: Thermal analysis of the resins

Thermal analysis of polymers provides information on polymer molecular architecture as well as degradation mechanism under specified conditions. It also provides useful temperature range for various applications. Thermal properties of co-polyurethanes of BANF, BCFM, EBAN, EBANRA, EBANOA and EBANA were investigated by TG method at the heating rate of 10°C/min in an N₂ atmosphere and discussed in light of structure of the based resins.

Section-6: Density measurements of the polyurethane

The density of polyurethane of BCFM-PEG-200 film was determined by floatation method by using CCl₄-n-hexane as a solvent system and discussed in terms of structure/composition of the resin.

Section-7: Mechanical and electrical properties of the polyurethane
The tensile strength, electric strength and volume resistivity of polyurethane of BCFM-PEG-200 film is determined according to standard methods and discussed their usefulness.

**Section-8: Chemical resistance of the polyurethane**

The chemical resistance of the above mentioned polyurethane film against water, 10% of each acids, alkalis and salt was carried out by change in weight method at the interval of 24h till the equilibrium was established and interpreted the data in light of nature of environment and possible applications.

**Chapter-4: Fabrication and physico-chemical studies of composites**

Composite materials are made up of two or more solid phases: fibers (dispersed phase) responsible for stress resistances and matrix (continuous phase) responsible for stress propagation. Because of the flexibility and excellent abrasion resistance of the polyurethane resins, now a day they are widely used to fabricate the composite matrices. Recently natural fibers (jute, sisal, bamboo, etc.) reinforced composites are emerging as realistic alternatives to synthetic fibers reinforced composites in many applications due to their low cost, light weight, low density, easy availability and bio degradability as compared to synthetic fibers [10,11].

From the prehistoric times mankind has depended on the renewable biomass or agro waste as its primary source for material needs. Here we are concerned with the conversion of biomass or agro waste to marketable industrial products. In India, rice husk, wheat husk, coconut fibers, papaya fibers, sugarcane husk are

the byproducts from the crops and vegetables [12-14]. Currently, the scientific community all over the world has focused their attention on utilization of these agro wastes in fabricating low cost, light weight hybrid composites, in combination with natural fibers. Hybrid composites offer a range of properties that can not be obtained with a single kind of reinforcement and by careful selection of agro wastes along with natural reinforcing fibers; the material cost can be reduced substantially. Now a day polyurethane based composites are widely used as seat frames, sun shades, door panels, package trays and truck box panels. This chapter is further subdivided into three sections.

**Section-1: Fabrication of composites**

Hybrid composites of jute, glass, rice husk and sugarcane are prepared by hand lay up compression molding under 7.6 MPa pressure at 70°C for 2h and at room temperature for 12h.

**Section-2: Mechanical and electrical properties of the composites**

Polymeric composites have found their applications in a variety of fields because of their excellent physico-chemical properties and low cost as compared to conventional materials. Tensile strength, flexural strength, volume resistivity and electric strength of the composites are determined according to standard ASTM methods. The results are discussed in light of related materials.

Section-3: Water absorption study

Moisture absorption study of composites was carried out at room temperature as well as in boiling water. The composites of 5cm X 5cm were prepared and the edges of the composites were sealed with the same materials which used in composites. The Chemical resistance of the composites is tested against water, 10% each of HCl and NaCl till equilibrium was established.

Chapter - 5: Ultrasonic studies of resins

Recently ultrasonic has become the subject of extensive research because it finds applications in numerous fields of science like consumer industries, medical fields, engineering, process industries, etc.[15]

Knowledge of acoustical properties of solutions furnishes a wealth of information on molecular interactions occurring in the solutions, the nature and the strength of interactions. The density, viscosity and ultrasonic velocity measurements of EBANRA, EBANOA and EBANAA solutions in different solvents at 30°, 35° and 40° C are determined. Various acoustical parameters such as isentropic compressibility (Ke), specific acoustical impedance (Z), classical absorption coefficient (α/f^2)cl, viscous relaxation time (τ), intermolecular free path length (Lf) are determined and discussed in light of effect of solvent, temperature, concentration, etc.

CHAPTER 6: Summary

This chapter of the thesis summarizes the output of the work incorporated in the thesis.

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CHAPTER – 1

LITERATURE SURVEY

ON

MONOMERS AND RESINS
Materials have such an influence on our lives that the historical periods of humankind have been dominated and named after materials with the advent of the modern civilization and development of scientific knowledge, there has been an upsurge in demand for developing newer materials for novel applications.

Historians frequently classify the early ages of man according to the materials that he used for making his implements and other basic necessities. The well-known of these periods are the Stone Age, the Iron Age and the Bronze Age.

From the ancient civilizations of Egypt and Babylonia man was employing a range of materials such as stones, woods, ceramics, glasses, skins, horn and fibers. Until the 19th century man’s inanimate possessions, his home, his tools, his furniture, were made from varieties of these classes of materials.

During last century and a half, two new closely related classes of materials have been introduced, which have not only challenged the older materials for their well-established uses but have also made possible new products, which have helped to extend the range of activities of mankind. Without these two groups of materials, rubber and plastics, it is difficult to conceive everyday features of modern life such as the car, telephone, television set could ever be developed.

The most ancient polymeric material, mentioned in the book of ‘Genesis’ (Chapter-11) described that the builders in the “Babylonia” had a brick of stone and slime they had for mortar”.

In ancient Egypt mummies were wrapped in a cloth dipped in a solution of bitumen in oil of lavender, which was known variously as Syrian Asphalt. On exposure to light, the product hardened and became insoluble. It would appear that this process involved the action of chemical cross-linking, which in modern times became of great importance in the vulcanization of rubber and production of thermosetting plastics.

Synthetic polymers have a long history before their commercialization began. The polymer industry itself was started in the early 1800’s with the use of natural rubber for easers and rubberized fabrics. Synthetic polymers have not only challenged the conventional materials for their well established uses but
have also made possible new products, which are constantly replacing older ones. It is difficult to believe modern life without polymers.

They are highly useful in the rapidly developing fields such as space exploration, terrestrial transportation, modern communications, energy saving, environmental protection, public health, microbiology, medicine, etc.

The term polymer is derived from the Greek words “meros” meaning parts and “poly” meaning many. Thus, a polymer is a large number of subunits or building blocks linked together by covalent bonds. According to IUPAC a polymer is defined as “a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or group of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units.”

[A] LITERATURE SURVEY ON BISPHEROLS

Bisphenols are the important constituents or intermediates in dyes, drugs, paints and varnishes, coatings, pesticides, plasticizers, fertilizers, bactericides and in other applications. Bisphenols find their applications as anti-oxidants for rubbers, oil, fat, soap and carotene; and stabilizer for polyolefin and against UV radiation, and for increasing the flex life of rubbery material. They are also used as fog inhibitors in electro photography, electroplating solvent and as wash fastening agents. They are widely applied in manufacturing thermally stable polymers, epoxy resins and polyester resins.

Farbenind [1, 2] has reported the condensation of phenols and ketones in the presence of acetic acid, hydrochloric acid at 50°C and also reported the melting points of 1,1'-bis(4-hydroxy phenyl)cyclohexane (186°C), 1,1'-bis(4-hydroxy phenyl)-4-methyl-cyclohexane (179°C). The products are useful as intermediates for dyes and drugs.

Mc Greal et al [3] have reported the condensation of ketones (0.5 mole) and phenols (1.0 mole) in acetic acid. The solutions were saturated with dry HCl for 3-4h and kept the reaction mixture for varying periods up to 4 weeks until the crystallized. The yields with aliphatic and aromatic, ketones were 10-25% and with cyclic ketones 50-80%.

They have also proposed the following mechanism

1. The addition of phenol to ketone
\[ \text{PhOH} + R_2\text{CO} \rightarrow R_2\text{C(OH)}\text{C}_6\text{H}_4\text{OH} \]

2. \[ R_2\text{C(OH)}\text{-C}_6\text{H}_4\text{OH} + \text{PhOH} \rightarrow R_2\text{C(}\text{C}_6\text{H}_4\text{OH})_2 + \text{H}_2\text{O} \]

Johnson and Musell et. al [4, 5] have reported synthesis of 1,1'-bis(4-hydroxy phenyl)cyclohexane (1) using 5 moles of phenol, 1 mole of a cyclohexanone, H$_2$S or BuSH below 40°C with 0.1-0.3 mole dry HCl gave (I) m.p. 186-87°C; 2Me-I, 236-40°C; 4-Me I 178°C; 1,1'- bis(4-hydroxy-3-methyl phenyl)cyclohexane m.p. 187°C and 1,1'-bis(4-hydroxy-3-isopropyl-phenyl) cyclohexane, m.p. 109-111.5°C. Mash containing small quantities of bisphenol (I) protect chickens from coccidiosis better than does a sulfaguanidine.

Bender et al [6] have reported preparation of various bisphenols by reacting phenol, NaOH and acetone. The mixture was refluxed for 16 h and acidified to pH 2-3 with 6N HCl. The Yield was 47.5%. Similarly they have also synthesized 1,1'-bis(4-hydroxyphenyl) cyclo- hexane (m.p.187°C); 1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane (m.p.186-9°C) and 1,1'-bis(3-chloro-4-hydroxyphenyl) cyclohexane (m.p. 134-41°C).

Bender et al [7] have reported the preparation of bisphenols by irradiating a mixture of ketone and phenol at 20-100°C with β-rays or ultra violet in the presence of 37% aq. HCl or 70% aq. H₂SO₄ as condensing agent and stirring at 30-37°C. 1,1’-Bis(4-hydroxy phenyl)cyclohexane (m.p. 186-9°C) was obtained in 93% yield from 1 mole cyclohexanone and 4 moles phenol.

Farbenfabriken [8] has reported the preparation of 4, 4’-dihydroxydiphenyl cyclohexane (m.p. 186°C) using cyclohexanone (78 kg) and excess phenol (400 kg) in the presence of 38% HCl (80 kg) as a catalyst at room temperature for 6 days.

Tumerman et al. [9] have reported condensation of o-cresol with aliphatic, aromatic and cyclic ketones in the presence of HCl and BF₃ as catalysts. The highest reaction rate was observed in the case of Me₂CO and cyclohexanone. The condensation of o-cresol with pinacolone yielded 10-12% after 450 h of condensation.

Farbenfabriken [10] has reported chlorination of bisphenols by chlorine gas with stirring for 1h at 15°C in nitrogen atmosphere and steam distillation of 1,1’-bis(4,4’-dihydroxydiphenyl)cyclohexane gave 1,1’-bis(3,3’,5,5’-tetrachloro-4,4’-dihydroxy phenyl)cyclohexane (m.p. 148.5 - 9.5°C).

Bilik et al. [11] have reported the preparation of bis(3-chloro-4-hydroxy phenyl)alkanes by the reaction of bis(4-hydroxy phenyl)alkanes with SOCl₂ and a
catalyst containing or generating a SH group in chloroform or carbon tetrachloride. A mixture of 1,1’-bis(4-hydroxy phenyl)cyclohexane (7.4 g), SOCl₂ (40 ml) and Na₂S (0.28 g) in CCl₄ (40 ml) was heated with stirring for 3 h at 55°C, 1 h at 70°C yielded 63-75% 1,1’-bis(3-chloro-4-hydroxy phenyl)cyclohexane of m.p. 142.5°C (CCl₄) 82-6% 2,2’-bis(3-chloro-4-hydroxy phenyl) propane of m.p. 89-91°C (30% aq. AcH) and 100% 3,3’-bis-(3-chloro-4-hydroxy phenyl)pentane. The title compounds are used in the preparation of combustible polycarbonate, nonflammable epoxy resins and herbicides.

Maeda et al. [12] have reported that polyurethane can be stabilized by 4,4’-thiobis(6-tert-butyl-3-methyl phenyl) with 1,1’-bis(4-hydroxy phenyl) cyclohexane thermally and against UV light by adding a mixture of 4, 4’-thio bis (6-tert-butyl-3- methyl phenyl) with 1, 1’-bis (4-hydroxy phenyl)cyclohexane or 1, 1’-bis (3-methyl-4-hydroxy phenyl)cyclohexane.

Masai and Nakanishi [13] have reported that 1,1’-bis (4-hydroxy-3, 5-dialkylphenyl)cyclohexane and 1,1’-bis (4-hydroxy-3-methyl-5-tetrabutylphenyl) cyclohexane are useful as antioxidant.

Farnham et al. [14] have reported condensation of ketone with a methyl group in α-position to the CO group such as acetone, PhCOMe or cyclohexanone with an excess of phenol like phenol, o-cresol and o-chlorophenol (ratio 1.3-2.0) with a free para position at 40-100°C in the presence of an insoluble anhydrous sulfonated cation exchange resin.

Freudewald et al. [15] have reported the condensation of phenol (94 g)

with cyclohexanone (98 g) in the presence of 2.0 g EtSH and anhydrous HCl (4.7 g) and heating at 70°C in closed system for 3h to give 97% 1,1′-bis(4-hydroxy phenyl) cyclohexane.

Popova et al. [16] have reported the synthesis of monomers by condensing phenol and o-cresol with cyclohexanone to give 1,1′-bis(4-hydroxy phenyl)cyclohexane and 1,1′-bis(3-methyl-4-hydroxy phenyl) cyclohexane, respectively. These bisphenols are treated with HNO₃ in AcOH at 0°C to give 1,1′-bis(3-nitro-4-hydroxy phenyl)cyclohexane and 1,1′-bis(5-nitro-3-methyl-4-hydroxy phenyl)cyclohexane, respectively. These monomers are useful for coordination polycondensation.

Kozlov et al. [17] have reported the condensation of o-cresol with cyclohexanone in the presence of polyphosphoric acid. The optimum conditions for this condensation were 40-45°C, 70-100 wt % H₃PO₄ (72% P₂O₅), o-cresol to cyclohexanone molar ratio (3:1) for 3h; 94% 1, 1′-bis (4-hydroxy-3-methylphenyl) cyclohexane was obtained with small quantities of other isomers.

Alexandru [18] has reported the preparation of bisphenols by reaction of a ketone (cyclohexanone) with phenol, BuSH, ClCH₂CH₂Cl and Me₃SiCl. The mixture was stirred and heated to 50-55°C and finally at 65°C to give bisphenol-Z.

Nagata et al. [19] have reported condensation of 4-hydroxy cyclohexanone with PhOH in 36% HCl at 60°C for 4h to give 77% biphenyl cyclohexanol derivative. The decomposition and dehydrogenation of which in a mixture of NaOH, PhCMe: CH₂, H₂O and 5% Pd/C under N2 at 250°C for 4h gave 83% 4, 4′-bisphenol.

Subramaniam et al. [20] have reported the synthesis of 4,4'-isopropylidene bisphenyl dicinnamate, 4,4'-cyclohexylidene bisphenyl dicinnamate, 4,4'-isopropylidene bisphenyl disalicylate, 4,4'-cyclohexylidene bisphenyl disalicylate, dioxyacetic acid and dimethyl ether of bisphenol-A and bisphenol-C. They have tested the compounds for their activity against a fungi Fusarium oxysporum by filter paper disc method and reported that dimethyl ether and the dioxyacetic acid are inactive even at the highest concentration level used, whereas both the esters are active even at the minimum concentration level used.

Islam et al. [21] have reported the synthesis of tetra halogenated 4,4'-dihydroxydiphenylalkanes. The condensation of PhOH with MeCOMe, cyclohexanone, cyclopentanone and AcPh gave respective bisphenols in 66-80% yields. The condensation of o and m-cresol with ketones gave 70, 68 and 60% yields of respective bisphenols. They have also reported bromination of bisphenols by Br-AcOH in 61-70% yields. Chlorination of bisphenols by HCl in presence of H$_2$O$_2$ gave the respective tetrachlorobisphenol derivatives in 67-87% yields. The condensation of bisphenols with ClCH$_2$COOH in aqueous NaOH gave dioxyacetic acid derivatives of bisphenols in 61-75% yields.

Dietzler [22] has reported bromination of bisphenol in methanol-water system. Thus bisphenol was treated with bromine at 42$^\circ$C with stirring (4h). The mixture was kept for 2h at 40$^\circ$C yielded 94.4% 4, 4'-isopropylidene-bis (2,6-dibromophenol) (181-182$^\circ$C), 4, 4'-cyclohexylidene bis(2,6-dibromo-phenol) (m.p. 190$^\circ$C).

Rao et al. [23] have reported a convenient method for the preparation of bisphenols. Cyclohexanone was treated with phenol at 40°C and with o-cresol at room temperature in the presence of hydrochloric acid and acetic acid to give 1, 1'-bis (4-hydroxy phenyl) cyclohexane and 1, 1'-bis (3-methyl-4-hydroxy phenyl) cyclohexane, respectively.

Garchar et al. [24, 25] have studied optimization reaction conditions for the synthesis of 1, 1'-bis (R, R'-4-hydroxy phenyl) cyclohexane by condensing cyclohexanone (0.05 mole) and phenol, o-cresol and 2, 6-dimethylphenol (0.1 mole) in the presence of varying mixture of hydrochloric acid and acetic acid (2:1 v/v) at four different temperatures: 40°, 50°, 60° and 70°C. They have reported optimum catalyst concentration (10-15 ml), time (30-90 min) and temperature (55-70°C) for obtaining yields greater than 80%. They have also synthesized chloro, bromo and nitro derivatives and screened for their potential antimicrobial and antifungal activities against microbes. Some of these compounds are significantly found active against B. subtilis, S. pyogens and A. niger. The nitro compounds are found to be the most active as antifungal agents.

[B] LITERATURE SURVEY ON EPOXY AND PHENOLIC RESINS, EPOXY ESTER (POLY ESTER POLYOLS) AND THEIR HYBRID COMPOSITES

Epoxy and phenolic resins are the most versatile class of contemporary plastics. Due to tendency of undergoing variety of chemical reactions, both resins 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 [26]. Epoxy is best for laminates in combination with glass fiber to achieve excellent electrical insulators, while phenolics are best with wood based cheap composites due to excellent adhesion with cellulosic materials. Excellent chemical and corrosion resistance, thermal and dimensional stability, superior mechanical and electrical properties, together with the ease of handling and processability, have made epoxy resins highly useful as surface coatings, and structural adhesive [27–30]. Use of epoxy resins in composite matrix in high technology areas is limited, as these areas require material with inherent low

thermal expansion coefficients and high toughness [31,32] 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. Urea-formaldehyde and silicon resins have been reported to have excellent properties as modifiers for the epoxy resins. The first commercial attempts to prepare resins from epichlorohydrin were made in 1927 in the United States. Credit for the first synthesis of bisphenol-A-based epoxy resins is shared by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee of the United States in 1936. Dr. Castan's work was licensed by Ciba, Ltd. of Switzerland, which went on to become one of the three major epoxy resin producers worldwide. Ciba's epoxy business was spun off and later sold in the late 1990s and is now the advanced materials business unit of Huntsman Corporation of the United States. Dr. Greenlee's work was for the firm of Devoe-Reynolds of the United States. Devoe-Reynolds, which was active in the early days of the epoxy resin industry, was sold to Shell Chemical (now Hexion, formerly Resolution Polymers and others).

Phenol formaldehyde condensation polymers often referred as phenolic resins, were the first true synthetic polymers to gain commercial acceptance. They have maintained a prominent position in the polymer market to the present time. About 70% of all the thermosetting polymers produced are made up of phenol, urea and melamine-formaldehyde polymers, with phenolics enjoying the lion's share. The ability of formaldehyde to form resinous substance had been observed by chemists in the second half of the 19th century. In 1859 Butlerov described formaldehyde polymers, while in 1872 Adolf Bayer reported that phenol and aldehyde react to give resinous substances.


In 1899 Arthur Smith took out British patent 16274, on phenol–aldehyde reaction. In due course Leo Hendrik Baekeland discovered techniques of controlling and modifying the reaction that useful products could be made. The first of his 119 patents on phenol–formaldehyde plastics was taken out in 1907 and in 1910; the general Bakelite Company was formed in United States. Within a very few years the material had been established in many fields, particular for electrical insulation. The initial phenol-formaldehyde products may be of two types, novolacs and resoles. Phenolic resin chemistry has been discussed in detail elsevier [33-37].

(1)

Novolacs
The novolacs are prepared by reacting phenol with formaldehyde in a molar ratio of approximately 1:0.8 under acidic conditions. Under these conditions there is a slow reaction of the two reactants to form the o- and p-hydroxymethyl phenols. These materials will then slowly react with further formaldehyde to form their own methylol derivatives, which in turn rapidly react with further phenol to produce higher polynuclear phenols. The novolacs are sometime referred as two stage

resins as it is necessary to add some curing agents that will enable additional methylene bridge to be formed.

**Resoles**

A resole is produced by reaction of phenol with an excess of formaldehyde under basic conditions. In this case, the formation of phenol-alcohols is rapid but their subsequent condensation is slow. Thus, there is a tendency for polyalcohols, as well as mono alcohols, to be formed. The resulting polynuclear polyalcohols are of low molecular weight, while a solid resole may have only three to four benzene rings per molecule. Heating of these resins will result in cross-linking via the uncondensed methyol groups or by some complex mechanism. It is also called as one stage resin. Phenolic resins are well known for two major applications in molding and laminates. They are also applied in other applications.

Cast phenolic resins are important plastic material. Self extinguishing phenolic resin foams are developed recently but are more expensive than well expanded polystyrene. Other commercially practiced phenol formaldehyde resins are ‘fiber-resin performs moldings’, which provides characteristics of molded powder and laminates. Such perform moldings are particularly useful in carrying containers, protective covers, television receiver backs, molded suitcases and in computer parts. Phenolic resins are useful in surface coating materials and in adhesive preparation. They are also applied to impregnate wood and metal coil to give a rigid, heat and water resistance structure.

Today’s technology of epoxy resins had started only by late 1930’s and early 1940s, when a number of patents were applied simultaneously in U.S.A. and Europe. Special mention may be made of the work carried out by Dr. Castan
of Switzerland and Dr. Sylvan Greenlee of the United States simultaneously around the year 1938, who had patented the first epoxy resin out of reaction of epichlorohydrin and bisphenol-A.

![Chemical structure of epoxy resin](image)

Various types of epoxy resins have been produced: glycidyl ethers, glycidylamines, linear aliphatics and cycloaliphatics. However, epoxy resin, which is a reaction product of epichlorohydrin and bisphenol-A, is most commonly used epoxy resin today, known as diglycidyl ether of bisphenol-A (DGEBA) (III).

The resin can be obtained with different degrees of polymerization ranging from low viscosity liquids to high melting solids [38] as shown in Table 1.1. In order to prepare high molecular weight resin and to avoid contamination the epoxy resin can be prepared by two-stage process. This involves first the preparation of lower molecular weight polymers with a degree of polymerization of about three and then reacted with bisphenols-A in the presence of a suitable polymerization catalyst such that the reaction takes place without evolution of by product [39].

The epoxide resins of the glycidyl ether are usually characterized by six parameters:

- Resin viscosity (of liquid resin)
- Epoxide equivalent
- Hydroxyl equivalent
- Average molecular weight
- Melting point (of solid resin)
- Heat distortion temperature (of cured resin)
The epoxy resin can be converted into three dimensional infusible networks together by covalent bonds. This conversion from a liquid or a friable brittle solid into tough cross-linked polymer is called curing or hardening in epoxy technology. Mainly amine hardening and acid hardening systems are employed for curing of epoxy resins.

Epoxy resins are widely used for land, marine and space transportation, automobile and electrical components, rehabilitations products and pollution control equipments. The characteristic properties of epoxy resins make them suitable for an increasing number of engineering applications, such as high strength and stiffness, good dielectric behavior, resistance to chemicals, low shrinkage during cure, etc. Despite of excellent properties their brittle behavior with low elongation restricts their use for high performance applications [40].

Chemie Produkte [41] has reported the sealing composition for pipe joints and building materials. A typical composition consists of a mixture of an epoxy resin, a hardener and tar, which polymerized rapidly.

Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes [42], acrylates, etc. This modification of epoxy resin is feasible due to highly reactive epoxy ring, which

Table – 1.1: Effect of reactant ratios on molecular weight

<table>
<thead>
<tr>
<th>Mole ratio of epichlorohydrin/ bisphenol-A</th>
<th>Softening point (°C)</th>
<th>Molecular Weight</th>
<th>Epoxide equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>43</td>
<td>451</td>
<td>314</td>
</tr>
<tr>
<td>1.4</td>
<td>84</td>
<td>791</td>
<td>592</td>
</tr>
<tr>
<td>1.33</td>
<td>90</td>
<td>802</td>
<td>730</td>
</tr>
<tr>
<td>1.25</td>
<td>100</td>
<td>1133</td>
<td>862</td>
</tr>
<tr>
<td>1.2</td>
<td>112</td>
<td>1420</td>
<td>1176</td>
</tr>
</tbody>
</table>
can also undergo ring opening reaction in the presence of acids [43] to yield polyester polyol containing a free hydroxyl group that can be utilized to produce polyurethanes. To make an economic production of polyurethanes, efforts have been made to prepare polyester polyols from the low cost natural oils and their derivatives.

All the vegetable oil fatty acids are used for polyester polyols (epoxy esters) manufacturing but the most commonly used are listed Table-1.2 with their specific properties they confer on the polyester polyol (epoxy esters). Polyester polyol is more effective than polyether polyol in the production of polyurethane.

The commercial interest in epoxide resins was first made apparent by the publication of German patent 6,76,117 by I. G. Farben in 1939, which described liquid poly epoxides. In 1943 P. Casten filed US patent 23,24,483 covering the curing of the resins with dibasic acids. The Ciba Company subsequently exploited this important process. A later patent of Casten (US patent 24,44,333) covered the hardening of epoxide resins with alkaline catalyst used in the range 0.1–5 %.

The early stage of their development, epoxy resins were used almost entirely for surface coating. The developments in this field are due to the research work of S. O. Greenlee and described in a number of patents. These include work on the modification of epoxy resins with glycerol, the esterification with drying oil acids and reaction with phenolic and amino resins.

Wolfram and Jhan [44] have prepared phenolic composition, which is suitable for molding compositions. They have proposed the formation of resinous condensation product by reacting phenol or cresol with CH₂O in the presence of strong acid or base as a catalyst.

Table-1.2 Fatty acids and properties of epoxy esters

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Epoxy ester properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linseed</td>
<td>Fast air drying system with poor color retention</td>
</tr>
<tr>
<td>DCO</td>
<td>Fast air-drying or stoving system with good flexibility and chemical resistance.</td>
</tr>
<tr>
<td>Soya been</td>
<td>Air-drying systems with good color and soft flexibility films.</td>
</tr>
<tr>
<td>Coconut</td>
<td>Non-air drying system with very good color, chemical resistance and flexibility, good color on oven backing.</td>
</tr>
</tbody>
</table>
Greenlee [45] has prepared the rapid drying composition from diphenols and epichlorohydrin and esterified this product with Tall–oil. Chemie produkte [46] has reported the sealing composition for pipe joints and building materials. A typical composition consists of a mixture of an epoxy resin, a hardener and tar, which polymerized rapidly.

Lederman [47] has reported varnish based on bisphenols. A wrinkle varnish or base comprising a blend of tung-oil varnish and fish-oil varnish is described. It gives a fine texture wrinkle finish, good toughness and flexibility.

Petri et al. [48] have prepared epoxy resin foams from aqueous dispersions. Epoxy resin based on bisphenol-A, benzsulfohydrazide, dipropylene triamine were dispersed in water by 2,3-dibromopropyl phosphate as a dispersing medium. Rigid foam was obtained by this composition, which is suitable for architectural uses.

CIBA Ltd. [49] has reported coating composition for floors, roofs, walks and walls based on bisphenol–A epoxy resin. The composition was room temperature hardenable having quartz sand, epoxy resin, dibutyl phthalate together with triethylene tetramine. This composition has consistency of mortar and a pot life of 2.0 – 2.5h. It is spread on a concrete floor to a depth of 4mm. Hardening required 24-48h. The composition shows excellent adhesion in non-cracking and is highly resistance to chemical.

Union Carbide Co. [50] has reported curing of polyepoxides with liquid glycol diamines \( (\text{H}_2\text{N}(\text{CH}_2)_3\text{O}(\text{C}_n\text{H}_{2n}\text{O})_x \text{ (CH}_2)_3\text{NH}_2)(I) \), where \( n \) is 2-5 and \( x \) is 1-11. The cured compounds have excellent impact strength and flexibility and are stable as protective coatings. Thus, 100 g of diglycidyl ether of 2,2'-bis(p-hydroxy-phenyl) propane was mixed with 29.4 g stoichiometric amount of \( \text{H}_2\text{N} \text{(CH}_2)_3\text{O CH}_2\text{CH}_2\text{O}_2 \text{(CH}_2)_3\text{NH}_2 \) for 5 min. The mixture was applied on cold-rolled steel and was cured by storing 7 days at room temperature.

Minnesta Mining and Manufacturing Co. [51] have reported synthesis of flexible adhesive film having honeycomb structure. Thus, an epoxy resin mixture (I) was prepared by heating 100 parts of glycidyl ether of bisphenol – A at 121°C, adding 2-parts fine \( \text{SiO}_2 \) and stirring at 149°C for 10-20 min. A mixture of 145 parts isophthaloyl dihydrazide, 10 parts \( \text{MgO} \) and 1 part dimethyl diocta decyl ammonium bentonite was added to epoxy mixture at 104°C and the resulting mixture was milled at 77°C to complete dispersion.

Bremmer [52] has synthesized flame-retardant epoxy resin. In a typical composition tetra bromo bisphenol-A was added to bisphenol-A-diglycidyl ether (epoxide equivalent 186) at 70°C under an \( \text{N}_2 \) atmosphere with stirring. The composition was cured by triethyl amine.

Karl [53] has reported phenol-HCHO resins for building materials. A typical material composed of phenol-HCHO resin pre condensate, acid hardener, an ethylene glycol, \( \text{BuOH} \) or terpineol ester, mineral fillers [such as \( \text{CaO} \), \( \text{Ca(OH)}_2 \), \( \text{CaSO}_4 \) or \( \text{Ca(CO}_3)_2 \) and an additive such as sand were suitable for use as building material.

