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PHYSICO-CHEMICAL STUDIES OF SOME HIGH PERFORMANCE POLYMERS

A
THESIS
SUBMITTED TO THE SAURASHTRA UNIVERSITY
FOR
THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

THE FACULTY OF SCIENCE (CHEMISTRY)

BY

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UNDER THE GUIDANCE

OF

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SEPTEMBER-2006

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Statement under O. Ph. D. 7 of Saurashtra University

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.

Dt.: -09-2006 (Mr. Sunil I. Mavani)
Place: Rajkot.

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

Date : -09-2006
Place : Rajkot.

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Rajkot - 360 005

CONTENTS

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 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 [4-6], which permit the manufacturing the products ranging from expanded materials to highly compact materials. Polyurethane can be tailor made according to their application as adhesive, additives, a catalyst or a coating material [7].

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1. T. Jeevananda and Siddaramaiah, “Synthesis and characterization of polyaniline filled PU/PMMA interpenetrating polymer networks.” Eur. Polym. J. **39,**569-578, 2003.
2. B.K. Kendagannaswamy and Siddaramaiah, “Chain extended polyurethane-synthesis and characterization.” J Appl. Polym. Sci. **84,** 359-369, 2002.
3. A. Gandini, Comprehensive Polym. Sci., Suppl.1, 1992.
4. Y. Zhang and D. J. Hourston, “Rigid interpenetrating polymer network foams prepared from a rosin-based polyurethane and epoxy resin.” J. Appl. Polym. Sci. **69**,271-281, 1998.
5. C. B. Viek and F. A. Okkonen, Forest Prod. J. **48**, 71, 1998.
6. T. K. Roy, V. M. Mannari and D. A. Raval, J Sci and Ind. Research, **56**, 159 1997.
7. N. Nurdin, G. Helary and G. Sauvet, “Biocidal polymers active by contact II. Biological evaluation of polyurethane coatings with pendant quaternary ammonium salts.” J. Appl. Polym. Sci. **50**, 663-670, 1993.

The literature survey on epoxy/ polyester polyols, polyurethane resins based on bisphenols revealed that most of the work is confined on bisphenol-A. The work to be incorporated in the thesis is based on synthesis and physico-chemical studies of polyurethanes based on phenolic and epoxy resins.

A Comprehensive summary of the work is sub-divided into six chapters:

CHAPTER 1: Literature survey on phenolic and epoxy resins, epoxy esters (polyester polyols) and polyurethane resins and their composites

CHAPTER 2: Syntheses of monomers, epoxy and phenolic resins, polyester polyols and polyurethane resins

CHAPTER 3: Physico-chemical characterization of the resins

CHAPTER 4: Surface coating of polyurethane resins on different substrates and their chemical resistance

CHAPTER- 5: Fabrication and physico-chemical characterization of the composites

CHAPTER-6: A comprehensive summary of the work done

CHAPTER 1: Literature survey on phenolic and epoxy resins, epoxy esters (polyester polyols) and polyurethane resins and their composites

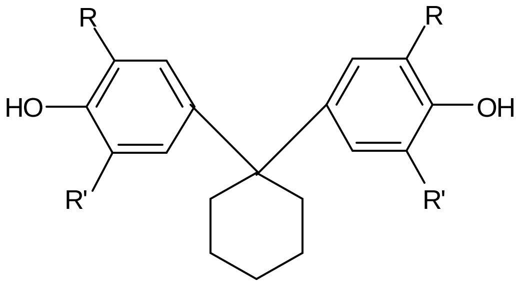
This chapter of the thesis describes the up to date literature survey on synthesis, applications and characterization of phenolic and epoxy resins, epoxy esters (polyester polyols), polyurethane resins and their composites in various fields of science.

CHAPTER 2: Syntheses of monomers, epoxy and phenolic resins, polyester polyols and polyurethane resins

This chapter is further subdivided into five sections:

Section-1: Syntheses of 1, 1’- bis (R, R’- 4-hydroxy phenyl) cyclohexane (I)

1,1’-bis(4-hydroxy phenyl) cyclohexane (BC) /1,1’-bis(3-methyl -4-hydroxy phenyl) cyclohexane (MeBC) were synthesized by Friedel – Crafts condensation of phenol/ o-cresol with cyclohexanone by using a mixture of HCl: CH_3COOH (2:1 v/v) as a catalyst at 50-55^{0}C for 4h and were repeatedly recrystallised from methanol-water system prior to their use.



(I)

BC: R=R'=H

MeBC: R=CH3 and R'= H

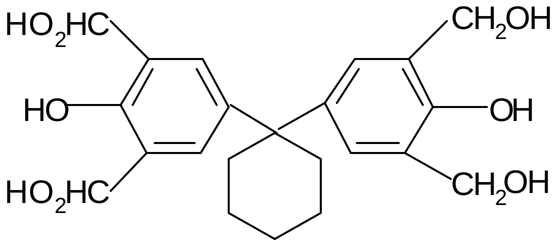
ClBC: R=R'=Cl

BrBC: R=R'=Br

BC was chlorinated by using thionyl chloride in carbon tetrachloride and sodium sulphide as a catalyst at 70^{0}C for 3h. BC was brominated by using bromine in glacial acetic acid at room temperature for 2h. Halogenated bisphenols were repeatedly recrystallised from appropriate solvent system (s) prior to use.

Section-2: Syntheses of bisphenol-C-formaldehyde resin (II)

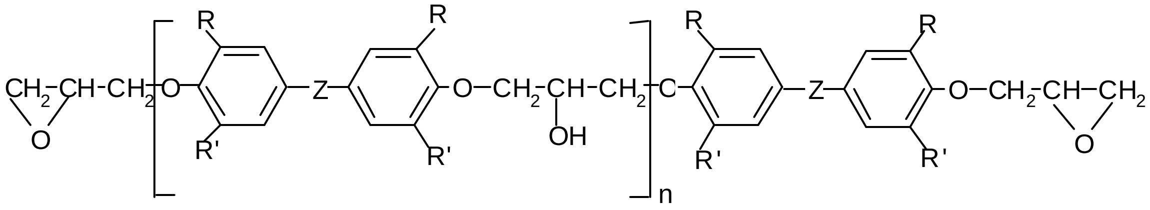
Bisphenol-C- formaldehyde resin (II) was synthesized by condensing bisphenol-C with formaldehyde by using alkali as a catalyst at 70^{0}C for 2h. A white crystalline resin was repeatedly purified from methanol-water system prior to its use.



(II)

Section-3: Syntheses of epoxy resins (III)

Epoxy resins of bisphenol-A (BA), BC, MeBC, BrBC and ClBC were synthesized by condensing bisphenols with epichlorohydrin by using isopropanol as a solvent and alkali as a catalyst at reflux temperature for 3.5 h. The resins were extracted from chloroform.



(III)

ER-1: R= R’=H and Z = isopropyl

ER-2: R=R’= H and Z = cyclohexyl

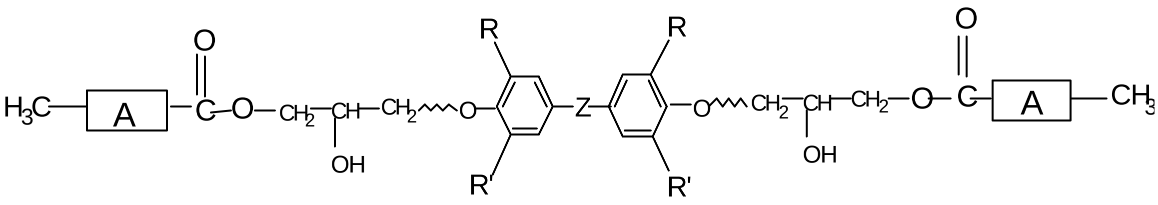
ER-3: R= CH_3 R’= H and Z =cyclohexyl

ER-4: R=R’= Cl and Z = cyclohexyl

ER-5: R=R’= Br and Z = cyclohexyl

Section-4: Syntheses of polyester polyols (IV)

The polyester polyols were synthesized by condensing ER-1 to ER-5 with ricinoleic acid/ oleic acid/ rosin (1:2 mole ratio) by using 1, 4- dioxane as a solvent and triethyl amine as catalyst at reflux temperature for 4-6h. The general structure of the polyester polyols is



(IV)

Polyester polyols

RAER-1: R=R'=H, Z= isopropyl and A= ricinoleic acid

RAER-2: R=R'=H, Z= cyclohexyl and A= ricinoleic acid

RAER-3: R=CH_3, R'= H, Z= cyclohexyl and A= ricinoleic acid

RAER-4: R=R'= Cl, Z= cyclohexyl and A= ricinoleic acid

RAER-5: R=R'=Br, Z= cyclohexyl and A= ricinoleic acid

OAER-1: R=R'=H and Z= isopropyl and A= oleic acid

OAER-2: R=R'=H and Z= cyclohexyl and A= oleic acid

OAER-3: R=CH_3, R'= H and Z= cyclohexyl and A= oleic acid

OAER-4: R=R'=Cl and Z= cyclohexyl and A= oleic acid

OAER-5: R=R'=Br and Z= cyclohexyl and A= oleic acid

RER-2: R=R'=H and Z= cyclohexyl and A= rosin
RER-3: R= CH_3, R'= H and Z= cyclohexyl and A= rosin

Section-5: Syntheses of polyurethane resins

[A] Syntheses and film preparation of polyurethanes of RAER-1 and RAER-2

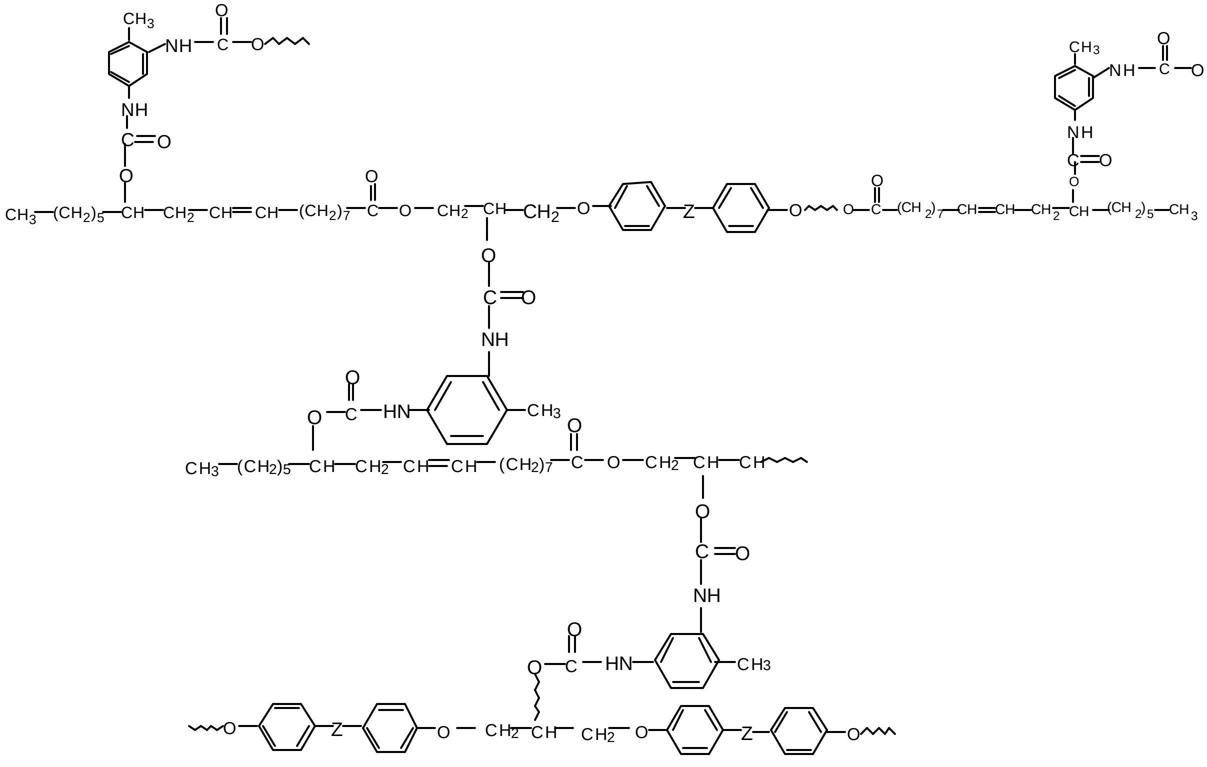
Polyurethanes of RAER-1 and RAER-2 were prepared by reacting polyester polyols (0.0029 mol) with 2,4-toluene diisocyanate (0.004 mol) by using MEK as a solvent at room temperature for 15 min. The films of the resins were cast by solution casting. The general structure of the resultant polyurethane is as under

[B] Syntheses of copolyurethane resin

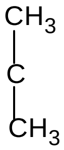
Copolyurethane resin of PU (synthesized according to above process) and PEG-400 (20% and 30% of polyester polyol) was synthesized and their film was cast by evaporation of MEK at room temperature. The structure of the resultant copolyurethane is as under.

[C] Syntheses of polyurethanes of BCF and ER-2

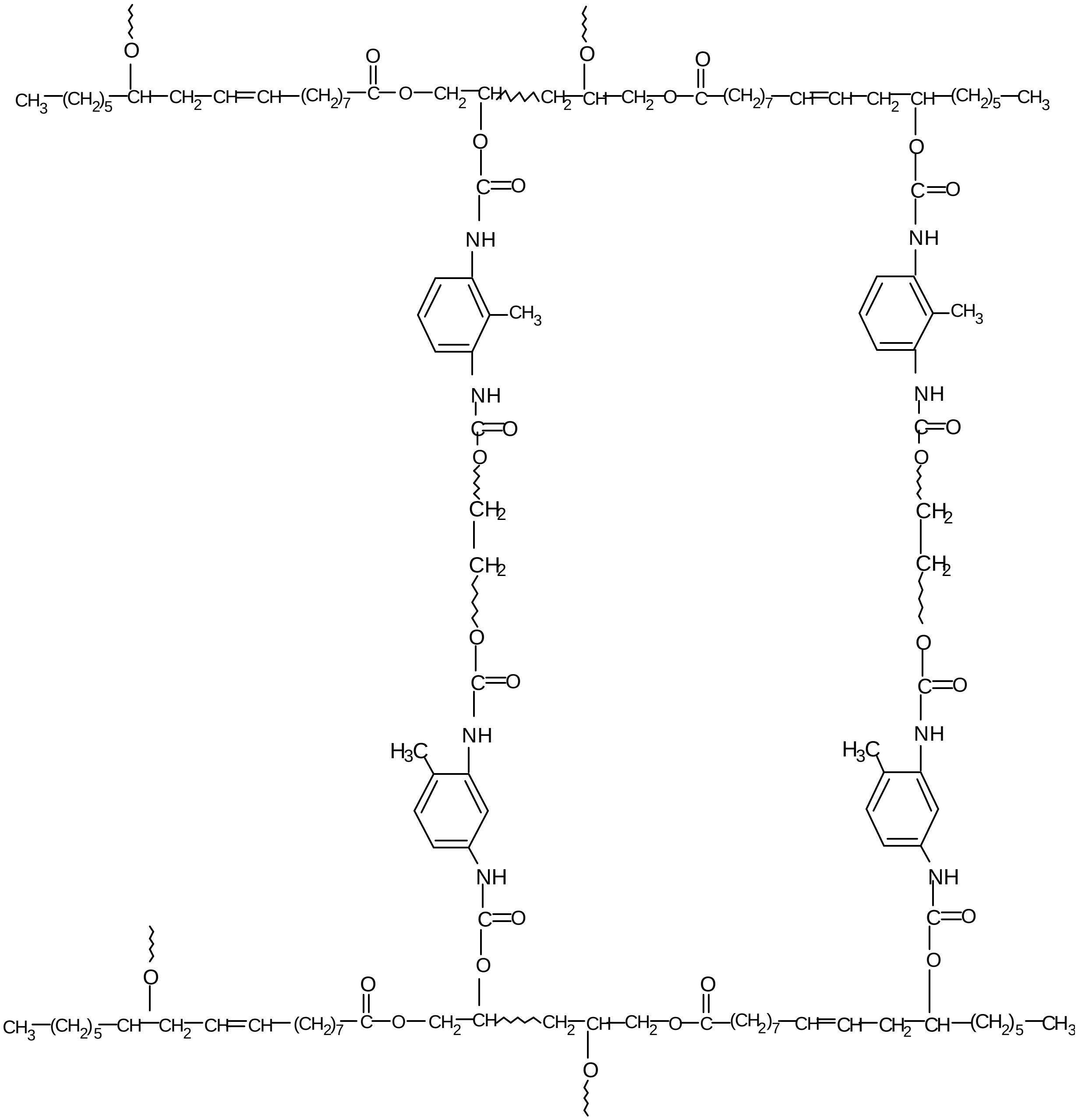
Polyurethane resins of BCF and ER-2 were synthesized by reacting BCF/ER-2 with toluene diisocyanate (1: 3 mole ratio) using MEK as a solvent at room temperature for 15-30 min.



(V)

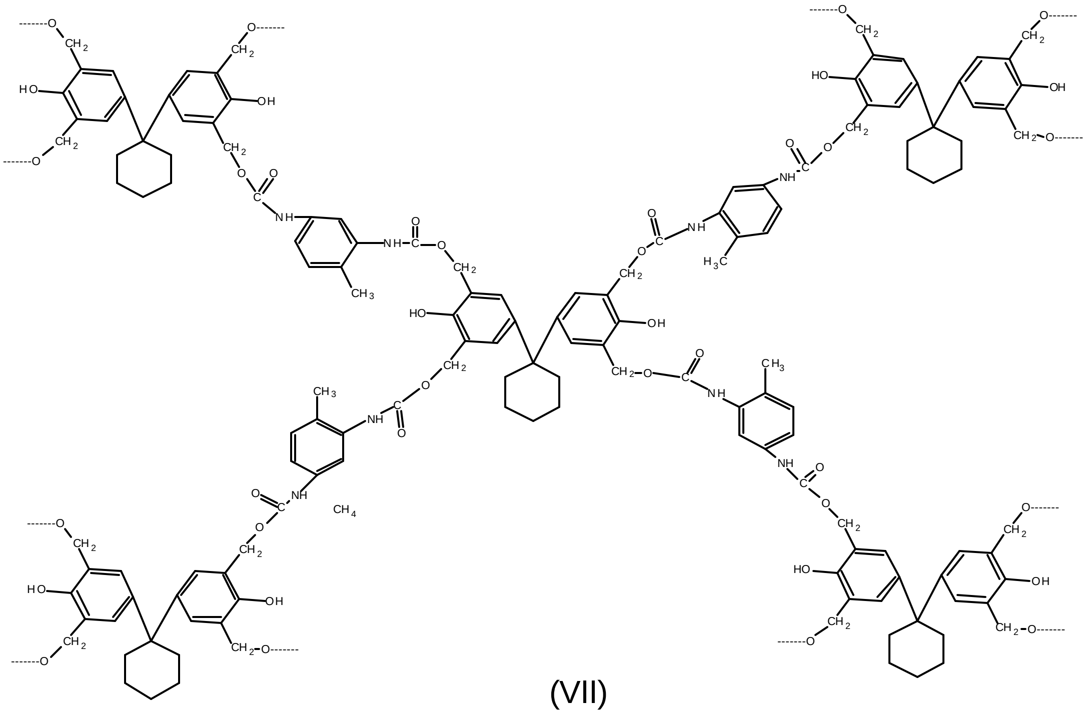
where Z=  $C(CH_3)_2$ for RAER-1 Z= cyclohexyl for RAER-2

Polyurethane resin based on RAER-1 & RAER-2 polyester polyol



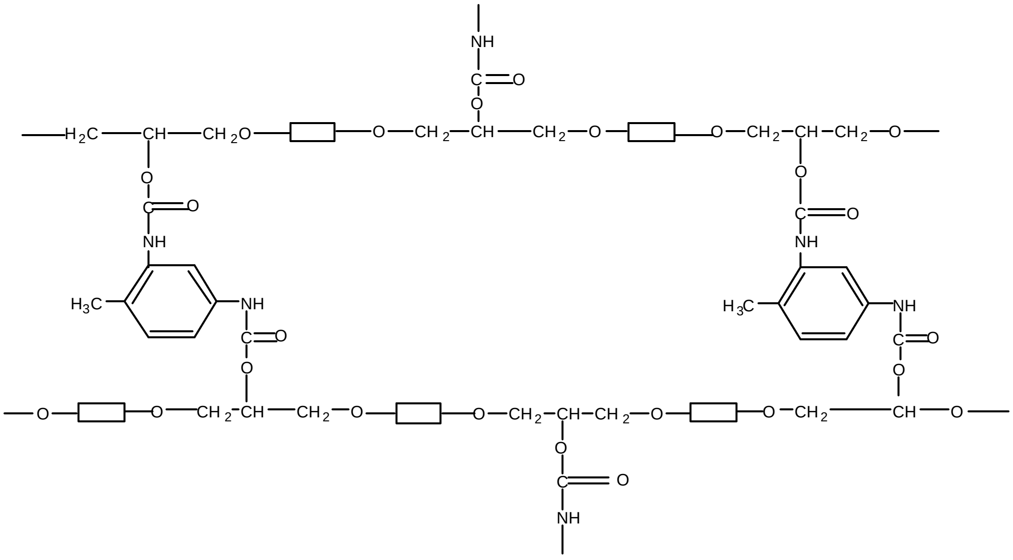
(VI)

Copolyurethane resin



(VII)

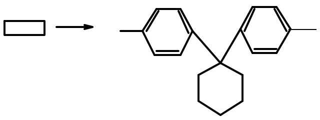
Polyurethane of BCF resin



(VIII)

Polyurethane of ER-2 resin

where



CHAPTER 3: Physico-chemical characterization of the resins

This chapter is further subdivided into eight sections:

Section-1: Spectral characterization of the resins

Formation of different linkages in the resins is supported by IR 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 and compared.

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 and compared.

Section-4: Determination of hydroxyl value of polyester polyols

The hydroxyl value of the polyester polyols were determined 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 polyurethanes of BCF, ER-2, RAER-1, RAER-2 and RAER-3-PEG-400 were investigated by TG method at the heating rate of 10 ^{0}C/min in an N_2 atmosphere and discussed in light of structure of the based resins.

Section -6: Density measurements of the polyurethanes

The densities of polyurethanes of RAER-1, RAER-2 and RAER-3-PEG-400 were determined by floatation method by using CCl_4-n-hexane as a solvent system and discussed in terms of structures/composition of the resins.

Section-7: Mechanical and electrical properties of the polyurethanes

The tensile strength, electric strength and volume resistivity of RAER-1, RAER-2, RAER-3-PEG-400 films are determined according to standard methods and discussed their usefulness.

Section-8: Chemical resistance of the polyurethanes

The chemical resistance of the films of above mentioned polyurethanes 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 discussed their stability in different environments.

Chapter-4: Surface coating of polyurethane resins on different substrates and their chemical resistance

This chapter describes coating application of the polyurethane resins on different substrates such as copper, mild steel, tin and glass. The hydrolytic stability of the coated resins in different environments was tested against water, acid and salt by change in weight method till equilibrium was established.

Chapter-5: Fabrication and physico-chemical characterization of the 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 fiber (jute, sisal bamboo etc.) reinforced composites are emerging as realistic alternatives to synthetic fibers reinforced composites in many applications due to its low cost, light weight, low density, easy availability and bio degradability as compared to synthetic fibers [8,9].

---

8. R.G. Schmidt and C. E. Frazier, “Network characterization of phenol formaldehyde thermosetting adhesive” Inter. J. Adhe. Adhesives, **18**,139-146, 1998.
9. J. Gassan and V. S. Gutowski, “Effect of corona discharge and UV treatment on the properties of jute-fiber epoxy composites.” Compos. Sci and Tech. **60**, 2857-2863, 2000.

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 [10-12]. 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 days polyurethane based composites are widely used as seat frames, sun shades, door panels, package trays and truck box panels.

Section-1: Fabrication of different types of composites

Composite materials are formed by combination of two or more materials that retain their respective characteristic properties when combined together. They are superior to those of the individual constituents. The main constituents of the composites are fibers, reinforcing materials (dispersed phase) responsible for stress resistance and resins, matrix material (continuous phase) responsible for stress propagation.

Hybrid composites are materials made by combining two or more different types of fibers in common matrix. They offer a range of properties that can not be

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10. C. N. Zarate, M. I. Aranguren and M. M. Reboredo, “Resole-vegetable fibers composites.” J. Appl. Polym. Sci,**77**, 1832-1840, 2000.
11. C. Y. Lai, S. M. Sapuan, M. Ahmad and N. Yahya, “Mechanical and electrical properties of coconut coir fiber-reinforced polypropylene composites.” Polym-Plastics Tech. and Eng. **44**, 619-632, 2005.
12. E.S. De Medeiros, J.A.M. Agnelli, J Kuruvilla, H. De Carvalho and H. C. Mattoso, “Mechanical properties of phenolic composites reinforced with jute/cotton hybrid fabrics” Polym. Compos. **26**, 1-11, 2005.

obtained with a single kind of reinforcement. In hybrid composites fabrication varieties of natural fiber jute, jute-rice husk and jute-wheat husk sandwich composites (15cm X 15cm / 5cm X 5cm) of polyurethanes of BCF and ER-2 were fabricated by hand lay-up technique under 30.4 MPa pressure and at 110-130 ^{0}C for 6-8 h.

Section-2: Mechanical and electrical properties of the composites

Mechanical and electrical properties of the composites are very important for the application viewpoint in diverse fields. Tensile strength, flexural strength, electrical strength and volume resistivity of the composites mentioned in previous section were determined according to standard methods. The results are discussed in light of related materials and their possible applicability.

Section-3: Chemical resistance study of composites

Moisture absorption study of composites was carried out at room temperature as well as in boiling water. For this composites of 5cm X 5cm were fabricated. The moisture uptake study was conducted periodically by change in mass method in water, acid and saline environments till equilibrium was established. The equilibrium moisture uptake, equilibrium time and diffusivity in different environments were determined and discussed in detail.

Chapter- 6: A comprehensive summary of the work done

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

Signature of the Guide **Signature of the candidate**

(P. H. Parsania)
Prof. and Head,
Department of Chemistry

(Sunil I. Mavani)

Historians frequently classify the early ages of man according to the materials that he used for making his implements and other basic necessities. The most 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, horne and fibers. Until the 19th century man's inanimate possessions, his home, his tools, his furniture, etc. 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 been 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.

[A] LITERATURE SURVEY ON BISPHENOLS

Bisphenols are most widely useful as intermediate for dyes, drugs, varnish and constituent of veterinary medicines, fungistats and pesticides, antiseptic, anticoccidial, lowering serum cholesterol in mammals. Several bisphenols are used as bactericides, disinfections, agriculture fungicides, herbicides, and drugs for treatment of seborrhea and acne and typical anti inflammatory agents. Various bisphenols have been shown to be effective fungicides specifically against mildew preventives on cotton fabric and against the fungi that cause peach brown rot.

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 also useful in manufacturing thermally stable polymers, epoxy resins, polyester and polyurethane resins.

Farbenind [1, 2] has reported the condensation of phenols and ketones in the presence of acetic acid, hydrochloric acid at 50^{o}C and also reported the melting points of 1,1'-bis(4-hydroxy phenyl cyclohexane) (186^{0}C), 1,1'-bis (4-hydroxy phenyl)-4-methyl cyclohexane (179^{0}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

$$\mathrm{PhOH + R_2CO \rightarrow R_2C\,(OH)\,C_6H_4OH}$$

(2) $\mathrm{R_2C\,(OH)\text{-}C_6H_4OH + PhOH \rightarrow R_2C\,(C_6H_4OH)_2 + H_2O}$

Johnson and Musell [4, 5] have reported synthesis of 1, 1'-bis(4-hydroxy

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1. I.G.Farbenind, Fr. Patent 647, 454 (1928); *C.A.* **23**, 2540, 1929.
2. I.G.Farbenind, Ger. Patent 467, 728 (1927); *C.A.* **23**, 1729, 1929.
3. M.E. McGreal, V. Niederl and J.B. Niederl, J. Am. Chem. Soc., 61, 345 (1939); *C.A.* **33**, 2130,1939.
4. J.E. Johnson and D.R. Musell, U.S. Patent 2,538,725 (1951); *C.A.* **4**5, 4412, 1951.
5. J.E. Johnson and D.R. Musell, U.S. Patent 2,535,014 (1950); *C.A.* **45**, 2635, 1951.

phenyl) cyclohexane (1) using 5 moles of phenol, 1 mole of a cyclohexanone, H_2S or BuSH below 40°C with 0.1-0.3 mole dry HCl gave (I) m.p. 186-87°C; 2Me-I, 236-240°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. They have also reported that coccidial infection in poultry may be suppressed by feeding a bisphenol (p-$HO(C_6H_4)_2$-CRR' in which R' is a phenyl or alkyl, R is H or alkyl).

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 p^H 2-3 with 6N HCl. The Yield was 47.5%. Similarly they have also synthesized 1,1'-bis(4-hydroxyphenyl) cyclohexane (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% aqueous HCl or 70% aqueous H_2SO_4 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'-dihydroxy diphenyl 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,

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6. H.L. Bender, L.B. Conte and F.N. Apel, U.S. Patent 2,858,342 (1958); *C.A.* **53**, 6165, 1959.
7. H.L. Bender, F.N. Apel and L.B. Conte, U.S. Patent 2,936,272 (1960); *C.A.* **54**, 19,604, 1960.
8. Farbenfabriken, Ger. Patent 1,031,788 (1958); *C.A.* **54**, 19,603, 1960.
9. B.M. Tumerman, E.S. Gervits and I.V. Vesela, Neffepererabotkai, Naftekhim, Nauchn,-Tekhum, 8, 46 (1965); *C.A.* **64**, 4977, 1966.

aromatic and cyclic ketones in the presence of HCl and BF_3 as catalysts. The highest reaction rate was observed in the case of Me_2CO 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^oC in nitrogen atmosphere and steam distillation of 1,1'-(4,4'-dihydroxydiphenyl) cyclohexane gave 1,1'-(3,3'5,5'-tetrachloro-4,4'-dihydroxy phenyl) cyclohexane (m.p. 148.5-9.5^oC).

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 $SOCl_2$ 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), $SOCl_2$ (40 ml) and Na_2S (0.28 g) in CCl_4 (40 ml) was heated with stirring for 3 h at 55^oC, 1h at 70^oC yielded 63-75% 1,1'-bis(3-chloro-4-hydroxy phenyl) cyclohexane of m.p. 142.5^oC (CCl_4) 82-6% 2,2'-bis(3-chloro-4-hydroxy phenyl) propane of m.p. 89-91^oC (30% aq.AcH) and 100% 3,3'-bis-(3-chloro-4-hydroxy phenyl)pentane. The title compounds are used in the preparation of incombustible 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)

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10. Farbenfabriken, Ger. Patent 1,073,504 (1960); *C.A.* **55**, 16,491, 1961.
11. I.M. Bilik, N.M. Bondarets, A.M. Serebryanyi, L.S. Rybkina and T.M. Cheryavskaya, Brit. Patent 1,047,058 (1966); *C.A.* **66**, 10,737, 1967.
12. S. Maeda, J. Yurimoto, S. Samukawa and Y. Kojima, Japan 14, 752(66) (1963); *C.A.* **66**, 86,263, 1967.
13. Y. Masai and M. Nakanishi, Japan 13, 248(`67) (1964); *C.A.* **68**, 3,557, 1968.

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^{o}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^{o}C in closed system for 3h to give 97% 1,1'-bis(4-hydroxyphenyl) 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 HNO_3 in AcOH at 0^{o}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, and were reduced with $SnCl_2$ in HCl and with Raney Ni to give 1,1'-bis(3-amino-4-hydroxy phenyl) cyclohexane, respectively. These monomers are useful for coordination polycondensation.

Serebryanyi et al. [17] have reported the preparation of 1,1'-bis(3-chloro-4-hydroxyphenyl)cyclohexane (0.056mole) in CCl_4 (90 ml) and $SOCl_2$ (0.13 mole) using fused Na_2S (0.005 mole) as a catalyst with stirring for 3h at 55^{o}C and 1 h at 70^{o}C gave 70% yield.

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14. A.G. Farnham, F.N. Apel and H.L. Bender, Ger. Patent 1,242,237 (1967); *C.A.* **68**, 59,282, 1968.
15. Freudewald, E. Joachim, Konrad and M. Frederic, Fr. Patent 1,537,574 (1968); *C.A*. **71**, 21,868, 1969.
16. T.K. Popova and G.P. Nedonoskova, Zh.Khim, 5Zh338 (1970); *C.A.***75**, 6,391,1971.
17. A.M. Serebryanyi, I.M. Bilik and N.M. Mironova, Metody Poluch Khim., Reaktive Prep. (U.S.S.R.) 20, 35 (1969); C.A. **76**, 85,493,1972.

Kozlov et al. [18] have reported the condensation of o-cresol with Me_2CO in the presence of polyphosphoric acid with a catalyst-o-cresol-Me_2CO ratio of 6:3:0.53 at 40^oC gave 94% $Me_2C-(C_6H_3(OH)Me-4,3)_2$. Similar results were obtained with o-cresol and MeCOEt, Et_2CO, MeCOPr, MeCOBu, $MeCO(CH_2)_4$-Me and $MeCO(CH_2)_5$-Me, condensation of cyclohexanone with o-cresol gave 90% 1,1'-bis(2-methyl- 4-hydroxyphenyl) cyclohexane.

Smirnova et al. [19] have reported acidity constants of chlorine containing bisphenols. The p^K values for the first and second ionization of bisphenol-A, bisphenol-C, and bisphenol-S derivatives are reported. Introduction of a Cl atom into the parent molecule decreases the p^K values and increases the difference between the 1st and 2nd p^K values whereas introduction of a methyl group increases the p^K value.

Kozlov et al. [20] have reported the condensation of o-cresol with cyclohexanone in the presence of polyphosphoric acid. The optimum conditions for this condensation were $40-45^oC$, 70-100 wt % H_3PO_4 (72% P_2O_5), 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 [21] has reported the preparation of bisphenols by reaction of a ketone (cyclohexanone) with phenol, BuSH, $ClCH_2CH_2Cl$ and Me_3SiCl.The mixture was stirred and heated to $50-55^oC$ and finally at 65^oC to give bisphenol-Z.

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18. N.S. Kozlov, A.G. Klein and V.P. Sukhodolova, Khim. Tekhnol, Obl. Tekh. Konf, (1973); *C.A.* **82**, 97,778, 1975.
19. O.V. Smirnova and E.Ya Robas, Zh. Prikl Khim, 48(3), 578 (1975); *C.A.* **82**, 139,099, 1975.
20. N.S. Kozlov, A.G. Klein and V.P. Sukhodolova, Vesti Akad Navuk B. SSR, Ser. Khim Navuk, 4, 109 (1976); *C.A*. **85**, 176, 992, 1976.
21. B.S. Alexandru, U.S. Patent 4,766,255 (1988); *C.A.* **110**, 38,737, 1989.

Nagata et al. [22] have reported condensation of 4-hydroxy cyclohexanone with PhOH in 36% HCl at 60°C for 4 h to give 77% biphenyl cyclohexanol derivative. The decomposition and dehydrogenation of which in a mixture of NaOH, PhCMe: CH_2, H_2O and 5% Pd/C under N_2 at 250°C for 4h gave 83% 4, 4'-bisphenol.

Subramaniam et al. [23] 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. [24] 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_2O_2 gave the respective tetrachlorobisphenol derivatives in 67-87% yields. The condensation of bisphenols with $ClCH_2COOH$ in aqueous NaOH gave dioxyacetic acid derivatives of bisphenols in 61-75% yields.