Taft [54] has reported new polymeric coating agents with improved properties. Such composition consists of a reaction product of hydroxy or epoxy containing compound capped with the bisphenol acid, 4-4’-bis (4-hydroxy phenyl) valeric acid (I) with a poly isocyanate and cross linked with an amine. Thus (I) reacts with 1,6-hexane diol and the reaction product was treated with Mondur HC (Poly isocyanate) to give a composition, which was sprayed to a 10-75 μ thick film on glass, metal or wood and cured for 5-15 sec in triethylamine.

\[
\begin{align*}
\text{HO} & \quad \text{C} & \quad \text{HOOC} & \quad \text{CH}_2 \\
\text{Me} & & & \\
\end{align*}
\]

(I)

Kogyo [55] has formulated epoxy resin composition hardened by phenol-polyamine-aldehyde reaction products at low temperature i.e. 10-15°C.

\[
\begin{align*}
\text{NH}_2 & \quad \text{CH}_2 & \quad \text{NH} & \quad \text{CH}_2 & \quad \text{NH} & \quad \text{CH}_2 & \quad \text{NH}_2 \\
\text{CH}_2 & \quad \text{NH} & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{NH}_2 \\
\end{align*}
\]

(I)

On heating 200g (I) and 50 g nonyl phenol for 1h at 66°C gave the blocked curing agent. A mixture of this compound, bisphenol-A-epichlorohydrin copolymer (epoxy equivalent ~190) and 2, 2-bis (o-hydroxy phenyl) propane-propylene oxide copolymer epoxide equivalent ~ 345) were cooked together. The composition has self-life of about 4 h and 70 min at 0°C.


Castan and Gandillon [56] have reported esterified epoxy resin of phenol formaldehyde with long chain fatty acids, which may be unsaturated, and dehydration is affected with acid catalyst to produce rapid drying films. Co or Pb naphthenate were also used. The resulting films are relatively resistant to alkali. The use of saturated acids in the esterification step gives resins, which can be hardened in the kiln.

Devoe and Raynolds Co. Inc. [57] has reported coatings of polyepoxy resin and dimeric fatty acids. Aliphatic polyepoxides or dihydric phenol react at 150º with dimeric unsaturated fatty acids, especially dilinoleic acid so that all carboxylic groups react only with epoxy groups to give high molecular weight linear polyether-polyester resins with epoxy end group for each carboxylic group > 1 but < 2 epoxy groups are used. Such resins give coatings after backing in the presence of amine catalysts and optically together with phenol or urea HCHO resins.

Kinck and Ditrych [58] had synthesized epoxy resin ester of Dian 1, epichlorohydrin 1.16, and NaOH 1.25 moles in organic solvents at 80-100º until the softening point was 100ºC. The resin obtained had an ester equivalent of 180 content of epoxy groups 0.11 mole / 100 g, and no. of OH groups 0.33 mole /100 g. Fatty acid (1600 parts) isolated from a soyabean oil was treated with 400 parts dicyclopentadiene at 280ºC during 3h. Volatile and unreacted components were distilled in vacuum. The prepared resin (900 parts) was mixed in a stainless steel vessel with the prepared acids (950 parts) and heated to 140ºC, and stirred under CO2. When the mixture was homogenized, the product was heated to 230ºC during 2 h and kept at the temperature until the acid no was 10 mg KOH /g, then the mixture was cooled to 170ºC and dissolved in a 1:1 mixture of xylene and ligronine to form a varnish containing 30% of dry substances. The hot

57. Devoe and Raynolds Co. Inc. (by John E. Masters), Ger. 1,130, 598 (1953); C.A., 57, 12,660, (1962).
varnish was filtered and used as an air drying varnish after adding 0.05% Co-naphthenate.

Nemours & Co. [59] has reported salt spray resistant coating composition of alkyd resin, drying oil (soyabean oil), and liquid epoxy resin (condensation) product of epichlorohydrin and diphenyl isoporpane. These compositions exhibit good adhesion and corrosion resistance under topcoats of acrylic enamel.

Shimizu et al. [60] have esterified epoxy resins with higher fatty acids like dehydrated linseed oil fatty acid in the presence of alkali metal salt catalyst and xylene for 8 h at 230 – 240°C under nitrogen atmosphere to give polyester with Q Gardner viscosity (as a 50% xylene solution).

Neumann and Hoenel [61] have prepared epoxy resins based on bisphenols useful in adhesive, coating, molded articles, where a part of bisphenols compounds are modified at the aromatic rings with an aryl alkyl group. For example bisphenol-F and styrene were reacted in presence of catalyst at 120°C, and equivalent weight 670-690 g/mol and viscosity at 25°C in 40% butyl diglycol solutions 480-510 mPas.

Nakahara et al. [62] have developed new type of epoxy resin containing a 4, 4'-biphenylene moiety in the backbone (Bis-EBP) and confirmed its structure by elemental analyses, infrared spectroscopy and 1H-nuclear magnetic resonance spectroscopy (NMR). In addition, to evaluate the influence of the

60. Shimizu, Shigeo; Tachibana, Akihiro; Aritomi, Michio; Mori, Akitshi; Suzuki, Tsotoma (Toko Chemical Industry Co., Ltd) Japan Kokai, 4,90,14,600 (1974); C.A. 81, 1,53,510, (1974).
4, 4'-biphenylene group in the structure, an epoxy resin having a 1,4-phenylene group in place of the 4,4'-biphenylene moiety (Bis-EP) was synthesized. The cured polymer obtained through the curing reaction between the new biphenyl-containing epoxy resin and phenol novolac was used for making a comparison of its thermal and physical properties with those obtained from Bis-EP and bisphenol-A (4,4'-isopropylidenediphenyl)-type epoxy resin (Bis-EA). The cured polymer obtained from Bis-EBP showed markedly higher fracture toughness of 1.32 MPa, higher glass transition temperature, lower moisture absorption, and higher thermal decomposition temperature.

Liu et al. [63] have prepared simultaneous interpenetrating polymer networks (IPNs) based on epoxy (diglycidyl ether of bisphenol-A) and unsaturated polyester resin (UP) using m-xylene diamine and benzoyl peroxide as curing agents. A single glass transition temperature for each IPN was observed with differential scanning calorimetry (DSC), which suggested good compatibility of epoxy and UP. This compatibility was further confirmed by the single damping peak of the rheometric dynamic spectroscopy. Curing behaviors were studied with dynamic differential scanning calorimetry and the curing rates were measured with a Brookfield RTV viscometer. It was noted that an interlock between the two growing networks did exist and led to a retarded viscosity increase. However, the hydroxyl end groups in UP catalyzed the curing reaction of epoxy; in some IPNs where the hydroxyl concentration was high enough, such catalytic effect predominated the network interlock effect, leading to fast viscosity increase. In addition, the entanglement of the two interlocked networks played an important role in cracking energy absorption and reflected in a toughness improvement.

Sanariya et al. [64] have reported a convenient method for the preparation of epoxy resins based on bisphenols-C. The epoxy resins of bisphenols-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mol in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was 75-80%.

Kagathara et al. [65] have reported a convenient method for the preparation of epoxy resins based on halogenated bisphenols-C. The epoxy resins of bisphenols-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mol in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was 75-80%.

Liu et al. [66] have reported combination of epoxy and novolac resins. In a typical study, a novel phosphorus-containing Ar-alkyl novolac (Ar-DoPo-N) was prepared. The Ar-DoPo-N blended with novolac and used as a curing agent for o-cresol formaldehyde novolac epoxy, resulting in cured epoxy resins with

various phosphorus contents. The epoxy resins exhibited high glass-transition temperatures (159-176°C), good thermal stability (>320°C).

Vikram Sarabhai Space Center [67] has reported phenolic resin prepared by treating HCHO with bisphenol / cardanol mixture in the presence of basic catalyst.

Aoki et al. [68] have reported the wood reinforced decorative molding board. In a typical formulation, wood was impregnated with an unsaturated polyester resin to prepare composites. Thus, a spruce veneer was immersed in unsaturated polyester containing 40% styrene and 1% benzoyl peroxide for 24 h to 95% pick-up of solution and 10 such veneers were laminated at 115°C and 3 Kg/cm² pressure under hydraulic press.

Joseph et al. [69] have developed composite boards from rice husk by coating and mixing the raw husks with water dispersible resin prepared by 1-step condensation of cardanol or cashew nut shell liquid with phenol formaldehyde using alkali as a catalyst. Coated husks were placed between hot pressing mats at 160-220°C. Thus, 8 Kg husk was sprayed coated with 1.6 Kg resin binder.

Li et al. [70] have studied properties of sisal fiber and its composites. They have modified the surface morphology of fibers by coupling agents such as N-substituted methacrylic acid, gamma-methacryloxy propyl trimethoxy silane, neopentyl (diallyl) oxy, tri (dioctyl) pyrophosphate titanate and neopentyl (diallyl) oxy triacryl zirconate. Composites were fabricated using modified fibers with polyester, epoxy, polyethylene, etc. both mechanical and moisture absorption.

resistance properties can be improved. They have also studied dynamic mechanical, electrical and ageing properties. They concluded that the modified sisal fiber reinforced composites are result of their good mechanical, environmental and economical properties.

Singh et al. [71] have fabricated jute fiber reinforced phenolic composites for the study of durability and degradation due to outdoor exposure. The physical and mechanical properties of jute composites have been studied under various conditions (humidity, hydrothermal and weathering). The ageing induced deterioration effect of their conditions on the dimensional stability, surface topology and mechanical properties of the composite was observed.

Joffe et al. [72] have studied the composites based on flex as a reinforcing fiber. They have fabricated natural fiber composites (NFC) and compared their mechanical properties with glass mat thermoplastics (GMT). The investigation showed that NFC have mechanical properties such as matrix/fiber compatibility, stiffness, strength and fracture toughness are as high as GMT or even higher in some cases. They have concluded that such a good mechanical properties in combination with lightweight makes use of NFC very attractive for automotive industries.

Biswas et al. [73] have described the importance of natural fibers for composite manufacturing. They have discussed the fabrication of jute-coir, jute-glass, jute-polyester composites, bamboo-mat veneered rice husk board and the use of cashew nut shell liquid as natural resin for biodegradable composites. The physical properties of composites were also measured.

LITERATURE SURVEY ON POLYURETHANE RESINS AND THEIR COMPOSITES

Polyurethanes (PUs) are known to be very attractive materials for various applications such as electrical/electronic potting and encapsulation, constructions, water proofing membranes, asphalt extended membranes, highway sealants, sound and vibration damping, automotive and rubber parts, etc. Due to their unique property, they offer the elasticity of rubber combined with the toughness and durability of plastics. Polyurethanes form an important class of polymers, whose structures and performances can be designed to meet the user’s needs. Polyurethane resins are mainly produced by isocyanation of diisocyanate with polydiols of various molecular weights or other reactants containing hydrogen donors that are reactive with isocyanates.

\[
\begin{align*}
O &\equiv C\equiv N \quad R' \quad N \equiv C\equiv O + \quad HO - C_2H_4O \quad \rightarrow \\
&\downarrow \\
\left[\begin{array}{c}
C\equiv N \quad R' \quad N \equiv C\equiv O + \quad C_2H_4O \\
\bigg| \quad \bigg| \\
H &\quad H &\quad O
\end{array}\right]_{m}
\end{align*}
\]

A urethane is essentially an ester of carbamic acid or substituted carbamic acid. The main advantage of polyurethane is that it can be tailor made to meet the diversified demands of modern technologies such as coatings, adhesives, foams, rubbers, reaction molding plastics, thermoplastic elastomers and composites. The pioneering work on polyurethane polymers was conducted by Otto Bayer and his coworkers in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany[74]. They recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities, especially when compared to already existing plastics that were made by polymerizing olefins, or by polycondensation. The new monomer combination also circumvented existing patents obtained by Wallace Carothers on polyesters [75].

Initially, work focused on the production of fibres and flexible foams. With development constrained by World War II (when PUs were applied on a limited scale as aircraft coating), it was not until 1952 that polyisocyanates became commercially available. Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams (initially called imitation swiss cheese by the inventors[2]) was thanks to water accidentally introduced in the reaction mix. These materials were also used to produce rigid foams, gum rubber, and elastomers. Linear fibres were produced from hexamethylene diisocyanate (HDI) and 1,4-butanediol (BDO).

In 1969, Bayer AG exhibited a plastic car in Dusseldorf, Germany. Parts of this car were manufactured using a new process called RIM, Reaction Injection Molding. RIM technology uses high-pressure impingement of liquid components followed by the rapid flow of the reaction mixture into a mold cavity. Large parts, such as automotive fascia and body panels, can be molded in this manner. Polyurethane RIM evolved into a number of different products and processes.

The history of polyurethane can be traced back to the 1930s in the World War II, when Germany was looking for the synthetic material for tyre. Bayer made aromatic diisocyanate in 1930 and he produced the first polyurethane in 1937 by reacting hexamethylene diisocyanate (HMDI) with 1, 4–butane diol(BDO).

\[
\begin{align*}
OCN—C_6H_{12}—NCO + HO—C_4H_8—OH
\end{align*}
\]
\[
\begin{align*}
\text{HMDI} & \quad 1, 4\text{-butane diol} \\
\begin{array}{c}
\text{C}—N—C_6H_{12}—N\text{C—O—C}_4H_8—O
\end{array} \\
\begin{array}{c}
\text{O—H} \quad \\
\text{H—O}
\end{array} \\
\text{[}]_n
\end{align*}
\]

During the late 1940s Dupont and Monsanto Company began supplying 2, 4-toluene diisocyanate (TDI) in pilot plant quantities. In 1950-1952 Farben Fabriken Bayer disclosed the development process of polyurethanes elastomers.
and of flexible foams based on polyesters, and shortly thereafter they came into commercial production.

Full scale commercial isocyanate manufacture began in the United States during 1954-55. The primary use for toluene diisocyanate was in flexible foam based on polyesters; the flexible foam obtained from these products, however, had two major drawbacks, high cost and poor hydrolysis resistance, which limited its commercial growth. In 1957, based on ethylene oxide and propylene oxide were introduced commercially into the polyurethane industry. These polyols lower the cost and improve the hydrolysis resistance of the products. Initially flexible foam prepared from the poly (alkylene oxide) was prepared through a "prepolymer" technique by which a prepolymer was formed from polyether and diisocyanate, and then catalyst, water and stabilizers were added to produce foam. First in 1958, “One-shot" foaming was developed in which polyether, diisocyanate, water, catalyst and foam stabilizers were mixed in one step.

Polyurethane (or polyisocyanate) resins are produced by the reaction of a diisocyanate with a compound containing at least two active hydrogen atoms, such as diol or diamine. Toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) and hexamethylene diisocyanate (HMDI) are frequently employed. They are prepared by the reaction of phosgene with the corresponding diamines.

\[
\begin{align*}
CH_3 & \quad NH_2 \\
NH_2 & \quad + \quad 2 \text{ClCOCI} \\
& \quad \text{Phosgene} \\
\end{align*}
\]

2, 4-Diamino-toluene

\[
\begin{align*}
CH_3 & \quad NCO \\
NCO & \quad + \quad 4\text{HCl} \\
\end{align*}
\]

2,4-Toluene diisocyanate

Aliphatic and aromatic isocyanates are the two classes of isocyanates used in the polyurethane coatings. The most commonly used isocyanates or the production of polyurethanes are listed in Table-1.3. The other component in the production of polyurethane is polyol. Polyols are hydroxyl terminated polyesters, polyethers, acrylic polyols and polyols based on natural oils.
Polyesters

Polyester resins are unsaturated resins formed by the reaction of dibasic organic acids and polyhydric alcohols. Among other uses, it is the basic component of sheet moulding compound and bulk moulding compound. Unsaturated polyesters are condensation polymers formed by the reaction of polyols (also known as polyhydric alcohols, organic compounds with multiple alcohol or hydroxy functional groups) and polycarboxylic that contain double bonds. Typical polyols used are glycols such as ethylene glycol. The usual polycarboxylic acids used are phthalic acid and maleic acid. Water, which is a by-product of this esterification reaction, is removed from the reaction mass as soon as it is formed to drive the reaction to completion.

Polyester resins are produced by different reactions such as the esterification of acids or alcohololysis or acidolysis of epoxies, etc. The wide selection of raw materials available allows a very large choice of finished products, with a wide range of properties. Polyester polyols are obtained by using a stoichiometric excess of di- or polyfunctional alcohols over the acid monomers during manufacture, which produces polyester backbones with hydroxyl reactive groups. The selection of raw materials and conditions of polymerization will produce polyesters with primary or secondary hydroxyl groups. The position of these groups will have a strong effect on the final properties of the polyurethane, especially reactivity.

Polyester resin is used for casting, auto body repair, wood filling, and as an adhesive. It has good wear and adhesive properties, and can be used to repair and bond together many different types of materials. Polyester resin has good longevity, fair UV resistance, and good resistance to water. It is important to recognize that all polyester resin products are not created equal; their chemical makeup is complex and can have a wide range of properties. As filler in auto repair, for example, this material is formulated for superior adhesion to paints and metals.
### Table-1.3: The common diisocyanates used for the production of polyurethanes

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Chemical Name</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene-2,4-diisocyanate</td>
<td>TDI</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>2</td>
<td>Hexamethylene diisocyanate</td>
<td>HMDI</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>3</td>
<td>Isophorone diisocyanate</td>
<td>IPDI</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>4</td>
<td>4,4’-Methylene bis phenylene diisocyanates</td>
<td>MDI</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>5</td>
<td>Cyclohexane-1,4-diisocyanate</td>
<td>CHDI</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>6</td>
<td>p-Phenylene-1,4-diisocyanate</td>
<td>PPDI</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
</tbody>
</table>
Polyethers

Hydroxylated polyethers are generally obtained by a polymerization of ethylene oxide, propylene oxide or even opening and then polymerization of tetrahydrofuran. The low viscosity of polyether resins (due to the absence of hydrogen bonding on the resin backbone and to their low molecular weight) is also an advantage in the production of solvent free formulations. The main advantage of polyether resins is their low cost due to the large availability of the raw materials used in their manufacture. The polyether polyol based polyurethanes are widely used to prepare rigid and flexible polyurethane foams, industrial flooring and underbody sealers for the automotive industry.

Acrylic resins

They are derived from acrylic or methacrylic acid or their esters polymerized by an addition reaction in the presence of initiators. Depending upon the monomers and process used to combine them, polymers with different properties can be obtained.

Other products with reactive hydroxyl groups

Epoxy resin possessing the secondary hydroxyl groups can be used as polyols. Special silicone resins are especially suitable for the heat stable PU coatings. Vinyl polymers alone or in combination with other polyols can be effectively used as polyols. Also the vegetable or plant oils such as castor oil, linseed oil, tall oil, etc. can be used as polyols. Coal tar contains numerous groups with active hydrogen so it can also be used as polyols.

The urethane reaction is catalyzed in a strict technical sense, i.e. the catalysts increase the rate of reaction without themselves being consumed. The most commonly used catalysts are organo tin compound for example dibutyl tindilaurate (DBTDL) and tertiary amines for example 1,4-diazobicyclo(2,2,2)-octane (DABCO), and tetramethyl butane diamine (TMBDA).

Polyurethane resins are characterized by a segmented structure, consisting of flexible segment, the polyol chains, and hard segments, crystallizability of segment, segmental length, intra and inter segment interactions such as H-bonding, overall compositions and molecular weight.
Polyurethanes possess a unique combination of performance and application properties with excellent abrasion resistance, flexibility, hardness, chemical resistance, UV light resistance and anti-microbial characteristics [76]. A great number of factors, which affect or influence the properties of polyurethane resins, are nature of polyol and diisocyanate, crosslinking density, NCO/OH ratio, curing conditions, etc [77, 78]. Various uses of polyurethanes (US data 2000) are summarized in Table 1.4.

Over the last few decades polyurethanes are widely used as adhesive materials and have developed a reputation for reliability and high performance in many applications including footwear industry, packaging applications, plastic bonding, furniture assembly and the automotive industry. Polyurethanes are rapidly developing products of coating and paint industry because of unique combinations of performance and application properties such as excellent elasticity, high hardness, high scratch and abrasion resistance, excellent impact resistance, high water, solvents, acids and alkali resistance and resistance to degradation from light and weathering. The polyurethane coated fabrics find applications in inflatable structures, conveyer belts, protective coatings, biomaterials, etc [79, 80].

Table-1.4 Applications of polyurethane in various fields

<table>
<thead>
<tr>
<th>Application</th>
<th>Amount of polyurethane used (millions of pounds)</th>
<th>Percentage of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Building &amp; Construction</td>
<td>1,459</td>
<td>26.8</td>
</tr>
<tr>
<td>Transportation</td>
<td>1,298</td>
<td>23.8</td>
</tr>
<tr>
<td>Furniture &amp; Bedding</td>
<td>1,127</td>
<td>20.7</td>
</tr>
<tr>
<td>Appliances</td>
<td>278</td>
<td>5.1</td>
</tr>
<tr>
<td>Packaging</td>
<td>251</td>
<td>4.6</td>
</tr>
<tr>
<td>Textiles, Fibers &amp; Apparel</td>
<td>181</td>
<td>3.3</td>
</tr>
<tr>
<td>Machinery &amp; Foundry</td>
<td>178</td>
<td>3.3</td>
</tr>
<tr>
<td>Electronics</td>
<td>75</td>
<td>1.4</td>
</tr>
<tr>
<td>Footwear</td>
<td>39</td>
<td>0.7</td>
</tr>
<tr>
<td>Other uses</td>
<td>558</td>
<td>10.2</td>
</tr>
</tbody>
</table>
Polyurethanes are very appealing class of polymers for use in the biomedical field. This is because of their relatively good biocompatibility, their physical properties and the ease with which their properties can be tailored to end use. They are widely used in the development of medical devices, for tissue and blood contact such as mammary prosthesis, vascular catheters, artificial skins, vascular grafts, artificial heart diaphragms and valves. They can be biodegradable depending upon their chemical structures [81].

Recent yearshave shown a growing interest in the development of bio based products that can reduce the wide spread dependence of fossil fuels. Indeed, the inevitable depletion of petroleum resources with the attending high cost has prompted the researchers to develop polymers from cheap and renewable resources such as cheap and renewable resources such as natural oils [82]. There are number of natural oils such as castor oil, linseed oil, tung oil, etc. are available in the market but among all of them castor oil and its derivatives are widely used due to its chemical structure [83, 84].


Castor oil is a triglyceride of fatty acids, whose main constituent is ricinoleic acid, extracted from Ricinus Communis [85, 86]. Commercial castor oil consists of triglycerides that contain 90% of ricinoleic acid and 10% of non-functional acid and it has an effective functionality of 2.7. Thus, castor oil acts as a polyol, which reacts with polyfunctional isocyanates to form polyurethanes, whose properties range from rigid polymers to elastomers. Because of unique structure of castor oil, it provides better water resistance and lower viscosity as compared to the polyols. Castor oil exhibits exceptional ability in pigment wetting and penetration due to the presence of ricinoleate. The castor oil based polyurethane systems have been widely used in the telecommunication/electrical industries, coatings, adhesives and sealants.

Owing to the versatility and broad range of properties now a day polyurethanes are widely used to fabricate the composites. Composite is a material that contains at least two different components clearly separated one from another and uniformly filling its volume, produced in order of creating particular property. The properties of the composites depend on those of individual components and on their interfacial compatibility. Composites are able to meet the diverse design requirement with significant weight saving as well as high strength to weight ratio as compared to conventional materials. Some advantages of composite materials over traditional materials are:

- Tensile strength of composite is four to six times greater than that of steel or aluminium
- Improved torsional stiffness and impact properties
- Composites have greater fatigue endurance limit (up to 60% of the ultimate tensile strength)
- Composite materials are 30-45% lighter than aluminium structures designed to the same functional requirement

Lower embedded energy as compared to other structural materials like steel, aluminium

Composites have lower vibration transmission than metal

Long life offers excellent fatigue, impact, environmental resistance and reduced maintenance

Composites enjoy reduced life cycle cost as compared to metals

Improved appearance with smooth surface and wood like finish

In addition to this, composite parts can eliminate joints and fasteners providing integrated design and fabrication of complex articles. FRP’s have higher strength capabilities and less susceptible to environmental degradation in saline environment, which curtails the life of conventional structures. Additionally FRP’s have strength to weight ratio of 50 times higher than that of steel.

Patel et al. [87] have synthesized starch and non-edible oil based polyester polyols and their reaction with isocyanate adducts to form urethane coatings. The mechanical and chemical properties of the coatings are comparable with that of commercial polyester polyols based polyurethane coatings and are considerably influenced by the type of oil used with starch in polyol synthesis and amount of isocyanate i.e. NCO/OH

Mehdizadeh and Yeganeh [88] have synthesized polyurethane elastomers based on difunctional castor oil and poly(propylene glycol), 2,4-diisocyanate and 1,4-butane diol and cured using toluene diisocyanate dimmer as cross linking agent. The elastomers were characterized by conventional methods. Physical, mechanical and thermal properties of the elastomers were studied. Investigation of these properties showed that the elastomers could be tailor made in order to fulfill industrial needs.


Kendagannaswamy et al. [89] have synthesized polyurethane elastomers using castor oil, 4, 4'-methylene bis (phenyl isocyanate) (MDI) and toluene 2, 4-diisocyanate (TDI) and studied the effect of different aromatic diamines on the physico-mechanical and optical properties of polyurethane. The study showed that tensile strength and percent elongation were in the range of 13-24MPa and 76-32%, respectively. Higher tensile strength was observed for 4,4'-diamino diphenyl sulphone (DDS) than the 4,4'-diaminodiphenyl methane (DDM) chain extender. The properties imparted by the chain extenders were explained on the basis of the groups present in the diamines and changes have been interpreted by wide angle X-ray scattering data.

Kluth and Meffert [90] have synthesized polyurethane prepolymers containing oleo chemical polyols as the polyol component. The oleo chemical polyols are the ring opened products or partial ring opened products of epoxidised fatty acids triglycerides with alcohols. The use of oleo chemical polyols having residual epoxide number from 1.0 to 4.0% by weight of epoxide oxygen is preferred. The polyurethane prepolymers are particularly suitable for use in one-component or two component PU foam formulations.

Swada [91] has synthesized epoxy modified polyurethane resin for a coating comprising curing agent (B) and an epoxy modified PU resin (A), which is the byproduct of reacting a carboxyl group containing polyurethane polyol containing repeat units derived from reacting an isocyanate compound (a) and a polyol (b) with a hydroxyl carboxylic acid (c) with an epoxy compound (d) in such a proportion that the epoxy group falls in a range of 0.1 to 1 equivalent per equivalent of the carboxyl group.


Schoener et al. [92] have synthesized moisture curable polyurethane coating compositions with improved pot life. Such enhancement is accomplished by blending with said coating composition a stabilized amount of stabilizing agent from the group of a mercapto compound, a polyphenol characterized by being reactable with an isocyanate group in the presence of a tertiary amine catalyst, and mixtures thereof. The amounts of stabilizing agents ranged from about 1% to 10% by weight. The enhanced pot life is realized even in the presence of significant quantities of water.

Ashraf et al. [93] have synthesized polyurethane from linseed oil epoxy and have developed anticorrosive coatings from it. Trans hydroxylation of linseed oil epoxy was carried out in situ. It is further reacted with TDI to synthesize polyurethane. Physico-chemical characterization of the synthesized resin was carried out as per standard methods. Structural elucidation was carried out using IR and NMR spectral data. Physico-mechanical and weather resistance performance of the coated samples were also studied and found that synthesized resin showed good performance in various corrosion tests.

Mao and Li [94] have studied the damping properties of epoxy resin/PU (EP/PU) semi interpenetrating polymer networks (IPNs) by dynamic mechanical analysis (DMA) method. It showed that the semi IPNs have excellent damping properties at ordinary temperature.

The maximum value of tanδ is about 1 when the weight composition of EP/PU is 70/30. Tensile tests also indicate that the system has good tensile strength and elongation at break at this ratio. The effect of structures on the properties of semi-IPNs is discussed. Applied to the cavitation corrosion resistant coating, the semi-IPNs showed good cavitation corrosion resistance.

Opera [95] has synthesized epoxy urethane acrylate from epoxy resins, acrylic acid and 4,4’-diphenyl methane diisocyanate using two stage polymerization. The oligomer obtained was studied by IR and ¹H NMR spectroscopy. The oligomer was cured using thermal treatment. All of these materials formed transparent films used for testing. The low molecular weight oligomers can be used as solvent less coating.

Kolekar and Athawale [96] have synthesized interpenetrating networks composed of glycerol modified castor oil based polyurethane (CG-PU) and PMMA. The effects of polyol modification, change in NCO/OH ratio and PU/PMMA composition, mechanical, chemical and thermal properties of IPNs were studied. It was found that among the three IPNs synthesized from (1) unmodified castor oil PU (2) glycerol modified castor oil PU (3) glycerol modified mixture of castor and linseed oil PU and PMMA, glycerol modified PU IPNs (CG-IPN) exhibited better tensile strength and chemical resistance. The detailed study of CG-IPNs revealed that tensile strength and hardness increased, while elongation decreased with increase in NCO/OH ratio. However, an exactly reverse trend was observed with increase in PU composition in PU/PMMA IPNs. The chemical resistance and thermal properties of the IPNs were unaffected by the change in NCO/OH ratio and PU/PMMA composition.

Mahesh and Alagar [97] have prepared the inter crosslinked networks of bismaleimide modified polyurethane-epoxy systems and cured in the presence of 4,4’-diaminodiphenyl methane. The grafting of PU onto epoxy skeleton was confirmed by the IR spectral analysis. The prepared matrices were studied by mechanical, thermal and morphological studies. The results revealed that the incorporation of PU into epoxy increased the mechanical strength and decreased the glass transition temperature and thermal stability, while incorporation of chain extended bismaleimide into PU modified epoxy system increased the thermal stability and tensile and flexural properties, while decreased the impact strength and glass transition temperature. The scanning electron microscopy was carried to study the surface morphologies of the matrices.

Prabu and Alagar [98] have prepared two different inter crosslinked networks (ICN) of siliconized polyurethane-epoxy / unsaturated polyester (UP) coatings. Epoxy and unsaturated polyester resins were modified with polyurethane prepolymer and hydroxyl terminated polydimethylsiloxane (HTPDSMS) using γ-amino propyl triethoxysilane and vinyl triethoxysilane as silane crosslinker and dibutyltindilaurate as a catalyst. The coating materials were obtained in the form of tough films and characterized for their mechanical properties such as tensile strength and impact strength as per ASTM methods, while thermal stability of the ICN coatings was studied using differential thermal analysis and thermogravimetric analysis and compared with unmodified epoxy/PU systems. The results revealed that the mechanical properties was increased by the incorporation of the PU (10 wt %) and silicone (10 wt %), while the thermal stability was decreased. Whereas, the incorporation of 10% silicone into the PU modified epoxy/PU system, the thermal stability was increased due to the partial ionic nature, high energy and thermal stability of Si-O-Si linkages.

Joshi and Athawale [99] have synthesized polyurethane resins from chemoenzymatically modified castor oil and different isocyanates and studied the difference in hardness, flexibility, impact strength and chemical resistance, when the different isocyanate precursors were used. The interesterification of castor oil and linseed oil was carried out near ambient temperature using lipase as a catalyst. The resultant interesterification product (IP) was reacted with isocyanate to form polyurethane resins. Polyurethane synthesized by this method is light in color and compared to conventional ones obtained from chemically catalyzed interesterification reactions at high temperature.

Somani et al. [100] have developed high solids polyurethane coating formulation by reacting different castor oil based polyester polyols with aromatic as well as aliphatic isocyanate adducts in different NCO/OH ratios. The structure of polyurethane resins was confirmed by FTIR spectroscopy, while molecular weight between the crosslinks and solubility parameter of the samples were determined by swelling method. The polyurethane resins were coated on test panels and tested for flexibility, scratch hardness, cross-hatch adhesion, impact, pencil hardness and solvent resistance as per standards. The effect of catalyst, structure of isocyanate and flexibility of polyols on the final properties was also studied. Thermal stability of these polymers was determined by thermo gravimetric analysis (TGA).


Jayabalan and Lizymol [101] have studied the effect of crosslinker on the stability of castor oil based aliphatic polyurethane potting compounds under thermal ageing, autoclaving, gamma radiation and sterilization. Two potting compounds, the first consisting of castor oil segments and an isocyanate crosslinker, while second with the smaller castor oil segment and a polyether polyl as a crosslinker. The first potting compound undergoes degradation under sterilization conditions, while second undergoes crosslinking under sterilization. A potting compound based on polyether polyl cross linker would be more promising for hollow fibers.

Lucas et al. [102] have prepared the thermoplastic polyurethane elastomers (TPUs) by reacting difunctional isocyanates with long or short chain polyesters or ethers containing terminal hydroxyl groups. Flexible hydroxyl polymers lowered the tensile modulus and gave high elongations. Typically thermoplastic of this type did not have both high strength and high elongation by polymerizing specific cross linkable monomers, networks could be formed, which were usually clear and homogenous with broad glass transitions. Compared to the thermoplastic polyurethanes, they were stronger and give higher elongation at break. Additionally, improvement in solvent resistance was provided through cross linking.

Huang et al. [103] have prepared polyurethane elastomers from bisphenol-S derivatives and studied the structure property relationship. The effect of soft segment of diol and the effect of structure of diisocyanate on the mechanical properties were also studied. The thermal properties of polyurethane elastomers were also investigated by using DSC and TGA analyses.

Kolekar and Athawale [104] have prepared the interpenetrating polymer networks (IPNs) from modified castor oil based polyurethane and poly(methyl methacrylate). Castor oil was first subjected to interesterification with linseed oil and tung oil. The resultant IPNs were characterized for their physico-mechanical, swelling and thermal properties. The morphologies of the IPNs were studied by differential scanning electron microscopy and differential scanning calorimetry. The results revealed that mechanical properties of the castor oil polyurethane (CU) and their IPNs (C-IPNs) with those of the castor oil modified with linseed and tung oil (L-IPNs and T-IPNs, respectively) it was found that L-IPNs showed higher tensile strength, hardness and better compatibility than C-IPNs. All the IPNs showed synergistic effect in elongation and exhibited similar thermal behavior with no significant change with respect to their composition. However, castor oil polyurethane and their IPNs showed relatively higher elongation and better resistance to solvents.

Keun et al. [105] have synthesized the two component polyurethane flame retardant coatings by blending chlorine containing modified polyesters (DCAOs) and polyisocyanates and compared the various properties of these coatings with non flame retardant coatings. The DCAOs used were synthesized by the polycondensation of dichloro acetic acid, a flame retardant carboxylic acid, with 1, 4-butane diol, trimethylo propane and adipic acid. The content of dichloro acetic acid was varied in 10, 20 and 30% in polycondensation reaction. The resultant flame retardant coatings were rapid drying and possessed the pot life of 8-10h. Coatings with 30% dichloroacetic acid were not fired by the vertical burning test.

Ajitkumar et al. [106] have carried out the swelling experiments of interpenetrating networks (IPNs) of castor oil based polyurethane and unsaturated polyesters and calculated their solubility parameters. Kinetics of swelling and sorption have also been studied in chlorobenzene at 25°C. IPNs with various weight composition of PU and UPE (80:20, 50:50, 20:80) and having various crosslinking densities (NCO/OH 1.2, 1.5, 2.0) have been employed. The results revealed that, the sorption was anomalous in nature, while diffusion coefficient (D) was found to increase with both crosslinking density and UPE content, whereas sorption coefficient showed reverse trend in all the cases. From the swelling studies, the molecular weight between two crosslinks (Mc) and the number of chains per unit volume (N) and degree of crosslinking were also calculated.

Vlad et al. [107] have synthesized series of interpenetrating polymer networks (IPNs) based on castor oil, 2,4- toluene diisocyanate and various amounts of polydimethylsiloxane-\(\alpha,\omega\)-diol (PDMS). The IPNs were characterized by means of DSC, TEM, TGA, \(^1\)H NMR and IR spectroscopies. All the IPNs exhibited phase separation and maximum extent at the point of phase inversion.

Jimenez et al. [108] have studied the effect of soft segment structure and molecular weight on the microphase separation in segmented polyurethane (SPU) by means of DSC, small-angle X-ray scattering, dielectric constant


measurements, pulsed nuclear magnetic resonance and thermoluminescence. Possible changes in the structural properties of SPU after cyclic mechanical fatigue were monitored using the same technique described as above. Samples were divided into two series according to their soft segment structure, i.e. one is linear poly (tetramethylene glycol) (PTMG) and another with methyl group on the PTMG chain. Hard segment consisted of 4, 4’-diphenyl methane diisocyanate (MDI) and 1, 4-butane diol as chain extender in both the sets. It was found that the phase separation increased for both types of SPU as the soft segment molecular weight increased. Samples with methyl group showed little soft segment crystallization. Upon fatigue, samples with methyl group showed a better fatigue resistance.

Chen et al. [109] have synthesized two parts adhesive having superior strength at cryogenic temperatures, which contains a urethane resin composition part and a hardner part. The urethane resin composition part comprises 50-99% by weight of a modified polyurethane prepolymer having an epoxy group at each of its respective end and 1-50% by weight of a modified urethane compound having substantially no ether cyanate (NCO) groups and at least two epoxy groups per molecule and a molecular weight less than 800 daltons. The hardener part is a polyamine containing primary or secondary amine groups. The equivalent ratio of the amine groups of the polyamine to the epoxy groups of the urethane resin composition part is 0.5-2.0.

Desai et al. [110] have synthesized polyester polyols using vegetable oil fatty acids having different characteristics (mainly in terms of hydroxyl functionality) and epoxy resin, using triethyl amine as a catalyst. Polyols were characterized by FTIR spectroscopy.


PU adhesives were synthesized from it and used in bonding the rubber. Treatment of sulphuric acid on the non-polar styrene-butadiene rubber (SBR) surface was studied for the bond strength improvement via an increase in wettability of the rubber surface. Wettability was found by measuring the contact angle using Goniometer. Bond strength was evaluated by 1800 T-peel strength test. The surface modification and mode of bond failure were studied by scanning electron microscopy (SEM).

Somani et al. [111] have synthesized polyurethane adhesives from different polyester polyols. The polyester polyols were synthesized by reacting castor oil derivatives with glycols (diols), while adhesives have been synthesized by reacting different polyester polyols with diisocyanate adducts in different NCO/OH ratios. The polyols and polyurethanes were characterized by FTIR spectroscopy. The effect of NCO/OH ratios, types of isocyanate adducts, and chain length of glycols were studied by determining wood to wood adhesion strength, i.e. by lap shear strength measurements and the change in lap shear strength after being placed in cold water, hot water, acid or alkali solutions was tested. Thermal stability of PU adhesives was determined by TGA.

Papon et al. [112] have synthesized the thermoplastic polyurethane elastomers (TPUs) of constant composition by prepolymer method and studied the influence of synthesis condition (pre polymerization and chain-extension time) on the final properties of TPUs. The TPUs were characterized by gel permeation chromatography, differential scanning calorimeter, stress-strain measurements and contact angle measurements. The adhesion properties of the


TPUs were determined by measuring the T-peel strength and found that above the threshold value the pre polymerization time influenced the final properties of the TPUs (viscosity of solutions, molecular weight, mechanical and adhesive behavior), whereas chain extension time does not. Therefore this is possible to prepare TPUs with specific properties by changing the polymerization conditions.

Papon et al. [113] have prepared thermoplastic polyurethane elastomers (TPUs) including different amounts of rosin in their composition, which is used either as an additive or as a reactant in the chain- extension step of the polymer synthesis. The properties of the materials are studied using solution viscosity measurements, size exclusion chromatography, stress controlled rheometry, differential scanning calorimetry (DSC), wide angle X-ray diffraction and contact angle measurements. Rosin as a chain extender led to increase the viscosity and molecular mass as well as improvements of rheological properties and changes in morphology. The crystalline regions are more affected (variations in the softening temperature and enthalpy) than the amorphous ones (quite constant glass transition temperature). The rosin act as actual chain extender and modified the organizations of both soft and hard segments of the polymers. The adhesive properties of the TPUs were determined by measuring the T-peel strength of the PVC/TPUs adhesive joints.

Kim et al. [114] have prepared polyurethane membranes by an immersion precipitation method. The effect of dope concentration, coagulation bath composition and the chemical structure of the polyurethane on the morphology of the membranes were studied. The degree of concentration was measured by quenching freshly formed polyurethane membranes in liquid nitrogen. A mechanism for the formation of the membrane morphology during immersion precipitation is proposed.


Bessaha et al. [115] have studied the role of prepolymer on the interfacial strength of polyurethane-based assemblies for two hydroxyl-terminated (telechelic) polybutadienes, R45M and R45HT. In this study, they showed that two main effects have to be considered: the length of the free chains, which could diffuse across the interface during the formation of the joint and the relative reactivity of the various hydroxyl groups of the chains and chain extenders with the isocyanate. The R45M chains were more efficient connectors than the R45HT chains. Migration of chain extenders and isocyanate over large distances created a thick interphase, where physical crosslinks appeared. This interphase was thicker for R45M-based polyurethane showing the role of the chain reactivity.

Pechar et al. [116] have synthesized the polyurethane networks (PUNs) using polyols derived from soybean oil, petroleum, or a blend of the two in the conjunction with diisocyanate. The soybean-based polyols (SBPs) were prepared using air oxidation, or by hydroxylating epoxidized soybean oil. Some of the networks were subjected to several solvents to determine their respective swelling behavior and solubility parameters. Sol-fractions were also determined, and DMA experiments were utilized to monitor the changes in storage modulus and tan δ with temperature for networks with sol and with the sol extracted. A linear relationship was noted between the hydroxyl number of a SBP and the glass transition temperature of its corresponding unextracted PU network within the range of hydroxyl numbers (i.e., 55-237 mg KOH/g) and glass transition temperatures (i.e., -21 to +83°C) encountered in this work. This same linear relationship was realized between the weighted hydroxyl number of soy and


petroleum-based polyol blends and the glass transition temperature of the resulting unextracted and extracted network PUs within the ranges utilized in this study (i.e., 44-57 mg KOH/g, -54-19°C).

Eren et al. [117] have synthesized simultaneous interpenetrating polymer networks (SINs) based on bromoacrylated castor oil polyurethane. In the first step, simultaneous addition of bromine and acrylate to the double bonds of castor oil was achieved. In the second step, bromoacrylated castor oil (BACO) was reacted with toluene diisocyanate (TDI), to form a prepolyurethane (BACOP). The prepolyurethanes were reacted with styrene (STY), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and 3-(acryloxy)-2-hydroxy propyl methacrylate (AHPMA) free radically, uses the acrylate functional group to prepare the simultaneous interpenetrating polymer networks (SINs). 2,2'-Azobis (isobutyronitrile) (AIBN) was used as the initiator and diethylene glycol dimethacrylate (DEGDMA) was used as the crosslinker. BACO and BACOP were characterized by IR, 1H-NMR, and 13C-NMR techniques. Synthesized polymers were characterized by their resistance to chemical reagents, thermo gravimetric analysis, and dynamic mechanical thermal analyzer (DMTA). All the polymers decomposed with 6-10% weight loss in a temperature range of 25-240°C. MMA-type SIN showed the highest Tg (126°C), while STY-type SINs showed the highest storage modulus ($8.6 \times 10^9$ Pa) at room temperature, with respect to other synthesized SINs.

Kumar et al. [118] have prepared polyethylene glycol-400 (PEG) based polyurethane (PU) and polyacrylonitrile (PAN) semi-interpenetrating polymer networks (SIPNs) (PU/PAN; 90/10, 70/30, 60/40 and 50/50) by sequential


polymerization method. The prepared SIPNs have been characterized by physico mechanical properties. The microcrystalline parameters such as crystal size ($\langle N \rangle$), lattice disorder ($g$), surface ($D_s$) and volume ($D_v$) weighted crystal size of SIPNs were estimated using wide angle X-ray scattering studies, and quantification of the polymer network has been carried out on the basis of these parameters. The microstructural parameters were established using exponential, lognormal, and reinhold asymmetric column length distribution functions and the results are compiled.

Rath et al. [119] have synthesized novel two component polyurethane sealant from hydroxy-terminated polybutadiene (HTPB) end capped with toluene diisocyanate (TDI) and polyoxypropylene triol. The 4,4'-diamino-3,3'-dichloro diphenyl methane (DADCDPM) and 4,4'-diamino-3,3'-dichloro triphenyl methane (DADCTPM) were used as chain extenders and fillers. Evaluation of mechanical properties and ageing studies indicated that the sealant possessed excellent mechanical properties and stability in different environments.

Bledzki et al. [120] have fabricated the polyurethane based composites reinforced with woven flax and jute fabrics with an evenly distributed microvoid foam structure. The influence on type of reinforcing fiber, fiber and microvoid content on the mechanical properties was studied. The investigation results for the static mechanical properties of the composites were described by approximate formulae. From the data, it was found that increasing fiber contents includes an increase in the shear modulus and impact strength, while increasing the microvoid content in the matrix results in decreased shear modulus and impact strength. The woven flax fibers result in composites with better mechanical strength than the woven jute fiber composites.


Yeo et al. [121] have fabricated the polyurethane composites with rice husk (RH) and polyethylene glycol (PEG-200) as a polyol. The effect of % RH (by weight), % of RH OH groups and RH sizes on tensile, flexural and impact properties were investigated. For most tests, properties increased as the % RH and % RH hydroxyl groups was increased but after the exceeding a threshold value, the properties started to decrease. This phenomenon was attributed to two factors, (i) % RH (by weight) or % RH OH groups (ii) amount of homogeneous PU matrix. The size of RH also played a significant role in the properties, which could be detected by scanning electron microscope (SEM) analysis. DMF immersion and water absorption tests, showed that as the % of RH increased DMF immersion decreased, while water absorption increased due to ability of RH OH groups to absorb water.

Khan et al. [122] have fabricated jute reinforced polyurethane composites under gamma irradiation. Thick polymer film was prepared under gamma irradiation using urethane acrylate in the presence of N-vinyl pyrrolidone, ethyl hexyl acrylate, and trimethylol propane triacrylate. Both jute dust and hessain cloth (jute fabric) were used to constitute composites based on the prepared resin matrix. Some of their mechanical and physical properties were studied.

Some additives such as acetic acid, acrylamide, urea, talc and titanium oxide were incorporated into the formulation to investigate their effect on the physical and mechanical properties, water absorption and weathering resistance of the resin and composites were also investigated.


Tay et al. [123] have fabricated oil palm empty fruit bunch composites with polyethylene glycol (PEG) molecular weight (MW) of 200 (PEG-200), 400 (PEG-400), polypropylene glycol (PPG) with MW of 400 (PPG-400) used as polyols. The effect of isocyanate (NCO) / hydroxyl (OH) ratio and PPG-400/ PEG-400 ratio on the impact strength, dimensional stability (immersion test), and thermal behavior were investigated. The study revealed that, as NCO/OH ratio was increased from 0.8 to 1.1 the impact strength and enthalpy increased, while swelling of composites either in water or DMF and onset and peak temperatures decreased. While for NCO/OH ratio above 1.1 the onset and peak temperature increased, while enthalpy decreased due to formation of allophanates. Thermal behavior of the composites made from the glycol mixture was predominantly influenced by the PPG -400.

Tay et al. [124] have fabricated the oil palm EFB-PU composites and investigated the effect of isocyanate (NCO)/ glycol (OH) ratio, glycol type and mixtures [polyethylene glycol PEG-400 (MW- 400) and polypropylene glycol PPG (MW-400)] on the flexural properties. Composites made with PEG-200 exhibited higher flexural properties than with PEG-400 and PPG-400. The flexural properties were also found to be influenced by the PPG-400/ PEG-400 ratio.

Wolcott et al. [125] have fabricated ligno cellulose fiber reinforced PU composites using difunctional and trifunctional poly(propylene oxide) based polyol. The mechanical properties of the composites were found to depend on the type of fiber and accessibility of hydroxyl functionality on the fiber. Dynamic mechanical analysis, swelling behavior and scanning electron micrographs of

failure surfaces all provided the evidence of a substantial interface in the composites that directly impacted the performance properties. Trifunctional polyols generally increased the strength and stiffness, regardless of fiber type. The data suggested that synthetic polyol functionality and relative accessibility of the internal polymer structure of the fiber wall are dominant factors in determining the extent of interphase development.

Silva and Silva [126] have prepared waste cellulose fiber based polyurethane composites. An elastomeric polyurethane based on polyether poly(tetramethylene glycol) and 4,4-diphenyl methane diisocyanate was used as polymeric matrix. Structural, thermal, and morphological characterization of the composites was carried out by infrared spectroscopy, thermogravimetry, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The results indicated that interfacial interaction between the cellulose fiber residue and the PU matrix occurred and that cellulose waste was a promising reinforcement for polyurethane composites.

Deng et al. [127] have prepared a series of water-resistant composites from a mixture of soy dreg (SD), castor oil, and 2,4-toluene diisocyanate (TDI) by a one-step reactive extrusion (REX) process. The structure and properties of the composites were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry, dynamic mechanical analysis, tensile testing, and swelling experiments. The results indicated that the toughness of the composites prepared from castor oil based polyurethane and SD was significantly improved. In this case, TDI played an in situ compatibilization role through the crosslinking reaction of —NCO groups with —NH$_2$, —NH—, and —OH groups in SD and castor oil. With an increase

in the molar ratio of —NCO groups of TDI and —OH groups of castor oil, the degree of crosslinking, tensile strength, glass-transition temperature, water resistivity, and solvent resistivity of the composites increased. With an increase in the SD content of the composites, the tensile strength and solvent resistivity of the composites increased because of the reinforcement of the cellulose component in SD.

**AIMS AND OBJECTIVES**

In the field of polymers, these have always been and will continue to be a need for new and novel resins and polymers for the economically viable and environmental beneficial applications. Our efforts are focused on use of the agriculture waste fibers in order to fabricate composites and polyurethane resins for coating and adhesive applications.

Following are the aims and objectives of the present work:

I. To collect literature on syntheses and characterization of monomers, resins, and their applications.

II. To synthesize and modify resins and evaluate their thermal, mechanical and electrical properties.

III. To fabricate glass, jute and sandwich composites based on agricultural wastes and evaluate their mechanical and electrical properties.

IV. To study water absorption behavior of the composites in various environments.

V. To study acoustical properties of the resin solutions in different solvents at different temperature.
CHAPTER – 2

SYNTHESSES OF

MONOMERS AND RESINS
This chapter is further subdivided into seven sections

**Section-I:** Synthesis of 1, 1’-bis (4-hydroxy phenyl) cyclohexane  
[bisphenol – C]

**Section-II:** Synthesis of 9, 9’-bis (4-hydroxy phenyl) anthrone-10 (BAN)

**Section-III:** Syntheses of bisphenol-formaldehyde resins (BCF/ BANF)

**Section-IV:** Syntheses of BCF Maleate resin

**Section-V:** Synthesis of epoxy resin of ban

**Section-VI:** Synthesis of polyester polyols

**Section-VII:** Synthesis of polyurethane resins

**Section-I: Synthesis of 1, 1’-bis (4-hydroxy phenyl) cyclohexane**  
[bisphenol – C]

\[
\text{Phenol} + \text{Cyclohexanone} \xrightarrow{\text{HCl : CH}_3\text{COOH 2:1 V/V}} \text{Bisphenol-C}
\]

55\(^{\circ}\)C, 4 h

1,1’- Bis (4-hydroxy phenyl) cyclohexane hereafter designated as BC was synthesized according to reported methods [1-2].


Thus, cyclohexanone (0.5 mol, 49 g) was treated with phenol (1.0 mol, 94 g) in the presence of mixture of HCl : CH₃COOH (2:1 v/v, 100:50 ml) as a Friedel-Craft catalyst at 55°C for 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution. The resinous material was removed by filtration through cotton plug. The yellowish solution so obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50°C. BC was further recrystallized repeatedly from benzene and methanol-water systems. The process was repeated to get pure, white, shining crystals of ~81% yield, and m. p. of BC was 186°C.

**Section-II: Synthesis of 9, 9'-bis (4-hydroxy phenyl) anthrone-10 (BAN)**

9, 9'-Bis (4-hydroxy phenyl) anthrone-10 (BAN) (II) was synthesized according to the reported method [3]. Thus, anthraquinone (0.1 mol, 20.8 g) was condensed with phenol (0.7 mol, 65.8 g) at 120°C in presence of stannic chloride (0.15 mol, 17.5 g) for 6h. Excess phenol was removed by steam distillation and product was boiled in an acetic acid to remove resinous material. The dark brown colored product was filtered, washed well with boiling water and dried at 50°C. Crude BAN (light gray) was dissolved in 2N NaOH solution and filtered through cotton plug.

The yellowish solution so obtained was acidified with dilute HCl, filtered, washed well with water and dried. BAN was further recrystallized repeatedly from dioxan-water system to get pure, white shining crystals of yield ~ 80 % and m.p. was 324 °C.

Section-III: Syntheses of bisphenol-formaldehyde resins (BCF/ BANF)

Bisphenol-formaldehyde resins (BCF/BANF) (III) were synthesized according to reported method [4]. Into a 1- liter flask equipped with a condenser, BC (0.5 mol, 134 g)/ BAN (0.5 mol, 189 g) and 37% formaldehyde solution (2.1 mol, 202 ml) were charged. Reaction mixture was heated at 50-55 °C for 1h/2h. A 47% sodium hydroxide (100 ml) solution was added gradually to the reaction mixture and temperature was raised to 70 °C during 15 min. Reaction mixture was cooled and neutralized by a dilute HCl and separated resin was isolated, washed well with distilled water and methanol and dried at 50 °C. BCF/BANF is soluble in acetone, 1, 4-dioxane, DMF and DMSO.

Section-IV: Synthesis of BCF Maleate resin

Bisphenol-C-formaldehyde-maleate resin (V) was synthesized by condensing BCF (0.01 mol / 3.88 g) and maleic anhydride (0.04 mol / 3.92 g) by using 1,4-dioxan as a solvent and phenothiazine as a catalyst at 80°C for 6h. Brownish green solid product was obtained, which was purified repeatedly from MEK-water system prior to its use. The process was repeated to get pure ~80% yield. BCFM is soluble in acetone, 1,4-dioxane, MEK, DMF and DMSO.

\[
\begin{align*}
\text{BCF} & \quad \text{Maleic anhydride} \\
\text{BCFM} & \quad \text{(IV)} \\
\text{Where } & \quad Z = \text{C} = \text{CH} = \text{CH} \cdots \text{COOH}
\end{align*}
\]

Section-V: Synthesis of epoxy resin of BAN

Epoxy resin of BAN (IV), hereafter designated as EBAN, was synthesized according to following method. Thus, BAN (0.5 mol, 189 g), epichlorohydrin (1.1 mol; 138.8 g) and isopropanol (250 ml) were placed in a 1lit round bottomed flask equipped with a condenser. The mixture was brought to reflux with stirring and 1.25mol NaOH in 50 ml water was slowly added to the solution and refluxed for 4.5 h. The separated solid resin was isolated by filtration and liquid resin by distillation of excess of isopropanol. The solid and liquid resins were washed well with water and extracted in chloroform and evaporated to dryness. Highly transparent yellowish color resin is soluble in CHCl₃, acetone, 1, 4-dioxan, DMF, 1, 2-dichloroethane and DMSO; and partially soluble in ethanol and isopropanol.
Section-VI: Synthesis of polyester polyols

The majority of epoxy esters are the reaction products of the epoxy resins and vegetable oil fatty acids. The main chemical reactions occurring during epoxy ester preparation are as under.

Esterification

\[
\text{(i) } \overset{\text{IPA, NaOH, Reflux}}{\text{C}}-\overset{\text{O}}{\text{OH}} + \overset{\text{O}}{\text{CH}}_2-\overset{\text{CH}}{-}\overset{\text{CH}}{-}\overset{\text{CH}}{\text{2}} \rightarrow \overset{\text{O}}{\text{C}}-\overset{\text{O}}{\text{CH}}_2-\overset{\text{CH}}{-}\overset{\text{CH}}{-}\overset{\text{CH}}{\text{2}} \overset{\text{OH}}{\text{H}}
\]
Hydroxy ester

\[
\text{(ii) } \overset{\text{C}}{\text{O}}-\overset{\text{OH}}{\text{OH}} + \overset{\text{CH}}{-}\overset{\text{CH}}{-}\overset{\text{CH}}{\text{2}} \rightarrow \overset{\text{C}}{\text{O}}-\overset{\text{O}}{\text{C}}-\overset{\text{CH}}{-}\overset{\text{CH}}{-}\overset{\text{CH}}{\text{2}} + \overset{\text{O}}{\text{H}}_2\overset{\text{O}}{\text{H}}
\]
Condensation ester

Esterification reactions are favored by removing water of reaction. Generally xylene is used as a solvent to remove water azeotropically.
This part of the thesis describes the synthesis of epoxy esters (polyester polyols) based on ricinoleic acid / oleic acid / acrylic acid.

\[
\begin{align*}
H_3C-(CH_2)_5-CH-CH_2-CH=CH-(CH_2)_7-COOH \\
\text{OH}
\end{align*}
\]

Ricinoleic acid (RA)

(A)

\[
\begin{align*}
H_3C-(CH_2)_5-CH=CH-(CH_2)_5-COOH
\end{align*}
\]

Oleic acid (OA)

(B)

\[
\begin{align*}
H_2C=CH-COOH
\end{align*}
\]

Acrylic acid (AA)

(C)

Ricinoleic acid is (+) 12-hydroxy-9-octadecanoic acid and has saponification value = 190 and iodine value = 80, while oleic acid has iodine value of (85-92).

The polyester polyols or epoxy esters were synthesized by condensing EBAN with RA/OA/AA(1:2 mole ratio) by using 1, 4- dioxane as a solvent and triethyl amine as a catalyst at reflux temperature. The reaction time, temperature, weight of acids and epoxy resin and the acid value of the corresponding polyester polyols are reported in Table-2.1. The reaction time was set in such a way that the acid value was decreased below 30 mg KOH / g of the resin. The resins are soluble in common organic solvents like chloroform, acetone, DMF, DMSO, THF, methyl ethyl ketone, 1, 4-dioxane, etc. indicating linear or branched chains. Prolonged reaction time resulted in cross linking of the resultant esters. The general structure of polyester polyol is shown in Scheme-VI.
Table-2.1: Time, temperature, weight of acids and epoxy resins and acid value of the polyester polyols

<table>
<thead>
<tr>
<th>Polyols</th>
<th>Weight in gm</th>
<th>Temperature</th>
<th>Time (h)</th>
<th>Acid value (mg KOH/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EANRA</td>
<td>26</td>
<td>19.04</td>
<td>Reflux</td>
<td>8</td>
</tr>
<tr>
<td>EANOA</td>
<td>17.2</td>
<td>19.04</td>
<td>Reflux</td>
<td>10</td>
</tr>
<tr>
<td>EANAA</td>
<td>14.4</td>
<td>19.04</td>
<td>Reflux</td>
<td>10</td>
</tr>
</tbody>
</table>

Polyester polyols

EANRA-1: \( A = \ce{H3C-(CH2)5-CH-CH2-CH=CH-(CH2)7-OH} \)

EANOA-2: \( A = \ce{H3C-(CH2)5-CH=CH-(CH2)5} \)

EANAA-3: \( A = \ce{H2C-CH} \)

(VI)
Section-VII: Syntheses of polyurethane resins

[A] Synthesis of polyurethane of EAN

Polyurethane resin of EAN was prepared by reacting 0.005 mol (13.19g) EBAN in 15 ml MEK with 0.0106 mol (1.85g) TDI in 15 ml MEK at room temperature. The reaction was stirred manually for about 25-30 min. The structure of polyurethane is shown in Schemes VII.

[B] Synthesis of polyurethanes of EANRA, EANOA, EANAA

Polyurethane resins of EANRA, EANOA and EANAA were synthesized by reacting 0.0025 mol (13.25g EANRA, 8.67g EANOA, 13.37g EANAA) polyester polyol in 10 ml methyl ethyl ketone (MEK) with 0.0053 mol (0.9g) TDI in 5 ml MEK at room temperature by manual stirring for about 15 min. The general structures of the polyurethanes are shown in Scheme VIII and (IX).
[C] Syntheses of co-polyurethanes of EANRA, EANOA, EANAA and TDI

In order to improve flexibility of PU an attempt has been made to use of PEG-200. Prepolyurethane of EANRA, EANOA and EANAA were synthesized according to previous section. To this prepolyurethane 30% PEG-200 in 5 ml MEK was added drop wise and the reaction mixture was stirred for further 10 min. The general structures of the copolyurethanes are shown in Scheme X and XI.