Dietzler [25] has reported bromination of bisphenol in methanol-water system. Thus bisphenol was treated with bromine at 42°C with stirring (4h). The

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22.Nagata, Teruyuki, Miura and Toru, Eur. Patent 251,614 (1988); *C.A.* **110**, 75,037, 1989.

23G. Subramaniam, R. Savithri and S. Thambipillai, J. Indian Chem. Soc., **66**, 797 (1989).

24 A. M. Islam, E.A. Hassan, M.E. Rashad, and M.M. Wassel, Egypt. J. Chem., **20(5)**, 483, 1980.

25.A.J. Dietzler, U.S. Patent, 3,029,291 (1962); C.A. **57**, 9,744, 1962.

mixture was kept for 2h at 40^{o}C yielded 94.4% 4,4’-isopropylidene-bis(2,6-dibromophenol) (181-2^{o}C), 4,4’-cyclohexylidene bis(2,6-dibromo-phenol) (m.p. 190^{o}C).

Rao et al. [26] have reported a convenient method for the preparation of bisphenols. Cyclohexanone was treated with phenol at 40^{o}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. [27, 28] 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^o, 50^o, 60^{o}and 70^{o}C. They have reported optimum catalyst concentration (10-15 ml), time (30-90 min) and temperature (55-70^{o}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.

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26. M.V. Rao, A.J. Rojivadiya, P.H. Parsania and H.H. Parekh, “A convenient method for the preparation of bisphenols”, J. Indian Chem. Soc., **64**, 758-759, 1987.
27. H.H. Garchar and P.H. Parsania, “Optimization reaction conditions for synthesis of 1,1’-bis(3,5-dimethyl-4-hydroxyphenyl) cyclohexane”, Asian J. Chemistry, **6**, 135-137,1994.
28. H.H. Garchar, S.H. Kalola and P.H. Parsania, “Synthesis and evaluation of bisphenol-C and its derivatives as potential antimicrobial and antifungal agents”, Asian J. Chemistry, **5(2)**, 340-347,1993.

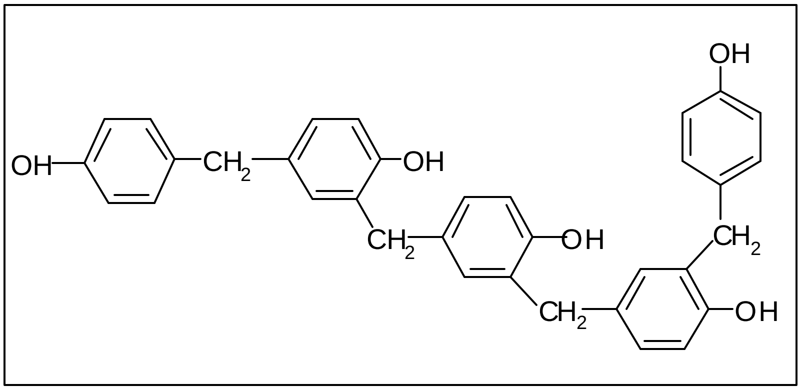
[B] LITERATURE SURVEY ON PHENOLIC RESINS, EPOXY RESINS, EPOXY ESTERS (POLYESTER POLYOLS) AND THEIR COMPOSITES

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.

The broad interest in epoxy resins originates from the extremely wide variety of chemical reactions that can be used for the curing that result many different properties. The chemistry is unique among the thermosetting resins. In contrast to the formaldehyde resins, no volatiles are given off during cure. Both epoxy and phenolics are individually superior in their respective fields. 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.

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 elsewhere [29-33].



(I)

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

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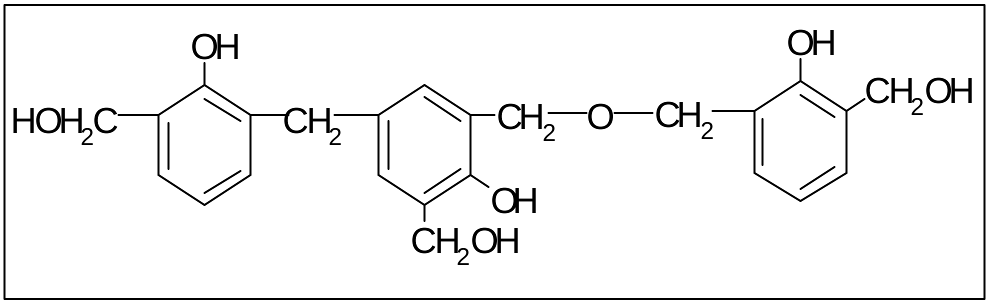
29. A.A.K. Whitehouse, E.G.K.Pritchett and G. Barnett,"Phenolic Resins", Iliffe, London, 1967.
30. P. Robitschek and A. Lewin, "Phenolic-Resins" Iiffe. London, 1950.
31. R.W. Martin, "The Chemistry of Phenolic Resins", John Wiley, New York, 1956.
32. N.J.L. Megson, "Phenolic Resin Chemistry", Butterworth, London, 1958.
33. T.S. Carswell, "Phenoplast", Inter science, New York, 1947.

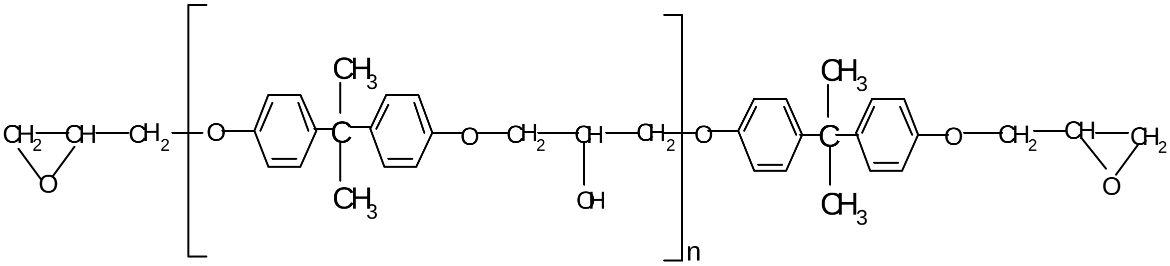
polyalcohols are of low molecular weight, while a solid resole may have only three to four benzene rings per molecule. Heating of these resins will result in cross-linking via the uncondensed methylol groups or by some complex mechanism. It is also called as one stage resin. Phenolic resins are well known for two major applications in molding and laminates. They are also applied in other applications.



(II)

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. Subsequently, in the early 1940s, CIBA A G of Basle took the authorization of patent by Greenlee et al.



(III)

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 [34] 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 [35].

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

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34. I. A. Brydson, “Plastics Materials” VIth edition, Butler Worth Heinemann Ltd., Oxford, p. 722, 1995.
35. Lee, H., and Neville, K., “Epoxy Resins in their Application and Technology”, Mc Graw-Hill New York, 1957.

Table – 1.1: Effect of reactant ratios on molecular weight

Mole ratio of epichlorohydrin/ bisphenol-A	Softening point (^{0}C)	Molecular Wt.	Epoxide equivalent
2.0	43	451	314
1.4	84	791	592
1.33	90	802	730
1.25	100	1133	862
1.2	112	1420	1176

- 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 [36]. Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes [37], acrylates, etc. This modification of epoxy resin is feasible due to highly reactive epoxy ring, which can also undergo ring opening reaction in the presence of acids [38] 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 polyol (epoxy esters) manufacturing but the most commonly used are listed below 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.

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36. A.F. Yee, and R.A. Pearson, “Toughening mechanisms in elastomer modified epoxies: Part-1 mechanical studies”, J. Mater. Sci. **21**, 2462-2474, 1986.
37. A.V. Cunliffe, M.B. Huglin, P.J. Pearce and D.H. Richards, “An anionically prepared flexible adhesive: 1: Synthesis”, Polymer **16**, 654-658, 1975.
38. C.A. May, Epoxy Resins- Chemistry and Technology, Marcel Dekker, New York, 1988.

Fatty acid	**Epoxy ester properties**
Linseed	Fast air drying system with poor color retention
DCO	Fast air-drying or stoving system with good flexibility and chemical resistance.
Soya been	Air-drying systems with good color and soft flexibility films.
Coconut	Non-air drying system with very good color, chemical resistance and flexibility, good color on oven backing.

The commercial interest in epoxide resins was first made apparent by the publication of Germans patent 676 117 by I. G. Farben in 1939, which described liquid poly epoxides. In 1943 P. Casten file US patent 2324483 covering the curing of the resins with dibasic acids. The Ciba Company subsequently exploited this important process. A later patent of Casten (US patent 2444333) covered the hardening of epoxide resins with alkaline catalyst used in the range 0.1–5 %. This patent, however, became of somewhat restricted value as the important amine hardeners are usually used in quantities higher than 5%.

In 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 [39] 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 CH_2O in the presence of strong acid or base as a catalyst.

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39. A. Wolfram and H. Jhan, “Synthetic resins suitable for various uses”, U.S.2, 322,990 (1943) C.A. **38**, 185, 1944.

Greenlee [40] has prepared the rapid drying composition from diphenols and epichlorohydrin and esterified this product with Tall–oil.

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.

Lederman [42] 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. [43] 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 dispersing medium. Rigid foam was obtained by this composition, which is suitable for architectural uses.

CIBA Ltd. [44] 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.

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40. S.O. Greenlee, “Tall-oil esters”, U.S. 2,493,486 (1949) C.A. **44** 2770, 1950.
41. Chemie Produkte, “Epoxy resins/containing sealing compositions”, Ger. 1,020,140 (1957) C.A. **54**, 179704, 1957.
42. B.E. Lederman (Midland Chemical Co.) ”Bisphenol-modified wrinkle varnish”, C.A. **53**, 1779, 1959.
43. R. Petri, H. Reinhard and L. Keller, “Epoxy resin foams from aqueous dispersions” Ger. 1,080,774 (1960) C.A. 2003, 55, 14982, 1961.
44. CIBA Ltd., “Epoxy resin containing coatings”, Brit. 883,521, 1961 C.A. **56** 11746, 1962.

Union Carbide Co. [45] has reported curing of polyepoxides with liquid glycol diamines ($H_2N(CH_2)_3O(C_nH_{2n}O)_x$ $(CH_2)_3NH_2)$(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 H_2N $(CH_2)_3O$ $(CH_2CH_2O)_2(CH_2)_3NH_2$ 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. [46] has synthesized flexible adhesive film having honeycomb structure. Thus an epoxy resin mixture (I) was prepared by heating 100 parts of glycidyl ether of bisphenol – A to 121^0C, adding 2-parts fine SiO_2 and stirring at 149^0C for 10-20 min. A mixture of 145 parts isophthaloyl dihydrazide, 10 parts MgO and 1 part dimethyl diocta decyl ammonium bentonite was added to epoxy mixture at 104^0C and the resulting mixture was milled at 77^0C to complete dispersion.

Bremmer [47] 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 70^0 under an N_2 atmosphere with stirring. The composition was cured by triethyl amine.

Karl [48] has reported phenol-HCHO resins for building materials. A typical material composed of phenol-HCHO resin pre condensate, acid hardener, an ethylene glycol, BuOH or terpineol ester, mineral filler [such as CaO, $Ca(OH)_2$, $CaSO_4$ or $Ca(CO_3)_2$and an additive such as sand were suitable for use as building material.

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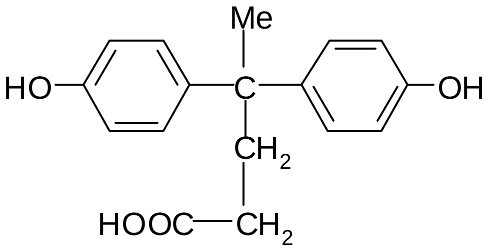
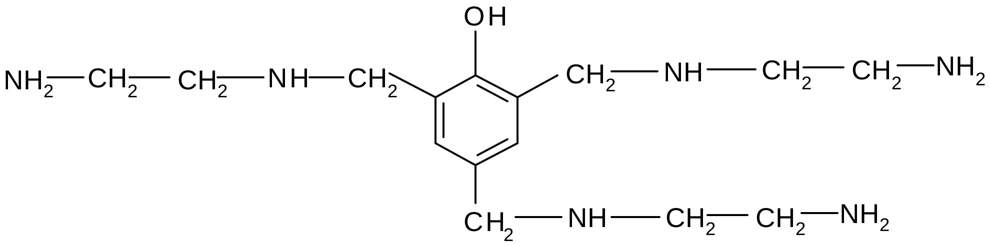
45. Union Carbide Co. (by Norman H. Reinking.), “Liquid glycol diamine curing agent for polyepoxides”, Brit. 904,403 (1962) C.A. **58**, 1643, 1963.
46. Minnesta Mining and Manufacturing Co. “Flexible adhesive film”, Ger. 1,100,213 (1961); C.A. **58**, 11551, 1963.
47. B.J. Bremmer (Dow Chemicals Co.), “Flame retardant epoxy resin”, U.S.3, 294,742 (1966); C.A. **66** 38487, 1967.
48. A. Karl, “Phenol-HCHO resins for building materials” Ger. 1,544,609 (1965); C.A. **73**, 4516, 1970.

Taft [49] has reported new polymeric coating agents with improved properties. Such composition consists 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 a triethylamine.



(I)

Kogyo [50] has formulated epoxy resin composition hardened by phenol-block-phenol-polyamine-aldehyde reaction products at low temperature i.e. 10-15^{0}C.



(I)

On heating 200g (I) and 50 g nonyl phenol for 1h at 66^{0}C gives the blocked curing agent. A mixture of this compound bisphenols-A-epichlorohydrin co polymer (epoxy equivalent ~190) and 2, 2-bis (o-hydroxy phenyl) propane-propylene oxide copolymer epoxide equivalent ~ 345) were cooked together. The

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49.D.D. Taft (Ashland Oil Inc.) "Polymeric coating agents" U.S. 2,203,594 (1971); C.A. **77**, 154, 099,1972.

50.A.D. Kogyo. "Hardenable epoxy resin composition", Japan 2,126,179 (1972); C.A. **78**, 137, 425,1973.

composition has self-life of about 4 h and 70 min at 0^0C.

Castan and Gandillon [51] 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. [52] 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 [53] have reported epoxy resins esters of Dian 1, epichlorohydrin 1.16, and NaOH 1.25 moles were condensed 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 were 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 140 °C, and stirred under CO_2. 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

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51. P. Castan and C. Gandillon (to Stella S.A.,), U.S. 3,028, 348 (1958); *C.A.*, **57**, 11,338, 1962.
52. Devoe and Raynolds Co. Inc. (by John E. Masters), Ger. 1,130, 598 (1953); *C.A.*, **57**, 12,660, 1962.
53. J. Kinck and Z. Ditrych, Czech., 101,431 (1961); *C.A.*, **58**, 674, 1963.

in a 1:1 mixture of xylene and ligronine to form a varnish containing 30% of dry substances. The hot varnish was filtered and used as an air drying varnish after adding 0.05 % Co-naphthenate.

Nemours & Co. [54] has reported salt spray resistant coating composition of alkyd resin, drying oil (soyabean oil), and liquid epoxy resin (condensation) product of epichlorohydrin and diphenylolporpane. These compositions exhibit good adhesion and corrosion resistance under topcoats of acrylic enamel.

Shimizu et al. [55] 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 – 240ºC under nitrogen atmosphere to give polyester with Q Gardner viscosity (as a 50 % xylene solution).

Neumann and Hoenel [56] 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 120^0C, and equivalent weight 670-690 g/mol and viscosity at 25^0C in 40% butyl diglycol solutions 480-510 MPas.

Nakahara et al. [57] 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 ^{1}H-nuclear magnetic resonance spectroscopy (NMR). In addition, to evaluate the influence of the 4, 4′-

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54. Nemours and Co. (by Ralph G. Swanson) Belg. 632, 997 (1963); *C.A.*, **59**, 14,734, 1964.
55. Shimizu, Shigeo; Tachibana, Akihiro; Aritomi, Michio; Mori, Akitshi; Suzuki, Tsotoma (Toko Chemical Industry Co., Ltd) Japan Kokai, 74, 14, 600; *C.A.* **80**, 1,53,510, 1974.
56. U. Neumann and M. Hoenel, Can. Pat. Appl. CA 2, 152,428(1995); C.A. **124**, 03,914c, 1996.
57. K. Nakahara, T. Endo and M. Kaji, “Synthesis of a bifunctional epoxy monomer containing biphenyl moiety and properties of its cured polymer with phenol novolac”, J. Appl. Polym. Sci. **74**, 690-698,1999.

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. [58] have prepared simultaneous interpenetrating polymer networks (IPNs) based on epoxy (diglycidyl ether of bisphenol-A) and unsaturated polyester resin (UP) using m-xylenediamine 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 increased. 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. [59] have reported a convenient method for the preparation

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58.C.C. Liu, C.T. Lee and M.S. Lin, “Toughened interpenetrating polymer network materials based on unsaturated polyester and epoxy”, J. Appl. Polym. Sci. **72**, 585-592,1999.

59. M.R. Sanariya, D.R. Godhani, S. Baluja and P.H. Parsania, “Synthesis and characterization of epoxy resins based on 1,1’-bis(4-hydroxyphenyl) cyclohexane and 1,1’-bis(3-methyl-4-hydroxyphenyl) cyclohexane”, J. Polym. Mater. **15**, 45-49, 1998.

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. [60] 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 mole 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. [61] 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 (159-117^{0}C), good thermal stability (>320^{0}C).

60.V.M. Kagathara, M.R. Sanariya and P.H. Parsania, “Selected Topics in Polymer Science”, S.K. Dolui Edi., Prof. Sukumar Maiti, Polymer Award Foundation, Kolkata, PP 1-8, 2001.

61. Y.L. Liu, C.S. Wu and K.Y. Hsu, “Flame retardant epoxy resins from o-cresol novolac epoxy cured with a phosphorus containing aralkyl novolac”, J. Polym. Sci. Part A, **40**, 2329-2339, 2002.

Vikarm Sarabhai Space Center [62] has reported phenolic resin prepared by treating HCHO with bisphenol / cardanol mixture in the presence of basic catalyst.

Aoki et al. [63] 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 115^0C and 3 Kg/cm^2 pressure under hydraulic press.

Joseph et al. [64] 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 160-220^0C. Thus, 8 Kg husk was sprayed coated with 1.6 Kg resin binder.

Li et al. [65] 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, neo-pentyl (diallyl) oxy, tri (dioctyl) pyrophosphate titanate and neo pentyl (dially) oxy triacryl zirconate. Composites were fabricated using modified fibers with polyester, epoxy, polyethylene, etc. both mechanical and moisture absorption

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62. Vikram Sarabhai Space Center “Phenolic resins”, Ind. 137,274 (1973); C.A. **92**, 59,687,1980.

63.Aoki, Eiichi, Fujii, Nobuyoshi, Sasakuri, Hirokai, “Reinforcement and decorative molding of wood”, Japan Kokai 77,125,607 (1977); C.A. **88**, 122,864, 1978.

64.G.Joseph, Zooland, Shri Shankarya, Shivasangayya and Surender, “Composite boards from rice husk”, Ind. Pat. 1,46,015 (1976); C.A. **91**, 2,12,346, 1979.

65. Y. Li, Y.W. Mai and L. Ye, “Sisal fiber and its composite: A review of recent developments” Compos. Sci. and Tech., **60**, 2037-2055, 2000.

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. [66] have fabricated jute fiber reinforced phenolic composites for the study of durability and degradation due to out door 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. [67] 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. [68] 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.

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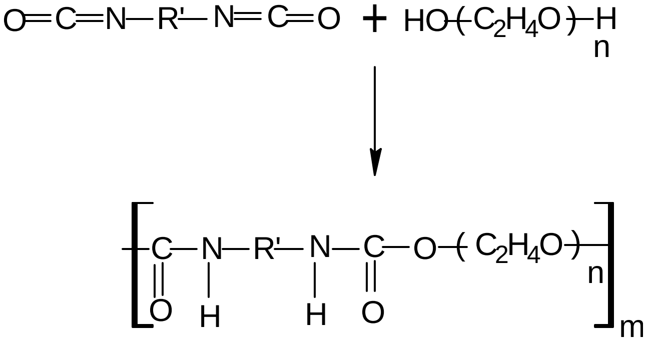
66. B. Shing, M. Gupta and A. Verma, “The durability of jute fiber reinforced phenolic composites”, Compos. Sci. and Tech., **60**, 581-589, 2000.

67. R. Joffe, L. Wallstrom and L.A. Berflund, “Natural fiber composites based on flax matrix effects”, Proceedings of International Scientific Colloquium, Modeling for Saving Resources, Riga, May 17, 2001

68. S. Biswas, G. Shrikanth and S. Nangia, “Development of natural fiber composites in India” Composite 2001 Convention and Trade Show, composite fabrication association, Oct. 3-6, 2001, Tampa, FL, USA.

[C] LITERATURE SURVEY ON POLYURETHANE RESINS AND THEIR COMPOSITES

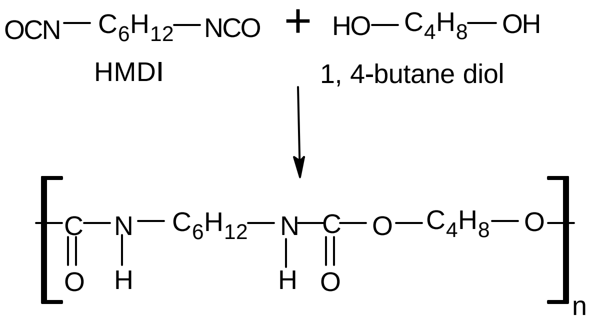
Polyurethane resins are a very unique class of a specialized materials, which are used industrially and on trade scale virtually in all sectors. Polyurethanes form an important class of polymers whose structures and performances can be designed to meet the user’s needs. Polyurethane resins are mainly produced by isocyanation of diisocyanate with polydiols of various molecular weights or other reactants containing hydrogen donors that are reactive with isocyanates.



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

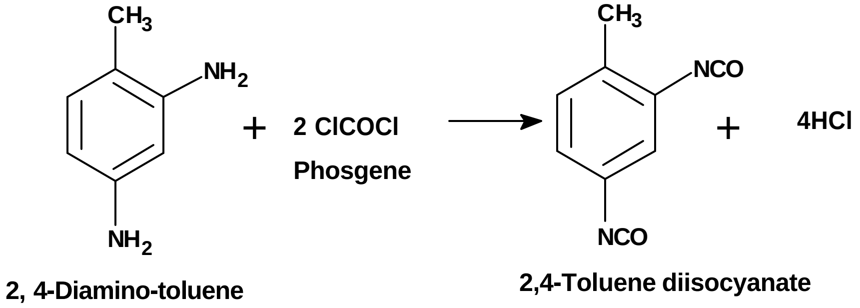
During the late 1940s Dupont and Monsanto Company began supplying 2, 4-toluene diisocyanate (TDI) in pilot plant quantities. In 1950-1952 Farben Fabriken Bayer disclosed the development process of polyurethanes elastomers and of flexible foams based on polyesters, and shortly thereafter they came into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



$$OCN-C_6H_{12}-NCO + HO-C_4H_8-OH \longrightarrow \left[\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-C_6H_{12}-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-C_4H_8-O \right]_n$$

Full scale commercial isocyanate manufacture began in the United State 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 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.



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-1.2. 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

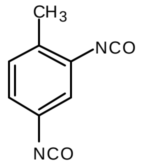
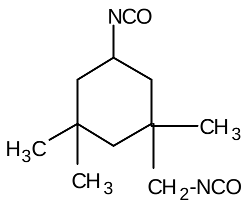
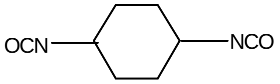
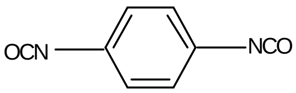
Polyester resins are produced by different reactions such as the esterification of acids or alcoholysis or acidolysis of epoxies, etc. The wide selection of raw materials available allows a very large choice of finished products, with a wide range of properties. Polyester polyols are obtained by using 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.

Polyesters exhibit good flexibility and chemical resistance so they are widely used in wood and plastic coatings in anti graffiti and aircraft coatings. The molecular weights of the polyester polyols used in the coatings may vary 500 to 5000.

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.

Table-1.2: The common diisocyanates used for the production of polyurethanes

Sr. No.	Chemical Name	Abbreviation	Structure
1	Toluene-2,4-diisocyanate	TDI	
2	Hexamethylene diisocyanate	HMDI	$OCN - C_6H_{12} - NCO$
3	Isophorone diisocyanate	IPDI	
4	4,4'-Methylene bis phenylene diisocyanates	MDI	$OCN - Ph - CH_2 - Ph - NCO$
5	Cyclohexane-1,4-diisocyanate	CHDI	
6	p-Phenylene-1,4-diisocyanate	PPDI	

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), 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.

Polyurethane possesses a unique combination of performance and application properties with excellent abrasion resistance, flexibility, hardness, chemical resistance, UV light resistance and anti-microbial characteristics [69]. 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 [70, 71].

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 [72, 73].

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 diaphrams and valves. They can be biodegradable depending upon their chemical structures [74].

69.M.X. Xu, W.G. Liu, Y.L. Guan, Z.P. Bi and K.D. Yao, “Study on phase behavior-impact strength relationship of unsaturated polyester/PU hybrid polymer network”, Polym. Inter. **38**, 205-209, 1995.

70.J.M. Buist, “Development in polyurethane-1”, Applied Science Publishers Ltd. London, 1978.

71. I.S. Lin, J. Biranowski and D.H. Lorenz, “Urethane chemistry and applications”, K.N. Edwards, Ed; ACS Symposium Series, 172, Ch. 34, p. 523, 1981.

72.J.A. Grapski and S.L. Cooper, “Synthesis and characterization of biocidal polyurethanes” Biomaterials **22**, 2239-2246, 2001.

73.A.Z. Okeema and S.L. Cooper, “Effect of carboxylate and/or sulphone ion incorporation on the physical and blood contacting properties of polyetherurethane” Biomaterials **12**, 668-676, 1991.

74.R. Jayakumar, M. Rajkumar, R. Nagendran and S. Nanjundan, “Synthesis and characterization of metal-containing polyurethanes with antibacterial activity”, J. Appl. Polym. Sci. **85**, 194-206,2002.

Recent years have 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 natural oils [75]. 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 [76, 77].

Castor oil is a triglyceride of fatty acids, whose main constituent is ricinoleic acid, extracted from Ricinus Communis [78, 79]. 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.

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75. G. Scott, “Polymer and environment” Cambridge: Royal Society of Chemistry; p27, 1999.
76. L.W. Barrett, L.H. Sperling, J. Gilmer and S.G. Mylonakis, “Crystallization kinetics of poly (ethylene terephthalate) in compositions containing naturally functionalized triglyceride oil”, J. Appl. Polym. Sci. **48**, 1035-1050,1993.
77. H.Q. Xi, X.D. Huang and G.G. Wang, “Electronic-ionic conducting interpenetrating polymer networks based on (castor oil-polyethylene glycol) polyurethane and poly(vinyl pyridine)”, Eur. Polym. J. **30**, 1227-1230, 1994.
78 K. Othmer, “Encyclopedia of Chemical Technology” 4th Edition, John Wiley and Sons, Inc. New York, 5, 1979.
79. R.W. Johnson and E. Iritz, “Fatty acids in industries process properties derivatives and applications” Marcel Dekker, New York, p13, 1989.

Owing to the versatility and broad range of properties now a days 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. [80] 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 [81] 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. [82] have synthesized polyurethane elastomers using castor oil, 4, 4'-methylene bis (phenyl isocyanate) (MDI) and toluene 2, 4-diisocyanate (TDI) and study 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

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80.J.V. Patel, P.K. Soni and V.K. Sinha, "Isocyanate adduct based two pack urethane coatings from biological material", J. Sci. Ind. Research. **58**, 579-585,1999.

81.M.R. Mehdizadeh and H. Yeganeh, "Synthesis and properties of isocyanate curable millable polyurethane elastomers based on castor oil as a renewable resource polyol", Eur. Polym. J. **40**, 1233-1238, 2004.

82.B.K. Kendagannaswamy, V. Annadurai, V. Siddaramaiah and R. Somashekar, "Physico-mechanical, optical and waxes studies on chain extended PU", J. Macromol. Sci., **37**, 1617-1625, 2000.

basis of the groups present in the diamines and changes have been interpreted by wide angle X-ray scattering data.

Kluth and Meffert [83] 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 [84] 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. [85] 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 there of. 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.

83.H. Kluth and A. Meffert, “PU prepolymers based on oleo chemical polyols.” U.S.P. 4,508,853. 1985.

84.H. Swada, “Epoxy-modified PU resin for a coating material” GB 2,369,123A, 2002.

85.Schoener, E. Thomas, B.A. Blakely and G.M. Carlson, “Stabilized moisture curable PU coatings.” EP 0,276,667, 1988.

Ashraf et al. [86] 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 [87] 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 tand 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 [88] 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 ^{1}H 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.

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86. S.M. Ashraf, E. Sharmin, F. Zafar, A. Hasant and S. Ahmad, “Studies on ambient cured PU modified epoxy coatings synthesized from sustainable resource.” Prog. Cryst. Grow. Chara. Mater. 83-88, 2002.
87. S. Mao and Y. Li, “Study on the properties and application of epoxy resin/PU semi-interpenetrating polymer networks”, J. Appl. Polym. Sci. **61**, 2059-2063, 1996.
88. S. Opera, “Epoxy-urethane acrylate”, Eur. Polym. J. **36**, 373-378, 2000.

Kolekar and Athawale [89] 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 [90] 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.

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89. S. Kolekar and V. Athawale, "Interpenetrating polymer networks based on polyol modified castor oil polyurethane and PMMA", Eur. Polym. J. **34**, 1447-1451, 1998.
90. K.P.O. Mahesh and M. Alagar, "Preparation and characterization of chain extended bismaleimide modified polyurethane-epoxy matrices", J. Appl. Polym. Sci. **87**, 1562-1568, 2003.

Prabu and Alagar [91] 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 (HTPDMS) using ?-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 [92] 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.

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91. A.A. Prabu and M. Alagar, “Mechanical and thermal studies of inter-crosslinked networks based on siliconized polyurethane-epoxy/unsaturated polyester coatings.” Prog. Org. Coatings. **49**, 236-243, 2004.
92. K.R. Joshi and V.D. Athawale, “Structure-property relationship in polyurethane coatings synthesized from chemoenzymatically modified castor oil”, J. Polym.Mater. **21**, 165-174, 2004.

Somani et al. [93] 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 [94] 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 polyol as a crosslinker. The first potting compound undergoes degradation under sterilization conditions, while second undergoes crosslinking under sterilization. A potting compound based on polyether polyol cross linker would be more promising for hollow fibers.

Lucas et al. [95] have prepared the thermoplastic polyurethane elastomers (TPUs) by reacting difunctional isocyanates with long or short chain polyesters

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93. K. Somani, S. Kansara, R. Parmar and N. Patel," High solids polyurethane coatings from castor-oil-based polyester polyols", Int. J. Polym. Mater. **53**, 283-293, 2004.
94. M. Jayabalan and P.P. Lizymol, "Studies on the effect of cross linker on the stability of castor-oil based aliphatic polyurethane potting compound", Polym. Degrad. Stab. **58**, 251-255, 1997.
95. H.R. Lucas, W.E. Mealmaker and N. Giannopouos, "Novel polyurethanes with interpenetrating networks for the coating industry", Prog. Org. Coat. **27**, 133-144, 1996.

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. [96] 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 [97] 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,

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96. C.C. Huang, B.Y. Liaw and D.J. Liaw, “Synthesis and properties of polyurethanes (PU) based on bisphenol-S derivatives”, Polymer **39**, 3529-3535, 1998.
97. S. Kolekar and V.D. Athawale, “Interpenetrating polymer networks based on oil modified castor oil urethane and poly (methyl methacrylate)”, J. Macromol. Sci. **37**, 65-79, 2000.

castor oil polyurethane and their IPNs showed relatively higher elongation and better resistance to solvents.

Keun et al. [98] 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, trimethylol 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. [99] have carried out the swelling experiments of interpenetrating networks (IPNs) of castor oil based polyurethane and unsaturated polyesters and calculated their solubility parameters. The kinetics of swelling and sorption have also been studied in chlorobenzene at 25^0C. 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 chains per unit volume (N) and degree of crosslinking were also calculated.

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98. J. Keun, K. Lee and H. Park, “Syntheses and physical properties of two-component polyurethane flame retardant coatings using chlorine containing modified polyesters”, J. Polym. Sci. Part-A **34**,1455-1464, 1996.

99. S. Ajitkumar, N.K. Patel and S.S. Kansara, “Sorption and diffusion of organic solvents through interpenetrating polymer networks (IPNs) based on polyurethane and unsaturated polyester”, Eur. Polym. J. **36**, 2387-2393, 2000.

Vlad et al. [100] have synthesized series of interpenetrating polymer networks (IPNs) based on castor oil, 2,4- toluene diisocyanates and various amounts of polydimethylsiloxane-a,? -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. [101] 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 thermoluminesence. 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. [102] 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 pre polymer having an epoxy group at each of its respective end and 1-50% by weight of a modified urethane compound

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100. A. Vlad, S. Opera and S. Vlad, "Interpenetrating polymer networks based on polyurethane and polysiloxane", Eur. Polym. J. **38**, 829-835, 2002.

101. G. Jimenez, A. Shishido, M. Sumita and S. Asai, "Effect of the soft segment on the fatigue behavior of segmented polyurethanes", Eur. Polym. J. **36**, 2039-2050, 2000.

102. D.S. Chen, H.C. Hsia, C.C.M. Ma and W.N. Wang, "Cryogenic adhesives made from epoxy terminated urethane" U.S.P. 5,484,853. 1996.

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. [103] 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 180^0 T-peel strength test. The surface modification and mode of bond failure were studied by scanning electron microscopy (SEM).

Somani et al. [104] 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.

103.S.D. Desai, A.L. Emanuel and V.K. Sinha, "Polyester-polyol based PU-adhesives; effect of treatment on rubber surface", J. Polym. Research. **10**,141-149, 2003.

104. K.P. Somani, S.S. Kansara, N.K. Patel and A.K. Rakshit, "Castor oil based PU adhesives for wood to wood bonding", Inter. J. Adhes. Adhe. **23**, 269-275, 2003.

Papon et al. [105] 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), where as chain extension time does not. Therefore this is possible to prepare TPUs with specific properties by changing the polymerization conditions.

Papon et al. [106] 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.

105.E. Papon, J.J. Villenave and M.S.S. Adsuar, “Influence of synthesis conditions on the properties of thermoplastic polyurethane elastomers”, J. Appl. Polym. Sci. **76**, 1590-1595, 2000.

106.E. Papon, J.J. Villenave and M.S.S. Adsuar, “Properties of thermoplastic elastomers chemically modified by rosin”, J. Appl. Polym. Sci. **82**, 3402-3408, 2001.

Kim et al. [107] 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. [108] 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. [109] have synthesized the polyurethane networks (PUNs) using polyols derived from soybean oil, petroleum, or a blend of the two in the

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107. Y.D. Kim, J.Y. Kim, H.K. Lee and S.C. Kim, “Formation of PU membranes by immersion precipitation II.Morphology formation”,J. Appl.Polym. Sci.**74**, 2124-2132, 1999.

108. N. Bessaha , J. Schultz , J. Maucourt , C. Combette and M. F. Vallat, “Adhesive behavior of polyurethane-based materials”, J. Appl. Polym. Sci. **76**, 665-671,2000.