Polyurethane resin of EANRA
(VIII)
Polyurethane resins of EANOA and EANAA

(IX)
Copolyurethane resin of EANRA
Copolyurethane resins of EANOA and EANAA (XI)
[D] Synthesis of polyurethane of BCFM and its copolyurethane

To a 250ml beaker 0.001mol (0.78g) BCFM was dissolved in 15ml methyl ethyl ketone (MEK) at room temperature. To this solution 0.002 mol (0.348g) toluene diisocyanate (TDI) in 50 ml MEK was added drop wise over a period of 10 min with stirring. The reaction mixture was stirred manually for about 15 min at room temperature. To this prepolyurethane 0.001 mol (0.2g) PEG-200 in 5 ml MEK was added drop wise and the reaction mixture was stirred for further 10 min. The resultant copolyurethane solution was poured into a leveled 15 cm X 15cm glass mold and the solvent was allowed to evaporate with a controlled rate. After 24h, the film was peeled from the mold. The suggested structures of the polyurethane and copolyurethanes are shown in Schemes XII and XIII:
Synthesis of monomers and resins

Copolyurethane of BCFM (XIII)
CHAPTER – 3
CHARACTERIZATION
OF
MONOMERS AND RESINS
This chapter of the thesis describes the determination of epoxy equivalent of the epoxy resins, acid and hydroxyl values of the polyester polyols, thermal, GPC and spectral characterization of the resins, density, mechanical and chemical resistance of BCFMPT-200 films. This chapter is subdivided into eight subsections.

Section-I: Spectral characterization of monomers and resins

Section-II: Determination of epoxy equivalent of the epoxy resin

Section-III: Determination of acid values of polyester resins

Section-IV: Determination of hydroxyl values of polyester resins

Section-V: Thermal analysis of polyester and polyurethane resins

Section-VI: Density measurements of the polyurethanes

Section-VII: Mechanical and electrical properties of copolyurethane films

Section-VIII: Chemical resistance study of copolyurethanes

Section-I: Spectral characterization of monomers and resins

This Section of the thesis includes the IR, Mass and NMR spectral characterization of the monomers, phenolic resins, epoxy resin, polyester polyols (epoxy ester) and polyurethane resins.

[A] IR spectral characterization

IR spectroscopy is an excellent technique for the qualitative analysis because except for optical isomers, the spectrum of compound is unique. Information about the structure of a molecule could frequently be obtained from its absorption spectrum. An infrared spectrum is obtained by passing infrared radiation through a sample. A detector generates a plot of % transmission of
radiation versus the wave number or wavelength of the radiation transmitted. At 100% transmission, all the energy of radiation passes through the molecule. At lower values of % transmission, some of the energy is being absorbed by the compound. Each spike in the infrared (IR) spectrum represents absorption of energy. These spikes are called absorption bands. Electromagnetic radiation with wave numbers from 4000 to 400 cm\(^{-1}\) has just the right energy to correspond to stretching and bending vibrations in molecules. Electromagnetic radiation with this energy is known as infrared radiation because it is just below the “red region” of visible light. (Infra is Latin word meaning “below”).

The intensity of an absorption band depends on the size of dipole moment change associated with the vibration. In other words, depends on polarity of the vibrating bond. Intensity of the absorption band also depends on number of bonds responsible for the absorption. The concentration of the sample used to obtain an IR spectrum also affects the intensity of absorption bands. Concentrated samples have greater wave numbers and therefore more intense absorption bands.

The IR spectra of resins and polymers were scanned on a Shimadzu-8400 FTIR spectrometer over the frequency range from 4000-400 cm\(^{-1}\). The IR spectra of resins and polymers are shown in Figs. 3.1 to 3.12. The characteristic IR absorption frequencies (cm\(^{-1}\)) are reported in Tables-3.1 and 3.3.
Fig. 3.1: IR (KBr) spectrum of BCF

Fig. 3.2: IR (KBr) spectrum of BANF
Characterization….

Fig. 3.3: IR (KBr) spectrum of BCF-M

Fig. 3.4: IR (KBr) spectrum of EAN
Fig. 3.5: IR (KBr) spectrum of EANAA

Fig. 3.6: IR (KBr) spectrum of EANRA
Fig. 3.7: IR (KBr) spectrum of EANOA

Fig. 3.8: IR (KBr) spectrum of EANPT
Characterization......

Fig. 3.9: IR (KBr) spectrum of EANOAPT

Fig. 3.10: IR (KBr) spectrum of EANRAPT
Fig. 3.11: IR (KBr) spectrum of EANAAPT

Fig. 3.12: IR (KBr) spectrum of BCFMPT
### Table-3.1: The characteristic IR absorption frequencies of BCF, BANF and BCFM

<table>
<thead>
<tr>
<th>Types</th>
<th>Group vibration mode</th>
<th>Observed IR frequencies,(cm(^{-1}))</th>
<th>Expected frequencies, (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BCF</td>
<td>BANF</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkane</td>
<td>C-H (u(_{as}))</td>
<td>2925.8</td>
<td>2921.0</td>
</tr>
<tr>
<td></td>
<td>C-H (u(_{s}))</td>
<td>2854.5</td>
<td>-</td>
</tr>
<tr>
<td>-CH(_3) and -CH(_2)-</td>
<td>C-H def, -CH(_3)</td>
<td>1454.2</td>
<td>1453.3</td>
</tr>
<tr>
<td></td>
<td>C-H def, -CH(_2)-</td>
<td>1454.2</td>
<td>1482.2</td>
</tr>
<tr>
<td></td>
<td>Twisting &amp; Wagging</td>
<td>1234.4</td>
<td>1251.7</td>
</tr>
<tr>
<td></td>
<td>Skeletal CH(_2) 4 or &gt;</td>
<td>-</td>
<td>746.4</td>
</tr>
<tr>
<td>Ar-OH</td>
<td>O-H (str.)</td>
<td>3346.3</td>
<td>3343.4</td>
</tr>
<tr>
<td></td>
<td>C-O (str.)</td>
<td>1172.6</td>
<td>1178.4</td>
</tr>
<tr>
<td>Aromatic</td>
<td>C-H (i.p.d.)</td>
<td>1110.9</td>
<td>1116.7</td>
</tr>
<tr>
<td></td>
<td>C-H (o.o.p.d.)</td>
<td>873.7</td>
<td>872.7</td>
</tr>
<tr>
<td></td>
<td>C=C (str.)</td>
<td>1604.7</td>
<td>1596.9</td>
</tr>
<tr>
<td>Ester</td>
<td>C=O (str.)</td>
<td>1747.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C-O(str.)</td>
<td>1234.4</td>
<td>1251.7</td>
</tr>
<tr>
<td>Ketone (cyclic)</td>
<td>C=O (str.)</td>
<td>1650.9</td>
<td>1649.0</td>
</tr>
</tbody>
</table>
### Table-3.2: The characteristic IR absorption frequencies of EAN, EANO, EANRA and EANAA

<table>
<thead>
<tr>
<th>Types</th>
<th>Group vibration mode</th>
<th>Observed IR frequencies, (cm⁻¹)</th>
<th>Expected frequencies, (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>EAN</td>
<td>EANO</td>
</tr>
<tr>
<td>Alkane</td>
<td>C-H (υax)</td>
<td>-</td>
<td>2939.6</td>
</tr>
<tr>
<td></td>
<td>C-H (υs)</td>
<td>2851.1</td>
<td>2857.36</td>
</tr>
<tr>
<td></td>
<td>C-H def, -CH₃</td>
<td>-</td>
<td>1446.66</td>
</tr>
<tr>
<td></td>
<td>C-H def, -CH₂⁻</td>
<td>1400.37</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Twistiing &amp; Wagging</td>
<td>-</td>
<td>1234.48</td>
</tr>
<tr>
<td></td>
<td>Skeletal CH₂ 4 or &gt;</td>
<td>-</td>
<td>742.6</td>
</tr>
<tr>
<td>-OH</td>
<td>O-H (str.)</td>
<td>3203.87</td>
<td>3317.17</td>
</tr>
<tr>
<td>Aromatic</td>
<td>C-H (i.p.d.)</td>
<td>1085.96</td>
<td>1182.40</td>
</tr>
<tr>
<td></td>
<td>C-H (o.o.p.d.)</td>
<td>877.64</td>
<td>825.56</td>
</tr>
<tr>
<td></td>
<td>C=C (str.)</td>
<td>1627.97</td>
<td>1595.18</td>
</tr>
<tr>
<td>Ester</td>
<td>C=O (str.)</td>
<td>-</td>
<td>1734.06</td>
</tr>
<tr>
<td></td>
<td>C-O(str.)</td>
<td>-</td>
<td>1329.0</td>
</tr>
<tr>
<td>Ketone(cyclic)</td>
<td>C=O (str.)</td>
<td>1693.56</td>
<td>1637.62</td>
</tr>
</tbody>
</table>
Table-3.3: The characteristic IR absorption frequencies of EANPT, EANOAPT, EANRAPT and EANAAPT

<table>
<thead>
<tr>
<th>Type</th>
<th>Absorption frequencies, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EANPT</td>
</tr>
<tr>
<td>-N-H Str.</td>
<td>3591.57</td>
</tr>
<tr>
<td>-CH₂Str. (sym.)</td>
<td>2875.96</td>
</tr>
<tr>
<td>-CH₂Str. (asym.)</td>
<td>2820.02</td>
</tr>
<tr>
<td>Urethane</td>
<td>1730.21</td>
</tr>
<tr>
<td>-C=O Str.</td>
<td>1224.84</td>
</tr>
</tbody>
</table>
[B] NMR spectral characterization

Some nuclei spin about their axes in a manner to that electrons spin. In the presence of an externally applied magnetic field, a spinning nucleus can only assume a limited number of stable orientations. Nuclear magnetic resonance occurs, when a spinning nucleus in a lower energetic orientation in a magnetic field absorbs sufficient electromagnetic radiation to be excited to a higher energetic orientation. The excitation energy varies with the type and environment of the nucleus. NMR spectroscopy can be used for the quantitative chemical analysis [1-5].

NMR spectroscopy consists of measuring the energy that is required to change a spinning nucleus from a stable orientation to a less stable orientation in the magnetic field. Different spinning nuclei at different frequencies in the magnetic field absorb different frequencies of radiation to change their orientations. The frequencies at which absorption occurs can be used for qualitative analysis. The decrease in intensity of incident radiation owing to absorption during a particular transition is related to the different spinning nuclei at different frequencies in the magnetic field absorb different frequencies of radiation to change their orientations. The frequencies at which absorption occur can be used for qualitative analysis.

The decrease in intensity of incident radiation owing to absorption during a particular transition is related to the number of nuclei in the sample that undergo the transition and can be used for quantitative analysis. NMR spectrometer was invented in 1945 by Falix Bloch (Stanford University) and Edward Purcell. They shared the Nobel Prize (1952) in Physics for their work.

The estimation of copolymer composition is of paramount importance for tailor making copolymers with the required physico-chemical properties. For quantitative copolymer composition, UV, IR and NMR spectroscopic techniques are well established [6-10]. NMR technique is more convenient for the quantitative estimation of copolymer composition as compared to other spectroscopic techniques.

The NMR spectra of polymers were scanned on a Bruker AVANCE II (400MHz) spectrometer by using CDCl₃ as a solvent and TMS as an internal standard. NMR spectra of polymers are shown in Figs. 3.13 to 3.16. The chemical shifts are reported in Tables-3.4 and 3.7.

Fig: 3.13 NMR (400MHZ) spectrum of EAN

Fig: 3.14 NMR (400MHZ) spectrum of EANAA
Fig: 3.15 Fig: 3.14 NMR (400MHz) spectrum of EANRA

Fig: 3.16 NMR (400MHz) spectrum of EANOA
Table-3.4: NMR chemical shifts of EAN

<table>
<thead>
<tr>
<th>Sample</th>
<th>NMR chemical shift, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAN</td>
<td>8.260-8.242 [ d, -CH(c) ]</td>
</tr>
<tr>
<td></td>
<td>7.442-7.399 [ m, -CH(e+d) ]</td>
</tr>
<tr>
<td></td>
<td>7.126-7.109 [ d, -CH(f) ]</td>
</tr>
<tr>
<td></td>
<td>6.880-6.861[ d, -CH(b) ]</td>
</tr>
<tr>
<td></td>
<td>6.861-6.726 [ d, -CH(a) ]</td>
</tr>
<tr>
<td></td>
<td>4.311 [s, -OCH_2(epoxy)]</td>
</tr>
<tr>
<td></td>
<td>4.181-4.177 [d, -OCH_2(open chain)]</td>
</tr>
<tr>
<td></td>
<td>4.061-3.863[ m, -CH-OH ]</td>
</tr>
<tr>
<td></td>
<td>3.316 [s, -OH]</td>
</tr>
<tr>
<td></td>
<td>2.878-2.874[d,-CH(epoxy))</td>
</tr>
<tr>
<td></td>
<td>2.722-2.687[m, -CH_2 (epoxy)]</td>
</tr>
</tbody>
</table>
Table-3.5: NMR chemical shifts of EANOA

<table>
<thead>
<tr>
<th>Sample</th>
<th>NMR chemical shift, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>EANOA</td>
<td>8.267-8.249[\text{d}, \text{-CH(c)}]</td>
</tr>
<tr>
<td></td>
<td>7.468-7.393 [ \text{m}, \text{-CH(e+d) } ]</td>
</tr>
<tr>
<td></td>
<td>7.132-7.115 [ \text{d}, \text{-CH(f) } ]</td>
</tr>
<tr>
<td></td>
<td>6.887-6.869[ \text{d}, \text{-CH(b) } ]</td>
</tr>
<tr>
<td></td>
<td>6.815-6.734 [ \text{d}, \text{-CH(a) } ]</td>
</tr>
<tr>
<td></td>
<td>5.349-5.334[t, \text{-CH=CH-(7,8)}]</td>
</tr>
<tr>
<td></td>
<td>4.321-4.309 [ \text{d}, \text{-OCH}_2(\text{epoxy chain})]</td>
</tr>
<tr>
<td></td>
<td>4.191-4.155 [\text{m}, \text{-OCH}_2(\text{open chain})]</td>
</tr>
<tr>
<td></td>
<td>4.103-3.873[ \text{m}, \text{-CH-OH(epoxy chain) } ]</td>
</tr>
<tr>
<td></td>
<td>3.326-3.319 [ \text{d}, \text{-OH} ]</td>
</tr>
<tr>
<td></td>
<td>2.901-2.878[d,\text{-CH(epoxy)}]</td>
</tr>
<tr>
<td></td>
<td>2.811-2.601[m, \text{-CH}_2 (\text{epoxy})]</td>
</tr>
<tr>
<td></td>
<td>2.338[s,\text{CH}_2(13)]</td>
</tr>
<tr>
<td></td>
<td>2.100-1.951[q, \text{-CH}_2(3-5,10-12)]</td>
</tr>
<tr>
<td></td>
<td>1.346-1.148[q,\text{-CH}_2(2)]</td>
</tr>
<tr>
<td></td>
<td>0.881-0.855[d, \text{-CH}_3(1)]</td>
</tr>
</tbody>
</table>
Table-3.6: NMR chemical shifts of EANRA

<table>
<thead>
<tr>
<th>Sample</th>
<th>NMR chemical shift, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>EANRA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.264-8.246 [ d, -CH(c) ]</td>
</tr>
<tr>
<td></td>
<td>7.487-7.407 [ m, -CH(e+d) ]</td>
</tr>
<tr>
<td></td>
<td>7.139-7.112 [ m, -CH(f) ]</td>
</tr>
<tr>
<td></td>
<td>6.884-6.849[ d, -CH(b) ]</td>
</tr>
<tr>
<td></td>
<td>6.749-6.733 [ d, -CH(a) ]</td>
</tr>
<tr>
<td></td>
<td>5.601-5.302[m, -CH=CH-(9,10)]</td>
</tr>
<tr>
<td></td>
<td>4.318 [s, -OCH(_2) (epoxy chain)]</td>
</tr>
<tr>
<td></td>
<td>4.263-4.156 [m, -OCH(_2) (open chain)]</td>
</tr>
<tr>
<td></td>
<td>4.066-4.056[ m, -CH-OH(epoxy chain) ]</td>
</tr>
<tr>
<td></td>
<td>3.501-3.392 [m, -OH]</td>
</tr>
<tr>
<td></td>
<td>2.888-2.876[d,-CH(epoxy)]</td>
</tr>
<tr>
<td></td>
<td>2.7368-2.719[m, -CH(_2) (epoxy)]</td>
</tr>
<tr>
<td></td>
<td>2.354-2.181[m,-CH(_2)(8,11)]</td>
</tr>
<tr>
<td></td>
<td>1.909-2.171[m, -CH(_2)(17)]</td>
</tr>
<tr>
<td></td>
<td>1.611-1.424[m,-CH(_2)(3-6,12-16)]</td>
</tr>
<tr>
<td></td>
<td>1.283 [s, -CH(_2)(2)]</td>
</tr>
<tr>
<td></td>
<td>0.871-0.856[d,-CH(_3)(1)]</td>
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</tbody>
</table>
Table-3.7: NMR chemical shifts of EANAA

<table>
<thead>
<tr>
<th>Sample</th>
<th>NMR chemical shift, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>EANAA</td>
<td>8.215-8.197[d,-CH(c)]</td>
</tr>
<tr>
<td></td>
<td>7.481-7.413[m, -CH(e+d)]</td>
</tr>
<tr>
<td></td>
<td>7.158-7.130[d, -CH(f)]</td>
</tr>
<tr>
<td></td>
<td>6.858-6.840[d,-CH(b)]</td>
</tr>
<tr>
<td></td>
<td>6.767-6.748[d,-CH(a)]</td>
</tr>
<tr>
<td></td>
<td>6.441-6.351[d,=CH₂]</td>
</tr>
<tr>
<td></td>
<td>6.192-6.098[m, =CH-C=O]</td>
</tr>
<tr>
<td></td>
<td>5.810-5.874[d, =CH₂]</td>
</tr>
<tr>
<td></td>
<td>4.754-4.778[t, -OCH₂(epoxy chain)]</td>
</tr>
<tr>
<td></td>
<td>4.262-4.273[d, -OCH₂(open chain)]</td>
</tr>
<tr>
<td></td>
<td>3.960-4.056 [m, -CH-OH(epoxy chain)]</td>
</tr>
<tr>
<td></td>
<td>3.347-3.357 [m, -OH]</td>
</tr>
</tbody>
</table>
Section-II: Determination of epoxy equivalent of the epoxy resins

Epoxy content is reported in terms of “epoxide equivalent” or “epoxy equivalent weight” and is defined as the weight of resin in grams, which contains one gram equivalent of epoxy. The term “epoxy value” represents the fractional number of epoxy groups contained in 100 grams of resins.

Epoxy equivalent and related terms gives information about the content of epoxy groups, which is very useful in determining the amounts of curing agents during the casting process. The principle of determination is addition of HCl, HBr or HF in presence of electron donor solvents like pyridine or dioxane to epoxide ring and the unreacted halide is back titrated with alkali.

Epoxy equivalent may be determined by infrared analysis. The characteristic absorption band for the epoxy group is from 877.2 to 806.45 cm\(^{-1}\) for terminal epoxy groups; from 847.45 to 775.2 cm\(^{-1}\) for internal epoxy groups; and from 769.2 to 751.8 cm\(^{-1}\) for triply substituted epoxy group [11]. The epoxide equivalent may be determined from changes in intensity as related to change in molecular weight using the absorption band of the epoxy group at 912.4 or 862.1 cm\(^{-1}\) in comparison to aromatic bands at 1610.3 cm\(^{-1}\).

Greenlee [12] has described the method for epoxy equivalent. The epoxide content of the complex epoxide resins were determined by heating a 1 g sample of the epoxide composition with an excess of pyridine containing pyridine hydrochloride at the boiling point for 20 min and back titrating the excess pyridine hydrochloride with 0.1 N sodium hydroxide by using phenolphthalein as an indicator and considering that 1 HCl is equal to 1 epoxide group [12].

Jungnickel et al [13] have reported some what better results than other hydrohalogenation methods with bisphenol-A epoxy resins and with water containing sample. They recommended the use of a stronger reagent (1 N pyridinium chloride in pyridine), larger sample sizes and a stronger hydroxide solution (0.5 N) for samples of relatively low molecular weight. They have developed a variation of the pyridinium chloride method in which pyridinium is replaced by chloroform. The precision and accuracy are somewhat better, due to the reduction of side reactions. The pyridinium chloride-chloroform method even permits the determination of epoxides sensitive acids, such as styrene and isobutylene oxides. However, the preparation of the reagent is cumbersome, and reaction periods of 2 h are required. Especially time consuming is the need for the exact equivalence of hydrogen chloride and pyridine.

Burge and Geyer [14] have also described an extensive procedure for the determination of epoxide equivalent. A weighed sample of an epoxide compound containing 2-4 milliequivalents of epoxy group is placed into a 250 ml round bottomed flask, and 25 ml of 0.2 N pyridinium chloride in pyridine was added. The solution was swirled and if necessary, heated gently until the sample was dissolved completely and refluxed for 25 minutes, cooled and then added 50 ml of methyl alcohol and 15 drops of phenolphthalein indicator and titrated with 0.5 N methanolic.

NaOH till pink end point. The epoxide equivalent was calculated according to following relationship:

\[
\text{Epoxide equivalent} = \frac{16 \times \text{Sample weight in grams}}{\text{grams oxirane oxygen in sample}}
\]

Where gram oxirane oxygen in sample = (ml NaOH for blank - ml NaOH for sample) x (Normality of NaOH) x (0.016)

The number 0.016 is the mili equivalent weight of oxygen in grams. The epoxide equivalent of the resin under study was determined according to above mentioned method and is observed value is 910 (mean of 3 measurements).

Section-III: Determination of acid values of the polyester polyols

Acid value is a measure of the free fatty acids content of oil and is expressed as the number of milligrams of potassium hydroxide required to neutralize the free acid in 1 gram of the sample. Acid value quantifies the reaction, which is in the beginning of the reaction, the acid value is high but as the reaction progresses acid is consumed to form ester and at the end of the reaction the acid value is low which signifies the completion of the ester reaction.

Acid values of polyester polyols were determined according to standard reported method [15]. Polyester polyol was exactly weighed (1- 2 g) in a small capsule and placed carefully in a 250 ml RBF and to it 50 ml of acetone was added. The flask was swirled for some time and heated gently for some time to dissolve sample completely. The solution was cooled and titrated with standard 0.1 N methanolic KOH by using phenolphthalein as an indicator. The procedure was repeated for blank titration under similar condition. The acid value of a given sample was determined according to following relationship.

15. ASTM-D-1639-61
Characterization......

\[
\text{Acid Value} = \frac{56.1 \times N \times (A - B)}{W}
\]

Where \( N \) = Normality of KOH

\( A \) = Sample burette reading

\( B \) = Blank burette reading

\( W \) = Weight of sample in grams

The average of three measurements of each of polyester polyols is reported in Table-3.8.

**Section-IV: Determination of hydroxyl values of polyester polyols**

Hydroxyl value is a measure of free hydroxyl groups present in the polyester polyols (epoxy esters) and it is expressed as number of milligrams of potassium hydroxide equivalent to the quantity of acetic acid that binds with 1 g of hydroxyl containing substances.

The hydroxyl value gives information about the number of free hydroxyl group present in a material. The determination is carried out by acetylation with acetic anhydride in pyridine. Aldehyde and primary and secondary amines interfere with the determination and if present than phthalic anhydride is used in place of acetic anhydride.

\[
\text{Resin-OH} + \text{CH}_3\text{C}=\text{O} \xrightarrow{\text{pyridine}} \text{Resin-O-CH}_3 + \text{CH}_3\text{COOH} + \text{N}
\]

\[
\text{CH}_3\text{COOH} + \text{KOH} \xrightarrow{} \text{CH}_3\text{COOK} + \text{H}_2\text{O}
\]

Hydroxyl values of polyester polyols and epoxy esters were determined according to standard reported method. Epoxy ester was exactly weighed (1-2 g) in a small capsule and placed carefully in a 250 ml RBF and to it 20 ml of acetylation mixture (1 volume of acetic anhydride and 3 volume of pyridine) was added.
Table-3.8: Acid values of polyester polyols

<table>
<thead>
<tr>
<th>Polyester polyol</th>
<th>Acid value, mg KOH/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>EANRA</td>
<td>6.62</td>
</tr>
<tr>
<td>EANOA</td>
<td>8.07</td>
</tr>
<tr>
<td>EANAA</td>
<td>7.92</td>
</tr>
</tbody>
</table>
The flask was swirled for some time and heated gently to dissolve sample completely. The content was refluxed on a boiling water bath for 30 min. The solution was cooled to room temperature and was added 50 ml cold water slowly down to the condenser and was titrated the free acetic acid with standard 1N NaOH using phenolphthalein as an indicator. The procedure was repeated for blank titration under similar condition. The average of three measurements was used to determine the hydroxyl value of given sample according to following relationship.

\[
\text{Hydroxyl value} = \frac{56.1 \times N \times (A - B)}{W}
\]

Where

- \( N \) = Normality of KOH
- \( A \) = Sample burette reading
- \( B \) = Blank burette reading
- \( W \) = Weight of sample in grams

**GPC analysis of epoxy and polyester resin**

Gel permeation chromatography is a separation technique, which is based on size exclusion principle, which separates analytes on the basis of their sizes and is also applied to polymers in particular. Size exclusion chromatography was first developed in 1955 by Lathe and Ruthven [16]. The term gel permeation chromatography can be traced back to J. C. Moore of the Dow Chemical Company, who investigated this technique in 1964 [17].

When characterizing polymers, it is important to consider the polydispersity index (PDI) as well the molecular weight. Polymers can be characterized by a variety of definitions for molecular weight including the number average molecular weight.

---


Table-3.9: Hydroxyl values of the polyester polyols (epoxy esters)

<table>
<thead>
<tr>
<th>Polyester polyols</th>
<th>Hydroxyl value mg KOH/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAN</td>
<td>541.08</td>
</tr>
<tr>
<td>EANRA</td>
<td>935.2</td>
</tr>
<tr>
<td>EANOA</td>
<td>741.48</td>
</tr>
<tr>
<td>EANAA</td>
<td>741.48</td>
</tr>
</tbody>
</table>
Characterization

\( \overline{M}_n \), the weight average molecular weight \( \overline{M}_w \), the size average molecular weight \( \overline{M}_z \), or the viscosity molecular weight \( \overline{M}_v \). GPC allows for the determination of PDI as well as \( \overline{M}_v \) and based on other data, the \( \overline{M}_n \), \( \overline{M}_w \) and \( \overline{M}_z \) can be determined.

**Gel**

Gels are used as stationary phase for GPC. The pore size of a gel must be carefully controlled in order to be able to apply the gel to a given separation. Commercial gels like Sephadex, Bio-Gel (cross-linked polyacrylamide), agarose gel and Styragel are often used based on different separation requirements [18].

**Eluent**

The most common eluents that dissolve polymers at room temperature are tetrahydrofuran (THF), o-dichlorobenzene and trichlorobenzene at 130–150 °C for crystalline m-cresol and o-chlorophenol at 90 °C for crystalline condensation polymers such as polyamides and polyesters.

**Pump**

There are two types of pumps available for uniform delivery of relatively small liquid volumes for GPC: piston or peristaltic pumps.

**Detector**

There are many detector types available and they can be divided into two main categories. The first is concentration sensitive detectors which include UV absorption, differential refractometer (DRI) or refractive index (RI) detectors, infrared (IR) absorption and density detectors. Molecular weight sensitive detectors include low angle light scattering detectors (LALLS), multi angle light scattering (MALLS) [19].

---


Advantages of GPC

As a separation technique, GPC has many advantages. First of all, it has a well-defined separation time due to the fact that there is a final elution volume for all unretained analytes. Additionally, GPC can provide narrow bands, although this aspect of GPC is more difficult for polymer samples that have broad ranges of molecular weights present. Finally, since the analytes do not interact chemically or physically with the column, there is a lower chance for analyte loss to occur. GPC provides a more convenient method of determining the molecular weights of polymers. In fact most samples can be thoroughly analyzed in an hour or less.[20].

Experimental

Molecular weights and molecular weight distribution of copolymers were determined by gel permeation chromatograph using Perkin Elmer GPC (series 200) using THF as a solvent and standard polystyrene mixed bed at 30°C. Molecular weight and molecular weight data of the epoxy and polyester polyols are summarized in Table-3.10 from which it is clear that chain extension resulted upon polyesterification of EAN with acrylic, oleic and recinolic acids.

Table-3.10 Molecular weight and molecular weight distribution data of EAN, EANOA, EANRA, EANAA

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>GPC data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_w$</td>
<td>$M_n$</td>
</tr>
<tr>
<td>EAN</td>
<td>2640</td>
<td>2040</td>
</tr>
<tr>
<td>EANOA</td>
<td>3470</td>
<td>2380</td>
</tr>
<tr>
<td>EANRA</td>
<td>5300</td>
<td>2830</td>
</tr>
<tr>
<td>EANAA</td>
<td>5350</td>
<td>2980</td>
</tr>
</tbody>
</table>
Section-V: Thermal analysis of polyester and polyurethane resins

Synthetic polymers are highly useful in the rapidly developing fields such as space exploration, terrestrial, transportation, modern communications, energy saving, environmental protection, public health, microbiology, medicine, etc. A major driving force for the growth and interest in the studies of thermally stable polymers is attributed to their extensive applications in aeronautics and in supersonic appliances. Considerable research work has been undertaken [21] on the thermal stability of polymers to derive the polymers, which may be useful for high temperature applications.

Data on thermal characteristics are an important tool for evaluating product performance as well as processability of polymeric materials. Thermal properties like specific heat and thermal conductivity are the determining factors in selection of processing parameters as well as designing the machines and tools for shaping of plastics. The data are also useful in screening the materials for specific applications.

On practical side, thermal analysis of polymers not only explains the behavior of polymers under conditions of high temperatures but also helps in selecting the right kind of material for the specific uses where high temperatures are encountered. It also suggests the design and synthesis of new materials for specific requirements in polymer technology such as high temperature resistant synthetic and natural fibers, transportation industries, electrical and electronic instruments, appliances, etc.

Kinetic study of thermal decomposition of epoxy resins containing flame retardant components was reported by Wang and Shi [22]. Hyperbranched polyphosphate ester (HPPE) and phenolic melamine (PM) were blended in

different ratios with a commercial epoxy resin to obtain a series of flame retardant resins. The thermal decomposition mechanism of cured ester was studied by thermogravimetric analysis and in situ Fourier-transform infrared spectroscopy. The degradation behaviors of epoxy resins containing various flame retardant components were found to be greatly changed.

Laza et al. [23] have studied the dynamic-mechanical properties of different mixtures formed by an epoxy resin (DGEBA type) and a phenolic resin (resole type) cured by triethylene tetramine and/or p-toluene sulphonic acid at different concentrations by means of dynamic mechanical thermal analysis (DMTA). All samples were cured by pressing at 90°C during 6h. The mechanical studies were performed between -100 to 300 °C at a heating rate of 2°C/min.

Thermal degradation and decomposition products of electronic boards containing BFRs have been studied by the Barontini et al. [24]. They have investigated the thermal degradation behavior of electronic boards manufactured using tetrabromobispheno-A and diglycidyl ether of bisphenol-A epoxy resins. Qualitative and quantitative information was obtained on the products formed in the thermal degradation process, and the bromine distribution in the different product fractions was determined. The more important decomposition products included hydrogen bromide, phenol, polybrominated phenols, and polybrominated bisphenol-A species.


Wang et al. [25] have reported the cure study of addition-cure-type and condensation-addition-type phenolic resins by the incorporation of propargyl and methylol groups onto novolac backbone, a series of addition-curable phenolic resins and condensation-addition dual-cure type phenolic resins (novolac modified by propargyl groups referred as PN, and novolac modified by propargyl and methylol groups simultaneously referred as MPN) were synthesized.

The processing characteristics, thermal cure and catalytic cure behavior for both resins were investigated mainly by means of viscosity measurements and non-isothermal differential scanning calorimetry (DSC). The effect of propargyl and methylol content of PN and MPN, the molecular weight and the configuration of the parent novolac, on the processing and cure behavior was studied in details. Processing parameters and curing kinetic parameters were obtained. Both resins exhibit excellent processing properties. Thermal cure of PN resins possessed one cure mechanism and that of MPN resins possessed two cure mechanisms according to DSC analysis. The dual-cure-type mechanism made MPN resins superior to PN resins in terms of a mild and controllable cure process. Compared with thermal cure, catalytic cure of PN resins showed lower initiation temperature and cure temperature by about 60 °C. These novel resins have a bright prospect of application as matrix for thermal-structural composite materials.

Nair et al. [26] have reported the thermal characteristics of addition-cure phenolic resins. The thermal and pyrolysis characteristics of four different types of addition-cure phenolic resins were compared as a function of their structure.


Characterization

Whereas the propargyl ether resins and phenyl azo functional phenolics underwent easy curing, the phenyl ethynyl and maleimide-functional required higher thermal activation to achieve cure. All addition-cure phenolics exhibited improved thermal stability and char-yielding properties in comparison to conventional phenolic resole resin. The maleimide-functional resins exhibited lowest thermal stability and those crosslinked via ethynyl phenyl azo groups were the most thermally stable systems. Propargylated novolac and phenyl ethynyl functional phenolics showed intermediate thermal stability. The maximum char yield was also given by ethynyl phenyl azo system. Non-isothermal kinetic analysis of the degradation reaction implied that all the polymers undergo degradation in at least two steps, except in the case of ethynyl phenyl azo resin, which showed apparent single step degradation.

Effect of various operating parameters

1. Atmosphere

The atmosphere associated with any thermal analysis, which is composed of gases that are introduced from outside and those are evolved from the samples. The presence or absence of such gases may have strong influence on the results. These gases may react with the sample or with each other and change the reaction mechanism or product composition. Inert atmosphere and vacuum will influence the decomposition processes as well. In vacuum the primary decomposition of gases will tend to be pumped away from the sample before the molecules collide with the surface and undergo secondary reactions. When these molecules collide with inert gas molecules, they may undergo homogeneous reactions or may be reflected back to the sample surface and react there.

2. Container geometry

The container geometry influences the gaseous environment and heat transfer to the samples. Even with a flowing gaseous atmosphere, a deep narrow
container will limit the contact between the sample surface and gas, whereas a shallow, broad container will promote the contact.

3. Container material

It is reasonable to expect that in some cases the container material will react with material being tested or some of the products.

4. Sample size

Two major effects are associated with the sample size, namely surface and bulk effects. In carrying out degradation studies, it is customary to reduce film thickness or particle size until the rate of the decomposition becomes independent of size.

5. Rate of heating

In the case where only kinetic considerations are significant, an increase in rate of temperature rise will cause the process to be displayed to a higher temperature because they will be at the lower temperature for a shorter length of time. The rate of change of the measured parameter will also be greater for faster heating.

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA)

Physical transformation [27] such as glass transition, cold crystallization and crystallization from melts, crystalline disorientation, and melting can be studied by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Glass transition involves the motion of short segments in the amorphous region and is related to the brittleness of the polymer. Crystallization from the melt is of great practical importance. A number of properties of polymers like melting range, heat of fusion and melting point depression, degree of crystallinity, random copolymer structure and stereo regularity and identification

27. E. Heisenberg; Cellulose Chemie, 12,159, (1931); C.A. 25, 59, 823, (1931).
of composition of a mixture may be studied through melting. DSC is a method where by the energy necessary to establish a zero temperature difference between a substance and a reference material is recorded as a function of temperature or time. The energy input to the sample is compensated by an increased energy input to the sample in order to maintain a zero temperature difference because this energy input is precisely equivalent in magnitude to the energy absorbed during the transition in direct calorimetric measurement. The combination of programmed and isothermal techniques has been used for characterizing unresolved multistep reactions in polymers [28]. DSC provides useful informations about crystallinity, stability of crystallites, glass transition temperature, cross linking, kinetic parameters such as the activation energy, the kinetic order, frequency factor, entropy change and heat of polymerization.

**Thermo Gravimetric Analysis (TGA)**

Thermogravimetry is a useful analytical technique for recording weight loss of a test sample as a function of the temperature or time, which may be useful for understanding the chemical nature of the polymer. Thus, the weight of a substance in an environment heated or cooled at a controlled rate is recorded as a function of time or temperature. There are three types of thermogravimetry namely

1. Static or isothermal thermogravimetry,
2. Quasistatic thermogravimetry and
3. Dynamic thermogravimetry

Most of the studies of polymers are generally carried out with dynamic thermogravimetry. Normally sample starts losing weight at a very slow rate up to a particular temperature and thereafter, the rate of loss becomes large over narrow range of temperature. After this temperature the loss in weight levels off. TGA curves are characteristic for given polymers because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at the rates that are function of the polymer structures.

The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evaluation of volatile products in the formation of heavier reaction products. Pyrolysis of many polymers yields TG curves, which follow relatively simple sigmoidal curves. In such a case weight of sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction gets completed. The shape of the curve depends on the kinetic parameters: reaction order (n), frequency factor (A) and activation energy (Ea). The values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation [29, 30].

Reich and Levi [31] have described several temperature characteristics for qualitative assessment of relative thermal stability of polymers:

1. Initial decomposition temperature (T₀)
2. Temperature for 10% weight loss (T₁₀)
3. Temperature for maximum rate of decomposition (Tₘₐₓ)
4. Half volatilization temperature (Ts)
5. Differential decomposition temperature
6. Integral procedural decomposition temperature (IPDT)

For the estimation of kinetic parameters from TG traces, several so called exact methods have been proposed. All these methods involve the two assumptions that thermal and diffusion barriers are negligible and that Arrhenius equation is valid. Since small quantities of materials are employed in TG studies, thermal and diffusion

barriers would be negligible. Since the shape of any TG curve is dependent on the nature of apparatus and the way in which it is used. Most kinetic treatments are based on relationship of the type.

\[
\frac{dC}{dt} = k f(C) \quad \ldots 3.1
\]

Where \( C \) = Degree of conversion, \( t \) = time; \( k \)=rate constant,

\( f (C) \) = temperature independent function of \( C \)

The constant \( k \) is generally assumed to have the Arrhenius form

\[
k = A e^{-Ea/RT} \quad \ldots 3.2
\]

\( C \) is defined as the conversion with respect to initial material

\[
C = 1 - \frac{W}{W_o} \quad \ldots 3.3
\]

where \( W_o \)= Initial weight of the material and \( W \)= weight of the material at any time.

The residual weight fraction is given by

\[
\frac{W}{W_o} = (1-C)
\]

and the rate of conversion is given by

\[
\frac{dC}{dt} = - \left( \frac{1}{W_o} \right) \frac{dW}{dt} \quad \ldots 3.4
\]

For homogeneous kinetics, the conversion would be assumed to have the form

\[
f(C) = (1-C)^n \quad \ldots 3.5
\]

Where \( n \) = order of the reaction

Upon substituting Eqns. 3.2 and 3.5 into Eqn. 3.1
\[
\frac{dC}{dt} = A \, e^{-\frac{E_a}{RT}} (1-C)^n
\]

OR

\[
\frac{dC}{dT} = \left( \frac{A}{\beta} \right) (e^{-\frac{E_a}{RT}}) (1-C)^n \quad \text{... 3.6}
\]

Where \( \beta \) = Rate of heating

Methods of single heating rate

1. **Freeman-Carroll [32] and Anderson-Freeman methods [33]**

   Freeman-Carroll has developed the following relation to analyze TGA data at single heating rate:

   \[
   \frac{\Delta \ln \frac{dC}{dt}}{\Delta \ln (1-C)} = n - \frac{E_a}{R} \left[ \frac{\Delta \left( \frac{1}{T} \right)}{\Delta \ln (1-C)} \right] \quad \text{... 3.7}
   \]

   A plot of L.H.S. against \( \Delta \left( \frac{1}{T} \right) / \Delta \ln (1-C) \) would yield a straight line with slope equal to \( -\frac{E_a}{R} \) and the intercept equal to \( n \). Using Eqn. 3.7 Anderson-Freeman derived the Eqn. 3.8

   \[
   \Delta \ln \left( \frac{dC}{dt} \right) = n \, \Delta \ln (1-C) - \frac{E_a}{R} \, \Delta \left( \frac{1}{T} \right) \quad \text{...3.8}
   \]

   According to Eqn. (3.8), the plot of \( \Delta \ln (dC/dt) \) against \( \Delta \ln (1-C) \) for equal interval of \( \Delta (1/T) \) would be a straight line with slope equal to \( n \) and the intercept equal to \( -E/R \, \Delta (1/T) \).

2. Sharp-Wentworth method [34]

For a first order process (n=1), Sharp-Wentworth derived the following relation to analyze TGA data.

\[
\log \left( \frac{dC/\,dt}{1-C} \right) = \log \left( \frac{A}{\beta} \right) - \frac{E_a}{2.303R} \frac{1}{T} \quad \cdots 3.9
\]

Where C= fraction of polymer decomposed at temperature T, \( \beta= \) rate of heating, A= Frequency factor and Ea= the activation energy of the process. The plot of \( \log \left( \frac{(dC/dt)}{(1-C)} \right) \) against \( 1/T \) would be a straight line with slope equal to \( -(Ea/2.303 \, R) \) and the intercept equal to \( \log \left( A/\beta \right) \).

3. Chatterjee method [35]

Chatterjee has developed the following relation for the determination of n from TG curves based on weight units.

\[
n = \frac{\log \left( \frac{dW}{dt} \right)_1 - \log \left( \frac{dW}{dt} \right)_2}{\log W_1 - \log W_2} \quad \cdots 3.10
\]

Where \( W_1 \) and \( W_2 \) are the sample weights.

29. Horowitz-Metzger method [36]

The value of Ea can be determined from a single TG curve according to Horowitz – Metzger method

\[
\ln \left( \frac{E_a}{RT_s^2} \right) = \frac{E_a}{RT_s^2} \theta \quad \cdots 3.11
\]

Where, C= fraction of the compound decomposed at time t, Ea= activation energy, Ts= Temperature at which the rate of decomposition is maximum and \( \theta= T-T_s \)

The frequency factor $A$ and entropy change $\Delta S$ can be determined respectively according to Eqns. 4.12 and 4.13.

$$\ln E - \ln \left( \frac{T_s}{2} \right)^2 = \ln A - \ln \beta - \frac{E}{RT_s^2} \quad \ldots 3.12$$

$$A = \frac{k_b T}{h} e^{\Delta S / R} \quad \ldots 3.13$$

where $k_b$ is Boltzmann constant.

**Experimental**

TGA and DSC thermograms of EAN, EANOA, EANRA, EANAA and their copolymers were scanned on Perkin Elmer DSC-TGA (Model Pyris-I) at the heating rate of 10°C/min in nitrogen atmosphere.

**Results and Discussion**

The TG-thermograms of EAN, EANOA, EANRA, EANAA and copolyurethanes are presented in Figs. 3.17-3.18, respectively. From TG thermograms it is found that EAN, EANOA, EANRA, EANAA, EANRAPT, BCFMPT resins involved single step degradation while EANPT, EANOAPT, EANAAPT resins involved double steps degradation. EAN and EANOA are found to be thermally stable up to about 300°C. EANRA and EANAA are thermally stable up to about 250°C. EANPT, EANOAPT, EANAAPT, EANRAPT and BCFMPT are thermally stable up to about 200°C.

DSC thermograms of EAN, EANOA, EANRA, EANAA and copolyurethanes are presented in Figs. 3.19-3.27. DCS transition temperature and the characteristic temperatures for the assessment of the relative thermal stability of polymers are initial decomposition temperature ($T_0$), temperature of maximum weight loss ($T_{\text{max}}$) and temperature of final decomposition ($T_f$) are presented in Tables 3.11 and 3.12. The detail calculations for resins and their copolyurethanes are reported in Tables 3.13 and 3.14, respectively.
The plots of $\Delta \ln \frac{dW}{dt}$ against $\Delta \ln W$ are presented in Figs. 3.28-3.35.

The energy of activation ($E_a$), frequency factor ($A$), temperature of maximum weight loss ($T_{\text{max}}$) and entropy change ($\Delta S^*$) are determined according to Anderson-Freeman method [33] (Eqn. 3.8) and are reported in Tables 3.15-3.16.
Fig. 3.17: TG thermogram of EAN, EANOA, EANRA and EANAA at the heating rate of 100°C/min in an N2 atmosphere

Fig. 3.18 TG thermogram of EAN, EANOA, EANRA and EANAA at the heating rate of 100°C/min in an N2 atmosphere
Fig. 3.19: DSC thermogram of EAN at the heating rate of $10^3$C/min in an N$_2$ atmosphere

Fig. 3.20: DSC thermogram of EANOA at the heating rate of $10^0$C/min in an N$_2$ atmosphere
Fig. 3.21 DSC thermogram of EANRA at the heating rate of 10°C/min in an N₂ atmosphere

Fig. 3.22 DSC thermogram of EANAA at the heating rate of 10°C/min in an N₂ atmosphere
Fig. 3.23 DSC thermogram of EANRAPT at the heating rate of 10°C/min in an N₂ atmosphere

Fig. 3.24 DSC thermogram of EANPT at the heating rate of 10°C/min in an N₂ atmosphere
Fig. 3.25 DSC thermogram of BCFMPT at the heating rate of $10^0\text{C/min}$ in an $\text{N}_2$ atmosphere.

Fig. 3.26 DSC thermogram of EANAAPT at the heating rate of $10^0\text{C/min}$ in an $\text{N}_2$ atmosphere.
Fig. 3.27 DSC thermogram of EANOAPT at the heating rate of $10^0$C/min in an N$_2$ atmosphere
Table-3.11: DSC and TGA data of resins

<table>
<thead>
<tr>
<th>Resin</th>
<th>DSC Transition Temp., °C</th>
<th>T₀, °C</th>
<th>Tᵣ, °C</th>
<th>Tₘₐₓ, °C</th>
<th>%Wt. loss</th>
<th>% Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAN</td>
<td>134.69 (Endo) 157.44 (Endo)</td>
<td>280</td>
<td>420</td>
<td>372.01</td>
<td>60</td>
<td>38.9</td>
</tr>
<tr>
<td>EANOA</td>
<td>63.92 (Endo) 138.19 (Exo)</td>
<td>283</td>
<td>426</td>
<td>372.01</td>
<td>72</td>
<td>26.3</td>
</tr>
<tr>
<td>EANRA</td>
<td>66.22 (Endo) 142.98 (Exo)</td>
<td>200</td>
<td>450</td>
<td>372.01</td>
<td>70.58</td>
<td>16.33</td>
</tr>
<tr>
<td>EANAA</td>
<td>71.09 (Endo) 173.28 (Endo)</td>
<td>250</td>
<td>420</td>
<td>363.38</td>
<td>61.3</td>
<td>32.6</td>
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</table>
Table-3.12: DSC and TGA data of polyurethane resins

<table>
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<tr>
<th>Resin</th>
<th>DSC Transition Temp., °C</th>
<th>T₀, °C</th>
<th>Tᵣ, °C</th>
<th>T,max, °C</th>
<th>%Wt. loss</th>
<th>% Residue</th>
</tr>
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<tr>
<td>EANPT</td>
<td>77.91 (Endo)</td>
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<td>317</td>
<td>279.34</td>
<td>30</td>
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<td>414</td>
<td></td>
<td>380.44</td>
<td>33.67</td>
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<td>274</td>
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<td></td>
<td>317</td>
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<td>353.81</td>
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<td>EANRAPT</td>
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<td>450</td>
<td>372.16</td>
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<td></td>
<td>303.53 (Endo)</td>
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<tr>
<td>EANAAPT</td>
<td>72.6 (Endo)</td>
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<td>361.37</td>
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<td>BCFMPT</td>
<td>89.32 (Endo)</td>
<td>250</td>
<td>414</td>
<td>398.13</td>
<td>67.03</td>
<td>20.10</td>
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</table>
Table 3.13 The calculation scheme for EAN, EANOA, EANRA and EANAA by Anderson-Freeman method

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<tr>
<th>10^3/T</th>
<th>% wt. loss</th>
<th>dw/dt</th>
<th>W</th>
<th>InW</th>
<th>ln dw/dt</th>
<th>ΔlnW</th>
<th>ΔIndw/dt</th>
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</tr>
<tr>
<td><strong>EAN</strong></td>
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<table>
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<th>InW</th>
<th>Indw/dt</th>
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<tr>
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<tr>
<td>$10^3/T$</td>
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<td>$dw/dt$</td>
<td>W</td>
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### Characterization

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Fig. 3.28 The Anderson-Freeman plots for EAN

\[ y = 1.174x - 0.222 \]
\[ R^2 = 0.998 \]

Fig. 3.29 The Anderson-Freeman plots for EANOA

\[ y = 0.687x - 0.155 \]
\[ R^2 = 0.984 \]
Characterization……

Fig. 3.30 The Anderson-Freeman plots for EANRA

\[
y = 1.282x - 0.251 \\
R^2 = 0.981
\]

Fig. 3.31 The Anderson-Freeman plots for EANAA

\[
y = 0.588x - 0.145 \\
R^2 = 0.936
\]
Figs. 3.32 The Anderson-Freeman plots for EANPT
Figs. 3.33. The Anderson-Freeman plots for EANOAPT
Figs. 3.34. The Anderson-Freeman plots for EANAAPT
Fig. 3.35. The Anderson-Freeman plots for BCFMPT

\[ y = 2.973x - 0.174 \]

\[ R^2 = 0.998 \]
Table 3.15: Kinetic parameters of EAN, EANOA, EANRA and EANAA resins

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<th>Resin</th>
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<th>$E_a$, kJ</th>
<th>$A$, S$^{-1}$</th>
<th>$\Delta S^*$, J deg$^{-1}$</th>
<th>Regression coefficient, $R^2$</th>
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<tr>
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<td>EANOA</td>
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<td>EANAA</td>
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<td>$5.31 \times 10^7$</td>
<td>103.3</td>
<td>0.936</td>
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Table 3.16: Kinetic parameters of EANPT, EANOAPT, EANRAPT, EANAAPT and BCFMTP

<table>
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<th>Resin</th>
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<th>$A$, S$^{-1}$</th>
<th>$\Delta S^*$, J deg$^{-1}$</th>
<th>Regression coefficient, $R^2$</th>
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<td>BCFMPT</td>
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Section-VI: Density measurements of the polyurethane

The density, specific volume and molecular mass are useful in evaluation of various thermodynamic properties of the simple as well as polymeric materials [37-39]. These data are most useful for the average distance between macromolecular chains and the extent of crystallinity in polymers.

Theoretical calculation of the density

The density of the polymer can be calculated from the knowledge of the structural aspects. According to Slonimskii et al. [40] the density of the polymer may be expressed as:

$$\rho = \frac{K \cdot M}{N_A \sum \Delta V} \quad \text{...3.14}$$

Where $K$ is the packing coefficient, $M$ is the molecular weight of the repeat unit of the polymer, $\sum \Delta V_i$ is the intrinsic volume of the polymer repeat unit and $N_A$ is the Avogadro’s number. The values of $\sum \Delta V_i$ can be calculated from the knowledge of the volume increments $\Delta V_i$ of the atoms and groups of atoms. The packing coefficient $K$ is the ratio of the intrinsic volume to the true volume and it can be calculated from the experimental density of the polymer.

$$K = \left(\frac{K_{\text{int}}}{K_{\text{true}}}\right) = \frac{N_A \sum \Delta V_i}{M/\rho} \quad \text{...3.15}$$

Determination of density by floatation method

The density of BCFMPT-200 film was determined by a floatation method by using CCl₄-n-hexane system at 35°C temperature. In six different wide mouth stoppered test tubes, a small piece of film and about 5ml CCl₄ were placed and n-hexane was added drop wise with shaking till the film remained suspended throughout and allowed to equilibrate at room temperature for 24 h. The densities of the resultant mixtures were determined by usual method. The average of six measurements and standard deviation from mean values were determined. The observed density of BCFMPT-200 is 1.2719 ± 0.00049 g/cm³.

Section-VII: Mechanical properties of polyurethane film

Physical properties of PUs largely depend upon polymer chain structure, soft and hard segments [41]. Materials properties associated with elastic and inelastic reactions to an applied force that is called mechanical properties. The mechanical properties of polymers are the foremost requirement for a designer. Mechanical and electrical properties are very useful for end use applications. Tensile data of polymers are useful for the purpose of engineering design and understanding the characteristics of the materials.

In recent years plastics have been increasingly used for mechanical applications principally as gears, spring and bearings. The usage of plastics for mechanical applications offers the advantages such as elimination of parts through design, elimination of finishing operations, simplified assembly,and reduced maintenance, obviations of lubrications, weight savings, noise reduction and freedom from corrosion.

The mechanical properties of plastics can be broadly classified as short-term, long term and surface properties. The short-term properties are measured

Characterization

... at a constant rate of stress or strain in different modes like tension, compression, flexural, shear, etc. The long term properties are measurements of deformation or stress decay with respect to time in static conditions e.g. creep and stress relaxation. The mechanical properties of the surface include hardness, scratch, friction, and abrasion. The study of stress in relation to strain in tension depicts the tensile properties of the material. Tensile test data are widely used for defining the quality of different lots of polymeric materials.

Choi et al. [42] have reported preparation and characterization of conductive polyurethane films. In this study, conductive polyurethane (PU) films were prepared by the condensation of poly (propylene glycol) (PPG), toluene 2,4-diisocyanate, and 3-methylthiophene (3-MT) under various preparation conditions. The effects that the reaction time and temperature have on the morphology and surface free energy were investigated by scanning electron microscopy (SEM) analysis and contact angle measurements, respectively. The mechanical properties, such as tensile strength and elongation at break were also studied. The conductivity of the composite was as high as 42 S/cm.

Kozakiewicz et al. [43] have studied the effect of introducing double bonds and siloxane segments to the polyurethane-urea chain on the properties of polyurethane and polyurethane-acrylic/styrene dispersions. Several properties of dispersions, coatings and films were determined, including particle size, stability, and MFFT (minimum film-forming temperatures) of dispersions, hardness, resistance to water and solvents, adhesion of coatings and mechanical properties, and the glass-transition temperature ($T_g$) of films.

Bharadwaj et al. [44] have prepared polyurethane (PU) elastomers from castor oil based polyol, polyethylene glycol (PEG) of various molecular weights (200, 400 and 600) and toluene diisocyanate in the form of transparent sheets. The sorption, mechanical and thermal properties have been studied. The solubility parameter, molecular weight between two crosslinks and degree of crosslinking of PU samples were calculated from equilibrium swelling experiments. The kinetic study of swelling revealed that sorption is anomalous in nature in all the samples. Diffusion coefficient (D) and sorption coefficient (S) were found to decrease with an increase in chain length of PEG. The stress-strain data showed that the elastomers obtained using PEG-200 gave the best mechanical properties. The thermal degradation of all elastomers starts at \( \sim 250^\circ C \), regardless of the PEG chain length. The values of activation energy of degradation were in the range of 600-725 kJ/mole.

**Measurements**

The tensile strength (ASTM D 638-91) measurements were done and average value is found to be 7.53 MPa. Mechanical properties of the materials depend upon various factors namely temperature, humidity, loading conditions, rate of loading, morphology, molecular architecture, molecular weight, molecular weight distribution, degree of cross-linking, extent of plasticization, fillers, sample thickness, impurities, etc. The low magnitude of tensile strength indicated brittle nature of the BCFMPT-200 film. Electrical properties of the BCFMPT-200 film could not perform due to brittle nature.

**Section-VIII: Chemical resistance study of copolyurethanes**

Polymeric materials absorb moisture in humid atmosphere and when immersed in water. The extent of water uptake mainly depends on the presence of hydrophilic polar groups, void volume, additives, humidity and temperature.

Hydrolytic stability of polymeric materials depends on the nature and molecular structure of the polymers. The tendency of water uptake by polar groups present in polymers increases the dissociation and hydrolysis and hence introduces ionic impurities, which affect electrical and mechanical properties to a greater extent.

Ajithkumar et al. [45] have performed equilibrium swelling experiments of interpenetrating polymer networks (IPNs) based on castor oil-based polyurethanes (PU) and unsaturated polyester (UPE) in various solvents, in order to calculate their solubility parameter. The kinetics of swelling and sorption were also studied in chlorobenzene at 25°C. IPNs with various weight compositions of PU and UPE (80:20, 50:50 and 20:80) (-NCO/-OH ratio) viz. 1.2, 1.5 and 2.0 were used in the study. The results were found to vary with the weight compositions of the components of the samples. The absorption behavior also varies with the hydroxyl number (mol. wt.) of the polyol used in the preparation of PU.

Somani et al. [46] have studied the equilibrium swelling of polyurethanes (PU) in various solvents in order to calculate their solubility parameter. The kinetics of swelling and sorption were also been studied in 1,4-dioxane at 30°C. The PU was synthesized by reacting a novel polyol (castor oil derivative and epoxy based resin, EpxR) and one of the polyethylene glycols (PEG 200, PEG 400, PEG 600) with different weight compositions, with a toluene diisocyanate (TDI) adduct (derived from toluene diisocyanate and R60 polyol). Different -NCO/-OH ratio viz. 1, 1.3 and 1.7 were employed in the study.


The results were found to vary with the weight composition of polyol components, as well as the crosslink density of the samples. The sorption behavior was also found to vary with the molecular weight of polyethylene glycol employed in the preparations of the polyurethanes. Kinetic studies of swelling revealed that the sorption was anomalous in nature. The diffusion coefficient (D) increased with an increase in the -NCO/-OH ratio and decreased with an increase in chain length of polyethylene glycol.

Water uptake of BCFMPT-200 film against various reagents at room temperature was determined according to change in weight method:

\[
\% \Delta M = \left( \frac{M_2 - M_1}{M_1} \right) \times 100 \quad \ldots 3.16
\]

Where \( \Delta M \) is the change in weight, \( M_1 \) is the initial weight and \( M_2 \) is the weight after chemical treatment with time.

Water uptake study of BCFMPT-200 film was tested against various reagents (water, 10% each of aq. HCl, HNO₃, H₂SO₄, NaOH, KOH and NaCl) at 35°C temperature at the interval of 24h by change in weight method (Figs. 3.3). The % weight gain increased with the passage of time till the equilibrium was established. Equilibrium % weight gain and equilibrium time data are reported in Table 3.17. From Table 3.17, it is observed that water uptake is high in acidic environments and the minimum in pure water. Ester and urethane linkages in the resin are polar groups, which from H-bonding with regents’ solutions and hence increase in weight gain. The Na⁺ and K⁺ ions of alkalis and salt are solvated by the resin molecules. Thus, resin has structure forming tendency in the reagents studied.
The nature of strong electrolytes affect water structure and hence water uptake tendency via H-bond formation of salvation due to presence of urethane and ester groups [47-48]. Strong electrolytes break water structure and hence result increase in diffusivity. The observed water absorption order is HCl > H₂SO₄ > HNO₃ > KOH > NaOH > NaCl > H₂O. Absorbed water induces irreversible changes namely chemical degradation and cracking, while hydrophilic polar groups are responsible for blistering. Cracking and blistering cause high water absorption [48]. From experimental finding it is concluded the copolymer film has good hydrolytic stability against water, saline, alkaline and acidic environments without any damage.


Table 3.17: Equilibrium % weight gain and time data for copolyurethane films

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<tr>
<td>NaOH</td>
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<td>KOH</td>
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</tbody>
</table>

Fig. 3.35 Plots of % weight gain with time in different reagents for BCFMPT-200.
CHAPTER – 4

FABRICATION AND

PHYSICO-CHEMICAL

STUDIES OF COMPOSITES
This chapter of the thesis describes the composites based on jute, cane sugar husk and rice husk and glass fibers.

This chapter is further subdivided into three sections:

Section-I: Fabrication of composites

Section-II: Mechanical and electrical properties of composites

Section-III: Water uptake study of composites

Section-I: Fabrication of composites

There are many processes which are applicable for fabrication of composites such as,

- Wet filament winding
- Hand lay-up technique
- Automated tape placement
- Resin transfer molding
- Pultrusion
- Injection molding
- Vacuum bagging
- Machine finishing

Among all the processes, hand lay-up technique is the cheapest process and all the composites reported in this chapter are fabricated by this technique. Many researchers have reported the fabrication of composites by hand lay-up technique since 1978 onwards [1-7].