109. T.W. Pechar , S. Sohn , S. Ghosh , C.E. Frazier , A. Fornof , T.E. Long and G.L. Wilkes, ‘Characterization and comparison of polyurethane networks prepared using soybean-based polyols with varying hydroxyl content and their blends with petroleum-based polyols”, J. Appl. Polym. Sci. **101**, 1432-1443, 2006.

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. [110] 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, using 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 ^{1}H-NMR, and ^{13}CNMR techniques. Synthesized polymers were characterized by their resistance to chemical reagents, thermo gravimetric analysis, and dynamic mechanical thermal analyzer (DMTA). All the polymers

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110.T. Eren, S. Çolak and S.H. Kusefoglu , "Simultaneous interpenetrating polymer networks based on bromoacrylated castor oil polyurethane", J. Appl. Polym. Sci.**100**, 2947-2955, 2006.

decomposed with 6-10% weight loss in a temperature range of 25-240°C. MMA-type SIN showed the highest T_g (126°C), while STY-type SINs showed the highest storage modulus (8.6×10^9 Pa) at room temperature, with respect to other synthesized SINs.

Kumar et al. [111] 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. [112] 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.

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111. H. Kumar, R. Somashekar, S.S. Mahesh, S. Abhishek, T.N. Guru Row, G.S. Kini and Siddaramaiah, “Structure-property relationship of polyethylene glycol-based PU/PAN semi-interpenetrating polymer networks”, J. Appl. Polym Sci **99**, 177-187, 2006

112. S.K. Rath, U.G. Suryavansi and M. Patri, “A novel polyurethane sealant based on hydroxy-terminated polybutadiene”, J. Appl. Polym. Sci. **99**, 884-890, 2006.

Bledzki et al. [113] 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. [114] 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. [115] have fabricated jute reinforced polyurethane composites

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113. A.K. Bledzki, W. Zhang and A. Chate, "Natural-fiber-reinforced polyurethane microfoams", Comops. Sci. Technol. **61**, 2405-2411, 2001.

114. Y.S. Yeo, G.S. Tay, A. Abubakar and H.D. Rozman, "The mechanical and physical properties of PU composites based on rice husk and PEG", Polymer Testing, **22**, 617-623, 2003.

115. M.A. Khan, S.K. Balo, M.U. Ahmad and K.M. Idriss Ali, "Effect of additives on reinforcement of radiation induced jute-urethane polymer composites", J. Appl. Polym. Sci. **67**, 79-85, 1998.

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. [116] 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. [117] 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

116.G.S. Tay, A. Abubakar and H.D. Rozman, “Oil palm EFB-PU composites: The extent of NCO/ glycol ratio, glycol type and glycol mixture on the impact strength, dimensional stability and thermal properties”, Polym. Plast. Technol. Eng. **42**, 811-826, 2003.

117.G.S. Tay, A. Abusamah and H.D. Rozman, “The effect of glycol type, glycol mixture and isocyanate/glycol ratio on flexural properties of oil palm EFB-PU composites”, J. Wood Chemi. Technol. **23**, 249, 2003.

(PEG) (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. [118] have fabricated ligno cellulosic 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 [119] 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.

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118. M.P. Wolcott, J.M. Nassar and T.G. Rials, “Interfacial contributions in lignocellulosic fiber reinforced PU- composites”, J. Appl. Polym. Sci. **80**, 546-555, 2001.
119. M.C. Silva, G.G. Silva, “A new composite from cellulose industrial waste and elastomeric polyurethane”J. Appl. Polym. Sci., **98**, 336-340, 2005.

Deng et al. [120] 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.

120.C.R. Deng , H. Liang and L. Zhang, "Toughened composites prepared from castor oil based polyurethane and soy dreg by a one-step reactive extrusion process", J Appl Polym Sci, **101**, 953-960, 2006.

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 their characterization by various techniques.
III. To study coating and chemical resistance of the resins.
IV. To fabricate jute and sandwich composites based on agricultural wastes.
V. To evaluate mechanical and electrical properties of the composites.
VI. To study water absorption behavior of the composites in various environments.

This chapter of the thesis describes the synthesis of bisphenol-C (BC) and its derivatives, epoxy resins based bisphenol-C and its derivatives, bisphenol-C-formaldehyde resin, polyester polyols (epoxy esters) and polyurethane resins. This chapter is further subdivided into five sections:

SECTION-1: SYNTHESES OF MONOMERS

SECTION-2: SYNTHESIS OF BISPHENOL-C-FORMALDEHYDE RESIN (III)

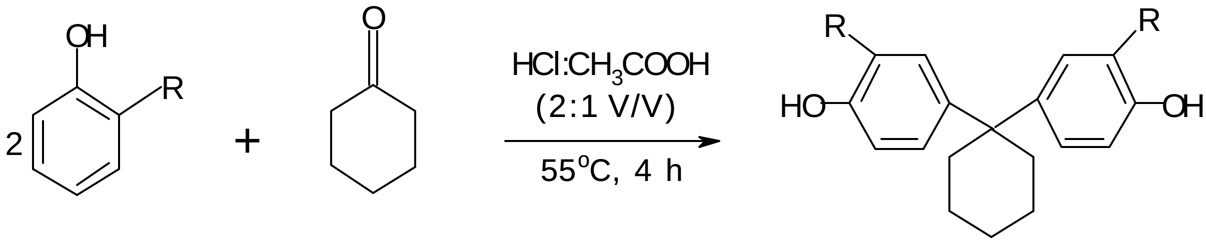
SECTION-3: SYNTHESES OF EPOXY RESINS (IV)

SECTION-4: SYNTHESES OF POLYESTER POLYOLS (V)

SECTION-5: SYNTHESES OF POLYURETHANE RESINS

SECTION-1: SYNTHESES OF MONOMERS

[A] Synthesis of 1, 1'-bis (3-R-4- hydroxy phenyl) cyclohexane



Phenol or O-cresol

cyclohexanone

BC: R = -H

MeBC: R = $-CH_3$

(I)

1, 1'-Bis(4-hydroxy phenyl) cyclohexane and 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane of general structure (I), here after designated as BC and MeBC were synthesized according to the reported methods [1, 2].

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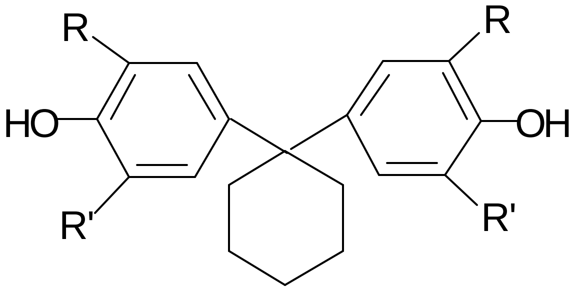
1. M.V. Rao, A.J. Rojivadia, P.H. Parsania, H.H. Parekh, “A convenient method for the preparation of bisphenols”, J. Ind. Chem. Soc., **4**, 758-9, 1987.
2. H.H. Garcher, H.N. Shukla and P.H. Parsania, “Kinetics of formation of 1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane”, Proc. Indian Acad., Sci. (Chem. Sci.), **103**, 149-153, 1991.

Thus, cyclohexanone (0.5 mol, 49 g) was treated with phenol and o-cresol (1.0 mol, 94 g) in the presence of mixture of HCl:CH_3COOH (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 filteration 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 and MeBC were further recrystallized repeatedly from benzene and methanol- water systems. The process was repeated to get pure, white, shining crystals of ~81% yield of BC and 77% yield of MeBC, m.p. of BC and MeBC was 186°C.

[B] Synthesis of 1,1'-bis(R, R'-4-hydroxy phenyl) cyclohexane (II):

BC was brominated by using bromine in glacial acetic acid at room temperature [3]. BC (27 g) was dissolved in 80 ml glacial acetic acid and 40 ml bromine in 20 ml glacial acetic acid was added drop wise with stirring. The mixture was stirred mechanically for 2 h. The product was isolated from chilled water, filtered, washed well with distilled water and dried at 50°C.



(II)

BrBC: R=R'=Br, ClBC: R=R'=Cl, ClMeBC: R=Cl and R'=-CH_3

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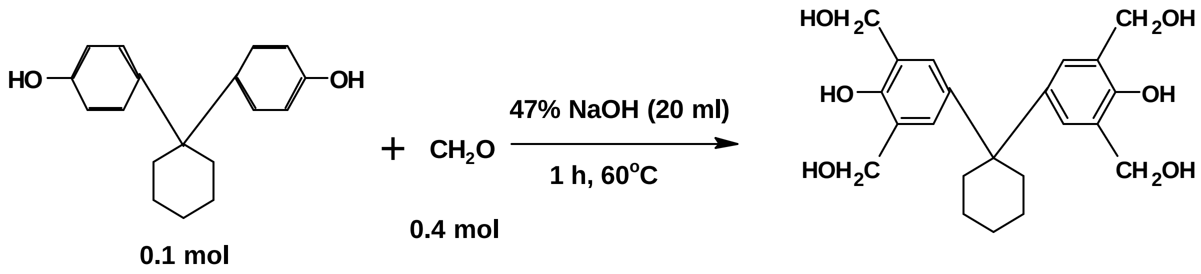
3. P.H. Parsania, **"**Physico-chemical studies on some industrially important bisphenols" Asian J. Chem.**2**, 211-213,1990.

BC and MeBC were chlorinated [4] by using thionyl chloride. Thus, 0.5 mol (134 g) BC was suspended in 600 ml of carbon tetrachloride, containing sodium sulphide (4 g) as a catalyst and 1.3 mol (95 ml) of thionyl chloride was added drop wise. The reaction mixture was refluxed for 4 h. After completion of the reaction, the excess of thionyl chloride and carbon tetrachloride were distilled off and the product was isolated from water, filtered, washed well with distilled water and dried at 50°C.

Halogenated bisphenols were repeatedly recrystallized from benzene and methanol-water systems prior to use. The yield and m.p. of ClBC, ClMeBC and BrBC were respectively 70, 70, 85% and 180, 181, 131°C.

SECTION-2: SYNTHESIS OF BISPHENOL-C-FORMALDEHYDE RESIN (III)

1,1'-Bis(4-hydroxy phenyl)cyclohexane-formaldehyde resin (BCF) was synthesized by reacting according to following method [5].



BC BCF

(III)

Into a 1-liter flask equipped with a condenser, BC (0.5 mol, 134 g) and 37% formaldehyde solution (2.1 mol, 202 ml) were charged. Reaction mixture was heated at 50-55°C for 1 h. 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

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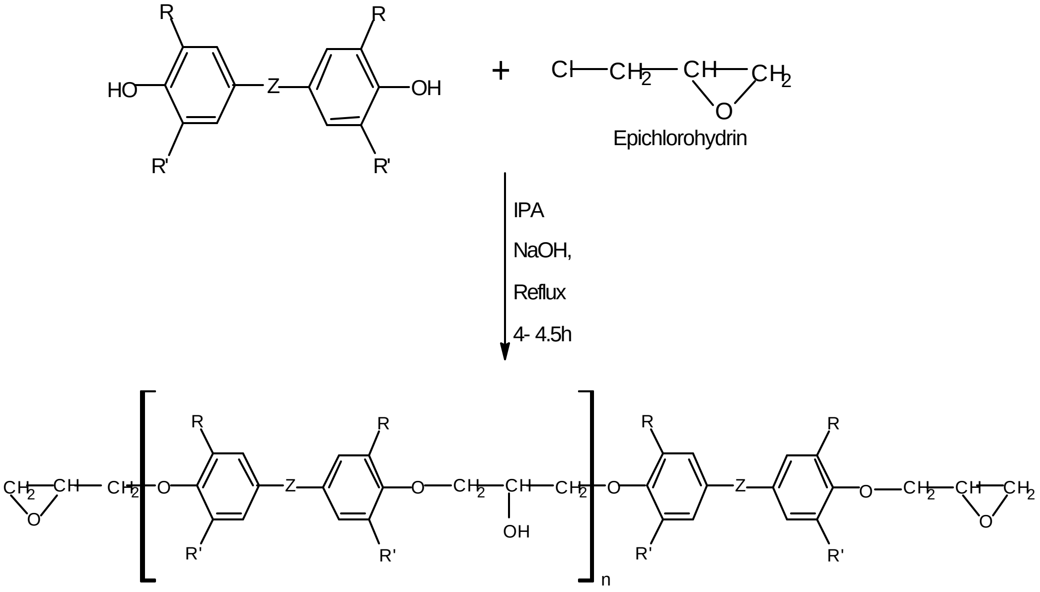
4. A.M. Serebryanyi, I.M. Bilik, N.M. Mironova, Metody Poluch Khim., Reaktive Prep. (U.S.S.R.) 20, 35 (1969); C.A. **76**, 85, 1972.
5. M.R. Sanariya and P.H. Parsania, "Synthesis of new bisphenol-C-formaldehyde and bisphenol-C-formaldehyde epoxy resin" J. Polym. Mater., **17**, 261-266, 2000.

separated viscous resin was isolated, washed well with distilled water and methanol and dried at 50^{o}C. BCF is soluble in acetone, 1, 4-dioxane, DMF and DMSO.

SECTION-3: SYNTHESES OF EPOXY RESINS (IV)

[A] SYNTHESES OF EPOXY RESINS OF BA, BC AND MeBC:

Epoxy resin of BA, BC, MeBC, ClBC and BrBC of general structure (IV), here after designated as ER-1 to ER-5, respectively, were synthsized according to the reported method [6].



(IV)

ER-1: R= R’=H and Z = isopropyl

ER-2: R=R’= H and Z = cyclohexyl

ER-3: R= CH_3 R’= H and Z =cyclohexyl

ER-4: R=R’= Cl and Z = cyclohexyl

ER-5: R=R’= Br and Z = cyclohexyl

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6. M.R. Sanariya, D.R. Godhani, S. Baluja and P.H. Parsania, “Synthesis and characterization of epoxy resins based on 1,1’-bis(4-hydroxy phenyl)cyclohexane and 1,1’-bis(3-methyl-4-hydroxy phenyl) cyclohexane”, J. Polym. Mater., **15**, 45-49, 1998.

BA / BC derivative (0.5 mol), epichlorohydrin (1.1 mol) and isopropanol (250 mol) were placed in a round bottomd flask equipped with a condenser. The mixture was brought to reflux temperature with stirring and 1-1.25 mol sodium hydroxide in 50 ml water was slowly added to the solution and the reflux was continue for 4- 4.5 h. The separated solid resin was isolated 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 colored resins was formed, which are soluble in $CHCl_3$, acetone, 1,4-dioxane, DMF, 1,2-dichloroethane, dichloromethane, and DMSO and partially soluble in ethanol and isopropanol.

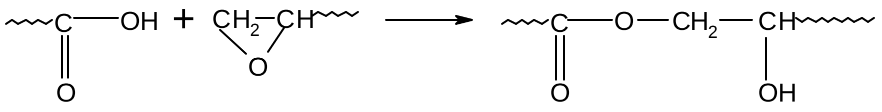
Similarly, epoxy resin of MeBC (0.25 mol) and epichlorohydrin (0.55 mol) was prepared by using isopropanol (100 ml) and sodium hydroxide (0.625 mol) in 25 ml of water. The liquid resin was isolated by distillation of excess isopropanol, was washed well with water, extracted in chloroform and evaporated to dryness. Highly transparent yellowish resin is soluble in $CHCl_3$, acetone, 1, 4-dioxane, DMF, 1, 2-dichloroethane, dichloromethane, and DMSO and partially soluble in ethanol and isopropanol.

SECTION-4: SYNTHESES OF POLYESTER POLYOLS (V)

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.

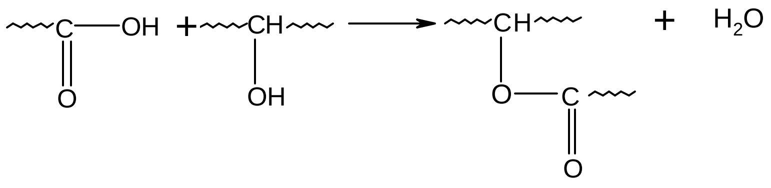
(1) Esterification

(i)



Hydroxy ester

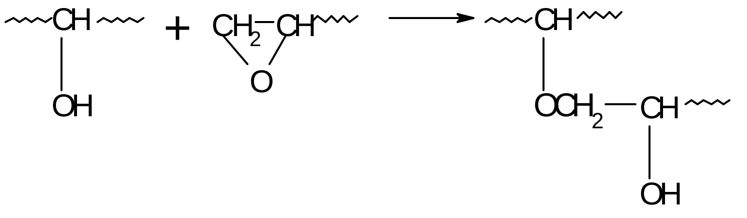
(ii)



Condensation ester

(2) Etherification

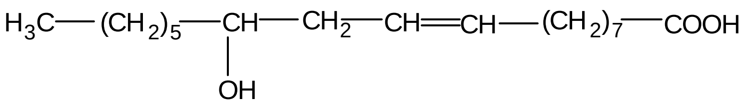
(iii)



Hydroxy ether

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 / rosin.



$$H_3C-(CH_2)_5-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH=CH-(CH_2)_7-COOH$$

or

$$H_3C-\boxed{RA}-COOH$$

Ricinoleic acid

(V)

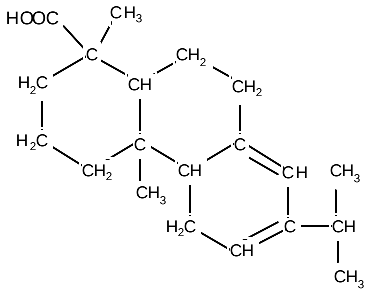
$$H_3C-(CH_2)_5-CH=CH-(CH_2)_5-COOH$$

or

$$H_3C-\boxed{OA}-COOH$$

Oleic acid

(VI)



or

$HOOC-\boxed{\text{Rosin}}$

Rosin

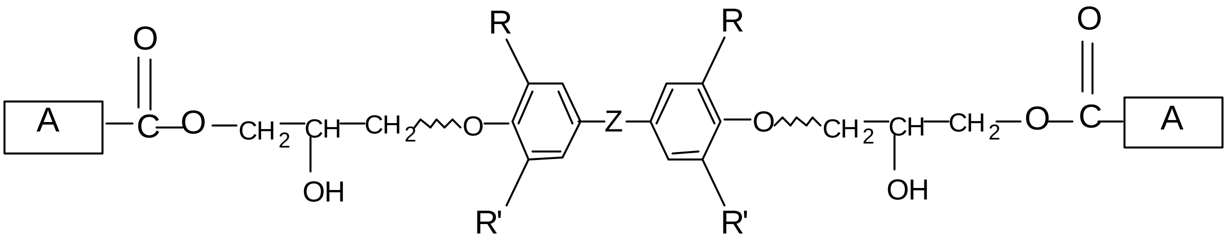
(VII)

Ricinoleic acid (RA), oleic acid (OA) and rosin (R) were used in the syntheses of polyester polyols. 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). Rosin contains about 90 % of acids, and small amount of esters. The acids are abietic acid; dextropimaric acid and levopimaric acid, out of all these abietic acid and levopimaric acid are the major part. The structures of ricinoleic acid, oleic acid, and rosin are shown in Schemes V, VI, VII.

The polyester polyols or epoxy esters were synthesized by condensing ER-1 to ER-5 with ricinoleic acid/ oleic acid/ rosin (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 resins 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-VIII.

Table-2.1: Time, temperature, weight of acids and epoxy resins and acid value of the polyester polyols

Polyols	Weight in gm		Temperature ^0C	Time (h)	Acid value mg KOH/gm
	Acid	Epoxy resin			
RAER-1	13	19	Reflux	4	3.0
RAER-2	13	17.68	Reflux	5	2.03
RAER-3	13	20.24	Reflux	6	2.14
RAER-4	13	20.120	Reflux	6	9.36
RAER-5	13	15.56	Reflux	5	7.025
OAER-1	11.28	19	Reflux	4	3.57
OAER-2	11.28	17.68	Reflux	6	2.79
OAER-3	11.28	20.24	Reflux	5	2.493
OAER-4	11.28	20.120	Reflux	6	6.25
OAER-5	11.28	15.56	Reflux	5	9.34
RER-2	12.08	17.68	Reflux	5	15.83
RER-3	12.08	20.24	Reflux	5	11.14



(VIII)

Polyester polyol

RAER-1: R=R'=H, Z= isopropyl and A= ricinoleic acid

RAER-2: R=R'=H, Z= cyclohexyl and A= ricinoleic acid

RAER-3: R=CH_3, R'= H, Z= cyclohexyl and A= ricinoleic acid

RAER-4: R=R'= Cl, Z= cyclohexyl and A= ricinoleic acid

RAER-5: R=R'=Br, Z= cyclohexyl and A= ricinoleic acid

OAER-1: R=R'=H and Z= isopropyl and A= oleic acid

OAER-2: R=R'=H and Z= cyclohexyl and A= oleic acid

OAER-3: R=CH_3, R'= H and Z= cyclohexyl and A= oleic acid

OAER-4: R=R'=Cl and Z= cyclohexyl and A= oleic acid

OAER-5: R=R'=Br and Z= cyclohexyl and A= oleic acid

RER-2: R=R'=H and Z= cyclohexyl and A= rosin

RER-3: R= CH_3, R'= H and Z= cyclohexyl and A= rosin

SECTION-5: SYNTHESES OF POLYURETHANE RESINS

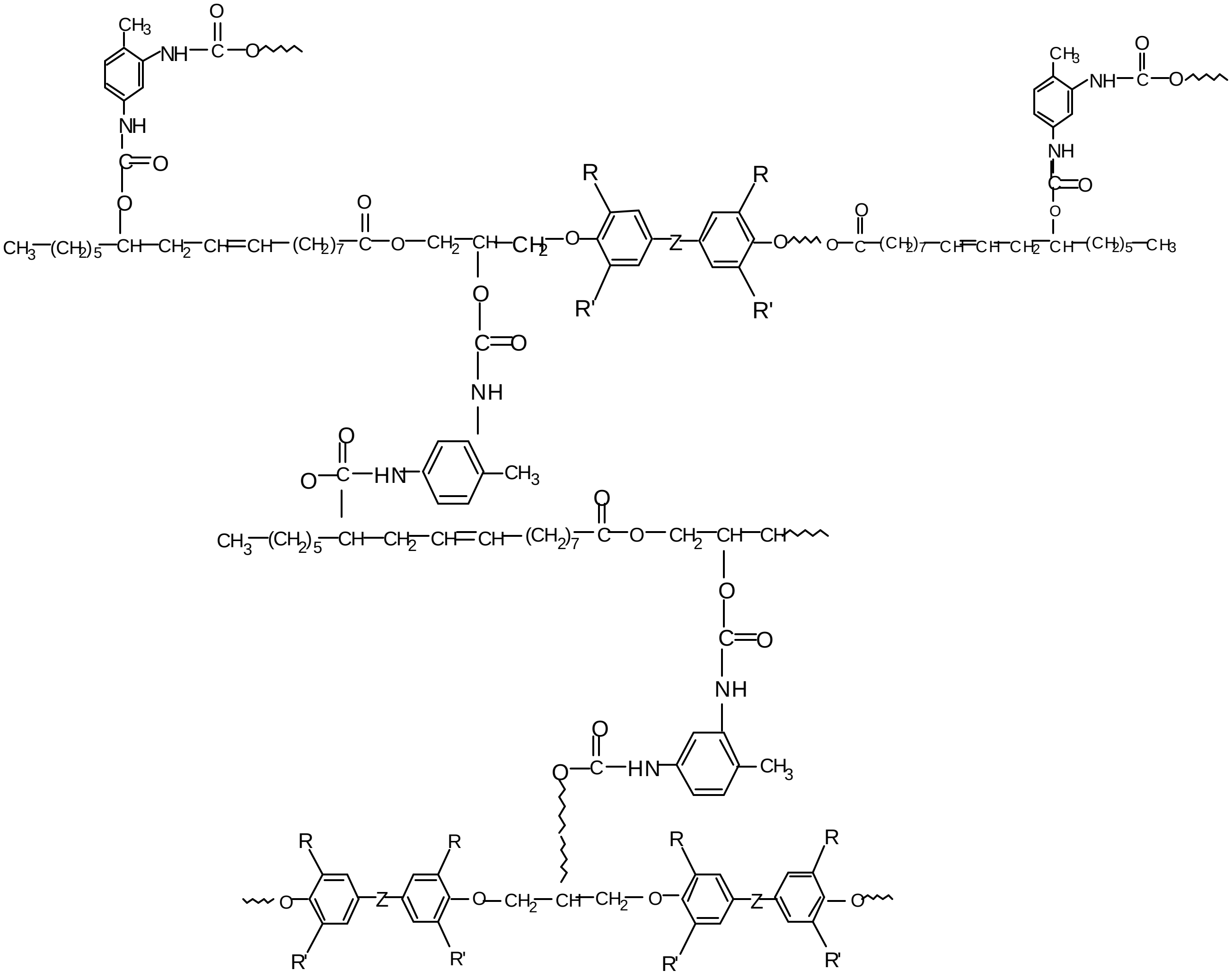
[A] Syntheses and film preparation of polyurethanes of RAER-1 and RAER-2

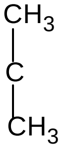
Polyurethane resins of RAER-1 and RAER-2 were synthesized by reacting 0.0029 mol (2.719g RAER-1/ 2.926g RAER-2) polyester polyol in 10 ml methyl ethyl ketone (MEK) with 0.004 mol (0.7 g) TDI in 5 ml MEK at room temperature by manual stirring for about 15 min. The resultant polyurethane solution was poured into a leveled 15 cm x15 cm glass mold. The solvent was allowed to evaporate with a controlled rate. After 24 h, the film was peeled out from the mold. The suggested structure of polyurethane resin is shown in Scheme IX:

[B] Syntheses of copolyurethane resins of RAER-3

In order to improve flexibility of PU an attempt has been made to use different proportions of PEG-400 as under:

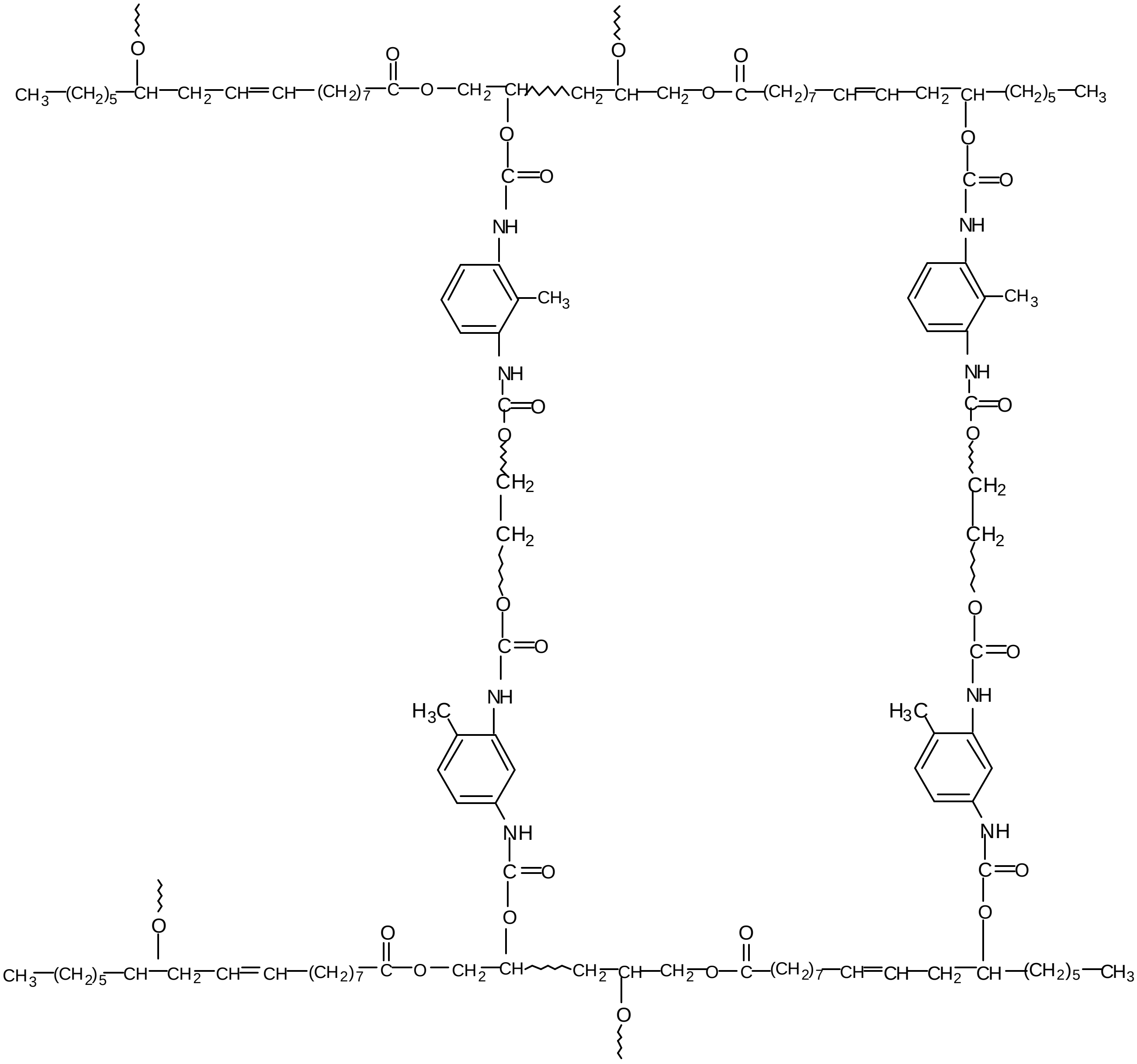
Pre polyurethane of RAER-3 was synthesized by reacting 3.0 g (0.002mol) RAER-3 in 10 ml methyl ethyl ketone (MEK) with 0.9 g (0.005 mol) toluene diisocyanate (TDI) in 5ml MEK at room temperature and stirred manually for 10 min. To this prepolyurethane 20% (0.6g) or 30% (0.9g) PEG-400 (based on polyester polyol) 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. The film was analyzed for their physico-chemical characterization. The suggested structure of the copolyurethane is shown in Scheme X:



where Z=  $-C(CH_3)_2-$ for RAER-1 Z= cyclohexyl for RAER-2

(IX)

Polyurethane resin based on RAER-1 & RAER-2 polyester polyol



(X)

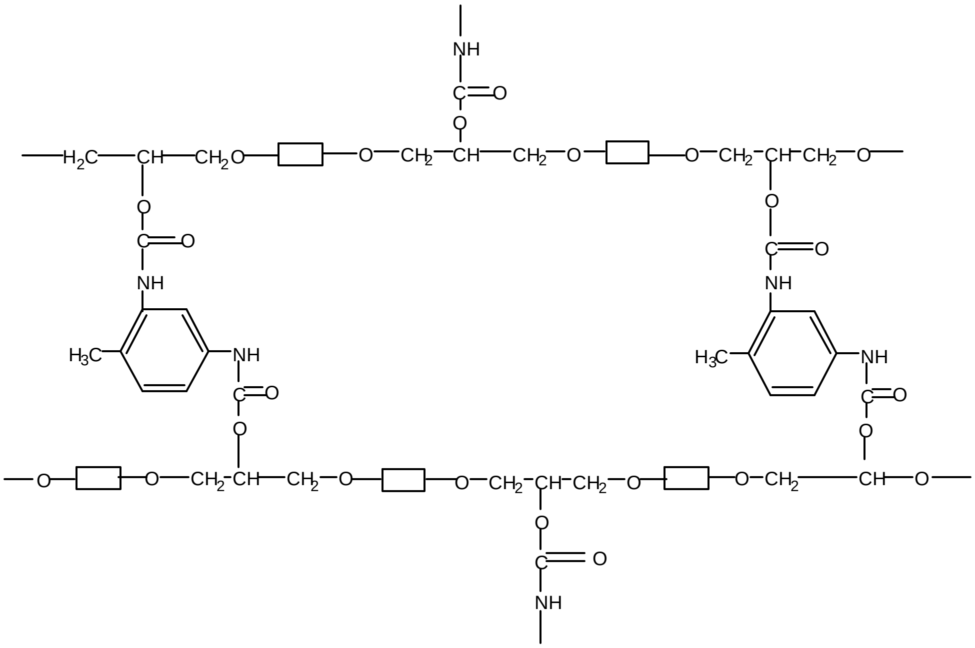
Copolyurethane resin

[C] Syntheses of polyurethanes of BCF and ER-2

Polyurethane resins of BCF and ER-2 was synthesized as follows:

To a 250ml beaker 0.023mol (9g) BCF was dissolved in 100ml methyl ethyl ketone (MEK) at room temperature. To this solution 0.155 mol (27g) toluene diisocyanate (TDI) in 50 ml MEK was added drop wise over a period of 10 min. The reaction mixture was stirred manually for about 15-30 min. at room temperature. The prepared polyurethane resin was used in the manufacturing of the composites.

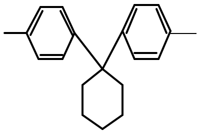
Polyurethane resin of ER-2 was prepared by reacting 0.005 mol (6.5g) ER-2 in 15 ml MEK with 0.0106 mol (1.85g) TDI in 15 ml MEK at room temperature. The reaction was stirred manually for about 25-30 min. The structures of polyurethanes are shown in Schemes XI & X. Here after the polyurethane resins are designated as BCFPU and ER-2PU for BCF and ER-2 resin, respectively.

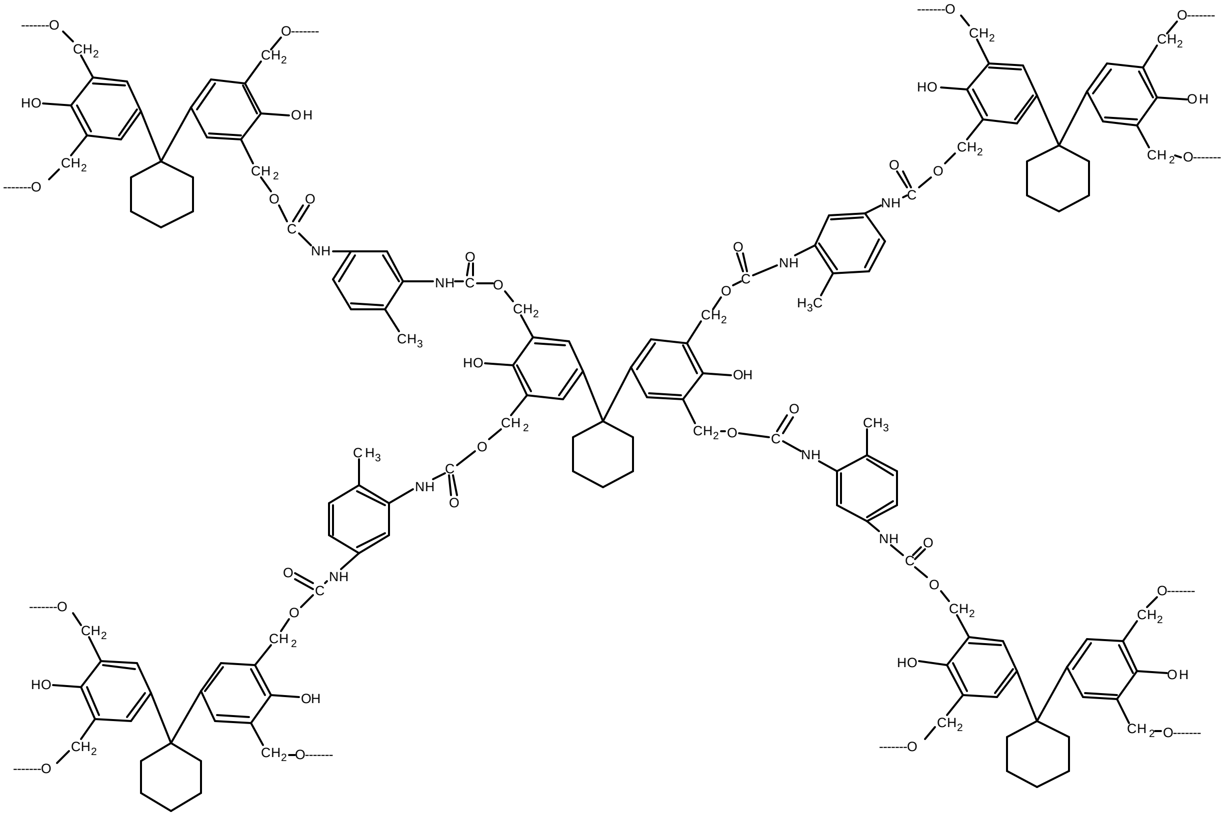


XI

ER-2PU

Where ▭ →





XII

BCFPU

This chapter of the thesis describes the determination of epoxy equivalent of the epoxy resins, acid and hydroxyl values of the polyester polyols and thermal, mechanical, electrical, chemical and spectral characterization of the resins.