Appropriate selection of fabrication-process is important part in composite preparation because manufacturing process is directly affects the cost of the composite. When the uses of composite at any specific applicable field like space application, where cost is not prior point than applicability, at that field any suitable process can be
used. But hand lay-up technique is better for routine application fields like manufacturing hardboard, construction devices, partition board, medium density fiber boards, panels, packaging, etc. than any other techniques. Many composite industries and research institutes, which are working on composites in India using hand lay-up technique for fabrication of composites.

Woven jute fibers (Brown jute, Corchorus Capsularis), rice husk and can sugar fibers used in present study were collected from the local market. Epoxy resin of 9, 9' bis(4-hydroxy phenyl) anthrone-10(EAN) was synthesized and purified according to section 5 of Chapter 2. Silane treated E-glass fabric (7 mil) (Unnati Chemicals, India) was used for composite purpose.

[A] Fabrication of jute, glass and their hybrid (glass-jute-glass) fiber reinforced polyurethane composites

Glass, jute and their hybrid composites (15cmx15cm) of EAN and PEG-200 polyurethane resin were fabricated by hand layup technique. EAN used for composite preparation was 50 % of jute/glass fabrics. 2, 4-Toluene diisocyanate (TDI) and PEG-200 used were 30 % of EAN. Types of composites, weight of (fibers, EAN, PEG-200 and TDI) are summarized in Table 4.1.

Thus, to a 250 ml beaker, required quantity of EAN was dissolved in 90 ml chloroform at room temperature. To this solution required quantity of TDI was dissolved in 15 ml chloroform and was added dropwise with stirring over a period of 10 min. To this reaction mixture required quantity of PEG-200 was added dropwise with stirring. The resultant reaction mixture was stirred for 20 min at room temperature and applied to jute/glass fabrics with the help of a smooth brush and prepregs were allowed to dry in the sunlight for about 15 min. Ten such prepregs were stacked one over the other and pressed between the two preheated stainless steel plates under the hydraulic pressure of 15.4 MPa at 80°C for 2h and 12h at room temperature. For hybrid composite the prepregs were stacked alternatively, i.e. glass-jute-glass. Silicone spray was used as a mold releasing agent. Here after composites are designated as EANPT-J, EANPT-G and EANPT-GJG.

[B] Fabrication of hybrid polyurethane composites

EANPT resin used for the preparation of hybrid composite was prepared according to method discussed above. BANFPT was synthesized by following method.

Thus, to a 250 ml beaker, required quantity of BANF was dissolved in 90 ml MEK at room temperature. To this solution required quantity of TDI was dissolved in 15 ml MEK and was added dropwise with stirring over a period of 10 min. To this reaction mixture required quantity of PEG-200 was added dropwise with stirring. The resultant reaction mixture was stirred for 20 min at room temperature.
Table 4.1 Fiber-matrix, TDI and PEG-200 compositions for epoxy jute, glass and their hybrid 15cm X 15cm size composites

<table>
<thead>
<tr>
<th>Type of Composite</th>
<th>Wt. of fabrics, g</th>
<th>Wt of resin (50% of fabrics), g</th>
<th>Wt of TDI (30% of resin), g</th>
<th>Wt of PEG-200 (30% of resin), g</th>
</tr>
</thead>
<tbody>
<tr>
<td>EANPT-J</td>
<td>82</td>
<td>41</td>
<td>12.3</td>
<td>12.3</td>
</tr>
<tr>
<td>EANPT-G</td>
<td>58</td>
<td>29</td>
<td>8.7</td>
<td>8.7</td>
</tr>
<tr>
<td>EANPT-GJG</td>
<td>(22 + 42)</td>
<td>32</td>
<td>9.7</td>
<td>9.7</td>
</tr>
</tbody>
</table>
The hybrid composites are made by one shot method. Ordinary sieves were used to separate the different sizes of rice husk (RH) /cane sugar (CS) fillers. The average fillers size used in the present study were 2-3mm (RH) and 5-6mm (CS). Types of composites, weight of (fibers, EAN, BANF, PEG-200 and TDI) are summarized in Table 4.2.

Above described BANFPT/EANPT resin (50% of total weight of jute and filler material) solution was applied to two 15cmx15cm woven jute fiber sheets with the help of a smooth brush and remaining resin was mixed with 25g RH/CS filler at room temperature. Resin coated jute sheets and RH/CS filler were allowed to dry at room temperature for about 15 min. Resin coated RH/CS filler was uniformly sandwiched between two resin coated jute sheets (Fig. 4.1) and placed between two preheated stainless steel plates and pressed under hydraulic pressure of 15.4 MPa at 150°C (BANFPT-RH-J) / 100°C (EANPT-CS-J) for 2.5 h and 12h at room temperature. Silicone spray was used as a mold releasing agent.

Figure-4.1: Arrangement of Jute-Biomass composite
Table 4.2 Fiber-matrix, TDI and PEG-200 compositions for hybrid 15cm X 15 cm size composites

<table>
<thead>
<tr>
<th>Type of Composite</th>
<th>Wt. of fabrics, g</th>
<th>Wt of resin (50% of fabrics), g</th>
<th>Wt of TDI (30% of resin), g</th>
<th>Wt of PEG-200 (30% of resin), g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Jute</td>
<td>CS/RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EANPT-CS-J</td>
<td>20</td>
<td>30</td>
<td>25</td>
<td>7.5</td>
</tr>
<tr>
<td>BANFPT-RH-J</td>
<td>22</td>
<td>25</td>
<td>24</td>
<td>25</td>
</tr>
</tbody>
</table>
Section-II: Mechanical and electrical properties of composites

Mechanical properties

The foremost requirement for a designer of a composite product is the data on the mechanical properties, which enable him to select the one best suited for the desired application. Recently, composites are being widely used as load bearing and engineering applications by allowing various fibers of high strength as a base for composite fabrication. By selection of appropriate matrix-reinforcing systems, desired properties can be achieved.

During service, composite has to suffer the cyclic stress, tensile, flexural, impact forces, bending, friction, wear and different types of stresses on it. Depending upon the mode of application, composite must be mechanically strong to suit the job. The geometrical response to loading leads to a wide range of mechanical properties grouped under stress-strain properties, visco-elasticity and failure properties. The various mechanical properties of the composites depend upon following factors:

- Type of reinforcing fiber
- Fiber-matrix adhesion
- Time and temperature of cure
- Molecular weight of polymer
- Fiber strength, modulus, fiber length and orientation
- Compatibilizers and impact modifiers
- Fiber content
- Presence of soft and hard segments
- Fiber loading, etc.

Depending on the property to be measured, standard test methods have been developed. However, they vary from each other in terms of loading conditions, shape and size of the test specimens, etc.

The mechanical properties of the plastic materials can be broadly classified into the following types:
Short-term mechanical properties

They are measured at a constant rate of stress or strain in different modes
- Tensile strength
- Flexural strength
- Compression strength
- Shear strength

Long-term mechanical properties

They are the measurements of deformation or stress decay with respect to time in static conditions
- Visco-elasticity
- Creep
- Stress relaxation

Surface properties

The mechanical properties of the surface include
- Hardness
- Scratch resistance
- Friction
- Abrasion resistance

The study of stress in relation to strain in tension depicts the tensile properties of the material. Tensile properties of materials are most widely useful for engineering design and understanding quality characteristics of polymeric materials. In tensile testing, samples can be prepared by different ways namely molding, compression molding and punching. In present investigation samples were prepared by compression molding as per prescribed standard tests for tensile and flexural testing.

The tensile strength ($\sigma$) of the composites was determined according to Eqn.4.1:

$$\sigma = \frac{W}{A} \quad \ldots 4.1$$

Where $W=$ the load value at break and $A=$original cross sectional area of the sample
Flexural strength is the resistance of material under the bending mode. Flexural properties are useful for quality control and classification of materials with respect to bending strength and stiffness. They depend upon various factors namely

- Type and amount of additives, which can soften or reinforce the material
- Method of sample preparation e.g. molding or machining
- Temperature
- Surface roughness, sinks, voids and other imperfections
- Anisotropy
- Accuracy in measured dimensions.

Flexural strength of the composites was determined according to Eqn.4.2:

\[
\text{Flexural strength} = \frac{1.5FL}{wt^2} \quad \cdots 4.2
\]

Where \( F \) = breaking load, \( L \) = span length (60-65mm), \( w \) = sample width (mm) and \( t \) = sample thickness (mm)

The mechanical behavior of polymers can be divided into three main groups: (I) Elastic (II) Plastic and (III) Brittle. The same sample can behave as a brittle, tough or rubber-like above and below the glass transition temperature. Slow rate of testing will simulate stiffer molecules and harder properties. The mechanical tests are classified as impact, tensile, flexural, hardness, etc. based on applied deforming stress.

The mechanical properties may best be divided into three sections:

1. Reversible rigidity/flexibility or modulus, which measures the stiffness of the polymer
2. Mechanical failure by yielding (Permanent deformation) or breaking at low or high rates of test or under a multiple cyclic stress
3. Complex mechanical properties involving a combination of these simpler processes
Joffe et al. [8] have studied the composites based on flax as a reinforcing fiber. They have fabricated natural fiber composites (NFC) and compared their mechanical properties with glass mat thermoplastics (GMT). The investigation showed that NFC have mechanical properties such as matrix/fiber compatibility, stiffness, strength and fracture toughness are as high as GMT or even higher in some cases. They have concluded that such a good mechanical properties in combination with lightweight makes use of NFC very attractive for automotive industries.

Vajrasthira et al. [9] have investigated the mechanical and dynamic mechanical properties of thermoplastic polyurethane (TPU) elastomers reinforced with two types of aramid short fibers, m-aramid (Teijin-Conex) and copoly(p-aramid) (Technora) with respect to the fiber loading. In general, both types of composites exhibited very similar stress-strain behaviors, except that Technora-TPU was stronger than Conex-TPU. This was primarily due to the intrinsic strength of the reinforcing fibers. The morphologies of cryogenically fractured surfaces of the composites and extracted fibers, investigated with scanning electron microscopy, revealed possible polar-polar interactions between the aramid fibers and TPU matrices.

Reboredo et al. [10] have fabricated the composites of unsaturated polyester using saw dust and Eucalyptus saligna oil or calcium carbonate as reinforcing fillers and studied the effect of filler concentration and surface treatment on the ultimate strength, elongation, modulus and dynamic mechanical properties.


Tay et al. [11] have fabricated the empty fruit bunch–polyurethane (EFB–PU) composites reacting EFB and polyethylene glycol (PEG) with diphenyl methane diisocyanate (MDI) and determined their tensile properties. The results revealed that the tensile properties were influenced by the percentage of -OH groups of EFB, coupled with the reinforcing effect of EFB filler. In addition to that, the formation of PU matrix from PEG and isocyanate proved to be crucial in producing good stress transfer from the matrix to the filler. SEM study showed that surface area of the filler also contributed towards the strength of the composites.

Ahmadhilmi et al. [12] have fabricated the treated and untreated polyurethane (PU)-oil palm empty fruit bunch (EFB) composites. The PU matrix employed consisted of diphenyl methane diisocyanate (MDI) and polyethylene glycol (PEG) with a molecular weight of 200. EFB fibers were used in the form of mats. The fibers were treated with two types of isocyanate: hexamethylene diisocyanate (HMDI) and toluene diisocyanate (TDI). The properties of the composites were believed to be predominantly influenced by the type of bonding produced. In general, the composites with isocyanate treated fibers showed superior tensile and flexural strength than those without treatment. These were believed to be attributed to the additional reaction sites in the form of urethane functional groups produced as the result of -NCO reactions with -OH of EFB prior to subsequent interaction with PU/PEG mixtures. The relatively superior properties of composites with HMDI treated fibers over those treated with TDI were probably due to the longer chain of the former, which render it more accessible to the reaction with -OH of PEG and also to its increased capability in absorbing more energy transferred from the matrix.

Gassan et al. [13] have fabricated flax fiber reinforced polyurethane composites and determined their mechanical properties. Flax fibers coated with two types and various amounts of silicones. Coating conditions have been found to affect strongly the composites properties. The effect of these two types and different amounts of silicone on the impact toughness, flexural strength and modulus, dynamic modulus and loss-energy and notch sensitivity are determined.

Carvalho et al. [14] have evaluated the tensile and impact behavior of jute fabrics—polyester composites as a function of the fabric style (knitted or weaved clothes), fiber weight fraction, and direction of the applied load. The tensile properties of plain-weave-fabric-reinforced composites (PWF) were higher than those of plain weft knit cloth composites (WKT) and were dependent on fiber content and test direction. The properties of the WKT, however, were independent of these variables. The obtained results indicate that the orthogonal fiber alignment of weaved cloths favors anisotropy, while the interconnected loops in knit fabrics favors isotropy. The results also indicated weak fiber-matrix interactions in both fabrics and a better fabric impregnation for the plain weave fabric, if compared with that of the knit fabric. The impact strength of both composites was higher than that of the matrix and was shown to increase with fiber content. WKT-reinforced composites showed better impact absorption capacity than PWF composites.

Sastra et al. [15] have determined the tensile strength of arenga pinnata fiber as

a natural fiber and epoxy resin as a matrix. For this the arenga pinnata fibers were mixed with epoxy resin at the various fiber weight percentages of 10%, 15%, and 20% arenga pinnata fiber and with different fiber orientations such as long random, chopped random, and woven roving. Results from the tensile tests of arenga pinnata fiber reinforced epoxy composite were that the 10 wt% woven roving arenga pinnata fiber showed the highest value for maximum tensile properties. The tensile strength and Young's modulus values for 10 wt. % of woven roving arenga pinnata fiber composite are 51.725 MPa and 1255.825 MPa, respectively. The above results indicated that the woven roving arenga pinnata fiber has a better bonding between its fiber and matrix compared to long random arenga pinnata fiber and chopped random arenga pinnata fiber. Scanning electron microscopy (SEM) tests were also carried out after tensile tests to observe the interface of fiber and matrix adhesion.

Wang et al. [16] have fabricated waterborne polyurethane (WPU) composites and have studied the effect of crosslinking agent on the different properties. Waterborne polyurethane (WPU) and casein (1:1 by weight) were blended at 90°C for 30 min, and then were crosslinked by adding 1-10 wt % ethane diol to prepare a series of sheets. Their structure and properties were characterized by using infrared spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), dynamic mechanical analysis, and tensile testing. The results indicated that crosslinked blend sheets exhibited a certain degree of miscibility, and exhibited much higher tensile strength and water resistivity than did the WPU, casein, and the uncrosslinked blend from WPU and casein. When the ethane diol content was 2 wt %, the tensile strength and elongation at break of crosslinked sheets achieved 19.5 MPa and 148% in the dry state, and 5.0 MPa and 175% in the wet state, respectively. A 2 wt % content of ethane diol played an important role in the enhancement of mechanical properties, thermal stability, and water resistivity of the blends of WPU and casein.

Cao et al. [17] have fabricated waterborne polyurethane (WPU)/starch (ST) with different contents (10-90 wt %) composites and studied the effect of different starch content on the various properties of the composites. Their miscibility, structure, and properties were investigated by wide-angle X-ray diffraction (WAXD), scanning electron microscope (SEM), different scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and the tensile tests, respectively. The results indicated that tensile strength of composite materials not only dependent on the starch content, but also related to the microstructure of WPU. The sample WPU2 (1.75 of -NCO/-OH molar ratio) exhibited hard-segment order, but WPU1 (1.25 of -NCO/-OH molar ratio) had no hard-segment order. The blend material from 80 wt % WPU1 and 20 wt % starch exhibited better tensile strength (27MPa), elongation at break (949%), and toughness.

Fengchang and Weibo [18] have studied the dynamic mechanical and vibration damping properties of polyether urethane and epoxy composites. The experimental results showed that the crosslink density was an important factor that influenced the loss factor of polyether-urethane damping materials; increasing the amount of pendant methyl of the backbone contributed to raising the value of the loss factor (tanδ) and broadened the damping temperature range; adding the planar filler can increase the shear motion and the internal dissipation in polyurethane materials. As the thickness ratio and the Young's modulus of the constraining layer increase, the composite loss factor increased significantly.


Kumar and Siddaramaiah [19] have fabricated the alkali treated and untreated bamboo fibers (Bambusa balcooa) reinforced polyurethane/ PMMA interpenetrating polymer network (IPN) based composites. The mechanical properties, like tensile strength and tensile modulus, and the chemical resistance of bamboo fibers before and after coating with PU and PU/PMMA IPN have been studied. Improvement in tensile strength, tensile modulus and chemical resistance of bamboo fibers were observed after coating with polymers. The PU/PMMA coated system showed better performance as compared to PU-coated bamboo fiber composite.

Musa et al. [20] have produced rice husk (RH)-unsaturated polyester (USP) composites and investigated their tensile, flexural, impact and dimensional properties. From the results, it was observed that the tensile, flexural and impact properties decreased as the percentage of filler was increased. The composites with smaller filler size displayed higher tensile, flexural and impact properties than those with larger filler size. This might be attributed to the higher surface area of the RH, which resulted in more interaction between the -OH groups of RH of the polyester matrix. The water absorption and thickness swelling of the composites showed an increasing trend as the immersion time was increased. However, samples with smaller filler size showed lower water absorption and thickness swelling than those with larger filler size.

Hazlan et al. [21] have produced rice husk (RH)–glass fiber (GF) hybrid polyester composites and investigated their tensile, flexural, impact and dimensional properties. From the results, it was observed that the tensile, flexural and impact properties decreased as the percentage of filler was increased. The composites with smaller filler size displayed higher tensile, flexural and impact properties than those with larger filler size. This might be attributed to the higher surface area of the RH, which resulted in more interaction between the -OH groups of RH of the polyester matrix. The water absorption and thickness swelling of the composites showed an increasing trend as the immersion time was increased. However, samples with smaller filler size showed lower water absorption and thickness swelling than those with larger filler size.


composites have been produced. Tensile, flexural, impact, and dimensional properties of the composites have been investigated. From the results, it was observed that GF imparted higher tensile, flexural, and impact properties. The presence of RH in the matrix produced composites with comparable tensile, flexural, and impact properties especially in the middle range of RH:GF ratios. Longer GF had a profound effect on the strength and toughness, while the shorter GF contributed the modulus of the composites. The incorporation of RH in the composites resulted in an increase in water absorption and thickness swelling. Overall, the study shows that RH together with GF produced composites with acceptable properties.

Ang et al. [22] have fabricated polyurethane composites with rice husk (RH) with polypropylene glycol, molecular weight (Mw) of 400 used as polyols and investigated the effect of percentage of RH (by weight), percentage of RH hydroxyl (-OH) groups, and RH size on the flexural, tensile, and impact properties. For most tests, the properties increased as the percentage of RH or percentages of RH -OH groups were increased. However, after exceeding a threshold value, the properties started to decrease. A dimethylformamide (DMF) immersion test showed that absorption and swelling decreased as the percentage of RH was increased. The size of RH also played a significant role in the properties, where smaller size RH produced composites with higher strength. This is due to the greater surface area for interaction between the -OH groups from the RH and -NCO groups from MDI, which could be detected by scanning electron microscope (SEM) analysis. The increased in water absorption and thickness swelling as the percentage of RH was increased was attributed to the ability of RH -OH groups to absorb water, causing the cell wall to swell.

Fujii et al. [23] have fabricated bamboo reinforced polypropylene composites for ecological purposes (Eco-composites) and have studied their basic mechanical properties. The steam explosion technique was applied to extract bamboo fibers from raw bamboo trees. The experimental results showed that the bamboo fibers (bundles) had a sufficient specific strength, which is equivalent to that of conventional glass fibers. The tensile strength and modulus of PP based composites using steam-exploded fibers increased about 15 and 30%, respectively, due to well impregnation and the reduction of the number of voids, compared to the composite using fibers that were mechanically extracted. The steam explosion technique was an effective method to extract bamboo fibers for reinforcing thermoplastics.

**MEASUREMENTS**

Tensile strength and flexural strength (IS 6748:1994) measurements were made on a Shanta Engineering Tensile Testing Machine, Model No. SET/T/50 at a speed of 50 mm/min.

Comparative tensile strength and flexural strength of EANPT-J, EANPT-G and EANPT-GJG are reported in Table 4.3 from which, it is clear that tensile strength of EANPT-GJG (49 MPa) is intermediate of EANPT-J, (33 MPa) and EANPT-G (52 MPa). As glass fibers (1200-1800 MPa) is much stronger than that of jute fibers (300-700MPa). From Table 4.3, it is observed that flexural strength is improved to a considerable extent. Stiffness of EANPT-GJG is improved by 142 % and 18 % as compared to EANPT-J and EANPT-G, respectively due to stiff nature of glass fibers. Thus, moderate tensile and flexural properties of the composites signify their importance for low load bearing applications especially for housing units. The mechanical properties of the composites depend on number of factors namely fiber content, fiber orientation, nature of fibers, fiber modification, interfacial bonding, additives like fillers, compatibilizer and impact modifier, humidity and mode of testing, etc[24].
Table 4.3 Mechanical properties of EANPT-J, EANPT-G, EANPT-GJG and EANPT-CS-J, BANFPT-RH-J composites

<table>
<thead>
<tr>
<th>Composite</th>
<th>Tensile strength, MPa</th>
<th>Flexural strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>EANPT-J</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>EANPT-G</td>
<td>52</td>
<td>39</td>
</tr>
<tr>
<td>EANPT-GJG</td>
<td>49</td>
<td>46</td>
</tr>
<tr>
<td>EANPT-CS-J</td>
<td>18</td>
<td>14</td>
</tr>
<tr>
<td>BANFPT-RH-J</td>
<td>21</td>
<td>11</td>
</tr>
</tbody>
</table>


From Table-4.3, it is clear that mechanical properties of sandwich composites are decreased considerably due to random orientation of fillers (CS and RH). There are two types of interfacial interactions namely covalent and H-bonding. Hydroxyl groups of cellulosics serve as reaction sites with various functional groups present in the resin. Thus, RH and CS both can be used as fillers as well as reactive components. In sandwich composites biomass fibers are not lined up in any direction and they are just tangled mass. The composites can be made stronger by lining up all the fibers in the same direction as in woven jute fabric (Fig. 4.1).

Oriented fibers are strong when pulled in fiber direction but they are weak at right angle to the fiber direction. The woven fibers give a composite a good strength in many directions and under tension, the strength of the composite is entirely due to reinforcement. The observed decrease in tensile strength and flexural strength of sandwich composites are due to random orientation of filler fibers, which are responsible for discontinuous stress transfer and decrease in strength and stiffness of PU. The lone pairs of electrons of urethane linkages form H-bonds with hydroxyl groups of jute and RH/CS fibers and hence resulted in improved

In present case glass composite possesses good tensile and flexural properties but sandwich composites possess fairly good tensile and flexural properties indicating their usefulness as low load bearing applications especially for housing units and others.

**Electrical properties**

Synthetic polymers are known for their electrical insulation characteristics. The majority of them are organic in nature, having covalent linkages; they provide high resistance to electric current flow. Earlier materials like wood, amber, ceramic, gutta-percha and natural rubber were the main materials used as insulating materials. Their limited range of mechanical properties and difficulties in fabrication were some of the reason why these materials could not provide the support to the electrical industry. Nowadays large numbers of synthetic polymers are available, which possess excellent
mechanical properties in combination with high electrical resistance. When assessing a potential insulating material, information on the following properties will be required.

• Dielectric constant (specific inductive capacity, relative permeability) over a wide range of temperature and frequencies
• Power factor over a range of temperature and frequency
• Dielectric strength (usually measured in kV/cm)
• Volume resistivity (usually measured in Ω cm or Ω m)
• Surface resistivity (usually measured in Ω cm)
• Tracking and arc resistance

The electrical properties of polymer materials are of considerable importance, where plastics are used in or near electrical equipments as insulating materials, supporting assemblies, connectors, housing, etc. The use of polymers in engineering as dielectrics is becoming increasingly important. The choice of polymeric dielectrics for each concrete case depends on its dielectric and other physical properties over a wide range of temperatures and electrical field frequencies. Investigations of dielectric properties are most important for studying polymer structure.

Electrical properties of the polymeric composites are affected by several factors namely

✓ Humidity
✓ Impurities
✓ Degree of resin cure
✓ Temperature
✓ Nature of polymers and nature of fillers and additives
✓ Geometry, electrode area and electrode material
✓ Sample thickness,
✓ Time of voltage application
✓ Current frequency and
✓ Extent of ageing.
Typical electrical properties of some selected plastic materials are reported in Table 4.4. In order to study the dielectric properties of composites, an ideal contact should be satisfied the certain conditions.

1. It should not induce a resistance to the flow of the current
2. It should not react chemically with semi conducting material
3. The contact properties should not be affected by variation of ambient conditions like illumination, temperature, electrical field, etc.
4. The -OHm’s low should apply to the semiconductor with contacts

The working voltage applied to an electrical insulating material must be much lower than the voltage, which causes the material rupture. Electrical discharge through a material at a minimum voltage called break down or disruptive voltage $V_{br}$ [25]. In some cases voltage lower than the break down voltage gives rise to a surface discharge that dose not penetrate deep into the bulk of a material. This is a surface or creeping, breakdown occurring at a surface break down voltage.

The basic characteristic of an electrical insulating material is its breakdown or dielectric strength $E_{br}$ (also called electric strength), which is a minimum strength of the uniform electric field that causes dielectric breakdown. The calculation of breakdown strength calls for measuring the breakdown voltage of the material under test.

The breakdown voltage ($U_{br}$) is proportional to the electric field strength ($E_{br}$) only if the field is uniform. Such a field exists between two electrodes, which have the shape of the bodies of revolution; the surface of these electrodes may be described by Rogovsky equation [25].

$$E_{br} = \frac{U_{br}}{t} \quad \cdots 4.3$$

Where, t is the thickness of the material

It is common practice to use electrodes of a simple shape in the form of discs with rounded edges or as spheres; the field produced between such electrodes is very nearly uniform under certain conditions in a uniform field, break down voltage allows calculation of dielectric strength with measure of the thickness of the specimen at the point of rupture. The dielectric strength is expressed in volts per millimeter.

Dielectric strength i.e. the minimum required voltage at which the insulating material fails to resist the electric current is called as dielectric strength, which is used to determine uniformity of the material and the manufacturing process. Although such determinations are not adequate for design purposes, they do give some relative indication of amount of insulating material that will be required to support a certain voltage level. Flexible plastics are characterized by high dielectric and mechanical strengths in thin sections are useful as insulating taps [26].

The dielectric strength of the materials can be determined by the following equation:

\[
\text{Dielectric strength} = \frac{V}{t} \quad \ldots \quad 4.4
\]

Where \( V \) = puncture voltage (volts) and \( t \) = sample thickness (mm)

Volume resistivity i.e. the property of a bulk material is defined as, “The electrical resistance between the two faces of a 1 cm cube of the material.” Volume resistivity data are useful for designers to compare the relative insulation quality for the purpose of material selection, to evaluate the effects of material composition and environment and for material specification. The resistivity data can also be useful in determining the effect of moisture, determination of presence of impurities, studying of resin cure and in investigating the fundamental characteristics of materials. Volume resistivity increases with increasing the degree of resin cure, while it decreases with increasing the temperature.

Table 4.4: Typical electrical properties of some selected plastic materials

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Volume resistivity (Ω cm)</th>
<th>Dielectric strength (kV/cm)</th>
<th>Dielectric constant</th>
<th>Power factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>60 Hz</td>
<td>10^6 Hz</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60 Hz</td>
<td>10^6 Hz</td>
</tr>
<tr>
<td>PTFE</td>
<td>&gt;10^{20}</td>
<td>180</td>
<td>2.1</td>
<td>&lt;3 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.1</td>
<td>&lt;3 x 10^{-4}</td>
</tr>
<tr>
<td>PE</td>
<td>10^{20}</td>
<td>180</td>
<td>2.3</td>
<td>&lt;3 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.3</td>
<td>&lt;3 x 10^{-4}</td>
</tr>
<tr>
<td>PS</td>
<td>10^{20}</td>
<td>240</td>
<td>2.55</td>
<td>&lt;3 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.55</td>
<td>&lt;3 x 10^{-4}</td>
</tr>
<tr>
<td>PP</td>
<td>&gt;10^{19}</td>
<td>320</td>
<td>2.15</td>
<td>8 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.15</td>
<td>4 x 10^{-4}</td>
</tr>
<tr>
<td>PMMA</td>
<td>10^{16}</td>
<td>140</td>
<td>3.7</td>
<td>6 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.0</td>
<td>2 x 10^{-2}</td>
</tr>
<tr>
<td>PVC</td>
<td>10^{17}</td>
<td>240</td>
<td>3.2</td>
<td>1.3 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.9</td>
<td>1.6 x 10^{-2}</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>10^{15}</td>
<td>145</td>
<td>4.0</td>
<td>1.4 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.4</td>
<td>4 x 10^{-2}</td>
</tr>
<tr>
<td>PC</td>
<td>10^{18}</td>
<td>160</td>
<td>3.17</td>
<td>9 x 10^{-4}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.96</td>
<td>1 x 10^{-2}</td>
</tr>
<tr>
<td>Phenolic</td>
<td>10^{13}</td>
<td>100</td>
<td>5.0-9.0</td>
<td>8 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.0</td>
<td>4 x 10^{-2}</td>
</tr>
<tr>
<td>Urea Formaldehyde</td>
<td>10^{14}</td>
<td>120</td>
<td>4.0</td>
<td>4 x 10^{-2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>
The volume resistivity of the material can be determined by the following equation:

\[
\text{Volume resistivity} = \frac{R_v A}{t} \quad \cdots 4.5
\]

Where \( R_v \) = volume resistance (ohms), \( A \) = area of electrodes (19.6 cm\(^2\)) and \( t \) = sample thickness (cm)

Naik and Mishra [27] have fabricated wood polymer composites from agro-waste (banana, hemp, and agave fibers) and novolac resin and determined their electrical properties. Banana, hemp, and agave fibers were treated with novolac resin for the formation of their composites in the different ratios of 60:40, 55:45, 50:50, 45:55, and 40:60 (wt/wt). These fibers were also treated with maleic anhydride and the effect of maleic anhydride was studied on surface resistivity and volume resistivity of wood polymer composites. The maximum surface and volume resistivities were found in maleic anhydride treated and untreated banana fiber composites, respectively. The treatment of maleic anhydride improved the surface resistivity of respective fiber composites. Maleic anhydride treated banana fiber composites showed maximum surface resistivity, while untreated agave fiber composites showed minimum surface resistivity.