SECTION-1: SPECTRAL CHARACTERIZATION OF THE RESINS

SECTION-2: DETERMINATION OF EPOXY EQUIVALENT OF THE EPOXY RESINS

SECTION-3: DETERMINATION OF ACID VALUES OF THE POLYESTER POLYOLS

SECTION-4: DETERMINATION OF HYDROXYL VALUES OF POLYESTER POLYOLS

SECTION-5: THERMAL ANALYSIS OF THE RESINS

SECTION -6: DENSITY MEASUREMENTS OF THE POLYURETHANES

SECTION-7: MECHANICAL AND ELECTRICAL PROPERTIES OF THE POLYURETHANES

SECTION-8: CHEMICAL RESISTANCE OF THE POLYURETHANES

SECTION-1: SPECTRAL CHARACTERIZATION OF THE RESINS

This section of the thesis includes the IR spectral characterization of the epoxy resin, polyester polyols (epoxy esters) and polyurethane resins.

Information about the structure of a molecule could frequently be obtained from its absorption spectrum. The atomic and electronic configuration of a molecule is responsible for the position of absorption bands. The most structural information of organic molecules could be obtained from their IR spectra. The masses of the atoms and the forces holding them together are of such magnitude that usual vibration of organic molecules interacts with electromagnetic radiation so as to absorb and radiate in the IR region. During the absorption, it is necessary for the molecule to under go a change in a dipole moment. IR spectroscopy is an excellent method for the qualitative analysis because except for optical isomer, the spectrum of a compound is unique. It is most useful for the identification, purity and gross structural detail. This technique is faster than any other analytical method.

The IR spectra (KBr pellets) of the resins were scanned on a Shimadzu-8400 FT-IR spectrometer over the frequency range from 4000 – 400 cm^{-1}. The IR spectra of the resins are shown in Figs. 3.1-3.14.

The characteristic absorption bands (cm^{-1}) for each system besides the normal modes of alkane, alicyclic and aromatic groups are reported in Tables – 3.1-3.7

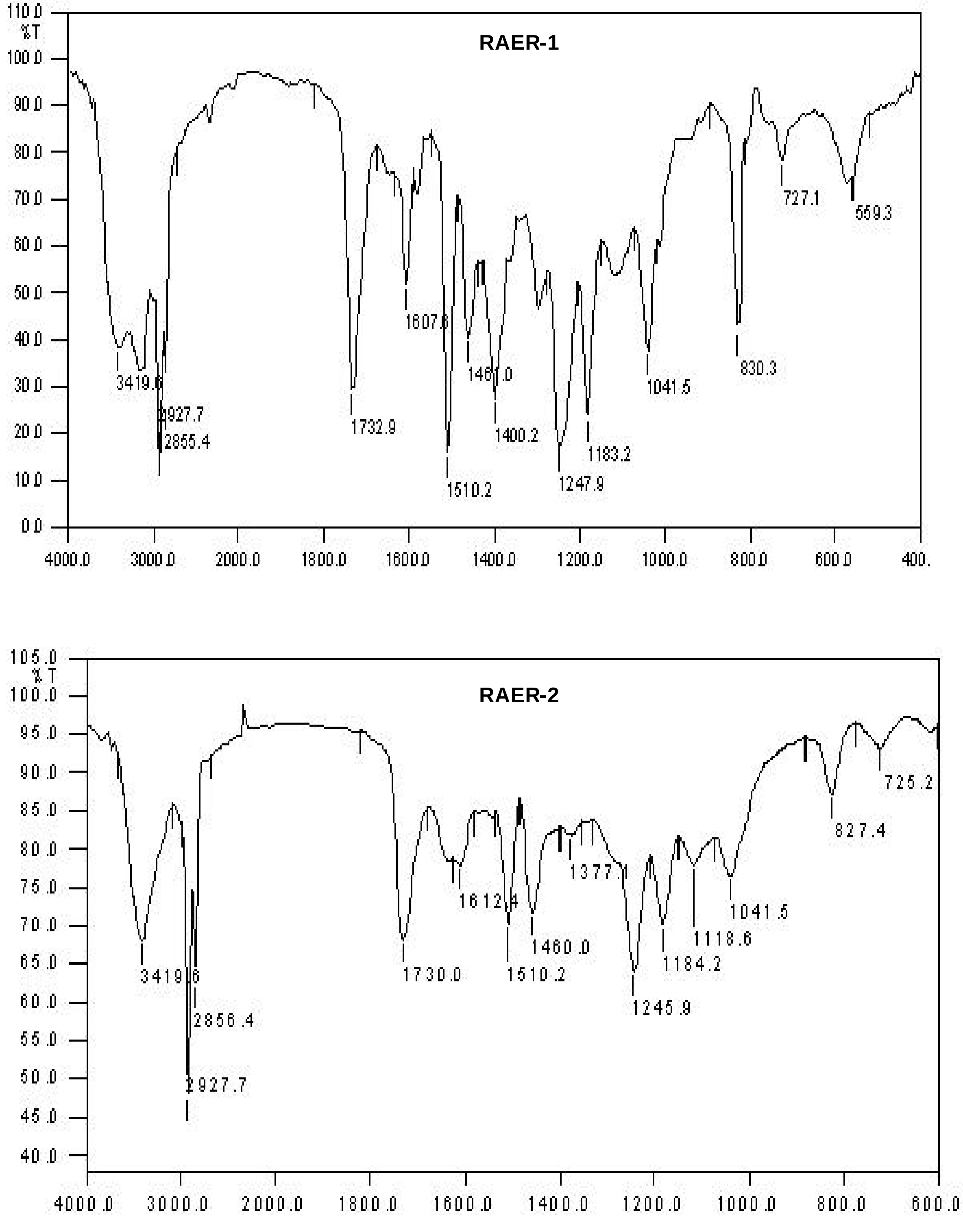


Figure-3.1: IR (KBr) spectra of RAER-1 and RAER-2

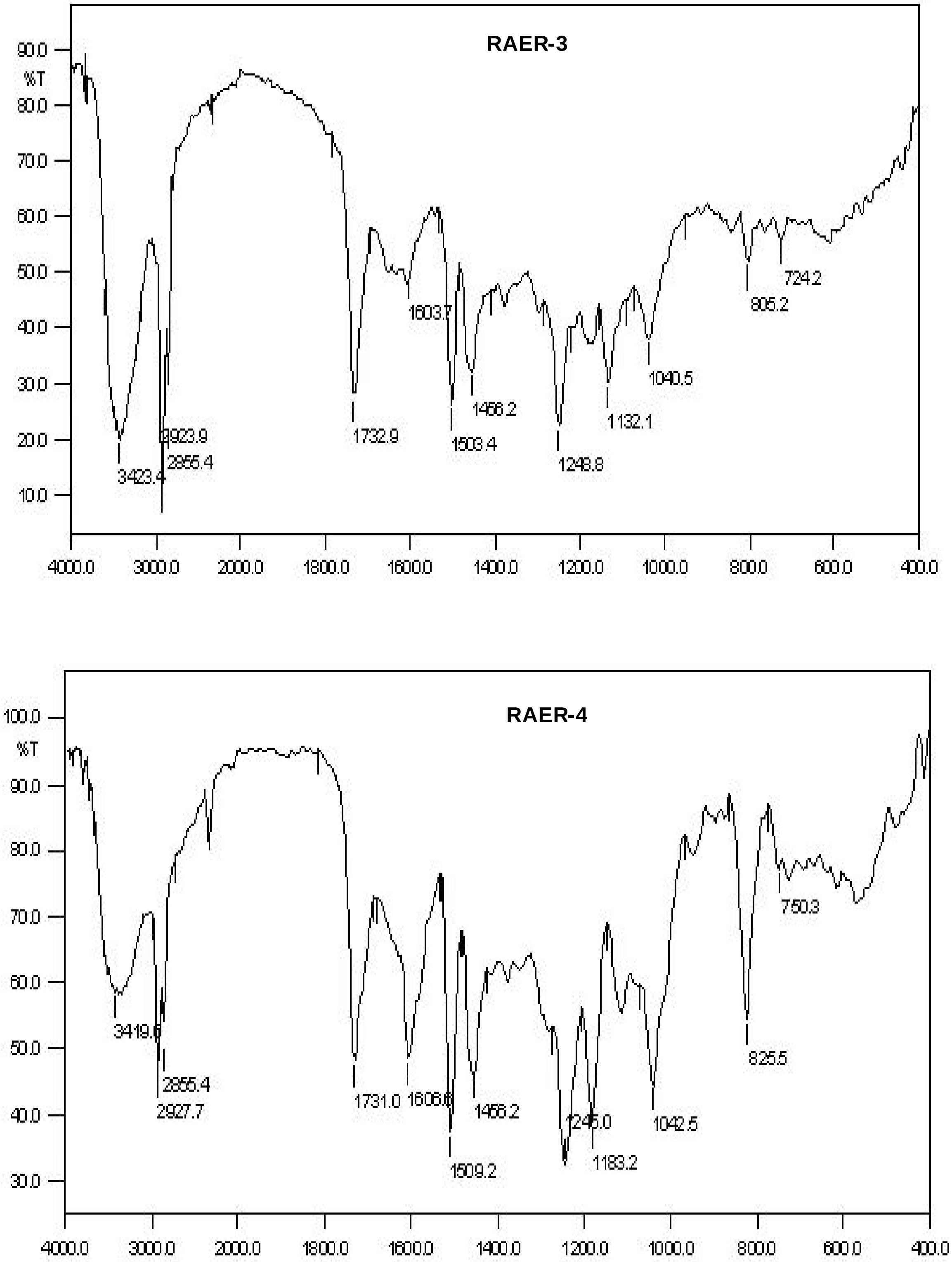


Figure-3.2: IR (KBr) spectra of RAER-3 and RAER-4

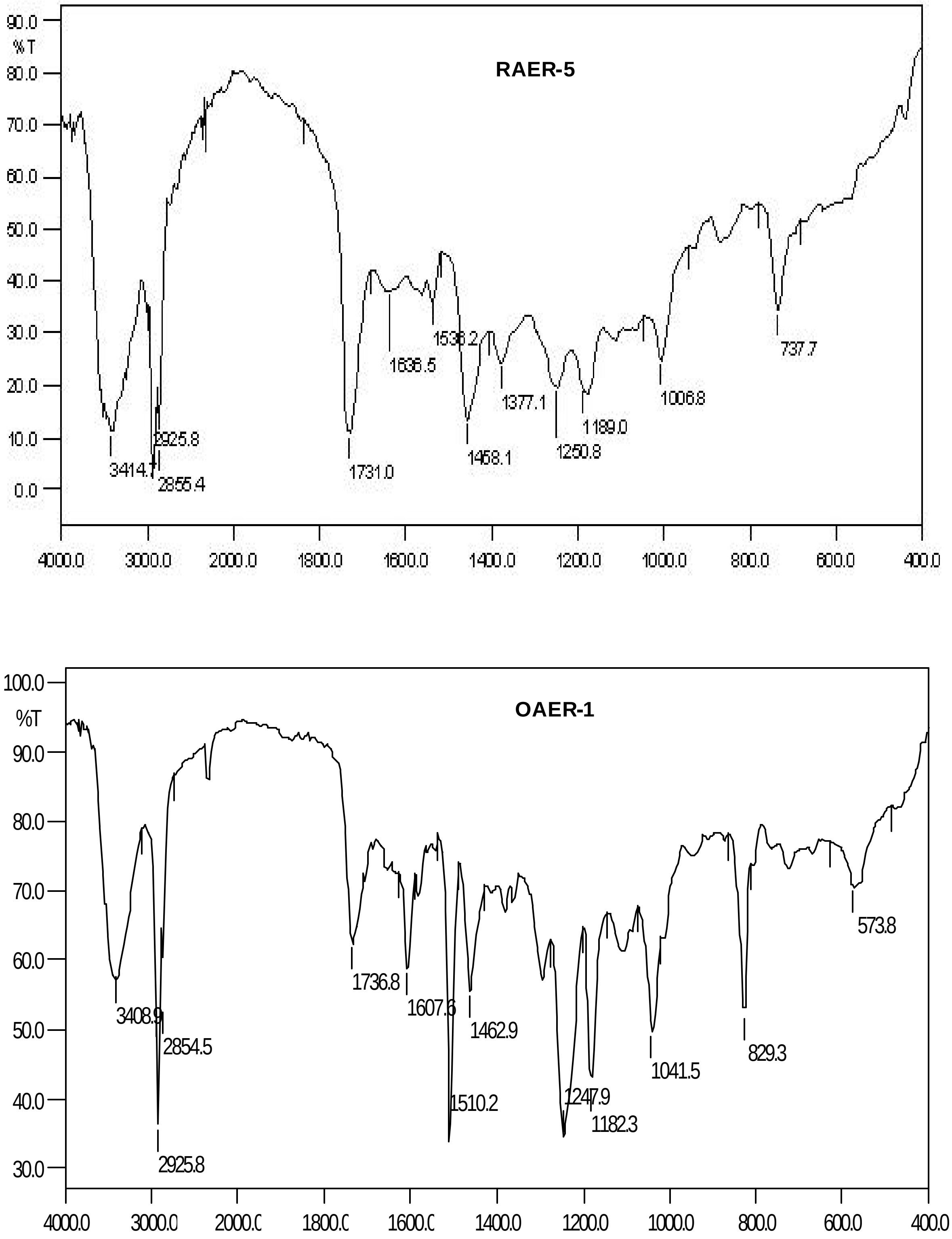


Figure-3.3: IR (KBr) spectra of RAER-5 and OAER-1

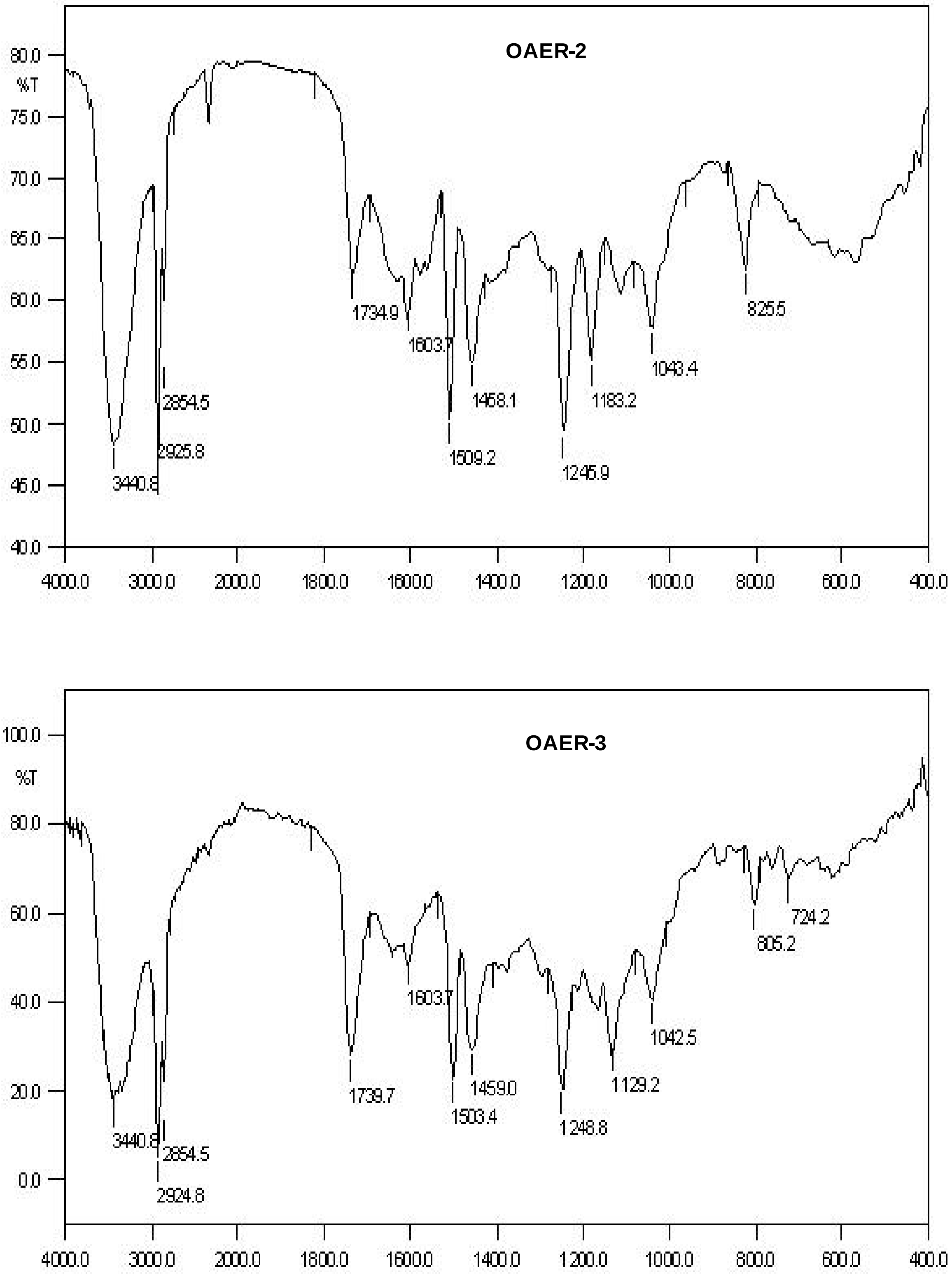


Figure-3.4: IR (KBr) spectra of OAER-2 and OAER-3

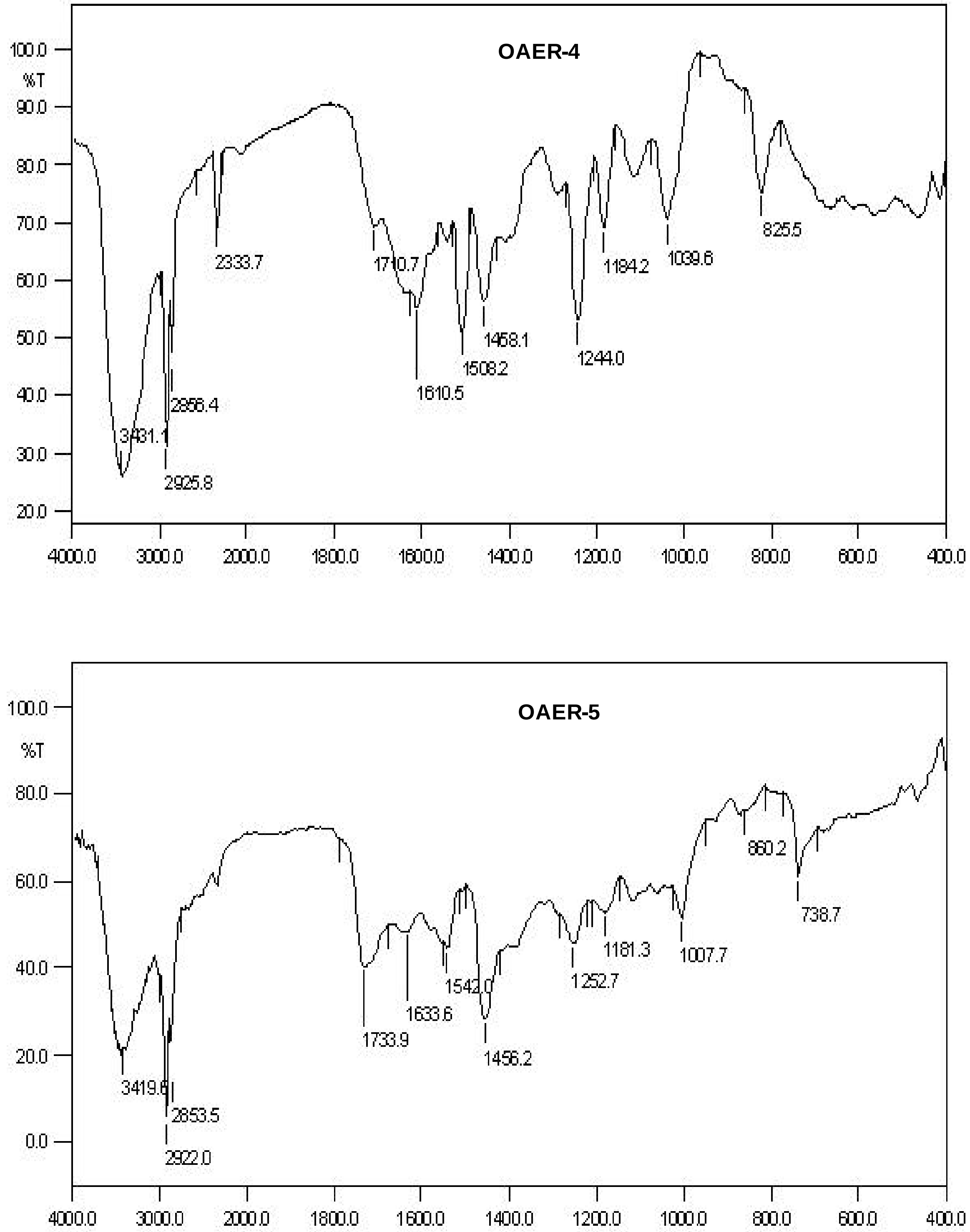


Figure-3.5: IR (KBr) spectra of OAER-4 and OAER-5

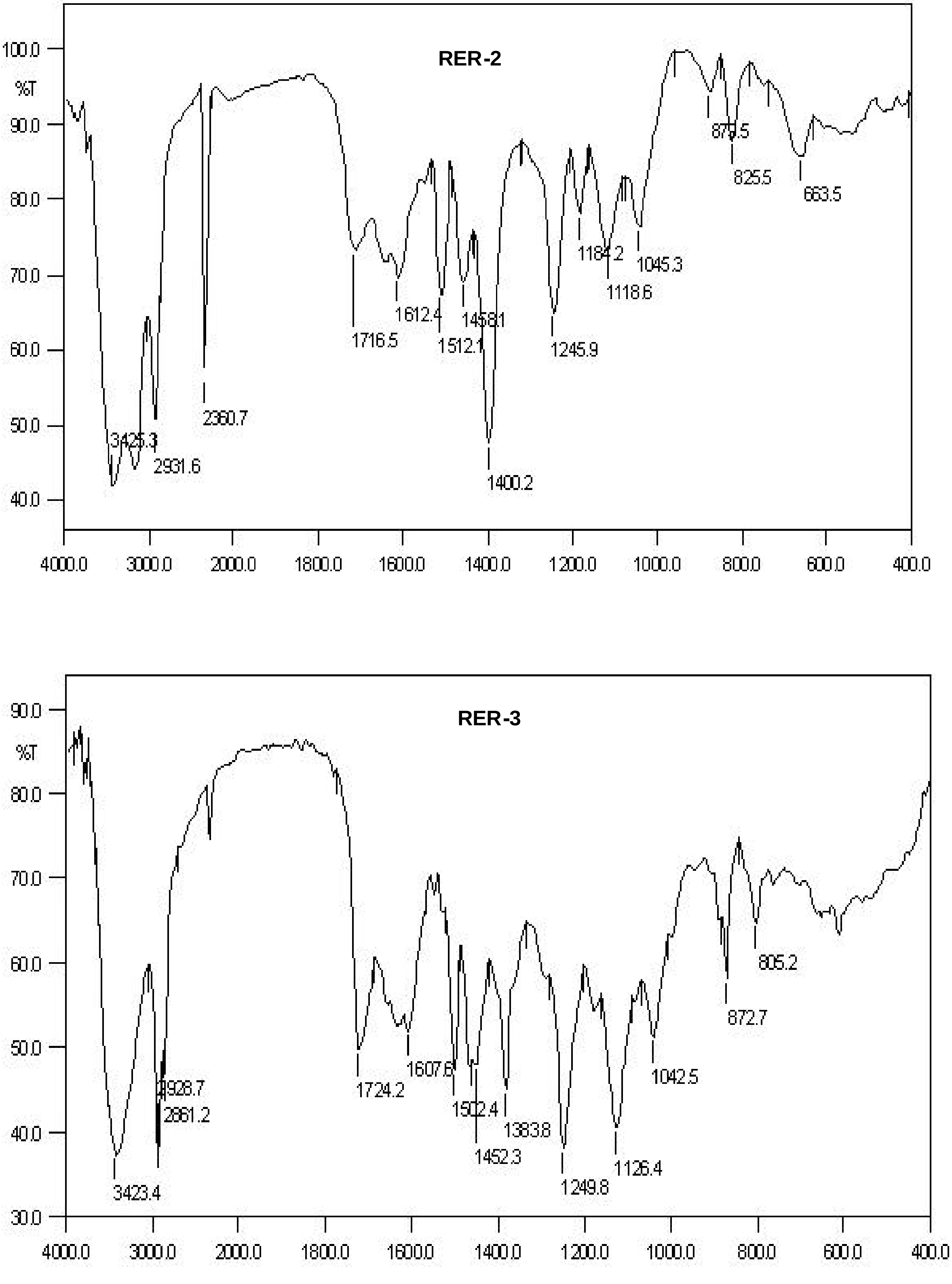


Figure-3.6: IR (KBr) spectra of RER-2 and RER-3

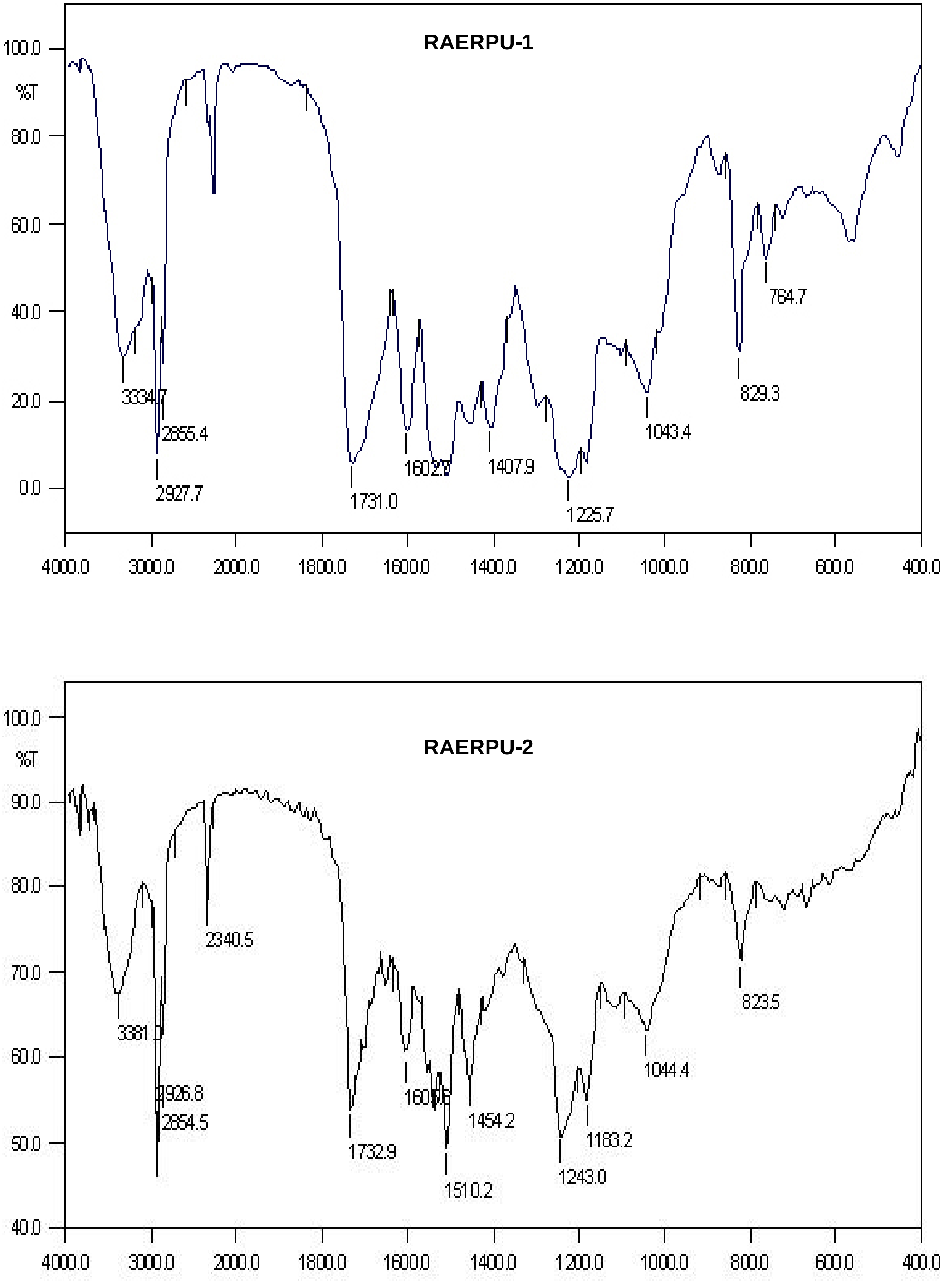


Figure-3.7: IR (KBr) spectra of RAERPU-1 and RAERPU-2

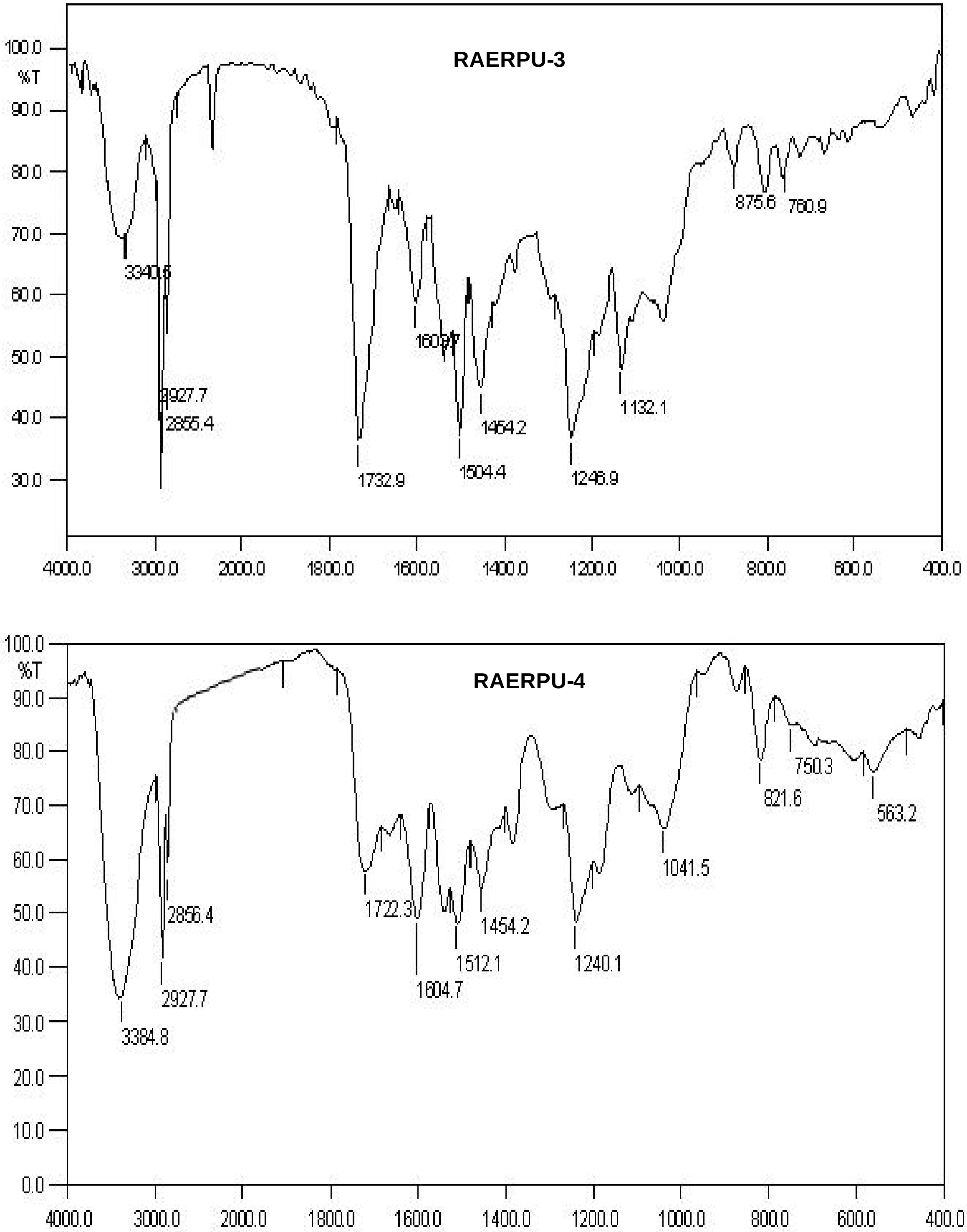


Figure-3.8: IR (KBr) spectra of RAERPU-3 and RAERPU-4

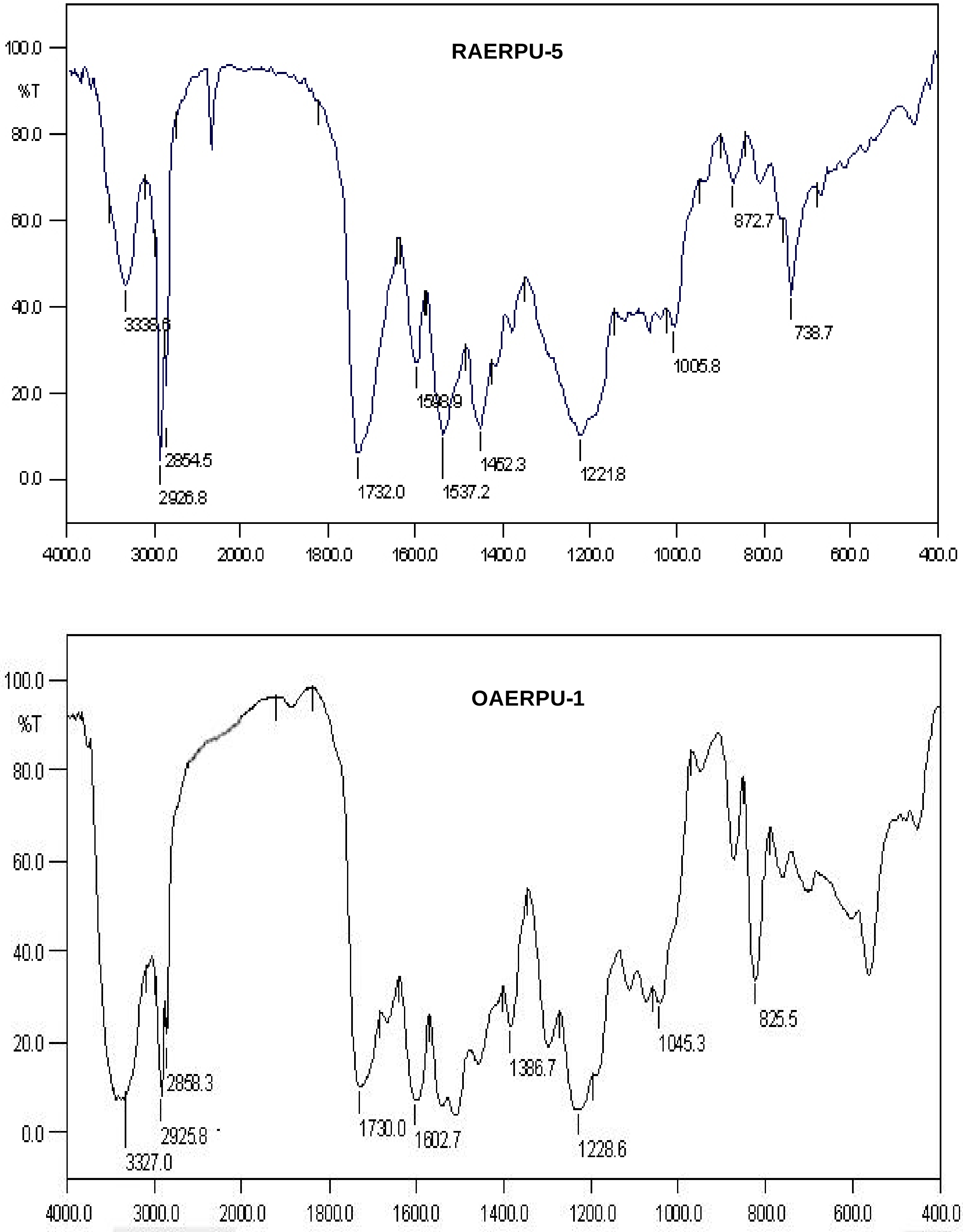


Figure-3.9: IR (KBr) spectra of RAERPU-5 and OAERPU-1

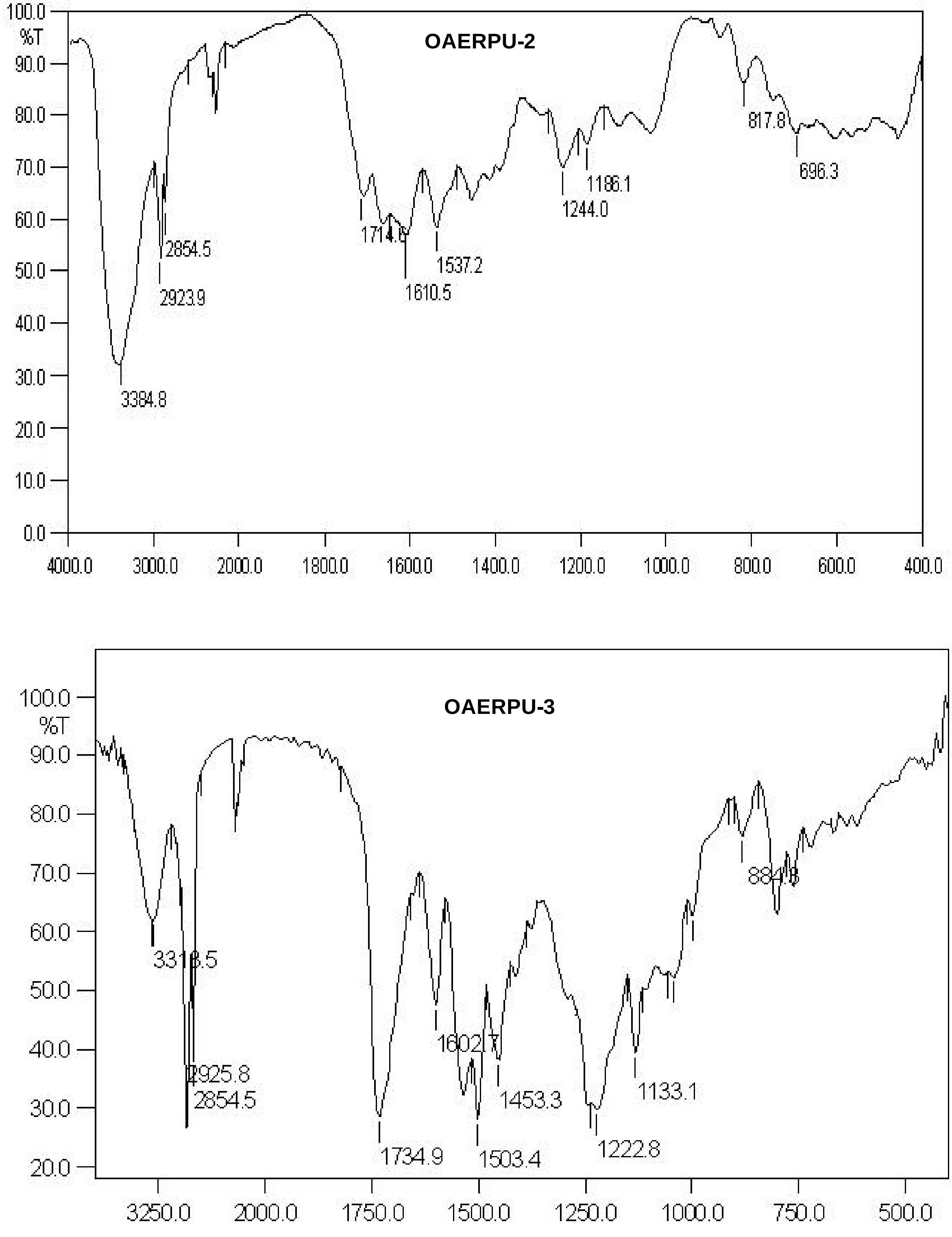


Figure-3.10: IR (KBr) spectra of OAERPU-2 and OAERPU-3

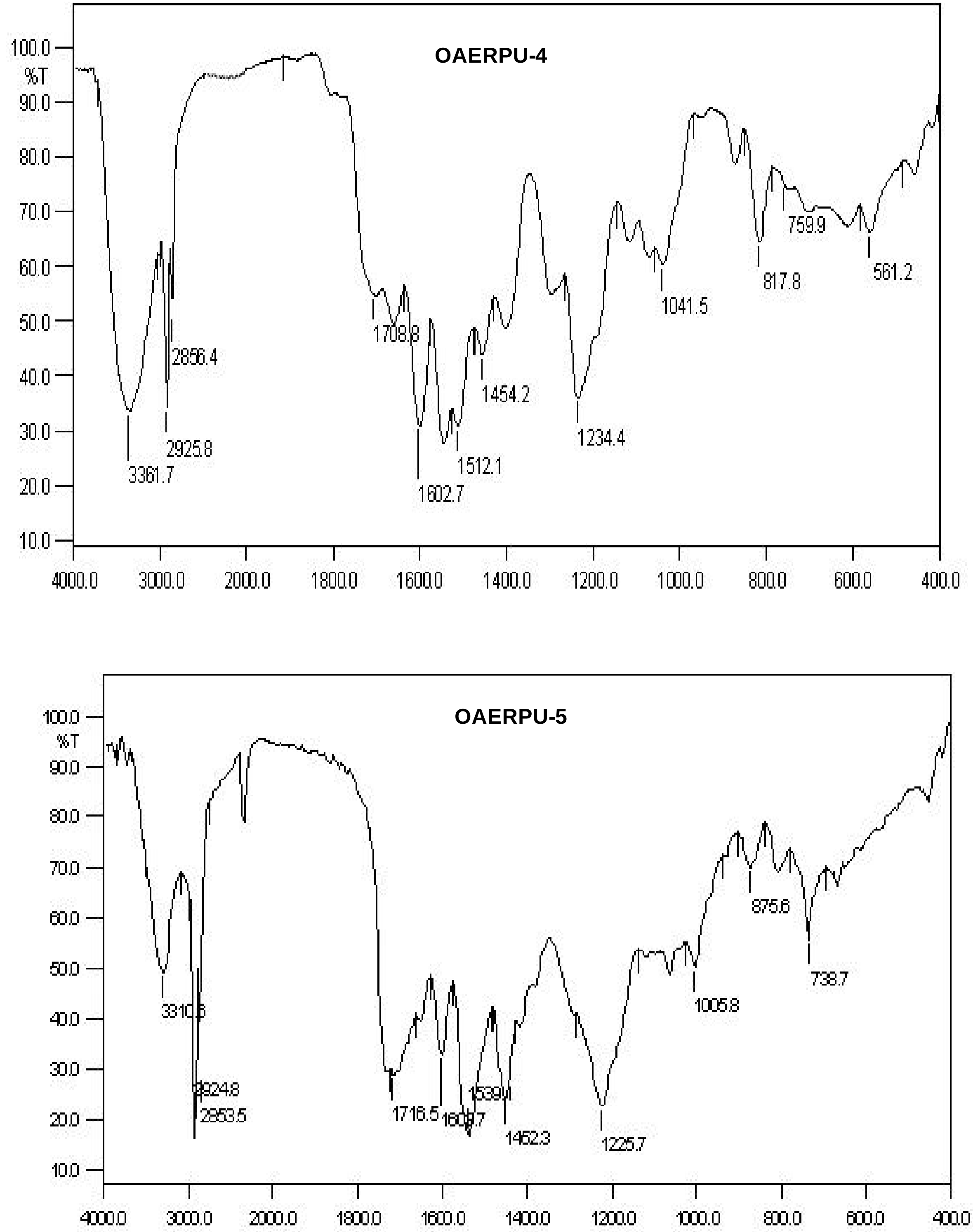


Figure-3.11: IR (KBr) spectra of OAERPU-4 and OAERPU-5

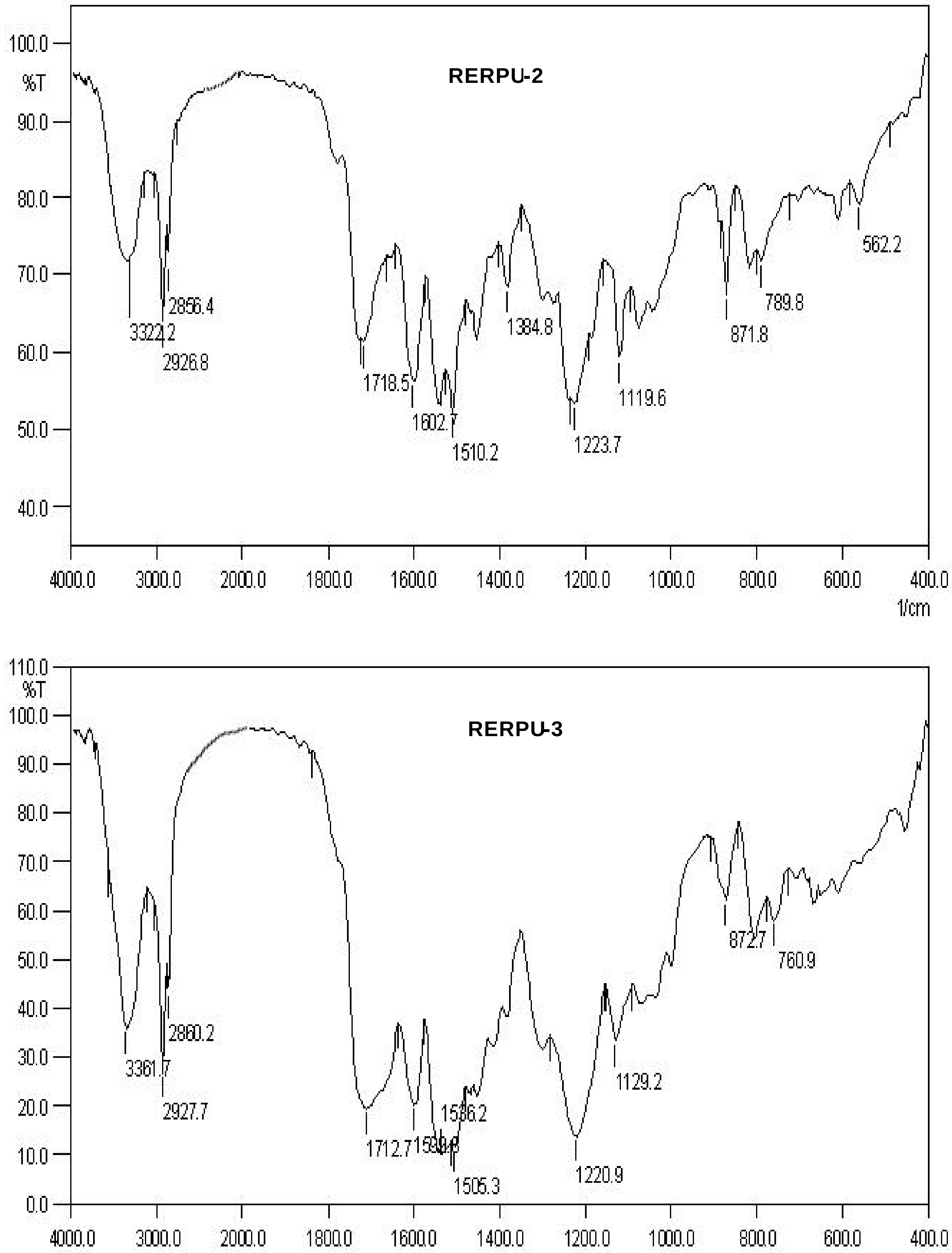


Figure-3.12: IR (KBr) spectra of RERPU-2 and RERPU-3

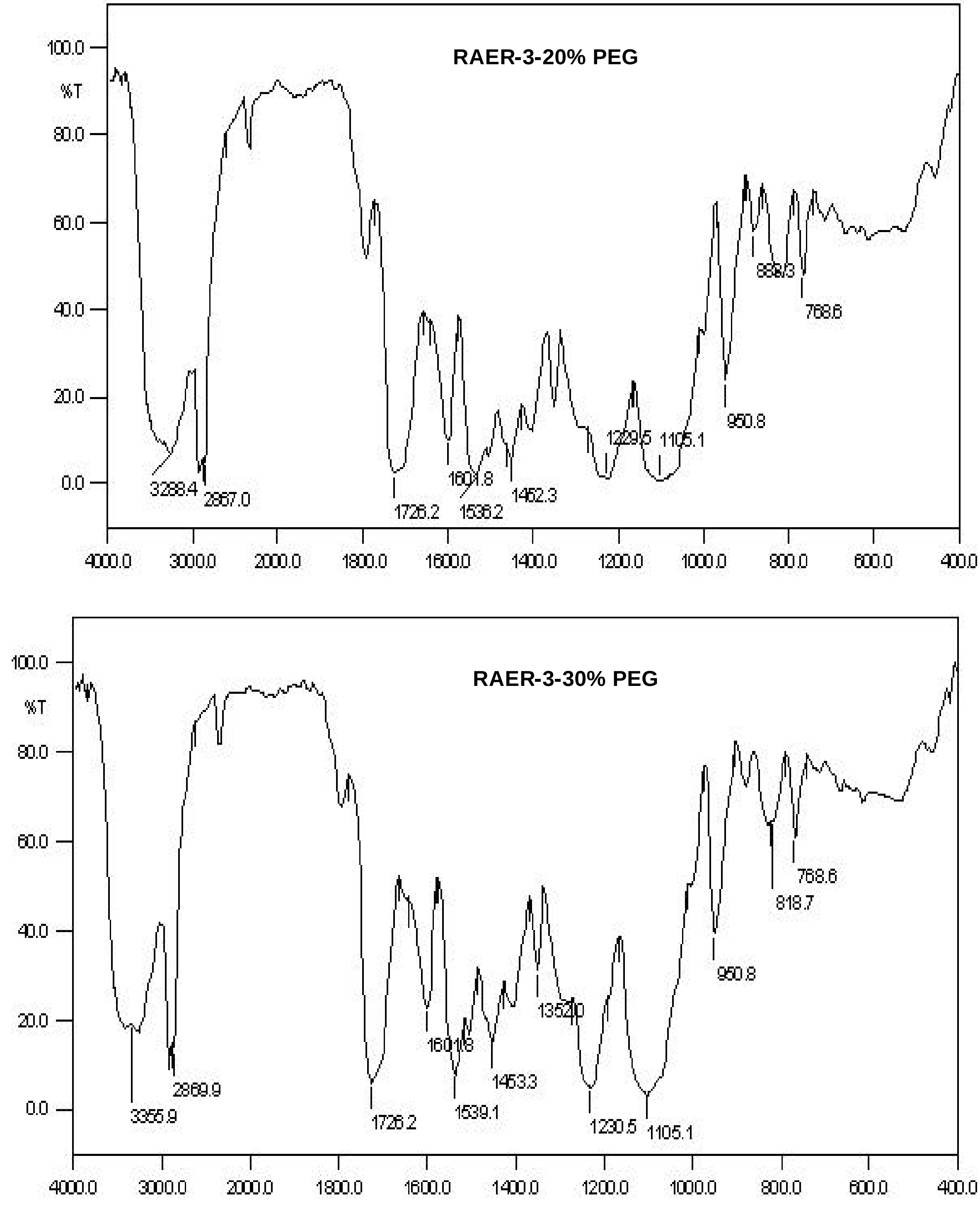


Figure-3.13: IR (KBr) spectra of RAER-3-20% PEG and RAER-3-30% PEG

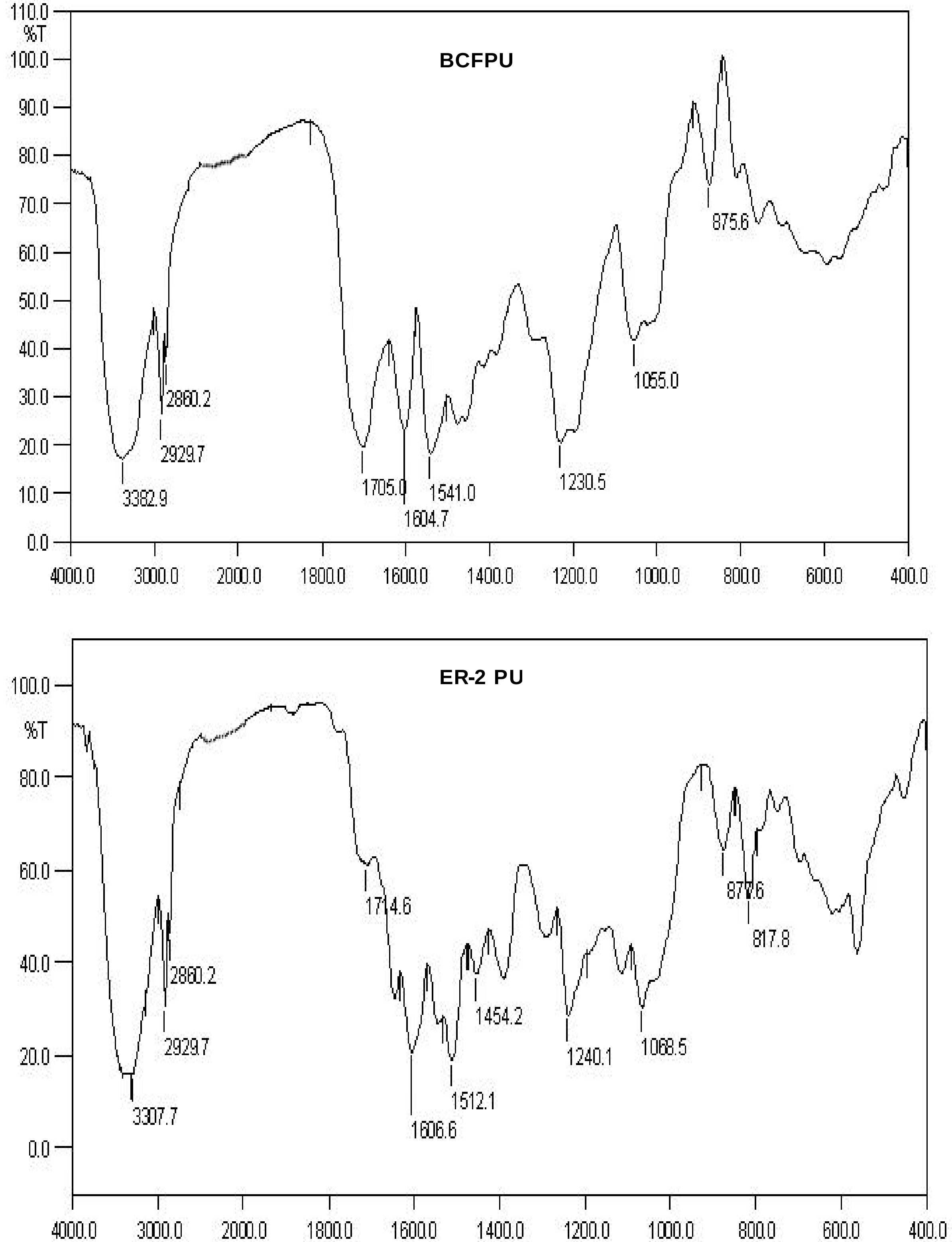


Figure-3.14: IR (KBr) spectra of BCFPU and ER-2 PU

Table-3.1: The characteristic IR absorption frequencies of RAER-1 to RAER-5

Type	**Absorption frequencies, cm^{-1}**				
	RAER-1	**RAER-2**	**RAER-3**	**RAER-4**	**RAER-5**
-OH Str.	3419.6	3419.5	3423.4	3419.6	3407.0
-CH$_2$Str.					
asym.	2927.7	2927.7	2923.9	2927.7	2925.8
sym.	2855.4	2856.4	2855.4	2855.5	2855.4
-C=O Str.	1732.9	1730.0	1732.9	1731.0	1731.0
-C-O-C Str.	1247.9	1245.9	1248.8	1245.0	1250.8
C-Cl Str.	-	-	-	750.3	-
C-Br.Str.	-	-	-	-	737.7

Table-3.2: The characteristic IR absorption frequencies of OAER-1 to OAER-5

Type	**Absorption frequencies, cm^{-1}**				
	OAER-1	**OAER-2**	**OAER-3**	**OAER-4**	**OAER-5**
-OH Str.	3408.9	3440.8	3440.8	3431.1	3419.6
-CH$_2$Str.					
asym.	2925.8	2925.8	2924.8	2925.8	2922.0
sym.	2854.5	2854.5	2854.5	2856.4	2853.5
-C=O Str.	1736.8	1734.9	1739.7	1710.7	1733.9
-C-O-C Str.	1247.9	1245.9	1248.8	1244.0	1252.7
C-Cl Str.	-	-	-		-
C-Br Str.	-	-	-	-	738.7

Table-3.3: The characteristic IR absorption frequencies of RER-2 and RER-3

Type	**Absorption frequencies, cm^{-1}**	
	RER-2	**RER-3**
-OH Str.	3425.3	3423.4
-CH$_2$Str. asym.	2931.6	2928.7
sym.		2861.2
-C=O Str.	1716.5	1724.2
-C-O-C Str.	1245.9	1249.8

Table-3.4: The characteristic IR absorption frequencies of RAERPU-1 to RAERPU-5

Type	Absorption frequencies, cm^{-1}				
	RAERPU-1	RAERPU-2	RAERPU-3	RAERPU-4	RAERPU-5
-N-H Str.	3334.7	3381.0	3340.6	3384.8	3338.6
-CH$_2$Str.					
asym.	2927.7	2926.8	2927.7	2927.7	2926.8
sym.	2855.4	2854.4	2855.4	2856.4	2854.5
Urethane -C=O Str.	1731.0	1732.9	1732.9	1722.3	1732.0
Urethane and ether -C-O Str.	1225.7	1243.0	1246.9	1240.1	1221.8
C-Cl Str.	-	-	-	750.3	-
C-Br Str.	-	-	-	-	738.7

Table-3.5: The characteristic IR absorption frequencies of OAERPU-1 to OAERPU-5

Type	Absorption frequencies, cm^{-1}				
	OAERPU-1	**OAERPU-2**	**OAERPU-3**	**OAERPU-4**	**OAERPU-5**
-N-H Str.	3327.0	3384.8	3318.5	3361.7	3310.6
$-CH_2$Str. asym. sym.	2925.8 2858.3	2923.9 2854.5	2925.8 2854.5	2925.8 2856.4	2924.8 2853.5
Urethane -C=O Str.	1730.0	1714.6	1734.9	1708.8	1716.5
Urethane and ether -C-O Str.	1228.6	1244.0	1222.8	1234.4	1225.7
C-Cl Str. C-Br Str.	- -	- -	- -	759.9 -	- 738.7

Table-3.6: The characteristic IR absorption frequencies of RERPU-2, RERPU-3, RAER-3-20% PEG and RAER-3-30% PEG

Type	Absorption frequencies, cm^{-1}			
	RERPU-2	**RERPU-3**	**RAER-3-20%PEG**	**RAER-3-30% PEG**
-N-H Str.	3322.2	3361.7	3288.4	3355.9
$-CH_2$Str. asym. sym.	2926.8 2856.4	2927.7 2860.2	- 2867.0	- 2869.9
Urethane -C=O Str.	1718.5	1712.7	1726.2	1726.2
Urethane and ether -C-O Str.	1223.7	1220.9	1229.5	1230.5

Table-3.7: The characteristic IR absorption frequencies of BCFPU and ER-2PU

Type	Absorption frequencies, cm^{-1}	
	BCFPU	ER-2PU
-N-H Str.	3382.9	3307.7
$-CH_2$Str. asym. sym.	2929.7 2860.2	2929.7 2860.2
Urethane -C=O Str.	1705.0	1714.6
Urethane and ether -C-O Str.	1230.5	1240.1

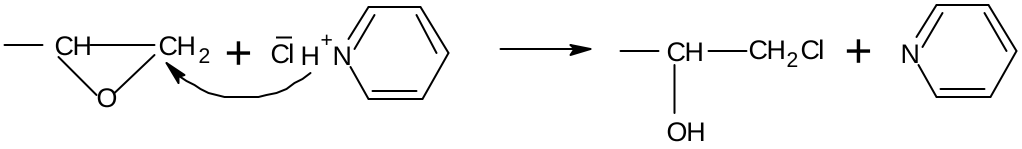
SECTION-2: DETERMINATION OF EPOXY EQUIVALENT OF THE EPOXY RESINS

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.

Epoxide equivalent may be determined by infrared analysis. The characteristic absorption band for the epoxy group is from 877.2 to 806.5 cm^{-1} for terminal epoxy groups; from 847.5 to 775.2 cm^{-1}?for internal epoxy groups; and from 769.2 to 751.8 cm^{-1} for triply substituted epoxy group [1].

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 band at 1610.3 cm^{-1}.



$$\underset{\text{(excess)}}{HCl} + NaOH \longrightarrow NaCl + H_2O$$

Greenlee [2] has described the method for epoxy equivalent. The epoxide content of the complex epoxide resins were determined by heating a 1 g sample

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1. J. Bomstein; Anal. Chem. **30**, 544-546, 1958.
2. S.O. Greenlee; (Devoe & Raynolds Co. New York) “Phenol aldehyde and epoxide resin compositions”, U.S. Pat. 2,502,145 (1949); C.A. **44**, 5614, 1950.

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 [2].

Jungnickel et al. [3] 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 some what 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 [4] have 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 is added. The solution is swirled and if necessary, heated gently until the sample is 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 standard 0.5N methanolic NaOH till pink end point. The epoxide equivalent is calculated according to following relationship:

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3. J.L. Jungnickel, E.D. Peters, A. Polgar and F.T. Weiss “Organic Analysis (J. Mitchell Jr., ed.)”, 1, 127, Interscience, New York, 1953.
4. R.E. Burge, Jr. and B.P. Geyer “Analytical Chemistry of Polymers” (G. M. Hline, ed.) Vol. XII/1, Interscience New York, 1959.

$$Epoxide\ equivalent = \frac{16 \times Sample\ weight\ in\ grams}{grams\ oxirane\ oxygen\ in\ sample} \quad \textbf{...3.1}$$

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 resins under study was determined according to above mentioned method and is reported in Table 3.8.

SECTION-3: DETERMINATION OF ACID VALUES OF THE POLYESTER POLYOLS

Acid value is a measure of the free fatty acid 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 reactions, i.e. 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.

Epoxy ester was exactly weighed (1- 2 g) in a 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 average of three measurements was used to determine the acid value of a given sample according to following relationship.

$$\text{Acid Value} = \frac{56.1 \times N \times (A-B)}{W} \quad \textbf{...3.2}$$

N = Normality of KOH

A = Sample burette reading

B = Blank burette reading

W = Weight of sample in grams

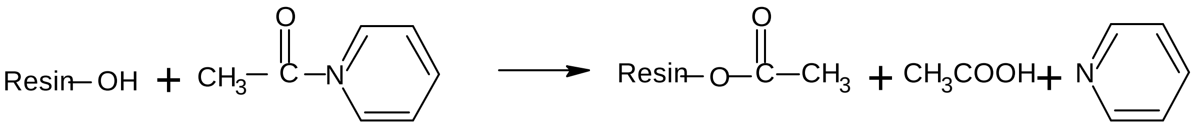
Table-3.8: Epoxy equivalent of the epoxy resin

Resin	**Epoxy equivalent**
ER-1	475
ER-2	442
ER-3	436
ER-4	389
ER-5	500

Acid values of polyester polyols and epoxy esters were determined by standard method [5] and are reported in Table-3.9.

SECTION-4: DETERMINATION OF HYDROXYL VALUES OF POLYESTER POLYOLS

The hydroxyl value is expressed as the number of mg of KOH equivalent to the quantity of acetic acid that binds with 1 g of hydroxyl containing substance. The hydroxyl value gives information about the number of free hydroxyl groups present in the polyester polyol, which can be utilized in the formation of polyurethane resin. 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 then phthalic anhydride can be used, which reacts much slower than acetic anhydride.



$$CH_3COOH + KOH \longrightarrow CH_3COOK + H_2O$$

Epoxy esters were exactly weighed (1- 2g) in a capsule and placed carefully in a 250 ml round bottomed flask and exactly 20 ml of acetylating mixture (1 volume of acetic anhydride and 3 volume of pyridine) was added. The mixture was refluxed for 30-50 min. Insoluble materials if present initially can be dissolved by adding 20 ml of benzene or ethylene chloride. The reaction mixture was cooled to room temperature and 50 ml cold water was added slowly down to the condenser. The mixture was titrated with standard 1N NaOH using phenolphthalein as an indicator. Similarly blank determination was carried out and the hydroxyl value of the polyester polyol was determined according to Eqn. 3.3. The hydroxyl values of the polyester polyols are reported in the Table-3.10.

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5. ASTM-D-1639-61

Table-3.9: Acid values of the polyester polyols

Polyester polyol	Acid value, mg KOH/g
RAER-1	3.0
RAER-2	2.03
RAER-3	2.14
RAER-4	9.36
RAER-5	7.025
OAER-1	3.57
OAER-2	2.79
OAER-3	2.493
OAER-4	6.25
OAER-5	9.34
RER-2	15.83
RER-3	11.14

The hydroxyl value can be determined according to following relationship

$$\text{Hydroxyl Value} = \frac{56.1 \times (A\text{-}B) \times N \text{ of NaOH}}{\text{Wt. of sample}} \qquad \textbf{…3.3}$$

Where N = Normality of KOH

A = Sample burette reading

B = Blank burette reading

W = Weight of sample in grams

SECTION-5: THERMAL ANALYSIS OF THE RESINS

This section of the thesis describes the thermal analysis of the resins.

Thermal analysis of polymers is very significant in predicting their utility under various environmental conditions, especially under high temperature applications. It is the best tool for understanding molecular architecture, decomposition mechanism, degradation pattern, etc.

For optimum performance of the finished products, it is of foremost important to know and monitor the curing reactions. Thermosets are difficult to study because of their insolubility and infusibility. Differential scanning calorimetric (DSC), differential thermal analysis (DTA) and thermogravimetric (TG) techniques provide considerable insight into reaction mechanism.

Increased emphasis on occupational safety and consumer protection has generated significant interest in analytical methods to evaluate safe processing, storage, shipping and safety conditions for a wide variety of materials. Thermal analysis techniques, particularly differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) have proven useful for evaluating kinetic parameters of various reactions and materials. Kinetic parameters provide usefulness of the potentially unstable nature of the materials.

Scientific and technological achievements together with demands based on industrial requirement have permitted the development of the many and various types of materials that can withstand at much higher temperature and environments that are more corrosive.

Table-3.10: The hydroxyl values of the polyester polyols

Polyester polyols	**Hydroxyl value mg KOH/g**
RAER-1	882
RAER-2	867
RAER-3	911
RAER-4	1020
RAER-5	805
OAER-1	790
OAER-2	626
OAER-3	848
OAER-4	878
OAER-5	770
RER-2	626
RER-3	870

Scientific studies help to reveal the molecular structure such as the sequence and arrangement of repeating units and side groups in the polymer as well as the nature of the chain ends and of the cross-links between chains. Such studies throw light on molecular architecture of polymer such as degree of polymerization, orientation, crystal perfection, percentage crystallinity, the extent of chain branching, strength of various bonds holding together polymer molecules, on the kinetic of depolymerization, on the effect of time, temperature, pressure, etc. and on the rates and products of degradation.

On practical side, thermal analysis of polymers, not only explain 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 and appliances, etc.

For any given application, it is likely that one or a few physical and / or chemical properties will be most important. A few that often encountered are structural integrity, tensile strength, viscosity, weight loss and susceptibility to oxidation.

Effect of various operating parameters

1. Atmosphere

The atmosphere associated with any thermal analysis, which composed of gases that are introduced from outside and those is evolved from the samples. The presence or absence of such gases may have a 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 influence decomposition processes. In vacuum, primary decomposition of gases tend to pump 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 reaction 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 sample. Even with a flowing gaseous atmosphere, a deep narrow container limits the contact between the sample surface and gas, whereas a shallow, broad container promotes the contact.

3. Container material

It is reasonable to expect that in some cases the container material reacts 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 polymer degradation studies, it is customary to reduce film thickness or particle size until the rate of decomposition becomes independent of size.

5. Rate of heating

In the case where only kinetic considerations are significant, and increase in the rate of temperature rise causes the process to be displayed to a higher temperature because the sample will have been at the lower temperatures for a shorter length of time. The rate of change of the measured parameters will also be greater for faster heating.

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

Physical transformations [6] such as glass transition, cold crystallization, crystallization from the melt, crystalline disorientation and melting can be studied by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The usefulness of DSC and TGA in various fields of chemistry is described in Table-3.11.

DSC is a method whereby 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. When an endothermic transition

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6. E. Heisenberg; Cellulose Chemie, 12, 159, (1931); C. A. **25**, 59823, 1931.

Table-3.11: The usefulness of DSC and TGA in various fields of chemistry

Properties	**Various fields of chemistry**				
	Polymers	**Pharma-ceutical**	**Organic products**	**Inorganic products**	**Food Stuffs**
(1) Physical Properties					
1. Specific heat	DSC	DSC	DSC	DSC	DSC
II. Phase transition:					
a)Melting / crystallization	DSC	DSC	DSC	DSC	DSC
b) Evaporation / drying	DSC and TGA	DSC and TGA	DSC and TGA	DSC and TG	DSC and TGA
	DSC	DSC	DSC	DSC	DSC
c)Solid–solid modification changes	DSC	-	-	-	-
d)Glass transition (Tg), softening	-	DSC	DSC	DSC	DSC
	-	-	-	-	DSC
	-	-	DSC	-	-
e) Polymorphism					
f) Liquid fraction	DSC	-	-	-	-
g)Liquid-solidphase transition	DSC	DSC	DSC	DSC	DSC
	-	DSC	DSC	DSC	-
h) Crystallinity					
i) Heat of fusion					
j) Purity					

Properties	Various fields of chemistry				
	Polymers	Pharma-ceutical	Organic products	Inorganic products	Food Stuffs
(2)Chemical Properties					
a)Decomposition/ pyrolysis	DSC and TGA	TGA	DSC and TGA	TGA	DSC and TGA
b)Oxidation, oxidative stability	DSC	DSC	DSC	TGA	DSC and TGA
c)Content determination, fillers	DSC and TGA	TGA\	TGA	TGA	DSC and TGA
d)Dehydration, moisture	DSC and TGA	DSC and TGA	DSC and TGA	DSC and TGA	DSC and TGA
e)Reaction profile, kinetics	DSC	-	DSC	DSC	-
f) Degree of cure, vulcanization	DSC	-	-	-	-
g)Safety investigations	-	DSC	DSC	-	-
h) Heat of reaction	DSC	-	DSC	DSC	-

occurs, the 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 reaction in polymers [7].