Jain and Chand [28] have fabricated different directionally oriented sisal fiber reinforced epoxy resin composites and studied the effect of temperature and frequency variation on dielectric constant (\( \varepsilon' \)), dielectric dissipation factor (\( \tan \delta \)) and on A.C. conductivity (\( \sigma_{a.c.} \)) of the samples. Measurements were in the temperature range 24–180 °C and in the frequency range 1–20 kHz. The sisal fiber epoxy composites were

oriented parallel and perpendicular to the electric field. It was found that the dielectric constant, \( \tan \delta \) and A.C. conductivity increased with increasing temperature. The dependence of dielectric constant, \( \tan \delta \) and A.C. conductivity with frequency have also been studied and it was found that \( \varepsilon' \) and \( \tan \delta \) of the epoxy and 0 and 90\(^0\)C oriented sisal fiber epoxy composites decreased with increasing frequency and A.C. conductivity increased with increasing frequency. Near the transition temperature of the epoxy the observed properties showed anomalous behavior. Peaks for dielectric constant, \( \tan \delta \) and A.C. conductivity were observed. Clear relaxation peaks for \( \tan \delta \) around 169 °C were observed in epoxy resin, shifting to the lower temperature side with increasing frequency. The relaxation time of epoxy and 0 and 90\(^0\) oriented sisal fiber epoxy composites has been calculated and it was found that \( \tau_{(s)} \) was 4.09×10\(^{-5}\), 5.52×10\(^{-5}\) and 5.47×10\(^{-5}\), respectively at 100\(^0\)C.

Paul et al. [29] have investigated the electrical properties of short-sisal-fiber-reinforced low-density polyethylene (LDPE) composites. Various surface treatments such as alkali, CTDIC, stearic acid, peroxide, permanganate and acetylation were carried out on the sisal fibers to improve interfacial bonding. The treated surfaces were characterized by infrared spectroscopy. The dielectric constant increased progressively with increase in fiber loading and decreased with increase in frequency for all composites. The dielectric constant values of the composites were found to have decreased as a result of chemical treatments. This is due to the fact that the hydrophilic nature of natural fiber decreased with treatment. Volume resistivity values of treated-sisal fiber/LDPE composites were found to be greater than those of raw-sisal-fiber/LDPE composites. Volume resistivity values of permanganate treated sisal fiber reinforced LDPE composites depended on the concentration of KMnO\(_4\) solution used for treatment. The value of volume resistivity increased, reached a maximum and then decreased with increase in concentration of potassium permanganate solution.

The dielectric loss factors of treated-sisal-fiber-reinforced/LDPE composites were found to be lower than that of untreated-sisal fiber/LDPE composites. The relaxation peak was found to be in the same region for all composites.

**MEASUREMENTS**

Dielectric strength (IEC-60243-Pt-1–1998), and volume resistivity (ASTM D-257–99) measurements were made on a high voltage tester (Automatic Electric-Mumbai) in air at 27°C by using 25/75 mm brass electrodes and a Hewlett-Packard high resistance meter at 500 V DC after charging for 60 s, respectively.

The comparative electric strength and volume resistivity of the polyurethane composites are reported in Table-4.5, from which it is clear that practically no change in dielectric strength is observed but volume resistivity has decreased considerably upon hybridization as compared to EANPT-J (53 %) and EANPT-G (71 %). Relatively low volume resistivity of the composites is due to presence of polar groups in fibers and polyurethane resin. Low volume resistivity of EANPT-J \(3\times10^{11}\Omega \text{ cm}\) as compared to EANPT-G \(5\times10^{11}\Omega \text{ cm}\) is due to polar nature of untreated jute fiber. Upon hybridization volume resistivity of EANPT-GJG \(1.4\times10^{11}\Omega \text{ cm}\) is decreased as a consequence of charge accumulation between glass and jute layers. This charge accumulation is mainly because of free hydroxyl and urethane groups.

Electrical properties of the composites rely on area and geometry of the electrodes, sample thickness, temperature, humidity, time of voltage application, extent of ageing, frequency of current, impurities, degree of resin cure, nature of reinforcing agents, etc. Moderate electric strength and volume resistivity of the composites may find their applications in electrical and electronic fields.

**SECTION-III: Water absorption study of composites**

The unique combinations of properties found in polymers have made it possible to use them in almost all areas of applications. Tailoring of polymer molecules to specifically achieve the required performance properties has further widened the scope of their applications. The performance and life span of polymeric materials depend on
Table 4.5 Comparative electric strength and volume resistivity of EANPT-J, EANPT-G, EANPT-GJG and EANPT-CS-J, BANFPT-RH-J composites

<table>
<thead>
<tr>
<th>Composite</th>
<th>Dielectric Strength (kV/mm)</th>
<th>Volume Resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EANPT-J</td>
<td>1.3</td>
<td>$3 \times 10^{11}$</td>
</tr>
<tr>
<td>EANPT-G</td>
<td>3.2</td>
<td>$5 \times 10^{11}$</td>
</tr>
<tr>
<td>EANPT-GJG</td>
<td>1.4</td>
<td>$1.4 \times 10^{11}$</td>
</tr>
<tr>
<td>EANPT-CS-J</td>
<td>1.4</td>
<td>$8.4 \times 10^{9}$</td>
</tr>
<tr>
<td>BANFPT-RH-J</td>
<td>1.0</td>
<td>$1.5 \times 10^{9}$</td>
</tr>
</tbody>
</table>
various factors, their molecular characteristics being the controlling one; exposure of polymers to different environmental conditions impairs their useful properties.

The highest consumption area of the plastic material is in packaging. This is mainly due to the superiority of plastic material over the other materials in terms of inertness and stability to contacting chemicals like water, oxidizing agents, oils, lubricants, industrial solvents and food stuffs. The selection of particular plastic materials for specific industrial applications has to be based on the chemical environment to which they will be exposed.

The interaction of chemicals with plastics can take place in different ways, affecting adversely their useful properties at varying rates and to varying degrees. The mechanisms involved can be chemical reaction, solvation, absorption, plasticization and stress cracking. The strength of chemical bonds, the degree of crystallinity, branching and polarity are the decisive factors for the chemical resistance of polymers. Rise in temperature increases the rate of chemical interaction. A number of standard chemical resistance tests have been developed, which include tests for moisture and water absorption, effects of immersion in chemicals, stain resistance and stress cracking. Most of these tests involve measurement of change in weight, dimensions and appearance and mechanical properties before and after the exposure to chemical reagents. Exposure time, temperature, concentration and reactivity of the reagents are the important factors for the tests. The most common methods used to determine chemical resistance are described below.

(1) Chemical resistance by change in mass method

(2) Chemical resistance by change in linear dimensions

(3) Chemical resistance by change in mechanical properties

All polymers and composites absorb moisture in humid atmosphere and when immersed in water. Natural fibers absorb more water as compared to synthetic fibers. Jute and other natural fibers are highly hygroscopic and possess low wettability with hydrophobic resins mainly due to hydroxyl groups of cellulose, hemi cellulose and lignin
Hemi cellulose is mainly responsible for water absorption although non-crystalline cellulose and lignin also play an important role in this process. The effect of absorbed water is to degrade tensile strength [34].

Absorbed water causes swelling of fibers and it continues till the cell walls are saturated with water. Beyond saturation point water exists as free water in the void structure leading to composite delamination or void formation. Absorbed water leads to weakening of interface and accelerates delamination and hence decreases the strength of the composites.

Absorbed water causes hydrolytic degradation of both matrix and interface during service [35].


Water absorption in polymeric composites is shown to be Fickian as well as non-Fickian in character [36, 37]. The visco-elastic nature of polymers and cracks are responsible for non-Fickian diffusion. Water absorption in composites depend upon fraction of fibers, void volume, additives, humidity and temperature.

**Diffusivity**

Various models have been proposed for water absorption in composites. It is well established that absorbed water in polymers and composites plays a significant role in mechanical behavior and long term durability. Assuming one-dimensional Fickian diffusion in composite, an attempt has been made to determine diffusivity ($D_x$) in different environments. Diffusivity is assumed to depend only on temperature and independent of the moisture content as well as stress levels in composites. For one-dimensional water absorption in semi-infinite plate exposed on both sides to same environment, the amount of water absorbed is given by Eqn. 4.6:

\[
G = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp \left[ -\frac{(2j+1)^2 \pi^2 D_x t}{h^2} \right] \quad \ldots \text{4.6}
\]

Where $D_x = \text{diffusivity}$, $t = \text{time (second)}$ and $h = \text{sample thickness (m)}$

The water content in the sample can be determined according to Eqn. 4.7:

\[
M = \frac{W_m - W_d}{W_d} \times 100 \quad \ldots \text{4.7}
\]

Where $M = \% \text{ water absorbed}$, $W_m = \text{weight of moist sample}$ and $W_d = \text{weight of dry sample}$.


The solution of diffusion equation in terms of % water absorption is given by eqn.4.8:

\[ M = \frac{4M_m}{h} \sqrt{t} \sqrt{D_x} \quad \ldots 4.8 \]

Where \( M_m \) = equilibrium water content. Diffusivity in a given environment can be determined from the initial slope of the plot of %M against \( \sqrt{t} \) according to Eqn. 4.8:

\[ D_x = \pi \left( \frac{h}{4M_m} \right)^2 (slope)^2 \quad \ldots 4.9 \]

In present case assuming one dimensional Fickian diffusion water absorption by EANPT-J, EANPT-G and EANPT-GJG in pure water, 10% HCl and 10% NaCl is carried out at 35\(^{\circ}\)C temperature. Moisture absorption study of EANPT-J, EANPT-G and EANPT-GJG composites were determined by a change in mass method. For these preweighed samples were immersed in distilled water, 10%HCl and 10%NaCl solutions at room temperature. Samples were periodically taken out from the solutions, wiped with tissue papers on both the sides, reweighed and reimmersed in the solutions. The process was carried out till equilibrium was established.

The percentage weight gained by the composites in water, 10 % aq. HCl and 10 % aq. NaCl solutions with the passage of time (\( t^{1/2} \)) is shown in Figs. 5-7. The % weight gained by each composite increased, reached maximum and then practically remained constant when equilibrium was established in each of the environment. The equilibrium time and equilibrium water content for composites in water, 10 % aq. NaCl, 10 % aq. HCl environments are recorded in Table 4.6. The observed trend in % equilibrium water content for EANPT-J, EANPT-G and EANPT-GJG is HCl > H\(_2\)O > NaCl, respectively. High equilibrium water content of EANPT-J is due to presence of hydrophilic -OH groups in jute and EAN and to some extent due to surface solvolysis. Glass composite showed a little water uptake tendency (6.46% in water, 9.67% in HCl and 4.89% in 10%
(NaCl) over a period of 96h due to silane treatment of glass fibers [38]. For hybrid composite it is intermediate of EANPT-J and EANPT-G.

The moisture absorption study of hybrid composites were not done due to delamination in the above media.

Diffusivity in different environments was determined according to Eqns. 4.8 and 4.9 and is reported in Table 4.6 from which it is clear that diffusivity in EANPT-GJG is intermediate of jute and glass composites. Observed diffusivity order is NaCl > H₂O > HCl. Water absorption tendency of jute composite is more than that of glass composite due to presence of hydrophilic hydroxyl groups in jute fibers. The presence of strong electrolytes in water affects water structure and hence diffusivity. The bigger the size of the solvated ions small is the diffusivity. Thus NaCl is found to break more water structure and hence high diffusivity. It is expected that the diffusion of hydrated ions will be more as compared to polymeric and clustered water molecules. Moreover, hydrated ions also undergo surface solvolysis because of the presence of polar groups in composite, which are responsible for high water uptake. The low water content in salt solution might be due to electrostatic repulsive forces acting among electronegative groups present in PU–jute composite [39].

Table 4.6 Moisture uptake and diffusivity data of composite at 35°C temperature

<table>
<thead>
<tr>
<th>Composite</th>
<th>%, Equilibrium water content at 35°C</th>
<th>Equilibrium time, h</th>
<th>Diffusivity ($D_x$), $10^{-11}$, m²/s</th>
<th>% Eqm. water content in boiling water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O 10% aq. NaCl 10% aq. HCl</td>
<td>H₂O 10% aq. NaCl 10% aq. HCl</td>
<td>H₂O 10% aq. NaCl 10% aq. HCl</td>
<td>H₂O 10% aq. NaCl 10% aq. HCl</td>
</tr>
<tr>
<td>EANPT-J</td>
<td>13.4 12.3 14.1 120 96 144 2.4 2.7 1.7</td>
<td>16.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EANPT-G</td>
<td>6.5 4.9 9.7 96 96 120 0.2 0.5 0.2</td>
<td>9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EANPT-GJG</td>
<td>10.3 8.1 10.9 120 96 120 0.7 0.8 0.6</td>
<td>13.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Absorption of water in composites causes swelling of fibers till the cell walls are saturated with water and beyond that water exists as free water in the void structure leading to composites delamination or void formation. Absorbed water causes weakening of interfacial adhesion and hydrolytic degradation of both matrix and fibers [40-42]. Cracking and blistering of fibers cause high water absorption, while degradation causes leaching of small molecules [43].

**Water absorption in boiling water**

Water absorption in composites mainly depends on temperature besides presence of hydrophilic groups in composites. The effect of boiling water on % water absorption with time is shown in Fig. 8 from which it is evident that the water absorption in composites is the maximum after 6h and remained almost constant (Table 4.7). From Table 4.7 and Fig. 8, it is evident that equilibrium water absorption time is reduced drastically without any damage to the composites. Thus, composites possess excellent hydrolytic stability against boiling water and even in harsh acidic and saline environments.


From experimental data it is clear that composites possess fairly good mechanical and electrical properties and excellent hydrolytic stability against harsh environmental conditions, which signify their usage as low load bearing housing units and in electrical and electronics and in marine field.
Table 4.7 The effect of boiling water on water absorption in EANPT-J, EANPT-G and EANPT-GJG composites with time

<table>
<thead>
<tr>
<th>Time, h</th>
<th>% Weight change</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EANPT-J</td>
<td>EANPT-G</td>
<td>EANPT-GJG</td>
</tr>
<tr>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1</td>
<td>11.77</td>
<td>5.37</td>
<td>7.21</td>
</tr>
<tr>
<td>2</td>
<td>13.34</td>
<td>7.22</td>
<td>9.21</td>
</tr>
<tr>
<td>3</td>
<td>15.18</td>
<td>8.02</td>
<td>11.69</td>
</tr>
<tr>
<td>4</td>
<td>15.88</td>
<td>9.12</td>
<td>12.42</td>
</tr>
<tr>
<td>5</td>
<td>16.05</td>
<td>9.25</td>
<td>13.35</td>
</tr>
<tr>
<td>6</td>
<td>16.15</td>
<td>9.25</td>
<td>13.38</td>
</tr>
<tr>
<td>7</td>
<td>16.15</td>
<td>9.25</td>
<td>13.38</td>
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<td>8</td>
<td>16.15</td>
<td>9.25</td>
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</tr>
<tr>
<td>9</td>
<td>16.15</td>
<td>9.25</td>
<td>13.38</td>
</tr>
<tr>
<td>10</td>
<td>16.15</td>
<td>9.25</td>
<td>13.38</td>
</tr>
</tbody>
</table>
Fig. 5. Plots of % weight gain against $t^{1/2}$ for EANPT-J, EANPT-G and EANPT-GJG composites in water at $35^0\text{C}$.

Fig. 6. Plots of % weight gain against $t^{1/2}$ for EANPT-J, EANPT-G and EANPT-GJG composites in 10% aq. HCl at $35^0\text{C}$.
Fig.7. Plots of % weight gain against $t^{1/2}$ for EANPT-J, EANPT-G and EANPT-GJG composites in 10 % aq. NaCl at 35°C

Fig.8. Plots of % weight gain against time for EANPT-J, EANPT-G and EANPT-GJG composites in boiling water.
CHAPTER – 5

ULTRASONIC STUDIES OF RESINS
This chapter describes the density, viscosity and ultrasonic velocity measurements of EANRA, EANOA and EANAA polymer solutions in different solvents at 303, 308 and 313 K. Various acoustical parameters of these polymers solutions are also discussed and determined in light of effect of structure, nature of solvents and temperature.

Ultrasonic is the study of high frequency sound waves, usually in excess of 20 KHz (20,000 cycles per sec). Around 1880 [1-3] Curies discovered the piezoelectric effect, which established the basis of ultrasound for the present day generation. Most modern ultrasonic devices rely on transducers (energy converters), which are composed of piezoelectrical material. Ultrasonic technology is now a day employed in a wide range of applications in medicine, biology, industry, material science, agriculture, oceanography, dentistry, consumer industry, sonochemistry research, etc. due to its non-destructive nature [4-10].

It is most useful in investigating various organic liquids, polymers and aqueous and nonaqueous electrolyte solutions. It provides a wealth of information about molecular interactions, the nature and strength of interactions. It offers a rapid nondestructive method for characterizing materials. The extensive uses of polymers in technology have promoted ultrasonic studies to understand the structures of polymers and furnish knowledge on solvophilic or solvophobic nature of polymers [11-14]. Applications in materials science include the determination of some properties of solids such as compressibility, specific heat ratios, elasticity, etc [15]. Ultrasound has also proved to be very useful for both soldering and welding. It is reported to improve the quality of homogenized milk. With the tracking of submarines, oceanographic applications include mapping of the sea bottom, discovering sunken ships and searching for schools of fish. Ultrasonic testing and evaluation techniques are widely used for obtaining information about micro structural and mechanical properties of metals and found wide applications in medical and biological fields [16-17]. Further, cleaning is the most common type of application of ultrasonic, which includes the removal of grease, dirt, rust and paint from metal, ceramic glass and crystal surfaces. Another area where ultrasonic is now-a-days being used, is to obtain the information

about microstructures [18, 19]. It is reported that these ultrasonic waves provide valuable information about the structure of solids [20, 21].

By ultrasonic velocity measurements, the molecular interactions in pure liquids [22-25], aqueous solutions [26] and liquid mixtures [27,29] can also be studied. It is a powerful, effective and reliable tool to investigate properties of polymers [30-33].

Non-destructive testing of ultrasonic involves incorporation of physical principles for determining flaws, dimensional variations, micro structural features and the mechanical properties of worked materials without impairing their usefulness. The non-destructive applications of ultrasonic for determining structural integrity, micro structural features and mechanical properties of worked materials.

Ultrasonic non-destructive and evaluation (NDTE) plays a major role in the present day life assessment program of nuclear installation, chemical industries, gas pipe lines, etc. during preservice and in service inspection/conditions. Typical casting defects are non-metallic inclusions, porosity, shrinkage, cavities, cold shut, hot tear (shrink crack) cold or stress crack, blow holes or inhomogeneity. All these defects can be tested ultrasonically by proper selection of probes (normal or angle) frequency and attenuation.

Sound velocity measurements on condensation polymers in protic or aprotic solvents are carried out by Parsania et al. [34-50] and investigated the influence of solvent, concentration, temperature and the nature of the substituents on the structure of polymers and molecular interactions in the solutions under investigations.

Acoustical properties


EXPERIMENTAL

Materials

The solvents: Chloroform (CF), tetra hydro furan (THF) and 1, 4-dioxan (DO) used in the present study were of laboratory grade and purified according to literature methods [51,52]. Polyester polyol resins EANRA ($\bar{M}_w = 5301$), EANOA ($\bar{M}_w = 3470$) and EANAA ($\bar{M}_w = 5350$) were synthesized and purified (Ch. 2).

Measurements

The density ($\rho$), viscosity ($\eta$) and ultrasonic velocity (U) of pure solvents and EANOA, EANRA, EANAA solutions were carried out at 303, 308 and 313 ± 0.1K by using specific gravity bottle, Ubbelohde suspended level viscometer and Mittal Enterprise Interferometer (New Delhi) Model No F-81, operating at 2 MHz, respectively. The $\rho$, $\eta$ and U measurements were accurate to ±0.1 kg/m$^3$, 0.01 mPas and ±0.15%, respectively.

Density measurements

The densities of pure solvents and solutions were measured by means of specific gravity bottle at three different temperatures: 303, 308 and 313 K by determining the weights of distilled water, solvents and solutions. The density ($\rho$) was calculated according to Eqn. 5.1 with an accuracy of ±0.0001 g/cm$^3$.

$$\rho, (g/cc) = \frac{Wt.\ of\ solvent/solution}{Wt.\ of\ water} \quad \cdots 5.1$$

Viscosity measurements

The method for determining the dynamic viscosity or coefficient of viscosity of liquids relies on Stoke’s law. In present investigation, suspended level viscometer developed by Ubbelohde was used. The viscometer was washed with chromic acid, distilled water, acetone and then dried at 50°C in an oven. Viscometer was suspended in a thermostat at 303K ± 0.1K and measured quantity of the distilled water / solvent / solution was placed into the viscometer reservoir by means of a pipette and thermally equilibrated for about 10 min. The efflux time of liquid between two marks was measured by means of digital stopwatch with an accuracy of ± 0.01 sec. Three replicate measurements on each liquid were made and the arithmetic mean was considered for the purpose of calculations.

Using the flow times (t) and known viscosity of standard (water) sample, the viscosities of solvents and solutions were determined according to Eqn. 5.2:

\[
\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2}
\]

Where \( \eta_1, \rho_1, t_1 \) and \( \eta_2, \rho_2, t_2 \) are the viscosities, densities and flow times of standard and unknown samples, respectively.

Sound velocity measurements

Ultrasonic interferometer (F-81) (Mittal Enterprises, New Delhi) was used in the present investigation. The working of interferometer was tested by measuring the sound velocity of pure solvents: chloroform, THF and 1,4-dioxan and comparing the results with literature data. The advantage of this instrument is that the quantity of sample needed for measurement is small (15-20 ml).

The measuring cell (2 MHz) with quartz crystal was filled with the solvent/solution and then micrometer with reflector plate was fixed. The circulation of water from the thermostat (at 303, 308 and 313 K) was started and
the experimental liquid in the cell is allowed to thermally equilibrate. The high frequency generator was switched on and the micrometer was rotated very slowly so as to obtain a maximum or minimum of the anode current. A number of maximum readings of anode current (n) were counted. The total distance (d) travelled by the micrometer for n=10 were read. The wave length (λ) was determined according to Eqn. 5.3:

$$\lambda = \frac{2d}{n} \quad \ldots5.3$$

The speed of sound (U) of solvents and solutions were calculated from the wave length (λ) and frequency (F) according to Eqn. 5.4:

$$U = \lambda \cdot F \quad \ldots5.4$$

The density (ρ), viscosity (η) and speed of sound (U) data of EANO, EANRA and EANAA solutions at three different temperatures are reported in Tables 5.1-5.9. The least square equations along with regression coefficients (R²) are reported in Tables 5.10-5.12.
Table-5.1: The density (\(\rho\)), viscosity (\(\eta\)), speed of sound (\(U\)) and pooled precision standard deviation (Sp) data of EANOA solutions in CF at three different temperatures: 303, 308 and 313 K.

<table>
<thead>
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<th>Viscosity (\eta), m Pas</th>
<th>Ave. Dist. d.10(^3),m</th>
<th>Wave length (\lambda.10(^3),m</th>
<th>(U) ms(^{-1}) (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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Table-5.2: The density ($\rho$), viscosity ($\eta$), speed of sound ($U$) and pooled precision standard deviation (Sp) data of EANOA solutions in DO at three different temperatures: 303, 308 and 313 K.

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<th>Density $\rho$, kg / m$^3$</th>
<th>Viscosity $\eta$, m Pas</th>
<th>Ave. Dist. d.10$^{-3}$,m</th>
<th>Wave length $\lambda.10^3$,m</th>
<th>U ms$^{-1}$ (F=2MHz)</th>
<th>Std. devi. mm($\pm$)</th>
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EANOA + DO at 308 K

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<th>Ave. Dist. d.10$^{-3}$,m</th>
<th>Wave length $\lambda.10^3$,m</th>
<th>U ms$^{-1}$ (F=2MHz)</th>
<th>Std. devi. mm($\pm$)</th>
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EANOA + DO at 313 K

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<th>Ave. Dist. d.10$^{-3}$,m</th>
<th>Wave length $\lambda.10^3$,m</th>
<th>U ms$^{-1}$ (F=2MHz)</th>
<th>Std. devi. mm($\pm$)</th>
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Table-5.3: The density ($\rho$), viscosity ($\eta$), speed of sound ($U$) and pooled precision standard deviation ($Sp$) data of EANOA solutions in THF at three different temperatures: 303, 308 and 313 K.

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<th>Viscosity $\eta$, m Pas</th>
<th>Ave. Dist. d.10$^3$,m</th>
<th>Wave length $\lambda$.10$^3$,m</th>
<th>$U$ m/s</th>
<th>Std. devi. mm(±)</th>
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Table-5.4: The density ($\rho$), viscosity ($\eta$), speed of sound ($U$) and pooled precision standard deviation (Sp) data of EANRA solutions in CF at three different temperatures: 303, 308 and 313 K.

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<th>Ave. Dist. d.10$^3$,m</th>
<th>Wave length $\lambda$.10$^3$,m</th>
<th>U ms$^{-1}$ (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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Table-5.5: The density ($\rho$), viscosity ($\eta$), speed of sound ($U$) and pooled precision standard deviation (Sp) data of EANRA solutions in DO at three different temperatures: 303, 308 and 313 K.

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<th>Ave. Dist. d.10²,m</th>
<th>Wave length $\lambda$.10²,m</th>
<th>$U$ ms⁻¹ (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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EANRA + DO at 308 K

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<th>Wave length $\lambda$.10²,m</th>
<th>$U$ ms⁻¹ (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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EANRA + DO at 313 K

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<th>$U$ ms⁻¹ (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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Table-5.6: The density ($\rho$), viscosity ($\eta$), speed of sound ($U$) and pooled precision standard deviation ($Sp$) data of EANRA solutions in THF at three different temperatures: 303, 308 and 313 K.

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<th>Ave. Dist. d.10$^3$,m</th>
<th>Wave length $\lambda$.10$^3$,m</th>
<th>U ms$^{-1}$ (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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Table-5.7: The density ($\rho$), viscosity ($\eta$), speed of sound ($U$) and pooled precision standard deviation (Sp) data of EANAA solutions in CF at three different temperatures: 303, 308 and 313 K.

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<th>Density $\rho$, kg/m³</th>
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<th>Ave. Dist. d.10³,m</th>
<th>Wave length $\lambda$.10³,m</th>
<th>U ms⁻¹ (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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Table-5.8: The density ($\rho$), viscosity ($\eta$), speed of sound (U) and pooled precision standard deviation (Sp) data of EANAA solutions in DO at three different temperatures: 303, 308 and 313 K.

<table>
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<th>Viscosity $\eta$, m Pas</th>
<th>Ave. Dist. d.10$^3$,m</th>
<th>Wave length $\lambda$.10$^3$,m</th>
<th>U m$^{-1}$ (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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</table>
**Table-5.9:** The density ($\rho$), viscosity ($\eta$), speed of sound ($U$) and pooled precision standard deviation (Sp) data of EANAA solutions in THF at three different temperatures: 303, 308 and 313 K.

<table>
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<th>Conc., %</th>
<th>Density $\rho$, kg / m³</th>
<th>Viscosity $\eta$, m Pas</th>
<th>Ave. Dist. $d.10^3$ m</th>
<th>Wave length $\lambda.10^3$ m</th>
<th>$U$ ms⁻¹ (F=2MHz)</th>
<th>Std. devi. mm(±)</th>
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<tbody>
<tr>
<td><strong>EANAA + THF at 303 K</strong></td>
<td></td>
<td></td>
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<tr>
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<td>879.1</td>
<td>0.466</td>
<td>3.136</td>
<td>0.6272</td>
<td>1254.4</td>
<td>0.001</td>
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<tr>
<td>0.25</td>
<td>880.8</td>
<td>0.472</td>
<td>3.14</td>
<td>0.628</td>
<td>1256</td>
<td>0.0007</td>
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<td>881.6</td>
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<td>3.142</td>
<td>0.6284</td>
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<td><strong>EANAA + THF at 308 K</strong></td>
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<tr>
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<td>876.4</td>
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<td>3.082</td>
<td>0.6164</td>
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<td>3.045</td>
<td>0.609</td>
<td>1218</td>
<td>0.0038</td>
</tr>
</tbody>
</table>
Acoustical properties.....

Specific acoustical impedance:

\[ Z = U \rho \] ...5.5

Isentropic compressibility:

\[ \kappa_s = \frac{1}{U^2 \rho} \] ...5.6

Intermolecular free path length [53]:

\[ L_f = K \left( \kappa_s \right)^{1/2} \] ...5.7

Where \( K = (93.875 + 0.375T) \times 10^{-8} \) is a temperature dependent constant

Classical absorption coefficient [54]:

\[ \left( \frac{a}{f^2} \right)_{cl} = \frac{8\pi^2 \eta}{3U^3 \rho} \] ...5.8

Viscous relaxation time

The resistance offered by viscous force in the flow of sound wave appears as a classical absorption associated with it is the viscous relaxation time (\( \tau \)):

\[ \tau = \frac{4\eta}{3\rho U^2} \] ... 5.9

From Tables 5.1-5.9, it is clear that the observed trends in \( \rho \), \( \eta \) and \( U \) are CF>DO>THF, DO> CF>THF and DO>THF>CF, respectively for EANOA, EANRA and EANAA. The \( \rho \) (except CF in which it is decreased with C), \( \eta \) and \( U \) are increased linearly with C and decreased with T in all the three solvent systems.

studied. From Tables-5.1-5.9, it is clear that the change in $\rho$ and $U$ with $C$ and $T$ are not as appreciable as $\eta$ due to intermolecular motion by molecular interactions [55-58].

The linear increase of $\rho$, $\eta$, and $U$ with $C$ confirmed increase of cohesive forces because of strong molecular interactions, while decrease of these parameters with $T$ supported decrease of cohesive forces. The increase in temperature has two opposite effects namely structure formation (intermolecular association) and structure destruction. The structure forming tendency is mainly due to solute-solvent interactions, while destruction of structure formed previously is due to thermal fluctuations. When thermal energy is greater than that of interaction energy, it causes destruction in structure formed previously.