DSC has proved to be a valuable technique for investigating parameters of the curing reactions of thermosetting polymers. This technique is applied to evaluate curing characteristics like the degree of cure, temperature and duration of the curing reaction, and the magnitude and variability of the heat of reaction as a function of time and temperature for thermosetting materials such as phenolics [8-10], diallyl phthalate [11], unsaturated polyester [12, 13] and various epoxy resins.

DSC provides useful informations about crystallinity, stability of crystallite, glass transition temperature, cross linking, kinetic parameters such as the activation energy, the kinetic order and heat of polymerization, etc.

DTA is more versatile and gives data of more fundamental nature than TGA. This technique involves recording of difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a programmed heating rate. Any transition, which the polymer sample undergoes, results in absorption or liberation of energy by the sample with a corresponding deviation of its temperature from that of the reference. In DTA, as soon as the sample reaches the temperature of the change of its state (chemical or physical), the differential signal appears as a peak. The

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7. A.A. Duswalt, Thermochemica Acta, **8**, 57, 1974
8. A. Siegman and M. Narkis; J. Appl. Polym. Sci., **27**, 2311, 1977.
9. R.Ray and A.R. Westwood; Eur. Polym. J., **11B**, 25, 1975.
10. M.Ezrin and G.C. Claver; Appl. Polym Symp., **8**, 159, 1969.
11. P.E. Willard; Polym. Eng. Sci., **12**, 120, 1972.
12. G.B. Jhonson, P.H. Hess and R.R. Miron; J. Appl. Polym. Sci., **6**, 497, 1962.
13. M.R. Kamal and S. Scyrour; Polym. Eng. Sci., **13**, 59, 1973.

number, position, shape and nature (exothermic or endothermic) of the DTA peaks give information about glass transition temperature, crystalline rearrangement, melting, curing, polymerization, crystallization, decomposition of polymer, etc.

Thermo gravimetric analysis (TGA)

Different polymers decompose over different ranges of temperature yielding different proportion of volatile and residues. Thermogravimetry is useful analytical technique for recording weight loss of a test sample as a function of temperature, which may be used 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

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 the sample starts losing weight at a very slow rate up to a particular temperature and there after, the rate of loss becomes large over a narrow range of temperature. After this temperature, the loss in weight levels off. TGA curves are characteristic for a given polymer because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at rates that are function of the polymer structure. 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 evaluation of volatile products in the formation of heavier reaction products.

Pyrolysis of many polymers yield sigmoidal TG curves. The weight of the sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction is completed. The shape of the curve depends on the kinetic parameters: reaction order n, frequency factor A and activation energy E. The values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation [14, 15].

Reich and Levi [16] have described several temperature characteristics for qualitative assessment of relative thermal stability of polymers:

1. Initial decomposition temperature (T_0)
2. Temperature for 10% weight loss (T_{10})
3. Temperature for maximum rate of decomposition (T_{max})
4. Half volatilization temperature (T_s)
5. Differential decomposition temperature and
6. Integral procedural decomposition temperature (IPDT)

With dynamic heating T_0 and T_{10} are some of the main criteria of the thermal stability of a given polymer.

For the estimation of kinetic parameters from TG traces, several so called exact methods have been proposed. All these methods involve two important 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. The shape of any TG curve is dependent on the nature of apparatus and the way in which it is used.

Macrovic et al. [17] have synthesized two-pack polyurethane coating and analyzed using thermo analytical techniques. The curing reaction was monitored using pressure differential calorimetry (PDSC), rheometry and dynamic mechanical analysis (DMA) showed the temperature dependency of activation

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14. D.W. Levi, L. Reich and H.T. Lee; Polymer Eng. Sci., **5**, 135, 1965.
15. H.L. Friedman; U.S. Dept. Com., Office. Tech., 24 PP (1959); cf. C. A. **55**, 26, 511, 1961.
16. L. Reich and D.W. Levi; Macromol. Rev. Eds. Peterlin Goodman Wiley Interscience, New York, 173, 1968.
17. M.G. Markovic, N.R. Choudhury, J.G. Matisons and D.R.G. Williams, "Characterization of polyurethane coatings using thermoanalytical techniques", J. Mater. Sci., **59**, 409-424, 2000.

energy and hence rate of curing. In-situ ATR-FTIR showed the formation of urethane linkage over time. The decomposition behavior carried out under non-isothermal mode using thermogravimetric analysis (TGA) showed bimodal behavior. The activation energies of the initial step (10% decomposition) from both iso and non-isothermal experiments were in very good agreement with each other. The use of dynamic mechanical analysis (DMA) showed the difference in glass transition behavior (T_g) and elastic modulus (E') due to the different state of cure. Also the coating exhibited a very broad loss modulus peak (E'') indicating higher energy dissipation with deformation.

Javni et al. [18] have synthesized a series of polyurethanes from polyols derived from soybean, corn, safflower, sunflower, peanut, olive, canola, and castor oil and their thermal stability in air and nitrogen assessed by thermogravimetric analysis, FTIR, and GC/MS. Oil-based polyurethanes generally had better initial thermal stability (below 10% weight loss) in air than the polypropylene oxide-based polyurethane, while the latter was more stable in nitrogen at the initial stage of degradation. If weight loss at a higher conversion was taken as the criterion of stability, then oil polyurethanes have better thermal stability both in air and in nitrogen.

Furukawa [19] has synthesized novel polyester-urethane elastomers with improved thermal stability and hydrolytic stability. The novel polyester glycols used were poly(β-methyl- δ-valerolactone) glycol (PMVL), poly(3-methyl pentamethylene adipate) glycol (PMPA), poly(nonamethylene-co-2-methyl octamethylene carbonate) glycol (PNCO). A mixture of PNCO and poly(dimethyl siloxane) glycol (PNCO/PDMS) was also used. Polyurethane network elastomers were prepared from 4,4′-diphenylmethane diisocyanate (MDI) (or2,4-tolulene diisocyanate (TDI)), and a mixture of 1,4-butane diol and trimethylol propane by a

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18.I. Javni, A. Guo, R. Fuller and Z.S. Petrovic, “Thermal stability of polyurethanes based on vegetable oils”, J. Polym. Appl. Sci., **77**, 1723-1730, 2000.

19.M. Furukawa, “Hydrolytic and thermal stability of novel polyurethane elastomers”, Angewante Makromolekulare Chemie, **252**, 33-43, 2003.

prepolymer method. Mechanical properties, T_g, thermal stability, and hydrolytic stability were measured. Morphology was also measured by means of polarizing microscopy, dynamic viscoelastometer and ESR. The novel polyurethane elastomers possessed good mechanical properties comparable to those of the general purpose polyester urethanes, and better thermal and hydrolytic stability than PTMG-based polyurethane. These polyurethane elastomers were exposed in out door during 2 year in Nagasaki, JAPAN. The novel polyurethane elastomers held almost constant values for gel fraction, swelling ratio, relative modulus during 12 months, while poly(oxytetramethylene oxide)-based polyurethane as a control decreased the these values. Relationship of degradation behaviors with chemical structure and morphology were discussed.

Song et al. [20] have synthesized polyurethanes from polyester and butanediol with three different diisocyanates, i.e., 4,4´-diphenylmethane diisocyanate (MDI), *m*-xylene diisocyanate (XDI), and 2,4-toluene diisocyanate (TDI). The effect of chemical structures of diisocyanate compounds on the degree of crystallinity and the thermal stability were observed. Differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS) were used to determine the degree of crystallinity of the hard segment. The thermal degradation of polyurethanes was studied by the thermogravimetric method. It has been shown that the polyurethane hard-segment crystallinity decreases in the following order: MDI> XDI> TDI>. The experimental results also indicated that polyurethanes with Ar-alkyl diisocyanates, i.e., XDI, had the best thermal stability. The polyurethanes synthesized from aromatic diisocyanates, i.e., MDI and TDI, had worst thermal stability than from XDI. However, owing to the higher degree of hard-segment, crystallinity for polyurethanes from MDI, these polyurethanes had a better thermal stability than those based on TDI.

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20. Y.M. Song, W.C. Chen , K. Linliu , Y.H. Tseng and T.L. Yu, “Effect of isocyanates on the crystallinity and thermal stability of polyurethanes”, J. Appl. Polym. Sci., **62**, 827-834, 1998.

EXPERIMENTAL

The TG thermograms of RAERPU-1, RAERPU-2, RAER-3-20% PEG, RAER-3-30% PEG, BCF PU and ER-2 PU were scanned on a Perkin Elamer, Model No. Pyris-1 TGA at the heating rate of 10 ^{0}C/ min in nitrogen atmosphere.

RESULTS AND DISCUSSION

Thermal analysis of polymers is very important in predicting their utility under various environmental conditions, especially under high temperature applications. The molecular architecture of polymers can be studied with the aid of DSC, DTA and TGA thermograms. The weight loss as a function of temperature data of thermogravimetric analysis provides a means to estimate kinetic parameters of thermal decomposition reaction.

Thermal methods are based upon the measurements of the dynamic relationship between temperature and some properties of a system such as mass, heat of reaction or volume, etc [21, 22].

TG thermograms of RAERPU-1, RAERPU-2, RAER-3-20% PEG, RAER-3-30% PEG, BCF PU and ER-2 PU at the heating rate of 10^{0}C/ min in nitrogen atmosphere are presented in Figs. 3.15-3.20, respectively. The initial decomposition temperature (T_0), temperature of 10% decomposition (T_{10}), temperature of 50% decomposition (T_{50}), decomposition range and % weight loss involved in each step are reported in Table-3.12.

Figs.3.15 and 3.16 show the TG thermograms of RAERPU-1 and RAERPU-2 at the heating rate of 10^{0}C/min in nitrogen atmosphere. From Figs.3.15 and 3.16, it is evident that RAERPU-1 and RAERPU-2 have followed

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21. W.W. Wendlant, “Thermal Methods of Analysis”, 2nd Ed. Wiley, New York, 1974; T. Meisel and K. Seytold, Crit. Rev. Ana. Chem. 12, 267, 1981.
22. R.C. Mackenzie “Differential Thermal Analysis”, Vol. 1&2, Academic Press, New York, 1970; W.W. Wendlant, Anal. Chem. 54, 97R (1982); 56, 250R, 1984.

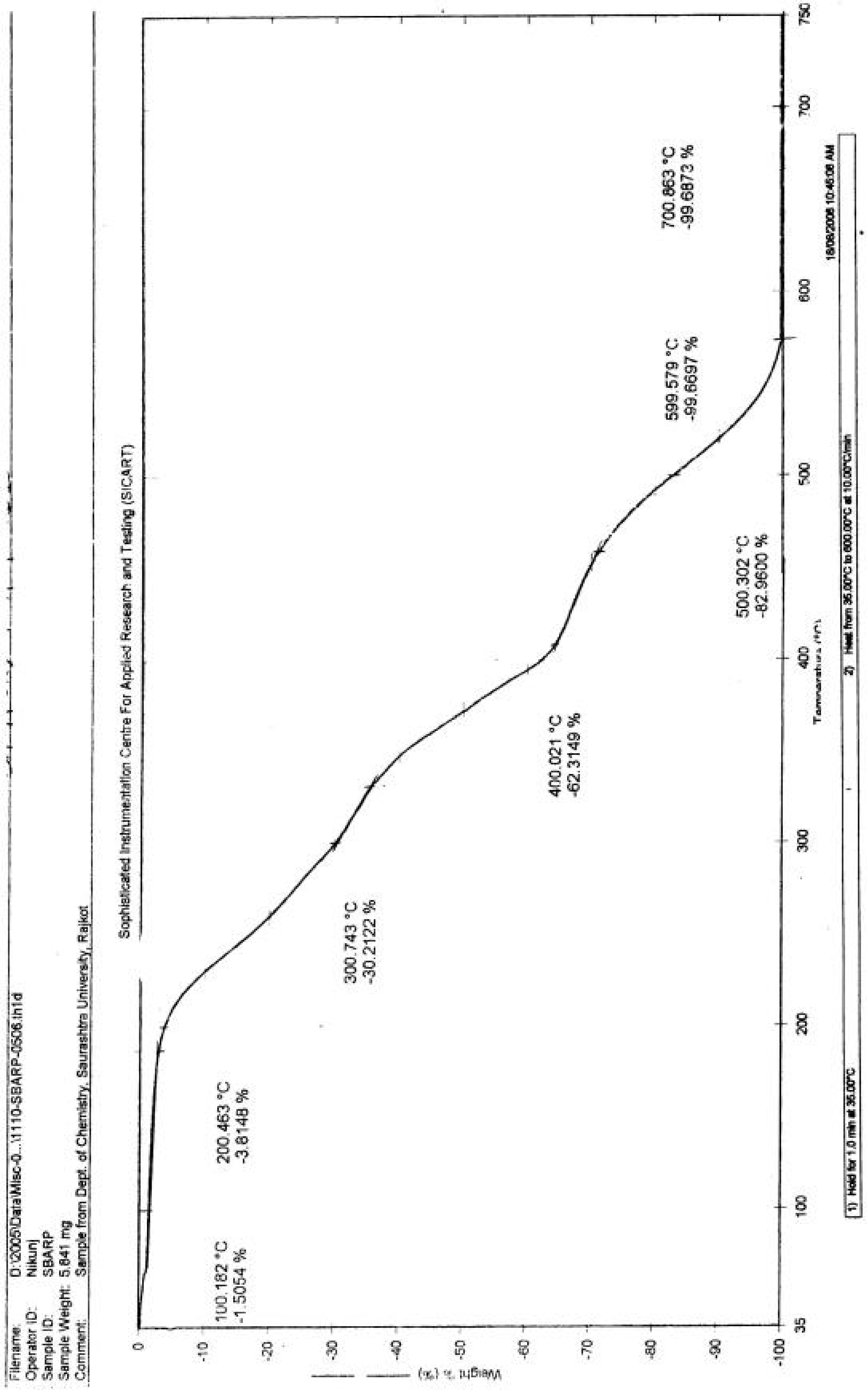


Fig 3.15 TG thermogram of RAERPU-1 at the heating rate of 10^{o}C / min in an N_2 atmosphere

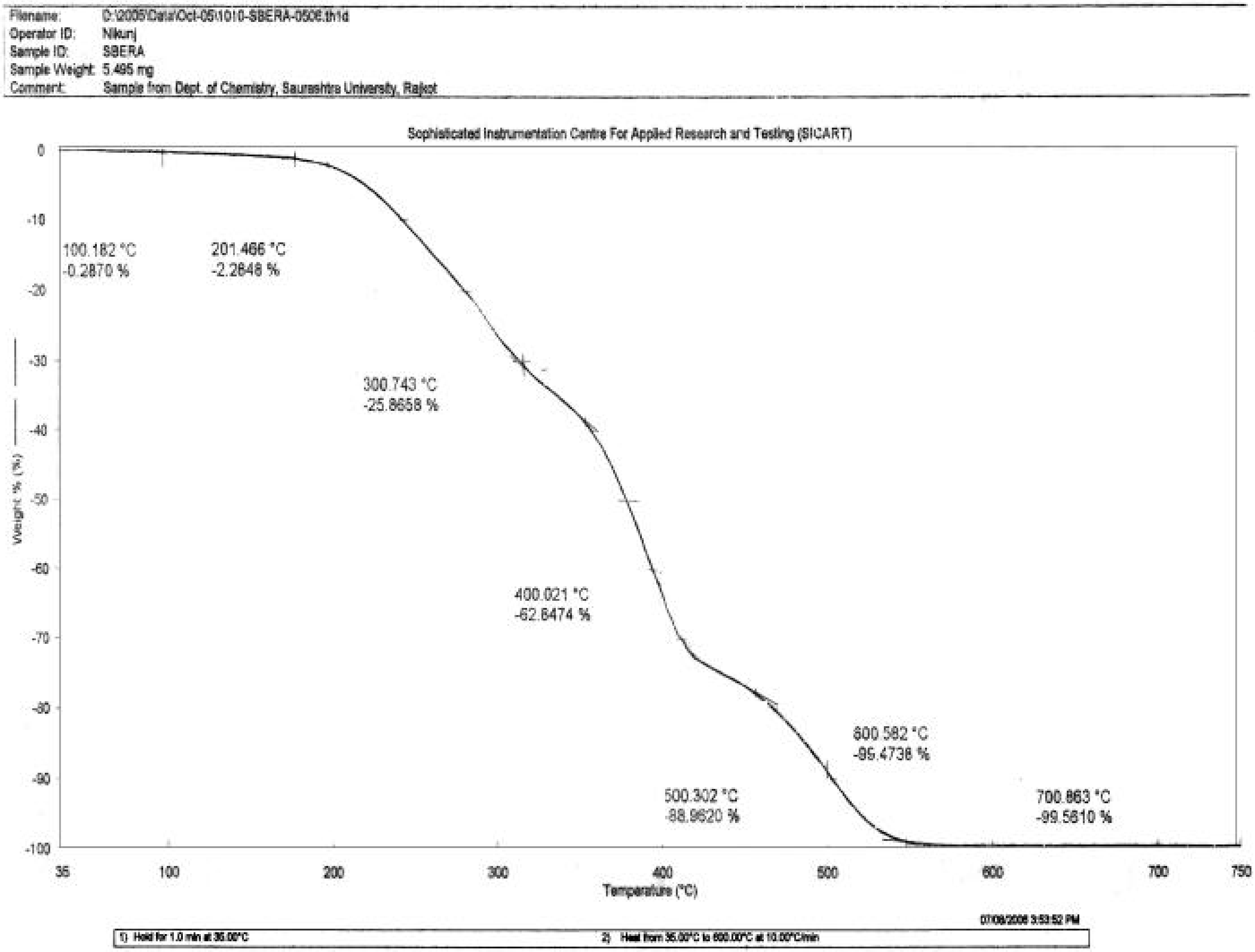


Fig 3.16 TG thermogram of RAERPU-2at the heating rate of 10^{o}C / min in an N_2 atmosphere

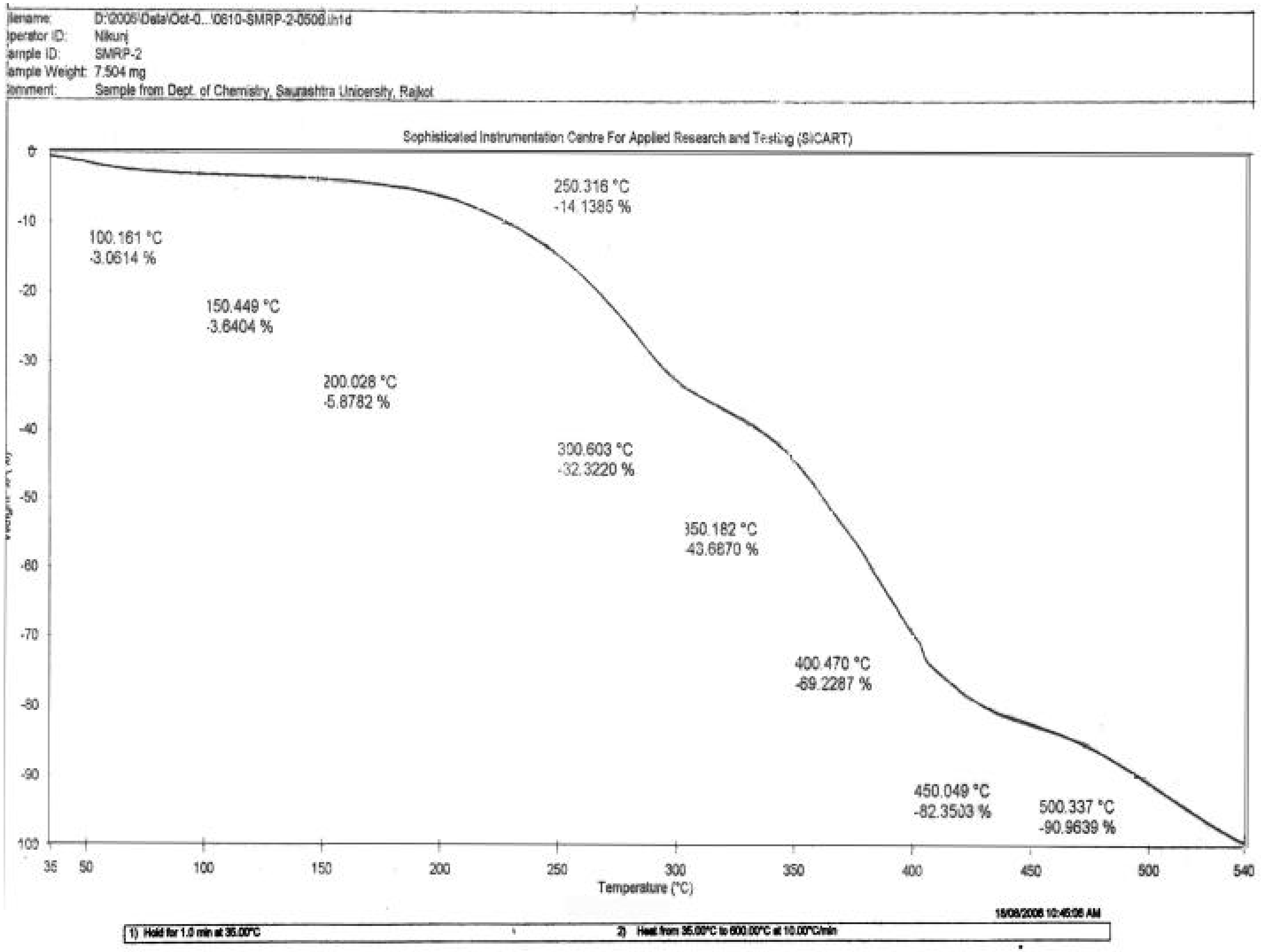


Fig 3.17 TG thermogram of RAER-3-20% PEG at the heating rate of 10^{o}C / min in an N_2 atmosphere

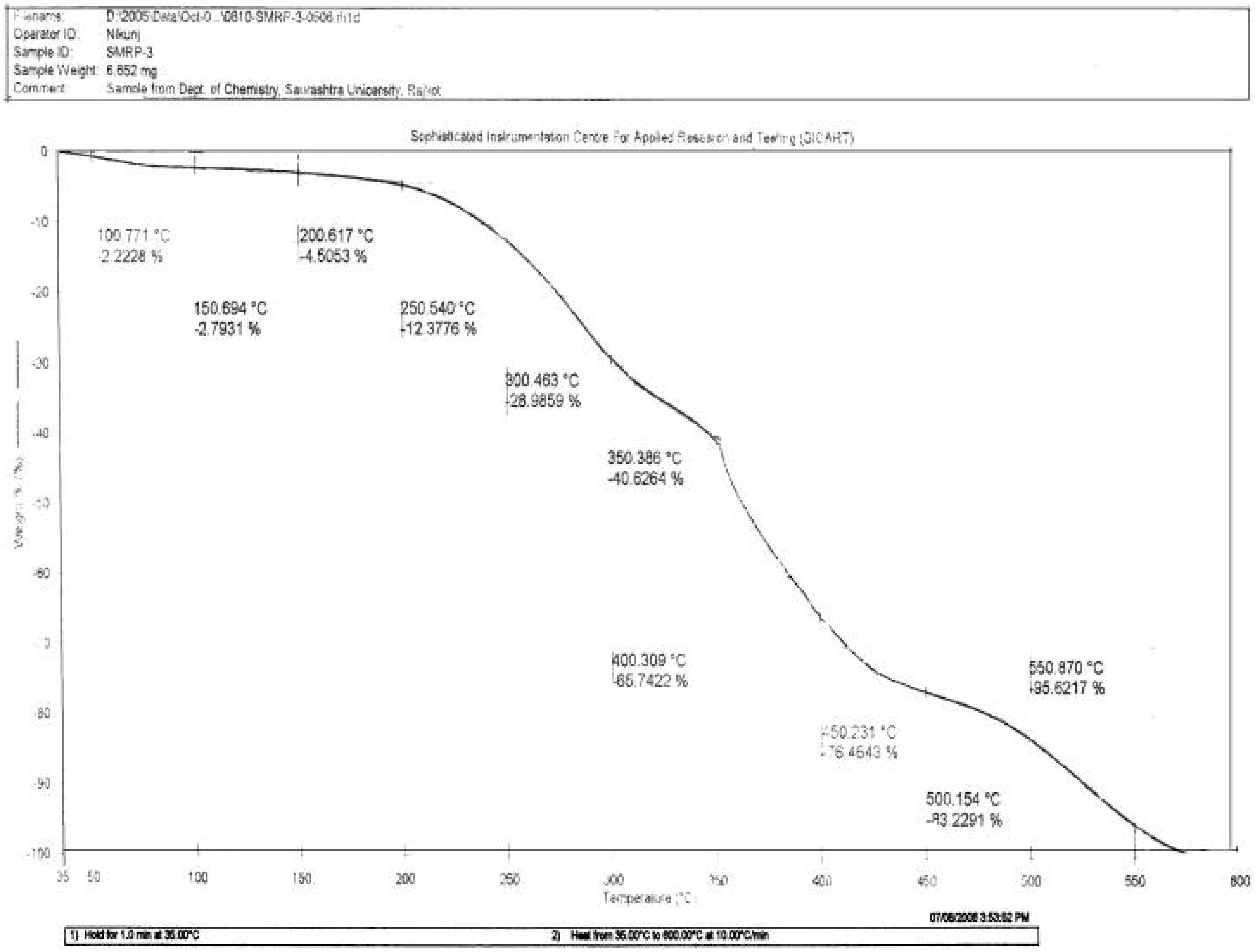


Fig 3.18 TG thermogram of RAER-3-30% PEG at the heating rate of 10^{o}C / min in an N_2 atmosphere

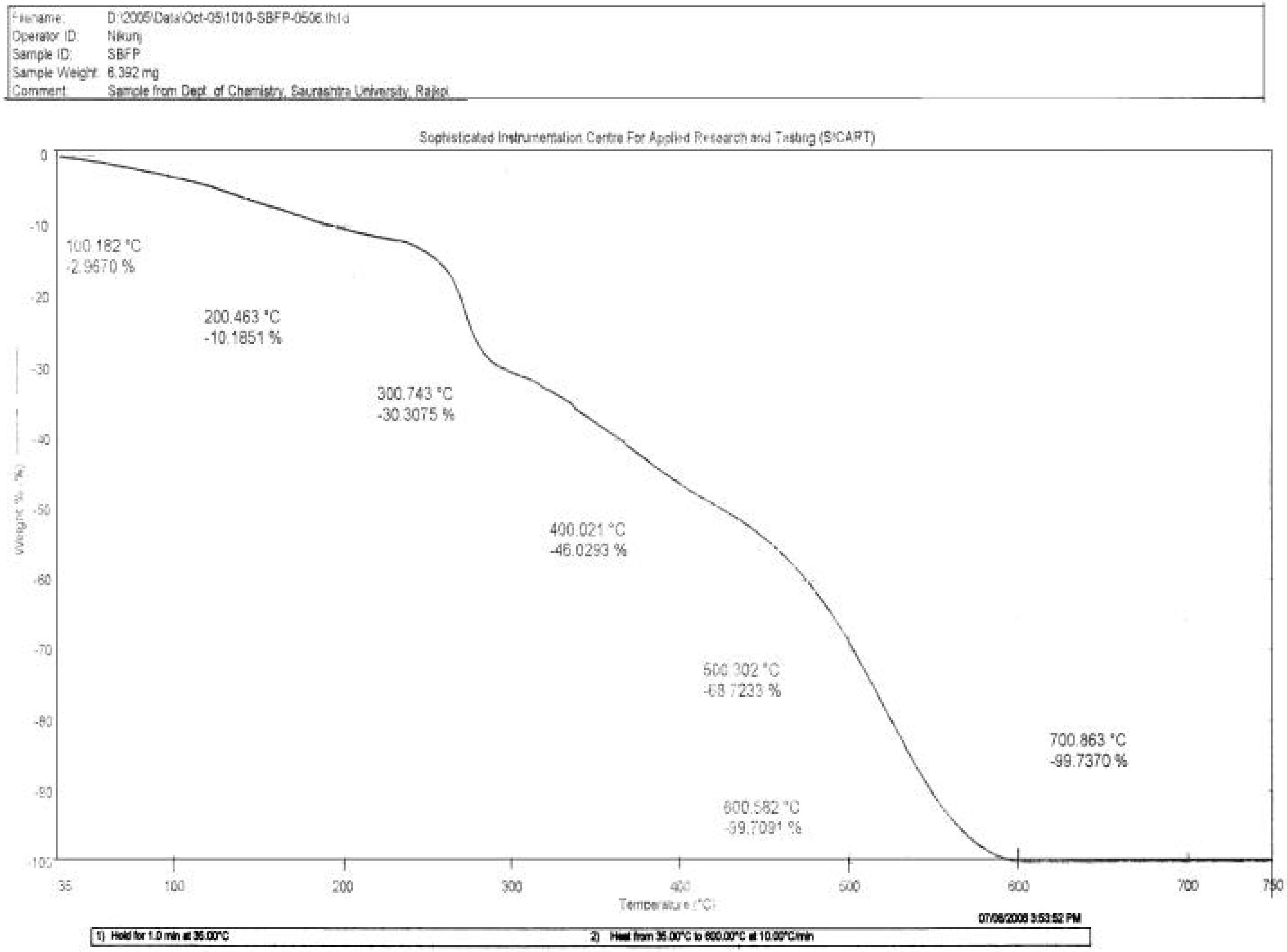
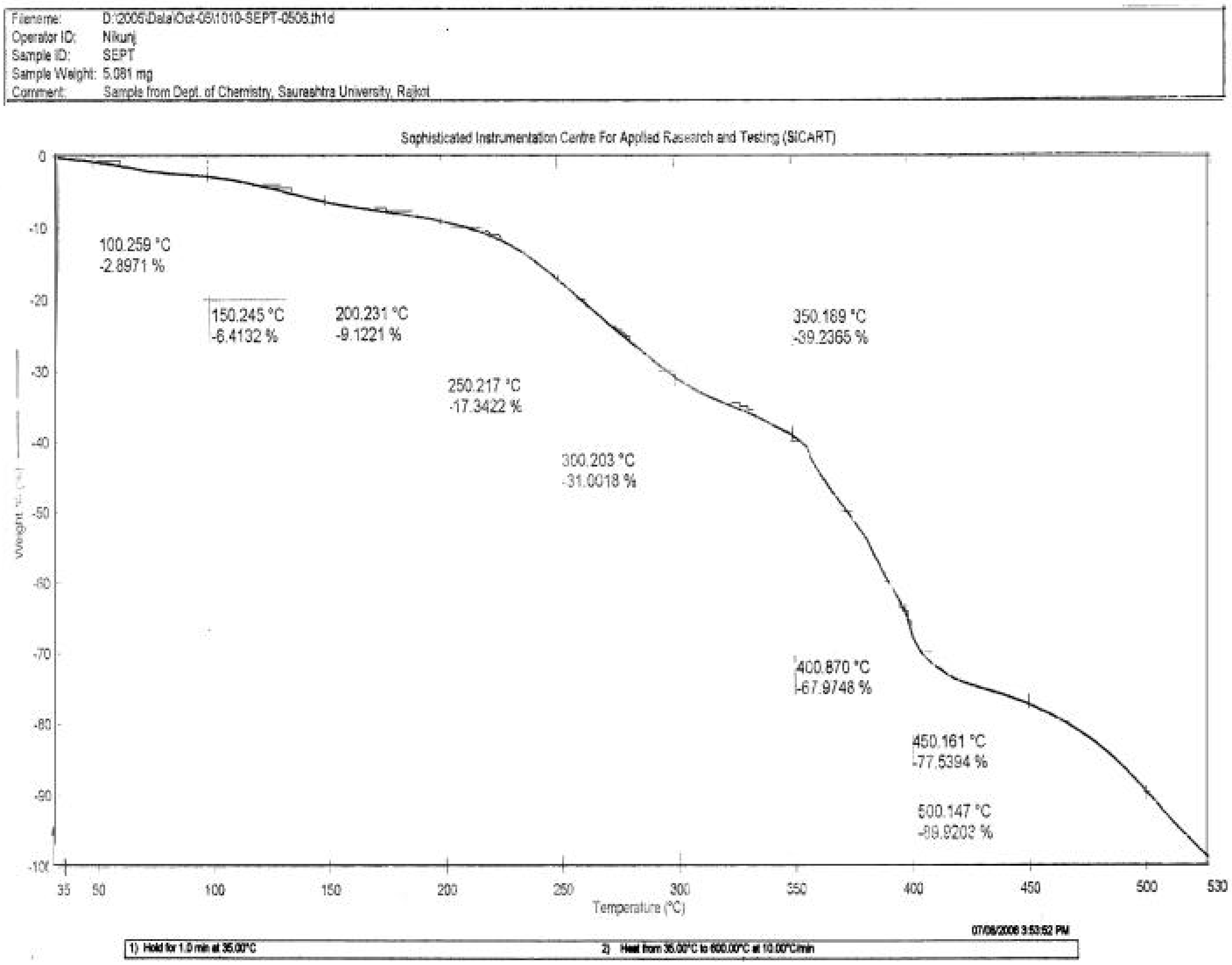


Fig 3.19 TG thermogram of BCFPU at the heating rate of 10°C / min in an N_2 atmosphere



Filename: D:\2005\Data\Oct-05\1010-SEPT-0506.th1d
Operator ID: Nikunj
Sample ID: SEPT
Sample Weight: 5.081 mg
Comment: Sample from Dept. of Chemistry, Saurashtra University, Rajkot

Fig 3.20 TG thermogram of ER-2 PU at the heating rate of 10^{o}C / min in an N_2 atmosphere

Table-3.11: TGA data of RAERPU-1, RAERPU-2, RAER-3-20%PEG, RAER-3-30% PEG, BCF PU and ER-2PU at the heating rate of 10^{o}C / min in nitrogen atmosphere

Resin	T_0	T_{10}	T_{50}	Decomposition range, ^{0}C	%Wt. loss
RAERPU-1	187	247	365	187-300 331-409 460-574	24.4 28.9 17.9
RAERPU-2	182	247	365	182-317 354-420 457-534	30.9 23.1 14.6
RAER-3-20%PEG	190	225.1	362.6	190-304 342-440 472-540	27.7 37.9 11.7
RAER-3-30%PEG	198	235.5	369.0	198-307 350-430 488-590	26.1 31.6 18.4
BCF PU	58.9	197.4	434.7	247-287 459-600	8.1 42.7
ER-2PU	58.8	205.3	368.7	211.7-306 355.8-413 465-530	21.1 27.8 16.2

three step degradation kinetics. From Table-3.11, it is clear that both the polyurethanes have comparable thermal properties and followed same degradation mechanism. They are thermally stable up to about 182- 188^{0}C and practically decomposed into low molecular mass substances. The observed three step degradation is due to three different weak linkages in the polyurethane chains ether, ester and urethane, which degrade selectively with the formation of free radicals. These free radicals may undergo variety of reactions such as chain cleavage, branching, rearrangement, cross linking, etc. Thus, incorporation of cardo group in polyurethane chains did not impart any change in thermal properties.