Thus, increase of $T$ favored increase of kinetic energy and volume expansion and hence resulted decrease of $\rho$ and $\eta$, while it increased intermolecular distance (free path length). The density and viscosity of medium, pressure, temperature, etc. affect the velocity. The molecular interactions caused chain expansion and hence increase of viscosity. A polymer-solvent interaction in solutions is of great value since the extension of chain is markedly influenced by the molecular interactions,

which furnish knowledge on solvophilic or solvophobic nature of the polymers under investigation. The solvated molecules affect polymer processing from solutions.

In order to understand the effect of concentration, temperature, nature of solvents and solute on molecular interactions in solutions, various acoustical parameters such as specific acoustical impedance \((Z)\), isentropic compressibility \((\kappa_s)\), intermolecular free path length \((L_f)\), classical absorption coefficient \((\alpha/f^2)_{cl}\) and viscous relaxation time \((\tau)\) are determined according to above mentioned standard relations and are correlated with \(C\) and \(T\) (Figs. 5.1-5.15). The least square equations and regression coefficients are summarized in Tables 5.10-5.12, from which a fairly good to excellent correlation between a particular parameter and \(C\) is observed for a given temperature and solvent system studied.

The \(Z\) \((R^2 = 0.889-0.998)\), \(\tau\) \((R^2 = 0.955-0.999)\) and \((\alpha/f^2)_{cl}\) \((R^2 = 0.948 \text{–} 0.999)\) increased linearly with \(C\) and decreased with \(T\), while \(\kappa_s\) \((R^2 = 0.922-0.998)\), and \(L_f\) \((R^2 = 0.913-0.997)\) both decreased linearly with \(C\) and increased with \(T\) in all three solvent systems for EANOA, EANRA and EANAA. Increase or decrease of acoustical parameters with \(C\) and \(T\) indicated presence of strong molecular interactions in the solutions. The ester, ether, carbonyl and hydroxyl groups of resins are polar groups, which are responsible for structure formation with solvents, i.e. molecular association. It is likely that OH groups of resins form H-bonds with Cl atoms of CF and lone pairs of electrons of THF and DO, while ester and carbonyl groups form H-bonds with H atom of CF. Due to modification of the structure of the solute both apparent molar volume as well as molecular weight will change and consequently \(\rho\), \(\eta\) and \(U\) also change with \(C\) and \(T\). Linear increase or decrease of the acoustical parameters with \(C\) confirmed predominant solvent-solute interactions over solute-solute interactions and dispersion forces.
Table-5.10: The least square equations and regression coefficients for EANOA solutions at different temperatures

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Least square equations (Regression coefficients, $R^2$) for EANOA-CF</th>
</tr>
</thead>
</table>
| $\rho$, kg m$^{-3}$ | 303 K: $-1.075C + 1474$ (0.909)  
308 K: $-1.990C + 1471$ (0.911)  
313 K: $-3.117C + 1467$ (0.948) |
| $\eta$, mPas | 303 K: $0.035C + 0.568$ (0.989)  
308 K: $0.034C + 0.533$ (0.993)  
313 K: $0.036C + 0.476$ (0.985) |
| $U$, ms$^{-1}$ | 303 K: $3.873C + 965.3$ (0.984)  
308 K: $3.502C + 950$ (0.989)  
313 K: $3.385C + 933.4$ (0.997) |
| $Z$, 10$^6$ kgm$^{-2}$s$^{-1}$ | 303 K: $0.004C + 1.423$ (0.991)  
308 K: $0.003C + 1.398$ (0.907)  
313 K: $0.001C + 1.370$ (0.931) |
| $\kappa$, 10$^{-10}$ Pa$^{-1}$ | 303 K: $-0.051C + 7.275$ (0.99)  
308 K: $-0.044C + 7.529$ (0.967)  
313 K: $-0.039C + 7.820$ (0.974) |
| $L_f$, 10$^{-11}$ m | 303 K: $-0.02C + 5.647$ (0.990)  
308 K: $-0.017C + 5.745$ (0.967)  
313 K: $-0.014C + 5.855$ (0.973) |
| $\tau$, 10$^{-13}$ s | 303 K: $0.296C + 5.514$ (0.986)  
308 K: $0.309C + 5.353$ (0.994)  
313 K: $0.346C + 4.965$ (0.983) |
| $(\alpha/f^2)_d$, 10$^{-14}$ s$^2$m$^{-1}$ | 303 K: $0.055C + 1.126$ (0.982)  
308 K: $0.059C + 1.111$ (0.994)  
313 K: $0.068C + 1.049$ (0.981) |
<table>
<thead>
<tr>
<th></th>
<th>( \text{EANOA-DO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ), ( \text{kg m}^{-3} )</td>
<td>1.907C + 1026 (0.974)</td>
</tr>
<tr>
<td>( \eta ), ( \text{mPas} )</td>
<td>0.079C + 1.122 (0.996)</td>
</tr>
<tr>
<td>( U ), ( \text{ms}^{-1} )</td>
<td>2.829C + 1328 (0.986)</td>
</tr>
<tr>
<td>( Z ), ( 10^6 \text{kgm}^{-2}\text{s}^{-1} )</td>
<td>0.005C + 1.362 (0.994)</td>
</tr>
<tr>
<td>( \kappa_s ), ( 10^{-10} \text{Pa}^{-1} )</td>
<td>-0.033C + 5.524 (0.997)</td>
</tr>
<tr>
<td>( L_r ), ( 10^{-11} \text{m} )</td>
<td>-0.015C + 4.921 (0.997)</td>
</tr>
<tr>
<td>( \tau ), ( 10^{-13} \text{s} )</td>
<td>0.525C + 8.273 (0.995)</td>
</tr>
<tr>
<td>( (\alpha/f^2)_{cl} ), ( 10^{-14} \text{s}^2\text{m}^{-1} )</td>
<td>0.075C + 1.228 (0.994)</td>
</tr>
</tbody>
</table>
### Table 5.10

<table>
<thead>
<tr>
<th>Variable</th>
<th>EANO-THF 1</th>
<th>EANO-THF 2</th>
<th>EANO-THF 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$, kg m$^{-3}$</td>
<td>3.143C + 881.6 (0.973 )</td>
<td>2.331C + 880.3 (0.989 )</td>
<td>2.407C + 878.5 (0.994 )</td>
</tr>
<tr>
<td>$\eta$, mPas</td>
<td>0.031C + 0.480 (0.995 )</td>
<td>0.024C + 0.454 (0.991 )</td>
<td>0.024C + 0.403 (0.970 )</td>
</tr>
<tr>
<td>$U$, ms$^{-1}$</td>
<td>1.434C + 1254 (0.902)</td>
<td>2.126C + 1233 (0.979)</td>
<td>2.048C + 1208 (0.927)</td>
</tr>
<tr>
<td>$Z$, 10$^5$, kgm$^{-2}$s$^{-1}$</td>
<td>0.005C+ 1.106 (0.990)</td>
<td>0.005C + 1.085 (0.982)</td>
<td>0.004C + 1.061 (0.971)</td>
</tr>
<tr>
<td>$\kappa$, 10$^{-10}$, Pa$^{-1}$</td>
<td>-0.041C + 7.204 (0.984)</td>
<td>-0.045C + 7.473 (0.941)</td>
<td>-0.047C + 7.791 (0.975)</td>
</tr>
<tr>
<td>$L_f$, 10$^{-11}$, m</td>
<td>-0.016C + 5.619 (0.983)</td>
<td>-0.017C + 5.723 (0.990)</td>
<td>-0.017C + 5.844 (0.975)</td>
</tr>
<tr>
<td>$\tau$, 10$^{-13}$, s</td>
<td>0.257C + 4.625 (0.989)</td>
<td>0.212C + 4.533 (0.961)</td>
<td>0.228C + 4.193 (0.955)</td>
</tr>
<tr>
<td>$(\alpha/f^2)_{cl}$, 10$^{-14}$, s$^2$m$^{-1}$</td>
<td>0.041C + 0.725 (0.992)</td>
<td>0.032C + 0.723 (0.984)</td>
<td>0.035C + 0.684 (0.948)</td>
</tr>
</tbody>
</table>
Table-5.11: The least square equations and regression coefficients for EANRA solutions at different temperatures

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Least square equations (Regression coefficients, $R^2$) for EANRA-CF</th>
<th>303 K</th>
<th>308 K</th>
<th>313 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$, kg m$^{-3}$</td>
<td>$-1.904C + 1477.$</td>
<td>$-2.253C + 1472.$</td>
<td>$-1.173C + 1467.$</td>
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<tr>
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<td>$R^2 = 0.987$</td>
<td>$R^2 = 0.990$</td>
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<tr>
<td>$\eta$, mPas</td>
<td>$0.041C + 0.568$</td>
<td>$0.035C + 0.532$</td>
<td>$0.027C + 0.481$</td>
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<tr>
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<td>$R^2 = 0.975$</td>
<td>$R^2 = 0.996$</td>
<td>$R^2 = 0.994$</td>
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<tr>
<td>$U$, ms$^{-1}$</td>
<td>$4.878C + 965.6$</td>
<td>$4.322 C + 948.8$</td>
<td>$4.546 C + 931.9$</td>
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<tr>
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<td>$R^2 = 0.937$</td>
<td>$R^2 = 0.992$</td>
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<tr>
<td>$Z$, 10$^6$ kgm$^{-2}$s$^{-1}$</td>
<td>$0.005C + 1.426$</td>
<td>$0.004 C + 1.397$</td>
<td>$0.005 C + 1.367$</td>
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<tr>
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<td>$R^2 = 0.899$</td>
<td>$R^2 = 0.987$</td>
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<td>$\kappa_s$, 10$^{-10}$ Pa$^{-1}$</td>
<td>$-0.063 C + 7.258$</td>
<td>$-0.056 C + 7.542$</td>
<td>$-0.069 C + 7.844$</td>
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<td>$R^2 = 0.922$</td>
<td>$R^2 = 0.990$</td>
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<tr>
<td>$L_f$, 10$^{-11}$ m</td>
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<td>$-0.021 C + 5.750$</td>
<td>$-0.026 C + 5.864$</td>
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<td>$R^2 = 0.923$</td>
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<tr>
<td>$\tau$, 10$^{-13}$ s</td>
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<td>$0.237 C + 5.034$</td>
<td>$0.309 C + 5.354$</td>
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<td>$(\alpha f^2)_{ch}$, 10$^{-14}$ s$^2$m$^{-1}$</td>
<td>$0.065C + 1.126$</td>
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<td>-------------------</td>
<td>--------------------------------------------------------------------------</td>
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</tr>
<tr>
<td>$\rho$, kg m$^{-3}$</td>
<td>$1.904 C + 1027.$ \hspace{0.5cm} $R^2 = 0.952$ \hspace{0.5cm} $2.443 C + 1025.$ \hspace{0.5cm} $R^2 = 0.984$ \hspace{0.5cm} $2.539 C + 1022.$ \hspace{0.5cm} $R^2 = 0.964$</td>
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<tr>
<td>$\eta$, mPas</td>
<td>$0.079 C + 1.132$ \hspace{0.5cm} $R^2 = 0.993$ \hspace{0.5cm} $0.065 C + 1.047$ \hspace{0.5cm} $R^2 = 0.996$ \hspace{0.5cm} $0.066 C + 0.891$ \hspace{0.5cm} $R^2 = 0.996$</td>
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<tr>
<td>$U$, ms$^{-1}$</td>
<td>$3.151 C + 1330.$ \hspace{0.5cm} $R^2 = 0.927$ \hspace{0.5cm} $6.107 C + 1305.$ \hspace{0.5cm} $R^2 = 0.965$ \hspace{0.5cm} $3.570 C + 1289.$ \hspace{0.5cm} $R^2 = 0.956$</td>
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<tr>
<td>$Z$, 10$^6$ kgm$^{-2}$s$^{-1}$</td>
<td>$0.005 C + 1.367$ \hspace{0.5cm} $R^2 = 0.989$ \hspace{0.5cm} $0.009 C + 1.339$ \hspace{0.5cm} $R^2 = 0.989$ \hspace{0.5cm} $0.006 C + 1.318$ \hspace{0.5cm} $R^2 = 0.970$</td>
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<tr>
<td>$\kappa$, 10$^{-10}$ Pa$^{-1}$</td>
<td>$-0.035 C + 5.497$ \hspace{0.5cm} $R^2 = 0.975$ \hspace{0.5cm} $-0.065 C + 5.715$ \hspace{0.5cm} $R^2 = 0.982$ \hspace{0.5cm} $-0.045 C + 5.881$ \hspace{0.5cm} $R^2 = 0.966$</td>
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<tr>
<td>$L_f$, 10$^{-11}$ m</td>
<td>$-0.016 C + 4.909$ \hspace{0.5cm} $R^2 = 0.975$ \hspace{0.5cm} $-0.029 C + 5.005$ \hspace{0.5cm} $R^2 = 0.982$ \hspace{0.5cm} $-0.020 C + 5.077$ \hspace{0.5cm} $R^2 = 0.966$</td>
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<tr>
<td>$\tau$, 10$^{-13}$ s</td>
<td>$0.516 C + 8.304$ \hspace{0.5cm} $R^2 = 0.989$ \hspace{0.5cm} $0.394 C + 7.986$ \hspace{0.5cm} $R^2 = 0.992$ \hspace{0.5cm} $0.457 C + 6.995$ \hspace{0.5cm} $R^2 = 0.995$</td>
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</tr>
<tr>
<td>$(\alpha/f^2)_{cl}$, 10$^{-14}$ s$^2$m$^{-1}$</td>
<td>$0.073 C + 1.231$ \hspace{0.5cm} $R^2 = 0.985$ \hspace{0.5cm} $0.053 C + 1.206$ \hspace{0.5cm} $R^2 = 0.988$ \hspace{0.5cm} $0.066 C + 1.069$ \hspace{0.5cm} $R^2 = 0.996$</td>
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### Table 5.11 Continue…

<table>
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<tr>
<th>Parameter</th>
<th>EANRA-THF</th>
</tr>
</thead>
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<td>$\rho$, kg m$^{-3}$</td>
<td>0.457 C + 6.995 R$^2 = 0.995$</td>
</tr>
<tr>
<td>$\eta$, mPas</td>
<td>0.040 C + 0.488 R$^2 = 0.994$</td>
</tr>
<tr>
<td>$U$, ms$^{-1}$</td>
<td>2.858 C + 1256. R$^2 = 0.941$</td>
</tr>
<tr>
<td>$Z$, 10$^6$ kgm$^{-2}$s$^{-1}$</td>
<td>0.006 C + 1.111 R$^2 = 0.980$</td>
</tr>
<tr>
<td>$\kappa$, 10$^{-10}$ Pa$^{-1}$</td>
<td>-0.055 C + 7.159 R$^2 = 0.970$</td>
</tr>
<tr>
<td>$L_f$, 10$^{-11}$ m</td>
<td>-0.021 C + 5.602 R$^2 = 0.970$</td>
</tr>
<tr>
<td>$\tau$, 10$^{-13}$ s</td>
<td>0.342 C + 4.667 R$^2 = 0.992$</td>
</tr>
<tr>
<td>$(\alpha/f^2)_{cl}$, 10$^{-14}$ s$^2$m$^{-1}$</td>
<td>0.517 C + 7.327 R$^2 = 0.990$</td>
</tr>
</tbody>
</table>
Table-5.12: The least square equations and regression coefficients for EANAA solutions at different temperatures

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Least square equations (Regression coefficients, $R^2$) for EANAA-CF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303 K</td>
</tr>
<tr>
<td>$\rho$, kg m$^{-3}$</td>
<td>$-1.387 \ C + 1474.$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.938$</td>
</tr>
<tr>
<td>$\eta$, mPas</td>
<td>$0.045 \ C + 0.560$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.950$</td>
</tr>
<tr>
<td>$U$, ms$^{-1}$</td>
<td>$2.439 \ C + 965.0$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.952$</td>
</tr>
<tr>
<td>$Z$, 10$^6$ kgm$^{-2}$s$^{-1}$</td>
<td>$0.002 \ C + 1.423$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.927$</td>
</tr>
<tr>
<td>$\kappa_S$, 10$^{-10}$ Pa$^{-1}$</td>
<td>$-0.029 \ C + 7.857$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.991$</td>
</tr>
<tr>
<td>$L_f$, 10$^{-11}$ m</td>
<td>$-0.011 \ C + 5.650$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.946$</td>
</tr>
<tr>
<td>$\tau$, 10$^{-13}$ s</td>
<td>$0.445 \ C + 5.446$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.996$</td>
</tr>
<tr>
<td>$(\alpha/f^2)_{cl}$, 10$^{-14}$ s$^2$m$^{-1}$</td>
<td>$0.087 \ C + 1.114$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.997$</td>
</tr>
<tr>
<td></td>
<td>EANAA-DO</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------------------------------</td>
</tr>
<tr>
<td>( \rho ), kg m(^{-3})</td>
<td>2.378 C + 1027. ( R^2 = 0.987 )</td>
</tr>
<tr>
<td></td>
<td>2.495 C + 1024. ( R^2 = 0.994 )</td>
</tr>
<tr>
<td></td>
<td>1.604 C + 1022. ( R^2 = 0.940 )</td>
</tr>
<tr>
<td>( \eta ), mPas</td>
<td>0.067 C + 1.080 ( R^2 = 0.994 )</td>
</tr>
<tr>
<td></td>
<td>0.088 C + 0.986 ( R^2 = 0.996 )</td>
</tr>
<tr>
<td></td>
<td>0.071 C + 0.860 ( R^2 = 0.996 )</td>
</tr>
<tr>
<td>( U ), ms(^{-1})</td>
<td>2.322 C + 1315. ( R^2 = 0.998 )</td>
</tr>
<tr>
<td></td>
<td>2.224 C + 1295. ( R^2 = 0.972 )</td>
</tr>
<tr>
<td></td>
<td>4.468 C + 1271. ( R^2 = 0.979 )</td>
</tr>
<tr>
<td>( Z ), 10(^6) kgm(^{-2})s(^{-1})</td>
<td>0.005 C + 1.350 ( R^2 = 0.997 )</td>
</tr>
<tr>
<td></td>
<td>0.005x + 1.326 ( R^2 = 0.997 )</td>
</tr>
<tr>
<td></td>
<td>0.006 C + 1.299 ( R^2 = 0.983 )</td>
</tr>
<tr>
<td>( \kappa_S ), 10(^{-10}) Pa(^{-1})</td>
<td>-0.051 C + 6.051 ( R^2 = 0.983 )</td>
</tr>
<tr>
<td></td>
<td>-0.033 C + 5.819 ( R^2 = 0.993 )</td>
</tr>
<tr>
<td></td>
<td>-0.051 C + 6.051 ( R^2 = 0.983 )</td>
</tr>
<tr>
<td>( L_f ), 10(^{-11}) m</td>
<td>-0.017 C + 4.971 ( R^2 = 0.913 )</td>
</tr>
<tr>
<td></td>
<td>-0.014 C + 5.051 ( R^2 = 0.993 )</td>
</tr>
<tr>
<td></td>
<td>-0.022 C + 5.150 ( R^2 = 0.983 )</td>
</tr>
<tr>
<td>( \tau ), 10(^{-13}) s</td>
<td>0.451 C + 8.111 ( R^2 = 0.993 )</td>
</tr>
<tr>
<td></td>
<td>0.629 C + 7.659 ( R^2 = 0.996 )</td>
</tr>
<tr>
<td></td>
<td>0.509 C + 6.945 ( R^2 = 0.994 )</td>
</tr>
<tr>
<td>( (\alpha/f^2)_{cl} ), 10(^{-14}) s(^2)m(^{-1})</td>
<td>0.065 C + 1.216 ( R^2 = 0.993 )</td>
</tr>
<tr>
<td></td>
<td>0.084 C + 1.172 ( R^2 = 0.990 )</td>
</tr>
<tr>
<td></td>
<td>0.074 C + 1.077 ( R^2 = 0.993 )</td>
</tr>
<tr>
<td></td>
<td>EANAA-THF</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>$\rho$, kg m$^{-3}$</td>
<td>$3.207 \ C + 880.1$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.988$</td>
</tr>
<tr>
<td>$\eta$, mPas</td>
<td>$0.042 \ C + 0.462$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.999$</td>
</tr>
<tr>
<td>$U$, ms$^{-1}$</td>
<td>$2.848 \ C + 1255.$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.988$</td>
</tr>
<tr>
<td>$Z$, 10$^5$ kgm$^{-2}$s$^{-1}$</td>
<td>$0.006 \ C + 1.104$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.998$</td>
</tr>
<tr>
<td>$k_S$, 10$^{-10}$ Pa$^{-1}$</td>
<td>$-0.058 \ C + 7.210$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.998$</td>
</tr>
<tr>
<td>$L_f$, 10$^{-11}$ m</td>
<td>$-0.039 \ C + 5.865$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.993$</td>
</tr>
<tr>
<td>$\tau$, 10$^{-13}$ s</td>
<td>$0.364 \ C + 4.448$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.999$</td>
</tr>
<tr>
<td>$(\alpha/k^2)_cl$, 10$^{-14}$ s$^2$m$^{-1}$</td>
<td>$0.553 \ C + 6.990$</td>
</tr>
<tr>
<td></td>
<td>$R^2 = 0.999$</td>
</tr>
</tbody>
</table>
Figs.5.1 The plots of $Z$ against $C$ for EANOA solution at 303, 308 and 313 K
Figs. 5.2 The plots of $Z$ against $C$ for EANRA solutions at 303, 308 and 313 K
Figs.5.3 The plot of Z against C for EANAA solutions at 303, 308 and 313 K
Figs. 5.4 The plots of $\kappa_s$ against C for EANOA solutions at 303, 308 and 313 K in THF
Figs. 5.5 The plots of $\kappa_3$ against C for EANRA solutions at 303, 308 and 313 K
Figs. 5.6 The plot of $\kappa_s$ against C for EANAA solutions at 303, 308 and 313 K
Figs. 5.7 The plots of $L_f$ against $C$ for EANOA solution at 303, 308 and 313 K in THF
Figs. 5.8 The plots of $L_f$ against $C$ for EANRA solutions at 303, 308, and 313 K
Acoustical properties of EANAA solutions at different concentrations and temperatures.

Figs. 5.9: The plot of $L_f$ against C for EANAA solutions at 303, 308 and 313 K.
Figs. 5.10 The plots of \((\alpha f^2)_c\) against C for EANOA solutions at 303, 308 and 313 K in THF.
Figs. 5.11 The plots of $(\alpha/\beta)_d$ against C for EANRA solutions at 303, 308 and 313 K.
Figs. 5.12 The plot of $(\alpha/f^{2})_{cl}$ against C for EANAA solutions at 303, 308 and 313 K.
Figs. 5.13 The plots of $\tau$ against C for EANO at 303, 308 and 313 K in THF
Figs. 5.14 The plots of $\tau$ against C for EANRA solutions at 303, 308 and 313 K
Figs. 5.15 The plot of $\tau$ against C for EANAA solutions at 303, 308 and 313 K
CHAPTER – 6

A BRIEF REVIEW

OF THE

WORK DONE
This chapter of the thesis deals with brief summary of the work incorporated in the thesis.

CHAPTER-1

This chapter of the thesis describes up to date literature survey on bisphenols, epoxy and phenolic resins, epoxy esters (polyester polyols), polyurethane resins, properties, application of natural and synthetic fibers and composites in diverse fields.

CHAPTER-2

This chapter deals with the synthesis of 9, 9'-bis (4-hydroxy phenyl) anthrone-10(BAN), its epoxy resin, polyester polyols based on RA, OA, AA and their polyurethane resins, bisphenol formaldehyde resin and its modification by maleic anhydride.

CHAPTER-3

This chapter describes the characterization of the resins by IR, $^1$HNMR spectral data, GPC, epoxy equivalent, acid values, and hydroxyl values of the epoxy resins and polyester polyols, DSC and TGA. The epoxy equivalent of the EAN is found to be 910. The acid values of the polyester polyols, EANOA, EANRA and EANAA were found to be 8.07, 6.62 and 7.92 mg KOH/g, respectively. The hydroxyl values of the polyester polyols EANOA, EANRA and EANAA were found to be 741.48, 935.2 and 741.48 mg KOH/g, respectively. TG thermograms of the EAN, EANOA, EANRA, EANAA and copolyurethanes were scanned at the heating rate of 10°C/min in the nitrogen atmosphere. EAN, EANOA, EANRA, EANAA, EANRAPT, BCFMPT resins involved single step degradation, while EANPT, EANOAPT, EANAAPT resins involved double steps degradation. EAN and EANOA are found to be thermally stable up to about 300°C. EANRA and EANAA are thermally stable up to about 250°C. EANPT, EANOAPT, EANAAPT, EANRAPT and BCFMPT are thermally stable up to about 200°C.

The density of BCFMPT-200 film is determined by a floatation method at 35°C by using CCl₄-n-hexane system. The observed density of BCFMPT film is 1.2719 ±
Water uptake study of BCFMPT-200 film was tested against various reagents (water, 10% each of aq. HCl, HNO₃, H₂SO₄, NaOH, KOH and NaCl) at 35°C by change in weight method. Water uptake is high in acidic environments and the minimum in pure water. Ester and urethane linkages in the resin are polar groups, which form H-bonding with reagents solutions and hence increase in weight gain. Thus, copolymer film has good hydrolytic stability against water, saline, alkaline and acidic environments without any damage. The observed water absorption order is HCl (13.02)> H₂SO₄ (10.95) > HNO₃ (10.63)> KOH (5.97)> NaOH (4.95)> NaCl (3.4)> H₂O (1.88).

CHAPTER-4

This chapter of the thesis elaborates the fabrication, mechanical, electrical and chemical resistance studies of the composites. Jute, Glass, Glass-Jute-Glass, Jute-Can and Jute-RH composites were prepared by hand-lay-up technique under 30.4MPa pressure. Tensile strength of EANPT-GJG (49 MPa) is intermediate of EANPT-J, (33 MPa) and EANPT-G (52 MPa). As glass fibers (1200-1800 MPa) is much stronger than that of jute fibers (300-700MPa). Flexural strength is improved to a considerable extent. Stiffness of EANPT-GJG is improved by 142 % and 18 % as compared to EANPT-J and EANPT-G, respectively due to stiff nature of glass fibers. No change in dielectric strength is observed but volume resistivity has decreased considerably upon hybridization as compared to EANPT-J (53 %) and EANPT-G (71 %).

The observed trend in % equilibrium water content for EANPT-J, EANPT-G and EANPT-GJG is HCl (9.67%)>H₂O(6.46%)>NaCl (4.89%), respectively. High equilibrium water content of EANPT-J is due to presence of hydrophilic -OH groups in jute and EAN and to some extent due to surface solvolysis. Glass composite showed a little water uptake tendency (6.46% in water, 9.67% in HCl and 4.89% in 10% NaCl) over a period of 96h due to silane treatment of glass fibers. For hybrid composite it is intermediate of EANPT-J and EANPT-G. Diffusivity in EANPT-GJG is intermediate of jute and glass composites. Observed diffusivity order is NaCl > H₂O > HCl. composites possess
excellent hydrolytic stability against boiling water and even in harsh acidic and saline environments.

CHAPTER-5

This chapter describes the acoustical properties of EANOA, EANRA and EANAA solutions at 30°, 35° and 40°C. Various acoustical parameters such as isentropic compressibility (κₚ), specific acoustical impedance (Z), classical absorption coefficient (α/f²)cl, viscous relaxation time (τ) and intermolecular free length (Lf) were determined and discussed in light of effect of solvent, temperature, concentration and nature of the polymer. The observed trends in ρ, η and U are CF>DO>THF, DO>CF>THF and DO>THF>CF, respectively for EANOA, EANRA and EANAA. The ρ (except CF in which it is decreased with C), η and U are increased linearly with C and decreased with T in all the three solvent systems studied. Change in ρ and U with C and T are not as appreciable as η because molecular motion is much more affected by polymer-solvent and polymer-polymer interactions in solutions.

The z, τ and (α/f²)cl increased linearly with C and decreased with T, while κₚ and Lf both decreased linearly with C and increased with T in all three solvent systems for EANOA, EANRA and EANAA. Increase or decrease of acoustical parameters with C and T indicated presence of strong molecular interactions in the solutions. The ester, ether, carbonyl and hydroxyl groups of resins are polar groups, which are responsible for structure formation with solvents, i.e. molecular association.
ACHIEVEMENTS
ACHIEVEMENTS

LIST OF PAPERS PUBLISHED/ACCEPTED/COMMUNICATED


6. Studies on jute/glass/hybrid composites of polyurethane based on epoxy resin of 9, 9' -bis (4-hydroxy phenyl) anthrone-10(EBAN) and PEG-200. B. D. Bhuva and P. H. Parsania*, Journal of Applied Polymer Science: Accepted


8. Speed of ultrasound and associated acoustical parameters of epoxy acrylate of 9, 9'-bis (4-hydroxy phenyl) anthrone-10 solutions at 303, 308

CONFERENCES/WORKSHOP/SEMINAR/SYMPOSIUM
PARTICIPATED AND PAPER PRESENTED

1. International Seminar on Recent Developments in Structure and Legend Based Drug Design, Saurashtra University, Rajkot (December 23, 2009).
2. National Seminar on Emerging Trends in Polymer Science and Technology (Poly-2009), Saurashtra University, Rajkot (October 08-10, 2009).
3. Two Days National Workshop on Patents & IPR Related Updates, Saurashtra University, Rajkot (September 19-20, 2009).
6. National Seminar on Emerging Trends in Chemical Science Research, Sardar Patel University, V.V. Nagar (January 20-21, 2009)
7. XXII Gujarat Science Congress, Bhavnagar University, Bhavnagar (March 9, 2008).
9. XXIII Carbohydrate Conference, Bhavnagar University, Bhavnagar (January 22-24, 2008).
11.XXI Gujarat Science Congress, Hemchandracharya North Gujarat University, Patan (March 11, 2007).
12.National Seminar on “Novel Trends in Polymer Science & Technology (NSNTPST)”, S. P. University, V. V. Nagar (March 8-9, 2007).

15. 2nd National Conference on “Thermodynamics of Chemical & Biological Systems”, V. N. South Gujarat University, Surat (October 30- November-1, 2006).