From the Figs 3.17 and 3.18, it is evident that RAER-3-20% PEG and RAER-3-30% PEG have followed three-step degradation kinetics. From Table-3.11, it is clear that practically there is no much change in thermal stability of RAER-3-20%PEG and RAER-3-30% PEG copolyurethanes. T_0, T_{10} and T_{50} are slightly increased with PEG-400 content in copolyurethane. Thus, PEG-400 content did not affect the thermal properties. The observed three step degradation is due to three different weak linkages in copolyurethane namely ether, ester and urethane. The first step weight loss (26-28%) in the temperature range 190-307^{o}C is due to decomposition of urethane linkage and moisture content leading to the formation of CO_2, alcohols, amines, aldehydes, CO, etc. The second step weight loss (32-38%) in the temperature range 342-440^{o}C is due to decomposition of polyester polyol. The third step weight loss (12-18%) in the temperature range 472-590^{o}C is due to complete decomposition of polyurethane. Degradation is complex process and involves a variety of reactions such as chain cleavage, branching, rearrangement, cross linking, etc. Selective degradation takes from a weak point in the chains and as a result free radicals will be formed, which further undergo variety of reactions. In present case both copolyurethanes are ultimately converted into low molecular weight substances as confirmed by negligible residue at the end of the degradation reaction.

Figs. 3.19 and 3.20 show the TG thermograms of BCFPU and ER-2PU at the heating rate of 10^{0}C/min in the nitrogen atmosphere. From the Figs 3.19 and

3.20, it is evident that BCFPU has followed two step degradation kinetics, while ER-2PU has followed three step degradation kinetics. In case of BCFPU the first step weight loss(8.1%) in the temperature range 247-287^{0}C is due to decomposition of urethane linkage and moisture content leading to the formation of CO_2, alcohols, amines, aldehydes, CO, etc. The second step weight loss (42.7%) in the temperature range 459-600^{0}C is due to the complete decomposition of the polyurethane. In case of ER-2PU the first, second and third step weight losses are 21.1%, 27.8% and 16.2%, respectively. The ER-2PU is completely degraded in the temperature range 465-530^{0}C.

SECTION – 5: DENSITY MEASUREMENTS

Qualitative and quantitative estimations provide enormous support to the plastic industry in quality control, development of new materials, product designing and process optimization. The measurement of density can be simple but it has great importance in quality control and screening of materials for specific applications. The molecular size and molecular weight distribution have profound effect upon processability and product quality. The density, specific volume measurements are useful for a designer in ascertaining component weight, in material identification, in assessing the crystallinity of semi crystalline plastics and in evaluation of various thermodynamic properties of the sample as well as polymer materials [23-27].

23.H.F. Mark, N.C. Gaylord and N.F. Bikales, "Encyclopedia of Polymer Science and Technology”, vol 12, Willey InterScience,NewYork ,1970.

24. C. Tanford, “Physical Chemistry of Macromolecules”, John Willey and Sons, Inc. New York, 1961.

25.V.R. Gowariker, N.V. Vishvanathan and J. Sreedhar, "Polymer Science”, Willey Eastern Ltd. ,1986.

26. T.M. Aminabhavi and P.Munk, Macromolecules, **6,** 1186, 1979.

27.L.Holiday and W.A. Holmes-Walker, “A new structural parameter of polymers- the relative number of network bonds per unit volume”, J. Appl.Polym.Sci.,**16**,139-155, 1972.

These data are most useful for the average distance between macromolecular chains and the extent of crystallinity in polymers.

Theoretical calculations of the density by floatation method:

The density of the polymer can be calculated from the knowledge of the structural aspects. According to Slonimskii [28] the density of polymer may be expressed as:

$$r = \frac{KM}{N_A \sum \Delta Vi} \qquad \text{...}\mathbf{3.4}$$

Where K is the packing coefficient, M is the molecular weight of the repeating unit of the polymer, S ?Vi is the intrinsic volume of the polymer repeat unit and N_A is the Avogadro’s number. According to Slonimskii [28] the values of ? ?V_i can be calculated from the knowledge of the volume increments ?Vi of the 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.

$$K = V_{int} / V_{true} = N_A S \ ? \ Vi / (M/?) \qquad \text{…}\ \mathbf{3.5}$$

Slonimskii et al. [28] have calculated packing coefficient of seventy polymers of widely different chemical and physical structure for both addition and condensation polymers. They have reported the average value of K 0.681 and 0.695 for bulk and film samples, respectively. In addition to intrinsic volume of the repeat unit, the knowledge of packing coefficient K is also necessary for the calculation of the density of polymer.

The densities of RAERPU-1, RAERPU-2, RAER-3-20% PEG and RAER-3-30% PEG films were determined by floatation method by using CCl_4-n-hexane system at 30^{o}C. In six different stoppered test tubes, a small piece of film and about 5ml of CCl_4 were placed and n-hexane was added drop wise with shaking till the polymer film remained suspended halfway in each test tube. The composition of the two solvents was adjusted in such a way that the film just

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28.G.L. Slonimskii, A.A. Askadskii and A.I. Kitaigorodkii, Polym. Sci. USSR, A-**12** , 556, 1970.

remained suspended throughout. The densities of the mixtures were determined after 24h by the usual method. The averages of six measurements along with the standard deviations are reported in Table-3.13.

According to equation 3.5 the density depends upon M and S?Vi and independent of intermolecular interactions. The formation of any organic molecule or repeat unit of a polymer involves replacement of H-atom by other elements. The polar group, which changes intrinsic volume and weight, and the ratio of these two quantities, is very important in deciding the density of a given polymer.

From Table 3.13, it is concluded that the observed difference in densities of RAERPU-1 and RAERPU-2 is mainly due to high packing density and cross linking density of RAERPU-2. This may be further supported by low acid and hydroxyl values of RAER-2 in comparison to RAER-1. Thus, urethane linkages in RAERPU-2 are more in number than that of RAERPU-1, while in case of copolyurethanes the density is decreased with increase in PEG-400 content and it is mainly due to increase in intrinsic volume of the copolymer network of repeating unit.

SECTION-7: MECHANICAL AND ELECTRICAL PROPERTIES OF THE POLYURETHANES

INTRODUCTION

The importance of synthetic polymers is growing fast because of their high demand in modern technology. In fact, various types of polymers are progressively being used to replace iron, steel, brass and other alloys, wood, etc. for many engineering items.

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

Table-3.13: The densities of polyurethanes or copolyurethanes determined by floatation method at room temperature

Polyurethane films	**r , g cm^{-3}**
RAER-1	1.2190±0.0004
RAER-2	1.2308 ± 0.0002
RAER-3-20% PEG	1.2379±0.0006
RAER-3-30% PEG	1.2016 ± 0.0006

Most applications of polymers need load-bearing capacity. The geometrical response to loading lead to a wide range of mechanical properties grouped under stress-strain properties, visco-elasticity and failure properties. These properties are in turn largely determined by the polymer structure (molecular weight, cross-linking, branching, segmental structure and morphology) and the nature and extent of compounding when characterizing the mechanical behavior of a polymeric system, external conditions like temperature, loading rate and environment must be considered [29-31].

The mechanical behavior of a polymer is divided into three main groups (i) elastic (ii) plastic and (iii) brittle. The same can behave as brittle, tough or rubber-like above or below the glass transition temperature. Slow rates of testing will stimulate stiffer molecules and harder properties. The mechanical tests are classified as impact, tensile, flexural, hardness, etc. on the basis of applied deforming stress.

Among the mechanical properties tensile strength, thermal expansion, thermal conductivity, high temperature resistance and chemical resistance, which determine the suitability of a plastic for a mechanical application. The wear resistance, fatigue resistance and impact resistance are particularly most important in the field of mechanical applications.

Polyurethane is among the most versatile material, which is widely used in many versatile applications because of its excellent mechanical properties and processability. Many researchers have synthesized polyurethanes and investigated their mechanical properties.

29.A. Krause, A. Lange, M. Ezrin, ”Plastics Analysis Guide, Chemical and Instrumental Methods”, Harver Pub, New York, 1983

30. T.R.Crompton, “The Analysis of Plastics”, Pergamon Press, Oxford, 1984

31. R.P.Brown, “Physical Testing of Rubbers”, Applied Science, London, 1979

MEASUREMENTS

The mechanical testing (tensile strength) was made on Instron Universal Testing Machine, Model No. 1185 (IS: 11298-Pt2-1987) at a testing speed of 50 mm/min by using 15mm wide strips. Of great importance in mechanical testing are the conditions in which the forces are applied. The loading can be considered basically static as in structure such as a bridge or building or dynamic as in an aero plane wing or in an oil-well drill rod. The strength of a material subject to dynamic loading is usually much less than its strength under the static loading.

A few mechanical tests have become popular because the results have been correlated well with performance data from a variety of applications. American Society for Testing Material (ASTM) has standardized several testing procedures for more universally accepted mechanical properties.

Mechanical properties

The mechanical properties of polymers can be divided in to three types:

(1) Reversible mechanical properties

(2) Mechanical failure, and

(3) Complex mechanical properties

The tensile behavior of polymer is probably most fundamental mechanical property used in the evaluation of polymers. The tensile strength of a material is the ratio of the stress applied to the material at the rupture to its original cross-sectional area. This property is typically called the ultimate tensile strength i.e. the strength at break.

RESULTS AND DISCUSSION

The comparative tensile strength of RAERPU-1, RAERPU-2, RAER-3-20% PEG and RAER-3-30% PEG films were determined according to Eqn. 3.6 and are reported in Table-3.14 with some useful plastics.

$$\text{Tensile strength} = \frac{\text{Load at break(g)} \times 10}{\text{Thickness in mm}} \qquad \textbf{...3.6}$$

Table-3.14: Tensile strength of copolyurethanes and some useful plastics [32]

Polymer	**Tensile strength, MPa**	**Polymer**	**Tensile strength, MPa**
Nylon-66	62-82.7	PP	32
PMMA	48.3-75.8	Teflon	13.8-34.5
UF-R	70	ABS	0.24-0.43
PC	55.2-65.5	RAERPU-1	37.4
PF-R	50	RAERPU-2	18.7
PS	50	RAER-3-20%PEG	33.0
PVC	49	RAER-3-30%PEG	4.5

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32. P. Ghosh, "Polymer Science and Technology of Plastics and Rubbers", Tata McGraw Hill Publishing Co. Ltd, New Delhi, 1982.

From Table-3.14, it is clear that RAERPU-1, RAERPU-2, RAER-3-20% PEG and RAER-3-30% PEG possess good to comparable tensile strength with other plastics. From the Table-3.14, it is observed that the tensile strength of RAERPU-1 is almost double than that of RAERPU-2. The rigid nature of RAERPU-2 is due to restricted free rotation of bulky cyclohexyl groups in polyurethane chains. In polyurethane ricinoleic acid moiety imparts chain flexibility, while polyester polyol moiety imparts chain rigidity to some extent due to partly aromatic nature. So when load is applied to the film, flexible moiety throws it away to the rigid part and consequently stress is concentrated at that point resulting in rupture at low load. The low tensile strength of RAERPU-2 is due to its rigid nature.

While in case of other copolyurethanes, it is observed that the tensile strength decreased with increasing amount of PEG-400. The observed decrease in tensile strength is due to incorporation of increasing PEG-400 soft segment in the chains, which imparted the flexibility of the copolyurethane network. When the load is applied to the film, because of high flexibility stress is concentrated at the junction of rigid and soft segments resulting in rupture at low load. Thus, due to lack of mutual coordination between hard and soft segments resulted non uniform stress distribution and hence caused decrease in mechanical properties especially tensile strength.

ELECTRICAL PROPERTIES OF POLYURETHANES

INTRODUCTION

Till about the first few decades of the twentieth century, insulator items consisted primarily of glass, wood, paper, rubber, asphalt, mica, amber and related materials mostly of natural origin. The availability of a large spectrum of synthetic polymers has changed our option in this regard quite remarkably. Matter can be classified according to its specific conductivity into electrical insulators, semiconductors and conductors. Macromolecules with certain constitutional characteristics possess semiconductor properties. The majority of the commercially used polymers however are insulators. For common organic polymers, high resistivity of the order of 10^{12} to 10^{18} Ohm cm is typical and decrease on addition of conducting fillers. The electrical resistivity also depends on the frequency and voltage.

For electrical applications, the selection is required to be made on the basis of evaluation of electrical property parameters. The basic properties of dielectrics are dielectric constant or permittivity, dielectric breakdown voltage, dielectric strength, volume conductivity, volume resistivity, dielectric loss, power factor and surface resistance, etc. The choice of dielectric for each particular purpose is determined by the temperature and electric field frequency dependencies of these quantities.

MEASUREMENTS

Electric strength (ASTM-D149-92) and volume resistivity (ASTM-D257-92) measurements were done respectively on a high voltage tester (Automatic Electric Mumbai) in air at 27^0C by using 25/75 mm brass electrodes and Hewlett Packard high resistance meter at 500 V DC after charging for 60 sec.

RESULTS AND DISSCUSION

(1) Volume resistivity

A good insulating material is one that offers a high electrical resistance under a variety of conditions. Volume resistivity of a material is the resistance between opposite faces of unit cube when the current flow is confined to the volume of rest specimen. This quantity is defined [33] as the ratio of the potential gradient that is the electric field strength E, in a specimen to the current density.

The volume resistivity ρ_v is proportional to the volume resistance R_v. the quantity that is reciprocal of ρ_v is known as the volume conductivity:

$$g_V = 1/\rho_V \qquad \textbf{... 3.7}$$

33.O.M. Kazarnovasky, “Testing of Electrical Insulating Materials”, Mir Pub.Moscow, 1982

In measuring R_v of a flat specimen, we determine the volume resistance of the specimen portion confined between the guarded and the unguarded electrode. In this case the calculated (effective) diameter d_m is equal to the arithmetic mean of d_1 and d_2:

$$d_m = (d_1+d_2) / 2 \qquad \textbf{...3.8}$$

where, d_1 is the diameter of the guard electrode and d_2 is the inner diameter of the ring shaped guard electrode.

The resistance R_v of the flat specimen is expressed in the form:

$$R_v = \rho_v . 4t / p (d_m)^2 \qquad \textbf{...3.9}$$

Where d_m is the diameter of the electrode and t is the thickness of the specimen. If R is measured in Ohm cm and t and d_m in meters the unit of measurements of ρ is the Ohm m. From Eqn. 3.10

$$\rho_v = 0.785 R_v (d_m)^2 / t \qquad \textbf{... 3.10}$$

Most high polymeric materials are very good to excellent insulating materials and they are less subject to conduction by imperfection and structural irregularities than other types of insulating materials such as ceramics in view of the polymeric materials being non-porous or of very low porosity in comparison. The ductility of many of polymeric insulators and the great control in keeping them free from ionic and metallic impurities during synthesis and progressing are also added factors in their favor.

Humidity affects the volume resistance of different insulators to markedly different extents. Non-polar polymers such as polystyrene and polyethylene are unaffected but the moisture measurably affects polar organic polymers. The extent to which they are affected depends on the degree of their moisture absorption and consequent solvation. Porosity favors moisture absorption and lowers volume resistance. Polar inorganic polymers such as quartz and glass however remain practically unaffected by moisture if they are non-porous because they undergo little solvation. Resistance of polymeric insulators suffers appreciably with increase in temperature. Volume resistivity or conductivity can be used as an aid in designing insulators for a specific application.

The change of resistivity with temperature and humidity may be great [34-36] and must be known when designing for operating conditions. Volume resistivity or conductivity determination are often used in checking the uniformity of insulating materials, either with regard to processing or to detect conductive impurities that affect the quality of the material and may not be readily detectable by other methods.

(2) Dielectric breakdown voltage or dielectric strength

The working voltage applied to an electrical insulating material must be much lower than the voltage, which causes the material rupture. Electrical breakdown results from an electrical discharge through a material at a minimum voltage called breakdown or disruptive voltage V_{br}. In some cases voltages for lower than the breakdown voltage give rise to a surface discharge that does not penetrate deep into the bulk of a material.

This is a surface or creeping, breakdown occurring at a surface breakdown voltage. Breakdown voltage is dependent on the duration and the rate of voltage application, thickness of the test sample, frequency of the applied voltage, temperature, dimensions and geometry of the electrodes and also the nature of the prevailing environmental conditions.

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.

34.H.L. Curtis, "Insulating Properties of Solid Dielectric", Bulletin, National Institute of Standards and Technology, Vol. **11**, 1915.

35.R.F. Field, "How Humidity Affects Insulation, Part-I, D.C. Phenomena", General Radio Experimenter, Vol. **20,** 1945

36. R.F. Field, "The Formation of Ionized Water Films on Dielectrics under Condition of High Humidity", J. Appl. Phys. Vol.**5**, 1946.

The calculation of breakdown strength requires the measurement of 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 [33].

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,

$$E_{br} = \frac{U_{br}}{t} \qquad \textbf{… 3.11}$$

Where, t is the thickness of the material. Thus, the determination of breakdown 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 mil (0.001 in) or volts per millimeters.

The voltage required to produce breakdown is dependent on many factors. The electric strength is influenced by various factors such as duration and rate of the voltage application, thickness of sample, frequency of the applied voltage, temperature, dimensions and geometry of the electrodes and nature of the prevailing environment.

Dielectric strength determinations are 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 strength in thin sections.

(3) Dielectric constant

Dielectric constant e' is defined as the ratio of capacitance C of a condenser filled with the dielectric to capacitance C_o of the same condenser with air as the dielectric:

$$e' = C / C_o \qquad \textbf{… 3.12}$$

The dielectric constant is measured in alternating field and depends on frequency and temperature. The mechanical analog of dielectric constant is the stiffness modulus. Most of the non polar polymers have dielectric constant of about 2-3. Introduction of polar and H-bonding considerably increases the dielectric constant of the polymer up to 10-12 and at the same time, introduction of polar groups increases the leakage current and the electrical energy is dissipated as heat. The dissipation factor tan d is a measure of the hysetresis in charging and discharging a dielectric. It is related to the dielectric loss e"

$$Tand = e'' / e' \qquad \textbf{…3.13}$$

The use of polymers in engineering as dielectrics is becoming increasing by important choice of the dielectric for each concrete case depends on its dielectric and other physical properties over a wide range of temperatures and electric field frequencies. Investigation of dielectric properties is one of the most convenient and sensitive methods of studying polymer structures.

The observed electrical strength and volume resistivity of RAERPU-1, RAERPU-2, RAER-3-20%PEG and RAER-3-30%PEG are listed in Table-3.15 along with some useful plastics [32], from which, it is clear that the electric strength and volume resistivity of RAERPU-1 are 80.7 kV/mm and 1.7 x 10^{15} ohm cm, while for RAERPU-2 they are 44.4 kV/mm and 2.18 x 10^{15} ohm cm, respectively. In case of RAER-3-20%PEG and RAER-3-30% PEG the electric strength and volume resistivity are 57.2 kV/mm and 4.6 x 10^{12} ohm cm and 43.1 kV/mm and 2.7 x 10^{12} ohm cm, respectively.

Tablel-3.15: Electrical properties of copolyurethanes and some useful plastics.

Polymer	**Electric strength kV/mm**	**Volume resistivity Ohm cm**
Acrylics	17.7 – 21.6	> 10^{14}
Cellulose acetate	10.2 -14.4	10^{12} – 10^{13}
Cellulose acetate butyrate	9.8 – 15.7	10^{10} – 10^{13}
Nylon-6	17.3 – 20.0	10^{12} -10^{13}
PF-R	7.9 – 16.7	10^{9} -10^{12}
PVC	55.1	10^{13}
Polyacetals	18.3	6 x 10^{14}
Cellulose propionate	11.8 – 17.7	10^{12} -10^{15}
RAERPU-1	80.7	1.7 x 10^{15}
RAERPU-2	44.4	2.18 x 10^{15}
RAER-3-20%PEG	57.2	4.6 x 10^{12}
RAER-3-30%PEG	43.1	2.7 x 10^{12}

The decrease in electrical properties in case of RAER-3- 20% PEG and RAER-3-30%PEG are mainly due to cross link density besides many more factors. As a result of incorporation of soft segment in polyurethane chains caused decrease in electric strength and volume resistivity. Inter chain distances in network is more due to PEG-400 segment, which imparted flexibility of network linkages. Thus, the structure of copolyurethanes affected electrical properties. Also large distances among polar groups, in polyurethane restricted partial charge transfer and hence resulted in good to excellent electrical properties signifying their usefulness as insulators in electrical and electronic industries.

SECTION-8: CHEMICAL RESISTANCE OF THE POLYURETHANES

Nonmetallic materials including textiles, wood, paper, plastics, elastomers, coatings, leather and ceramics are more widely used than metals. The nonmetallic materials are also subject to deterioration. The resistance of glass, cellulose and many organic polymers is related to the proportion of crystalline and amorphous region.

The chemical stability of a plastic is evaluated by change in the mass, linear dimensions and mechanical properties of material in the stress free state and also by the tendency to splitting in the stress-strain state after the samples has been exposed to reagents for a definite length of time [37, 38].

Test specification such as procedure of conditioning a specimen for testing purpose, concentration of reagents, time and temperature of testing, apparatus and instrument should be described in more detail for chemical resistance. The recommended reagents for testing chemical resistance of plastics are reported in Table-3.16. Other reagents used for testing plastics for chemical resistance are oleic acid, methanol, acetone, 1,2-dichloroethane (DCE),

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37.R.B. Seymour, “Treatise on Analytical Chemistry”- Interscience publication, New York, Vol III, pp 341-391

38.O.M. Kazarnovasky, B.M. Tareev, I.O. Forsilova and L.I. Lyuimov, “Testing of Electrical insulating materials” Mir Publishers , Moscow 1982.

Table-3.16: Recommended reagents and their concentrations for chemical resistance of plastics

Reagent	**Conc., %**
Sulfuric acid (1.84 g/cc)	3,30,100
Nitric acid (1.42g/cc)	10,40,100
Hydrochloric acid (1.91g/cc)	10,100
Chromic acid	40
Acetic acid	5,100
Citric acid	10
Sodium hydroxide	1,10,60
Sodium chloride	3,10
Sodium hypochlorite	10
Sodium carbonate	2,20
Ammonium hydroxide	-
Hydrogen peroxide	3,30
Ethyl alcohol	50,96
Phenol	5

carbon tetrachloride (CCl_4), heptane, benzene, toluene, aniline, mineral oil, transformer oil, olive oil, kerosene, gasoline, terpentine, 1%soap solution and other substances. The chemical resistance of material can be determined by change in mass, change in linear dimensions and by change in mechanical properties. A brief description of each method is described in Table 3.16.

(1) Chemical resistance by change in mass method

According to this method the change in the mass of a test specimen after exposure of a chosen reagent at temperature of 20^o, 40^o, 60^o, and 100^oC is determined. The test duration is dependent on the time required for plastic specimen to attain sorption, equilibrium or to loose stability in the test medium. The specimens are weighed after 12, 24, 36, 48, 96 and 128h and then every seven days. The specimen that has passed the test may either loose or gain in mass. The chemical resistance of the material is determined by averaging the changing in mass of several specimens.

The test specimen for molded or extruded plastics is in the form of a disc (50mm in diameter and 3mm in thickness). The specimens are cut from laminated or sheet plastics, the end faces of the laminated specimens are coated with same binder as used in the production of material in questions. In case of rod samples, a length of rod should be 50mm and diameter should be < 50 mm. A reagent is taken in amount of 8 ml per cm^2 surface area of plastic sample free from extractable substance and it is 20 ml per cm^2 surface area of an extractable plastics sample.

After loading the specimen in the bath, the reagent is mixed or stirred at least once in a day. After every seven days specimens are removed from the reagents once at a time, washed, wiped, dry and weighed. A percentage increase or decrease in the mass of a specimen is determined according to Eqn. 3.14

$$?M= [(M_2-M_1)/M_1] X100 \qquad \textbf{... 3.14}$$

Where ?M is the change in the weight, M_1 and M_2 are the weights of the specimen before and after immersion in the given reagent.

(2) Chemical resistance by change in linear dimensions

The method is based on change in linear dimensions of specimen after prolong exposure to a reagent. The form, size and no of specimens and the quantity of reagent must remain same as in the change in the mass method.

Before testing the thickness of central portion of the disc and two mutually perpendicular diameters of each specimen are measured after every seven days, the specimens are taken out from the bath, washed, wiped with a cloth and checked for the dimensions at the same place. A change in any of the linear dimensions in percent is determined according to following Eqn. 3.15.

$$?l= (l_2-l_1/l_1)\ X100 \qquad \textbf{... 3.15}$$

Where, l_1 and l_2 are linear dimensions of the specimens before and after immersion in the reagent.

(3) Chemical resistance by change in mechanical properties

This method is based on the stability of mechanical properties of plastics under prolonged exposure to reagent. The form, dimensions and number of specimens for plastic materials are chosen in compliance with the standard. After exposure to a reagent, the specimens are washed, wiped and tested for one or two most important characteristics such as tensile strength, flexural strength, impact strength, hardness, %elongation at break and mechanical stress in bending that causes a deflection equal to1.5 fold thickness of specimen. The relative change in mechanical properties may serve as a basis for dividing plastics into three groups as shown in Table-3.17.

In present investigation the hydrolytic stability of RAERPU-1, RAERPU-2, RAER-3-20% PEG and RAER-3-30% PEG films were determined by the change in weight method. For this purpose preweighed polymer films were immersed in pure water and 10% each of aqueous solutions of hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, potassium hydroxide and sodium chloride at room

Table -3.17: Stability characteristic of plastics on exposure to reagents

Type of plastics	**Relative change in mechanical stability characteristics, %**	
	Strength properties	**Deformation**
Thermoplastics	0-10 10.1-20 over 20	0-10……….Good 10.1-20….Adequate over 20……..Poor
Thermosets	0-15 15.1-25 over 25	-……….Good -……….Adequate -……….Poor

temperature at the interval of 24h for 15 days. For this the polymer films were taken out, washed, wiped, dried and weighed and reimmersed .The change in weight of film was evaluated according to equation 3.14. The comparative percentage weight loss or gain after regular interval of 24h was determined and reported in Tables-3.18- 3.21.

From Table- 3.18, it is observed that in HCl solution polyurethane film of RAERPU-1 has remained unaffected up to 24h but after that it has shown water absorption tendency. It gained weight up to 72h and then remained constant (6.4%). In H_2S0_4 solution it remained unaffected throughout the test but in HNO_3 solution it showed weight gain tendency up to 72 h and then remained constant (8.3%) and the film became yellowish after 6 days indicating nitration of aromatic rings. In NaCl solution, the film remained unaffected up to 48 h and then it showed weight gain tendency up to next 24 h and gained maximum weight (8.3%). Similarly in NaOH and KOH solutions, it remained unaffected up to 24h and then weight gain increased up to 72h and then remained constant. The equilibrium weight gain in NaOH solution is 6.6%, while it is 13% in KOH solution.

From Table-3.19 it is observed that the film of RAERPU-2 polyurethane remained unaffected in HCl, HNO_3 and H_2SO_4 solutions but it became yellowish after 7 days in HNO_3 solution. In NaCl medium it remained unaffected up to 13 days and gained equilibrium weight (2.4%) within next 24 h. In NaOH and KOH solutions, the film remained unaffected up to 8 days and gained equilibrium weights 4.8% and 1.9%, respectively. Both the films remained unaffected in water environment.

The weight gain tendency of both the film is probably due to micro cracks and partly surface solvolysis of polar groups by different electrolytic solutions. The absorbed moisture may induce the irreversible changes like chemical degradation, cracking and debonding. Cracking and blistering cause high water absorption, while leaching of small molecules results decrease in weight. Ether, ester and urethane linkages are polar groups and contain lone pairs of electrons, which may form H- bonds with solvated water molecules. The presence of electrolytes affect the water structure and hence moisture uptake behavior of the polyurethanes.

Table-3.18: Chemical resistance of RAERPU-1 film by change in weight method at room temperature

Time (h)	**H_2O**	**NaCl**	**NaOH**	**KOH**	**HCl**	**H_2SO_4**	**HNO_3**
24	0.00	0.00	0.00	0.00	3.3	0.00	4.14
48	0.00	0.00	3.3	8.65	6.64	0.00	8.29
72	0.00	8.26	6.54	12.98	6.64	0.00	8.29
96	0.00	8.26	6.54	12.98	6.64	0.00	8.29
120	0.00	8.26	6.54	12.98	6.64	0.00	8.29
144	0.00	8.26	6.54	12.98	6.64	0.00	8.29
168	0.00	8.26	6.54	12.98	6.64	0.00	8.29
192	0.00	8.26	6.54	12.98	6.64	0.00	8.29
216	0.00	8.26	6.54	12.98	6.64	0.00	8.29
240	0.00	8.26	6.54	12.98	6.64	0.00	8.29
264	0.00	8.26	6.54	12.98	6.64	0.00	8.29
288	0.00	8.26	6.54	12.98	6.64	0.00	8.29
312	0.00	8.26	6.54	12.98	6.64	0.00	8.29
336	0.00	8.26	6.54	12.98	6.64	0.00	8.29
360	0.00	8.26	6.54	12.98	6.64	0.00	8.29

Table-3.19: Chemical resistance of RAERPU-2 film by change in weight method at room temperature

Time (h)	**H_2O**	**NaCl**	**NaOH**	**KOH**	**HCl**	**H_2SO_4**	**HNO_3**
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00
72	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.00	0.00
144	0.00	0.00	0.00	0.00	0.00	0.00	0.00
168	0.00	0.00	0.00	0.00	0.00	0.00	0.00
192	0.00	0.00	4.8	1.9	0.00	0.00	0.00
216	0.00	0.00	4.8	1.9	0.00	0.00	0.00
240	0.00	0.00	4.8	1.9	0.00	0.00	0.00
264	0.00	0.00	4.8	1.9	0.00	0.00	0.00
288	0.00	0.00	4.8	1.9	0.00	0.00	0.00
312	0.00	0.00	4.8	1.9	0.00	0.00	0.00
336	0.00	0.00	4.8	1.9	0.00	0.00	0.00
360	0.00	0.00	4.8	1.9	0.00	0.00	0.00

Thus, low water uptake tendency of RAERPU-2 is probably due to somewhat more hydrophobic character than that of RAERPU-1.

Upon comparing above mentioned results clearly indicates the profound stability and low water uptake tendency of RAERPU-2 signifying its superior importance as a coating and adhesive material. Under harsh conditions, it is observed that both the copolyurethane films remained unaffected in water and saline environments, while in acidic and alkaline environments they gained weight within 24-48 h.

From Table-3.20 it is clear that RAER-3-20%PEG film has gained 14.2% weight in NaOH and KOH environments and 6.6% weight in HCl environment within 24h, while in H_2SO_4 and $HN0_3$ environments it gained 12.4% and 15.3% weight, respectively within 24h. In water and saline environments it remained unaffected.

From the Table-3.21, it is observed that the RAER-3-30%PEG film has gained 8.7% weight in NaOH, 4.7% in HCl and 8% in H_2SO_4 environments within 24h, while it gained 9% weight in KOH environment within 72h and 11.7% weight in HNO_3 environment within 48h. In water and saline environments it remained unaffected.

From the above mentioned data, it is clear that % weight gain in acidic and alkaline environments has decreased marginally with increase in PEG-400 content in co polyurethane. Increase in weight is probably due to unreacted hydrophilic carboxyl and hydroxyl groups, micro cracks and surface solvolysis due to highly electronegative urethane and ester linkages. From the observed fact it is clear that Na^+ and K^+ ions have almost same surface solvolysis effect but it is quite different in acids. The observed order is $HCl < H_2SO_4 < HN0_3$. Blistering can also increase the % weight gain. Thus, both films possess excellent resistance against water and 10% NaCl solution. They have moisture uptake and surface solvolysis tendency in acidic and alkaline conditions. Excellent hydrolytic stability of polyurethane and copolyurethane films in harsh conditions signify their applications in coating and adhesive industries.

Table-3.20: Chemical resistance of copolyurethanes of RAER-3-20%PEG film by change in weight method at room temperature

Time (h)	**H_2O**	**NaCl**	**NaOH**	**KOH**	**HCl**	**H_2SO_4**	**HNO_3**
24	0.00	0.00	14.18	14.21	6.62	6.21	7.63
48	0.00	0.00	14.18	14.21	6.62	12.42	15.26
72	0.00	0.00	14.18	14.21	6.62	12.42	15.26
96	0.00	0.00	14.18	14.21	6.62	12.42	15.26
120	0.00	0.00	14.18	14.21	6.62	12.42	15.26
144	0.00	0.00	14.18	14.21	6.62	12.42	15.26
168	0.00	0.00	14.18	14.21	6.62	12.42	15.26
192	0.00	0.00	14.18	14.21	6.62	12.42	15.26
216	0.00	0.00	14.18	14.21	6.62	12.42	15.26
240	0.00	0.00	14.18	14.21	6.62	12.42	15.26
264	0.00	0.00	14.18	14.21	6.62	12.42	15.26
288	0.00	0.00	14.18	14.21	6.62	12.42	15.26
312	0.00	0.00	14.18	14.21	6.62	12.42	15.26
336	0.00	0.00	14.18	14.21	6.62	12.42	15.26
360	0.00	0.00	14.18	14.21	6.62	12.42	15.26

Table-3.21: Chemical resistance of copolyurethanes of RAER-3-30% PEG film by change in weight method at room temperature

Time (h)	H_2O	NaCl	NaOH	KOH	HCl	H_2SO_4	HNO_3
24	0.00	0.00	8.65	4.52	4.73	7.96	2.92
48	0.00	0.00	8.65	4.52	4.73	7.96	11.69
72	0.00	0.00	8.65	9.04	4.73	7.96	11.69
96	0.00	0.00	8.65	9.04	4.73	7.96	11.69
120	0.00	0.00	8.65	9.04	4.73	7.96	11.69
144	0.00	0.00	8.65	9.04	4.73	7.96	11.69
168	0.00	0.00	8.65	9.04	4.73	7.96	11.69
192	0.00	0.00	8.65	9.04	4.73	7.96	11.69
216	0.00	0.00	8.65	9.04	4.73	7.96	11.69
240	0.00	0.00	8.65	9.04	4.73	7.96	11.69
264	0.00	0.00	8.65	9.04	4.73	7.96	11.69
288	0.00	0.00	8.65	9.04	4.73	7.96	11.69
312	0.00	0.00	8.65	9.04	4.73	7.96	11.69
336	0.00	0.00	8.65	9.04	4.73	7.96	11.69
360	0.00	0.00	8.65	9.04	4.73	7.96	11.69

This chapter of the thesis describes the surface coating and chemical resistance measuments of polyurethane resins on various substrates such as glass, copper, steel and aluminium.

INTRODUCTION

A coating is a covering that is applied to an object to protect it or change its appearance. They may be applied as liquids, gases or solids.

Ancient painted walls, to be seen at **Dendera, Egypt**, although exposed for many ages to the open air, still possess a perfect brilliancy of color, as vivid as when painted, perhaps 2000 years ago. The Egyptians mixed their colors with some gummy substance, and applied them detached from each other without any blending or mixture. They appeared to have used six colors: white, black, blue, red, yellow, and green. They first covered the field entirely with white, upon which they traced the design in black, leaving out the lights of the ground color. They used minimum red and generally of a dark tinge.

A brief look into the background of surface coatings industry gives an understaning of the position of polyurethane resins hold in this field today. At the outset it should be noted that the formulation and the manufacture of the coatings are going through the period of transition from a craft type of endevor to a scientifically regulated industry. For many years natural sources were the basis for the polymers and film forming materials used in paint and varnishes. Paint making at that time was a typical craft, with artists and painters mixing their own paints from pigment and oil.The properties of the finished product depended to a great degree on their judgement and experience.

Today coatings are not just used for decorative purposes but are used in almost ever facet of the human life. Applications of the sophisticated primers, surfaces and top coats have greatly increased the life of coated article. Coatings have also triggered the development in the field of marine, automobile, architectural, maintenance and fiber optics coatings. Also specifically coatings that control absorption or emission for temperature control, aircraft coatings that withstand the effect of UV radiation, absorption and the impact of air and dirt [1].

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1. J.H. Boatwright: Organic Coating,”Their Origin and Development”, R.B. Seymour and H.F. Mark, Elsevier, p-9, New York, 1990.

There are generally four components of paint and coatings: binder, diluent, filler, and additives. However, only the binder is absolutely required. The binder is the part, which eventually solidifies to form the dried paint film.

The diluent serves to adjust the viscosity of the paint. It is volatile and does not become part of the paint film. It remains as an additive.

Typical binders include synthetic or natural resins such as acrylics, polyurethanes, polyesters, melamines, epoxy, or oils. There are different kinds of binders: those that simply "dry", and those that undergo polymerization reactions. Binder that dries to form a solid film, when the solvent evaporates. Some polymerize into irreversibly bound network structures, which will not redissolve in the solvent.

Typical diluents include organic solvents such as alcohols, ketones, esters, glycol ethers, and the like. Water is a common diluent. Sometimes volatile low-molecular weight synthetic resins also serve as diluents.

Fillers serve to thicken the film, support its structure and simply increase the volume of the paint. Not all paints include fillers. Pigments that also function as fillers are called simply "pigments"; "fillers" are generally colored, neutral and opaque. It is necessary to adjust the resulting off-white color with pigments to give the desired color. Common fillers are cheap and inert, such as talc, lime, baryte, bentonite clay, etc. Depending on the paint, most of the paint films may consist of filler and binder, the rest being additives.

Typical additives include pigments, dyes, catalysts, thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, flatteners (de-glossing agents), and the like. Key developments in coating industries

- Early chemists relied on natural products for varnishes based on fossilized resins and natural oil.
- The attempts have been made to modify the natural resins to produce synthetic natural products.
- Another key development of rubber and then phenolic resin followed by alkyd, urea and melamine formaldehyde resins.

- Other 'Leap frog' achievements came in around 1944-silicone based paints and in 1947-epoxy resins.
- There after the coating industry was revolutionized by development of PVA and acrylic lacquers, powder coatings, water-borne paints, UV-cure coatings, cationic electro coatings and clear-over color top coats.

The high degree of cross-linking in the cured structure produces hardness, strength, heat-resistance, electrical resistance and broad chemical resistance. These properties are important in coatings, adhesives and reinforcements [2].

Polyurethanes are macromolecules or polymers formed by the reaction between a polyisocyanate and other polymer (commonly known as polyol) that contains active hydrogens (OH, COOH…). The choice of raw materials, both polyols and polyisocyanates are very large enabling many combinations with wide varieties of properties. There have been many developments in the 60 or so years and today polyurethanes are used in a wide range of applications such as foams, elastomers and coatings.

Polyurethanes were initially used to manufacture foams and plastic compounds, largely used in the Second World War II as thermal and sound insulation for German submarines.

The polyurethane coatings were first developed in the 1950's, when toluene diisocyanate derivatives were first manufactured on a large scale. Hexamethylene diisocyanate (HMDI) derivatives were patented in 1958, and first manufactured in a continuous process in 1967, leading to the development of new color stable coatings.

Rapid progress followed, enabling car manufactures to use polyurethane coatings. In 1967, Matra produced an all- plastic car finished in a two- pack polyurethane topcoat. This was followed in 1968, by German Railways using two-pack polyurethane to coat locomotives and passenger carriages. In 1970 polyurethane coatings were introduced for vehicle repair applications.

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2. R.D. Deanin, "Polymer Structure, Properties and Applications", Cabners books, division of Cabners Publishing Company, Inc., 1972.

Now a days polyurethane coating are used in numerous industrial applications and on a wide variety of substrates:

- Automotive industry: OEM, on line repair, refinishes.
- General industry: protective coatings, defense coatings, coil coatings.
- Other transportation: aerospace, trains, commercial vehicles.
- Plastics: car bumpers, dash-boards, computers.
- Industrial wood: kitchen furniture and flooring.
- Adhesives: sealants and sealers.

The automotive industry is the largest user of polyurethane coatings, using 30% of total volume. The breakdown markets for polyurethane coatings in Western Europe are shown in the Table-4.1.

With the evolution of legislation towards the reduction of VOC's, polyol and polyisocyanate procedures have worked with paint manufactures to develop low VOC complaint coatings. In, 1985, high solids two-pack polyurethane coatings were used as topcoats by Mercedes Benz, and 1989 saw the development of the first water-borne two-pack polyurethane coatings.

Polyurethane coatings are available in both one and two pack forms. A two component coatings will be simplified with the polyol, pigments, solvents and additives in one pack and the isocyanate in a second pack to be added and mixed just before use. When the two components are mixed together, the cross linking reaction begins, causing an increase in paint viscosity. Eventually, the viscosity increases in such that the coatings become unusable. This limit of use is known as the pot life and is normally expressed either as the time taken for coating to dwell or time taken for a specific viscosity increase. The pot life can vary enormously between one and eight hours. The pot life can be affected by type of polyol and polyisocyanate, NCO/OH ratio, temperature, solvent, level of catalyst, etc.

A one component coating is supplied with all the raw materials in the same pack. Two main types are available: moisture cured and blocked polyurethanes. Other radiation curing processes such as UV and electron beam can also be used to cure polyurethanes, blocked with specific protecting groups, polyurethane acrylates.

Table-4.1: European markets for PU coatings

Market Sector	**% Share**
Automotive Refinish	25%
General Industry & Maintenance	25%
Wood / Furniture	24%
Building & Civil Engineering	8%
Plastic Coatings	5%
Textiles / Leather	5%
Automotive OEM	3%
Commercial Vehicles	2%
Marine / Offshore	2%
Aviation	1%

The properties of the urethane network give polyurethane (PU) coatings with outstanding properties:

- Excellent mechanical properties

Due to the rapid elasticity of the urethane network, PU coatings can withstand extreme mechanical forces even at very low temperatures. They find their uses in aerospace for coatings.

- Excellent chemical resistance

The stability of the urethane network will provide resistance to chemicals as well as outdoor weatherability. Hence PU coatings are widely used in heavy duty protective coatings.

- High reactivity

The rapid reaction between polyol and polyisocyanate leads to the formation of a dense network even at room temperatures. This enables paint application outside, for example on petrochemical installations, and on heat sensitive substrates such as thermoplastics.

Under the ASTM D16 norm, the American Society for Testing and Materials has classified the polyurethane coatings into six categories as described in the Table-4.2.

1. Two – component polyurethanes (2K PU)

The first class covers the “true polyurethane” binders, i.e. those obtained through the cross linking of a hydroxylated resin by a polyisocyanate hardener.

This system is known as two pack (or twin or 2k) because the polyol and the polyisocyanate crosslinker are supplied in two different packages. In general part-A contains the hydroxylated resin plus pigments and additives such as dispersing agents, flow and leveling additives, UV absorbers, etc. Part-B also called as hardener or sometimes “catalyst” contains the polyisocyanates derivatives and occasionally additives designed to protect the isocyanates against the humidity. Solvents are added to both the part to achieve the desired viscosity. The two components are mixed together before use, either by manual stirring or by plural component pump. The mixed coating must be applied within the pot life of the resin.

Table-4.2: Classification of polyurethanes

ASTM-D16 classification	**Category**	**Curing process**
1	Oil modified urethanes	Oxidation of double bonds
2	Moisture cure PU	Reaction with moisture
3	Blocked urethanes	Thermal unblocking
4	Prepolymer + catalyst	Reaction with moisture
5	Two pack urethanes	NCO + OH reactions
6	Urethane lacquers	Physical drying

This reaction allows a great deal of flexibility in terms of drying conditions. This is due to very reactive isocyanate group, which is able to crosslink with hydroxylated resins over a wide range of temperatures or allowing air drying systems. The two component polyurethane system can achieve a very high performance level after drying. The drying time of two components polyurethane coating depends upon the type of the polyisocyanate used, which is shown in the Table-4.3. It is widely used to paint heat sensitive materials such as thermoplastics and heavy equipments such as tractors, which cannot be coated by thermosetting paints. Two pack polyurethane show very good resistance to water, aqueous chemicals and organic solvents. In case of water satisfactory formulations will show very good performance in immersion conditions. Thermal stability of these coatings is very good up to 180^0C. The most striking feature of the two pack PU coatings is their excellent weather ability and chalk resistance in comparison with other finish coatings.

The two pack polyurethane coatings give some excellent properties including

- Long pot life
- Very good chemical and stain resistance
- Excellent non yellowing (aliphatic isocyanates)
- Good mar resistance
- Long term flexibility
- Abrasion resistance
- Impact resistance
- High gloss

and in combination with the above properties relatively high solids can be obtained.

2. Polyurethanes for oven curing (1K PU)

This second family is similar to first one, but the isocyanate groups are protected by the blocking agents, which prevent the reaction with the hydroxyl groups at low temperatures. This allows the premixing of the two parts of the paint in a single pack with a very long shelf life. The blocking agent is released during the curing process.

Table-4.3: Relative drying times of two component PU coatings

Polyisocyanate	Relative drying time
TDI- Isocyanurate	1
TDI/HMDI- Isocyanurate	2
TDI- TMP adduct	6
HMDI- Biuret (with catalyst)	6
HMDI- Biuret (without catalyst)	30

Depending upon the nature of the isocyanates and nature of the blocking agents, unblocking temperatures can be as high as 200^0C or as low as 100^0 to 120^0C. A catalyst such as dibutyl tin dilaurate (DBTL) would then also be added at levels between 0.5 and 1%.

The basic rule of the formulation is the polyol must be non-yellowing on stoving and the solvents should have higher boiling points than those used in the two pack systems. The film possesses excellent hardness, abrasion resistance and solvent resistance.

3. Moisture cured polyurethanes

Moisture cured polyurethanes are one pack products with long pot lives. They use atmospheric moisture as crosslinking agents. This type of system is very old those based on aromatic isocyanates. Aliphatic polyurethanes are used in long durability topcoats, whilst aromatic based polyurethanes can be used in primers, undercoats or interior applications. The greater reactivity of aromatic isocyanates mean they have shorter drying times than aliphatic based products.

Formulations of moisture cure or one pack protective coatings provides products with many desirable properties. They are rapid drying even at low temperatures down to zero and below. They may also be applied at high humidities up to 100%. This allows for application under extreme conditions such as in fog and onto damp (but not wet) substrates. High humidity is advantageous to the curing of one pack moisture cured polyurethanes, since high moisture contents accelerate the drying process. To ensure satisfactory drying the minimum relative humidity should be 30%.

Moisture cured polyurethanes show very good surface tolerance and offer excellent adhesion to many substrates such as wood, concrete and metals because of reaction of isocyanate groups with the active hydrogen groups or moisture present in these materials. The coatings exhibit high resistance to water and chemicals, which make them suitable for immersion conditions and also in combination with cathodic protection.

This is widely used in open areas for painting large components, which can not be placed in an oven. Maintenance (offshore and marine topsides, motorway bridges, railway bridges and dock walls) and marine coatings are important markets for this type of technology.

Now a days polyurethanes are widely used in the textile coatings, leather and paper industries. Polyurethanes are being suitable for these applications because specific properties can be obtained during the application or from the finished material, i.e. by chemical crosslinking.

Polyurethanes are distinguished by their very good adhesion to different substrates and by high flexibility even at low temperatures. Their thermoplasticity (uncross-linked material) and resistance to most solvents are advantageous compared to the other polymers.

Polyurethane products for textile coating were first marketed in the fifties. At first small articles were produced but soon tent roofs, tent floors, blinds, ironing board covers, light rain coats and other products were manufactured.

The typical properties for polyurethane textile coatings are as follows:

- Leather like surface
- Warm comfortable touch
- Wash and cleaning stability
- Good adhesion between substrate and coating
- High elongation and elasticity
- Good abrasion resistance
- High flexibility at low temperature (without plasticizer)
- Very good resistance to oils and fats
- Low specific weight

Shamekhi and Yeganeh [3] have prepared versatile polyurethane material suitable as insulating coatings from novel kinds of polyhydroxy compounds (PHCs) via transesterification reaction of poly(ethylene terephthalate), different molecular weight of poly(ethylene glycol)s (PEGs), and castor oil. The final networks were prepared via crosslinking of polyhydroxy compounds with a novel

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3. M.A. Shamekhi and H. Yeganeh, “Novel polyurethane insulating coatings based on polyhydroxyl compounds, derived from glycolysed PET and castor oil”, J. Appl. Polym. Sci. **99**, 1222-1233, 2006.

blocked isocyanate curing agent made from trimethylol propane (TMP), toluene diisocyanate (TDI) and *N*-methyl aniline (NMA). Polyols and curing agent were characterized by conventional methods and the curing condition was optimized via gel content measurements. Curing kinetic of the polyurethane network formation was investigated by differential scanning calorimetric method and the kinetic parameters were derived. Crosslink density of the samples was determined via equilibrium swelling method and by using Flory-Rehner equations. Effects of crosslink density on electrical, physical, mechanical, and dynamic mechanical properties of the polyurethane coatings were investigated.

Mallu et al.[4] have synthesized interpenetrating polymer networks (IPNs) of polyurethane (PU)/polyacrylates have been synthesized by sequential polymerization of castor oil, methylene diisocyanate (MDI), and acrylate monomers such as methyl acrylate (MA), methyl methacrylate (MMA), and ethyl acrylate (EA); with benzoyl peroxide (BPO) and ethylene glycol dimethyl acrylate (EGDM) as an initiator and crosslinker, respectively and investigated the physico-mechanical properties, such as density, surface hardness, tensile strength, percentage elongation at break, and tear strength; and the optical properties, like total transmittance and haze, of PU/polyacrylate IPNs. Microcrystalline parameters of IPNs have been computed by using wide angle X-ray scattering (WAXS) recordings.

Cherian et al. [5] have modified unsaturated polyester resins (UPRs) by reactive blending with polyurethane prepolymers having terminal isocyanate groups and studied the effect of blending on various properties. Hybrid networks

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4. P. Mallu, S. Roopa, H. Somashekarappa, R. Somashekar and Siddaramaiah, “Studies on physico-mechanical and optical properties and WAXS of castor oil based PU/polyacrylates interpenetrating networks”, J. Appl. Polym. Sci. **95**, 764-773, 2005.
5. A.B. Cherian, B.T. Abraham, E.T. Thachil, “Modification of unsaturated polyester resin by polyurethane prepolymers”, J. Appl. Polym. Sci. **100**, 457-465,2006.

were formed by copolymerization of unsaturated polyesters with styrene and simultaneous reaction between terminal hydroxyl groups of unsaturated polyester and isocyanate groups of polyurethane prepolymer. The prepolymers were based on toluene diisocyanate (TDI) and each of hydroxy-terminated natural rubber (HTNR), hydroxy-terminated polybutadiene (HTPB), polyethylene glycol (PEG), and castor oil. Properties like tensile strength, toughness, impact resistance, and elongation at break of the modified UPRs show considerable improvement by this modification. The thermal stability of the copolymer is also marginally better.

Guhanathan et al. [6] have prepared tricomponent interpenetrating polymer network (IPN) systems involving castor oil, toluene diisocyanate (TDI), acrylonitrile (AN), ethylene glycol diacrylate (EGDA), and general-purpose unsaturated polyester resin (GPR) with various compositions. The mechanical properties such as tensile, flexural, impact, and hardness for the IPNs with various compositions were determined. It was found that the tensile strength of the GPR matrix was decreased and flexural and impact strengths were increased upon incorporating PU/PAN networks. The swelling properties in water and toluene were also studied. The morphology of the IPNs was studied using SEM.

Lenka et al. [7] have synthesized polyurethanes (PUs) by reacting castor oil with toluene-2,4-diisocyanate and hexamethylene diisocyanate and varying the NCO/OH ratio. All these polyurethanes were reacted with some acrylic monomers like ethyl acrylate, *n*-butyl acrylate, ethyl methacrylate, and butyl methacrylate using a crosslinker ethylene glycol dimethyl acrylate and benzoyl peroxide as the initiator. The physico-chemical properties of interpenetrating polymer networks (IPNs) were reported. Thermogravimetric analysis was used to

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6. S. Guhanathan, R. Hariharan and M. Sarojadevi, “Studies on castor oil-based polyurethane/polyacrylonitrile interpenetrating polymer network for toughening of unsaturated polyester resin”, J. Appl. Polym. Sci. **92**, 817-829, 2004.
7. S. Lenka, S.K. Panda, T. Pattnaik and P.L. Nayak, “Polymers from renewable resources. I.Castor oil-based interpenetrating polymer networks: Thermal and mechanical properties”, J. Appl. Polym. Sci. **47**, 1089-1096, 1993.

study the thermal behavior of IPNs and the evaluation of kinetic parameters. Degradation mechanism has also been investigated. Some of the mechanical properties viz. tensile strength, shore A hardness, elongation at break, etc. are also reported.

Ismail and Hussain [8] have synthesized adhesion of polyurethane (PU) coatings based on toluene diisocyanate, poly(propylene glycol) (PPG) 2000, polyethylene adipate (PEA) 2000 and castor oil (CO). The coatings were applied to glass slides with and without novalac primer (due to the high functionality of castor oil, the resultant PU coatings have limited shelf life). The studies showed that satisfactory adhesion strengths were achievable for immediate bonding. Furthermore, it was found that the adhesion of polyurethane to glass surfaces was increased by using a thin layer of novalac primer.

Rajan et al. [9] have synthesized three series of novel polyurethane elastomers containing phenolphthalein as chain extenders. The structure of the polyurethane was analyzed using IR and wide-angle X-ray diffraction studies. Tensile strength and percentage of elongation of all the series of polymers were studied. Thermal decomposition was studied using DSC.

Polus [10] has prepared polyurethane coatings by the "prepolymer mixing" method in two steps. The synthesis of the urethane prepolymer was carried out in presence of stannous 2-ethylhexanoate. The obtained prepolymer was exposed to the reaction with branched polyester polyols. This reaction was carried out in presence of the catalysts: DABCO, TEA and stannous 2-ethyl hexanoate. In the synthesis of polyurethanes the aliphatic diisocyanates with linear (TMDI) and cyclic (IPDI) structures were used. The polyurethanes obtained

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8. E.A. Ismail and M.H.M. Hussain, "Improvement of polyurethane adhesion to glass using novolac primer", J. Adhe. Technol. **16**, 1509-1513, 2002.
9. H. Rajan, P. Rajalingam, G. Radhakrishnan, "Synthesis and properties of segmented polyurethane using phenolphthalein as chain extenders", J. Appl. Polym. Sci. **48**, 2095-2099, 1992.
10. I. Polus, "Synthesis of polyurethane coating components with IPDI and TMDI", J. Mater. Sci. **61**, 238-240, 2003.

using these diisocyanates was oxidized. The changes in the quality were monitored by determining some properties of the cured coating, such as hardness, flexibility and scratch resistance.

Duffy et al. [11] have conducted studies on ternary blends consisting of poly(propylene oxide) and poly(methyl methacrylate co *n*-butyl methacrylate) blended with either poly(hexamethylene adipate) or poly(hexamethylene sebacate). These ternary blends formed the basis for preparation of high performance polyurethane-based hot-melt adhesives and coatings. Changes in polyester structure were found to strongly alter the miscibility behavior. Binary interaction parameters for the five polymer pairs were determined experimentally, permitting calculation of the phase behavior of the ternary polymer blends. Results predicted by the model are in excellent agreement with experimental observations. The influence of miscibility in the melt on the morphology development was also discussed.

Gite et al. [12] have synthesized polyurethane coatings from monoglycerides (MGs) of four oils (castor, linseed, soybean and sesame). These coatings were applied in the form of thin films on tin plates and analysed for various coating properties such as gloss, scratch resistance, flexibility and physico-chemical tests. A highly cross-linked product was obtained due to the higher functionality associated with MGs compared with their molecular weight. The trimer also imparted cross-linking due to its trifunctionality and a hard yet flexible, tough, glossy polyurethane coating was obtained.

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11. D.J. Duffy, H.D. Stidham, S. Sasaki, A. Takahara, T. Kajiyama and S.L. Hsu, “Effect of polyester structure on the interaction parameters and morphology development of ternary blends: Model for high performance adhesives and coatings”,J. Mater. Sci. **37**, 4801-4809, 2002.
12. V.V. Gite, R.D. Kulkarni, D.G. Hundiwale, U.R. Kapadi, “Synthesis and characterisation of polyurethane coatings based on trimer of isophorone diisocyanate (IPDI) and monoglycerides of oils”, Surface Coatings International Part B: Coatings Trans., **89**, 117-122, 2006.

Wounters et al. [13] have prepared polyurethane coatings with different network compositions in well-defined model systems as well as commercially-available formulations. The properties, such as glass-transition temperature, hardness and surface free energy of the model network were tuned by the choice of the ingredients. All coatings were studied with respect to their bulk properties as well as their surface properties. It was found that by the addition of a fluorinated additive, the surface free energy of the coating was lowered by approximately 15mNm^{-1}, leaving the bulk properties intact. It was also shown that these polyurethane coatings were able to adopt their surface free energy in a reversible manner, when exposed to water. The magnitude and rate of surface rearrangement was strongly dependent on the network density of the coating. The effect of coating properties on the formation of a biofilm and subsequent adhesion of diatoms was studied on a selection of the coatings used in this study, and the results obtained are discussed.

Shamekhi and Yeganeh [14] have prepared novel polyurethane insulating coatings from the reaction of glycerin-terminated polyurethane prepolymers (GPUPs) and a blocked isocyanate curing agent (BIC). The polyols and curing agent were characterized by conventional methods, while the curing condition was optimized via gel content measurements. The curing kinetics of the polyurethane coating was investigated and the kinetic parameters derived. The crosslink densities of the samples were determined via the equilibrium swelling method, using the Flory– Rehner equation. The relationships between the crosslink density and the electrical, physical, mechanical and dynamic mechanical properties of the coatings were also studied.

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13. M. Wouters, J. Zanten, T. Vereijken, D. Bakker, J. Klijnstra, "Fluorinated polyurethane coatings with adaptable surface properties",Surface Coatings International Part B: Coatings Trans., **89**, 23-30, 2006.
14. M.A. Shamekhi and H. Yeganeh, "Preparation and properties of novel polyurethane insulating coatings based on glycerin-terminated urethane prepolymers and blocked isocyanate", Polym. Inter., **54**, 754-763, 2005.

Paul et al. [15] have measured the elastic properties of films made of red oxide primers and polyurethane-based synthetic enamel paints. The measurements included the modulus of elasticity, Poisson's ratio, and strain energy. If taken into account, these findings may ultimately lead to improved primer-paint systems for the surfaces.

Ni et al. [16] have synthesized two series of polyesters with isomeric cyclohexane diacids. The first series of polyesters was synthesized with 1,4-cyclohexane dimethanol (CHDM) and three cycloaliphatic difunctional acids 1,4-cyclohexane dicarboxylic acid (1,4-CHDA), 1,3-cyclohexane dicarboxylic acid (1,3-CHDA), or hexahydrophthalic anhydride (HHPA). The second series was prepared with 1,4-CHDA and 1,3-CHDA with CHDM. Control polyesters with adipic, azelaic, and isophthalic acid (AA, AZA, IPA) were prepared for comparison. All the polyesters were cross-linked with hexamethylene diisocyanate (HMDI) isocyanurate, forming polyurethane films. General coatings, tensile, and viscoelastic properties were evaluated for the cured polyurethane films. In addition, fracture toughness and the mode of energy dissipation were investigated. The polyesters based on cycloaliphatic diacids have better solubility in MEK compared to the polyesters based on the aromatic or linear aliphatic diacids. The cycloaliphatic diacids based polyurethane coatings had intermediate mechanical and viscoelastic properties compared to polyurethane based on aromatic and linear aliphatic diacids. In addition, the cycloaliphatic diacids afforded polyurethane with a greater adhesion on aluminium substrate compared to the aromatic diacid IPA.

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15. K.C. Paul, A.K. Pal, A.K. Ghosh and N.R. Chakraborty, “Measurements of elastic properties of some coating materials”, Surface Coatings International Part B: Coatings Trans.,**87**, 47-50, 2004.
16. H. Ni, J.L. Daum, P.R. Thiltgen, W.J. Simonsick, W. Zhong, A.D. Skaja and M.D. Soucek, “Cycloaliphatic polyester-based high-solids polyurethane coatings II. The effect of difunctional acid”, Prog. Org. Coat. **45**, 49-58, 2002.

Narayan and Raju [17] have synthesized hydroxylated polyesters (HPs) with structural variation in the backbone used them in 2K polyurethane (PU) coatings. The HPs were characterized by gel permeation chromatography and DSC. The potentialities of these HPs in coating formulation have been studied by developing two pack PU clear coats with diphenylmethane diisocyanate. The results indicated that the structural variation of diol and acetoacetylation help in significant reduction of viscosity of HPs that was also reflected in an increase in percent application solids of coatings. The tensile and dynamic mechanical properties of the coating free films along with supported film properties such as adhesion, scratch resistance, flexibility, impact and abrasion were determined. The dynamic data was used to calculate cross-link density (XLD) and elastically effective network chain (M_c). The results indicated that the structural variation of building block and acetoacetylation were two potential tools to enhance or maintain the coating properties at higher application solids.

EXPERIMENTAL

This chapter of the thesis describes the surface coating of polyurethane resins on glass, copper, steel and aluminium plates and determined their chemical resistance in various reagants.

The detail procedure of synthesis of polyurethane of RAERPU-1 to RAERPU-5, OAERPU-1 to OAERPU-5, RERPU-2, RERPU-3, RAER-3-20%PEG and RAER-3-30%PEG polyurethanes are described below.

Into a 100ml beaker 0.0029 mol polyester polyol was dissolved in 10ml of methyl ethyl ketone at room temperature. To this solution 0.0051 mol toluene diisocyanate in 5ml MEK was added. The solution was stirred manually for about 15-20 min at room temperature. The resultant polyurethane was dissolved in 50ml methyl ethyl ketone (MEK) at room temperature.

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17. R. Narayan and K.V.S.N. Raju, "Properties of acetoacetylated hydroxylated polyesters based polyurethane coatings", Prog. Org. Coat., **45**, 59-67, 2002.

RAER-20% PEG and RAER-30% PEG were prepared by reacting 3.0 g (0.002mol) RAER-3 polyester polyol in 10 ml methyl ethyl ketone (MEK) with 0.9 g (0.005 mol) toluene diisocyanate (TDI) in 5ml MEK at room temperature and stirred manually for 10 min. To this prepolyurethane 20% (0.6g) or 30% (0.9g) PEG-400 (based on polyester polyol) in 5 ml MEK was added drop wise and the reaction mixture was stirred for further 10 min. The weight of polyester polyols and toluene diisocyanate are reported in Table-4.4.

The resultant polyurethane solution was applied on 5cm x 1.5cm glass, copper, steel and aluminium palates by immersion technique. All the plates were allowed to dry at room temperature and kept for seven days for complete curing in the presence of moisture. A very fine coating was observed on each plate with good adhesion to the substrates.

Chemical resistance of coatings

The chemical resistance of the coated plates was tested against various reagents such as water, 10% aq. HCl and 10% aq. NaCl solutions at room temperature by change in mass method at the interval of 24h for 15 days. The coated plates were taken out from the solutions at a regular interval, washed with distilled water, air dried reweighed and reimmersed and also checked their appearance.

RESULTS AND DISCUSSION

All the coated plates were touch dry within five minutes after the application of the resins. The coating remained unaffected in the distilled water and 10% aq. NaCl solution through out the tests. The coated glass plates immersed in 10% aq. HCl solution also remained unaffected through out the tests. The % weight change data of RAERPU-1 to RAERPU-5, OAERPU-1 to OAERPU-5, RERPU-2, RERPU-3, RAER-3-20% PEG and RAER-3-30%PEG polyurethanes coated copper, steel and aluminium plates in HCl solutions with time at room temperature are reported in Tables-4.5 to 4.13 as well as graphically in Figs. 4.1 to 4.9. The % equilibrium weight gain in acidic environment and corresponding equilibrium time data for all the systems are reported in Table-4.14.

Table-4.4: The weight of polyester polyols and toluene diisocyanate for the synthesis of polyurethane resins.

Polyurethane resin	Weight of polyester polyol (g)	Weight of toluene diisocyanate (TDI) (g)
RAERPU-1	2.726	0.9
RAERPU-2	2.926	0.9
RAERPU-3	4.35	0.9
RAERPU-4	3.22	0.9
RAERPU-5	3.64	0.9
OAERPU-1	2.30	0.9
OAERPU-2	2.412	0.9
OAERPU-3	2.494	0.9
OAERPU-4	2.77	0.9
OAERPU-5	3.28	0.9
RERPU-2	2.42	0.9
RERPU-3	2.50	0.9
RAER-3-20% PEG	3.0	0.9
RAER-3-30% PEG	3.0	0.9

Table 4.5: The % weight gain data of RAERPU-1 to RAERPU-5 coated copper plates in 10% HCl solutions with time at room temperature

Chemical	Time (h)	% Weight gain				
		RAERPU-1	RAERPU-2	RAERPU-3	RAERPU-4	RAERPU-5
HCl	24	0.4	0.0	0.0	0.7	0.0
	48	1.1	0.0	0.0	1.3	0.0
	72	2.2	0.6	0.0	2.5	0.7
	96	3.1	1.2	0.0	3.2	1.7
	120	3.9	1.7	0.0	3.7	2.6
	144	4.6	2.2	0.0	4.0	2.8
	168	4.9	2.6	0.3	4.1	3.1
	192	5.0	3.0	0.3	4.3	3.1
	216	5.0	3.0	0.3	4.3	3.1
	240	5.0	3.0	0.3	4.3	3.1
	264	5.0	3.0	0.3	4.3	3.1
	288	5.0	3.0	0.3	4.3	3.1
	312	5.0	3.0	0.3	4.3	3.1
	336	5.0	3.0	0.3	4.3	3.1
	360	5.0	3.0	0.3	4.3	3.1

Table 4.6: The % weight gain data of RAERPU-1 to RAERPU-5 coated steel plates in 10% HCl solutions with time at room temperature

Chemical	Time (h)	% Weight gain				
		RAERPU-1	RAERPU-2	RAERPU-3	RAERPU-4	RAERPU-5
HCl	24	0.9	0.0	0.0	0.9	0.0
	48	1.7	0.0	0.0	1.9	0.8
	72	2.9	0.8	0.13	2.3	2.1
	96	3.5	1.1	2.1	3.1	3.0
	120	4.2	1.7	3.5	3.7	3.7
	144	4.9	2.0	4.6	4.4	3.9
	168	5.3	2.6	5.3	4.4	4.0
	192	5.5	2.9	5.8	4.4	4.0
	216	5.5	2.9	6.1	4.4	4.0
	240	5.5	2.9	6.5	4.4	4.0
	264	5.5	2.9	6.6	4.4	4.0
	288	5.5	2.9	6.6	4.4	4.0
	312	5.5	2.9	6.6	4.4	4.0
	336	5.5	2.9	6.6	4.4	4.0
	360	5.5	2.9	6.6	4.4	4.0

Table 4.7: The % weight gain data of RAERPU-1 to RAERPU-5 coated aluminium plates in 10% HCl solutions with time at room temperature

Chemical	**Time (h)**	**% Weight gain**				
		RAERPU-1	**RAERPU-2**	**RAERPU-3**	**RAERPU-4**	**RAERPU-5**
HCl	24	0.0	0.0	0.0	1.0	0.0
	48	0.0	0.0	0.0	1.3	0.7
	72	0.0	0.9	1.4	2.0	1.6
	96	1.4	1.1	2.6	2.0	2.5
	120	2.7	1.5	3.4	2.5	3.4
	144	3.5	1.8	3.4	2.5	3.4
	168	3.9	2.0	3.4	2.5	3.4
	192	4.1	2.0	3.4	2.5	3.4
	216	4.1	2.0	3.4	2.5	3.4
	240	4.1	2.0	3.4	2.5	3.4
	264	4.1	2.0	3.4	2.5	3.4
	288	4.1	2.0	3.4	2.5	3.4
	312	4.1	2.0	3.4	2.5	3.4
	336	4.1	2.0	3.4	2.5	3.4
	360	4.1	2.0	3.4	2.5	3.4

Table 4.8: The % weight gain data of OAERPU-1 to OAERPU-5 coated copper plates in 10% HCl solutions with time at room temperature

Chemical	**Time (h)**	**% Weight gain**				
		OAERPU-1	**OAERPU-2**	**OAERPU-3**	**OAERPU-4**	**OAERPU-5**
HCl	24	0.0	0.0	0.0	0.6	0.4
	48	1.5	0.6	0.4	1.7	1.1
	72	3.0	1.8	1.7	2.5	2.2
	96	3.9	3.3	2.2	3.4	3.3
	120	5.2	4.0	2.7	4.1	4.3
	144	6.1	4.6	3.0	5.0	4.4
	168	6.6	4.9	4.1	5.8	4.6
	192	7.0	5.1	4.6	6.5	4.7
	216	7.6	5.3	4.7	7.6	5.4
	240	8.1	5.4	4.7	7.8	5.8
	264	8.4	5.4	4.7	7.8	6.0
	288	8.5	5.4	4.7	7.8	6.0
	312	8.5	5.4	4.7	7.8	6.0
	336	8.5	5.4	4.7	7.8	6.0
	360	8.5	5.4	4.7	7.8	6.0

Table 4.9: The % weight gain data of OAERPU-1 to OAERPU-5 coated steel plates in 10% HCl solutions with time at room temperature

Chemical	**Time (h)**	**% Weight gain**				
		OAERPU-1	**OAERPU-2**	**OAERPU-3**	**OAERPU-4**	**OAERPU-5**
HCl	24	0.0	0.0	0.0	1.3	0.5
	48	1.6	0.8	0.5	1.9	1.2
	72	2.1	2.2	1.5	2.8	2.3
	96	3.1	4.2	2.0	3.7	2.9
	120	3.7	5.3	2.5	4.8	3.5
	144	4.7	5.8	3.2	5.3	3.7
	168	5.4	6.4	5.3	6.0	4.0
	192	5.7	6.8	6.1	6.8	4.3
	216	6.0	6.9	6.5	7.2	4.6
	240	6.6	6.9	6.8	7.9	4.8
	264	7.0	6.9	7.0	8.2	4.8
	288	7.3	6.9	7.0	8.2	4.8
	312	7.3	6.9	7.0	8.2	4.8
	336	7.3	6.9	7.0	8.2	4.8
	360	7.3	6.9	7.0	8.2	4.8

Table 4.10: The % weight gain data of OAERPU-1 to OAERPU-5 coated aluminium plates in 10% HCl solutions with time at room temperature

Chemical	**Time (h)**	**% Weight gain**				
		OAERPU-1	**OAERPU-2**	**OAERPU-3**	**OAERPU-4**	**OAERPU-5**
HCl	24	0.0	0.0	0.0	0.5	0.5
	48	1.9	0.0	0.6	1.6	1.2
	72	2.8	1.1	1.4	2.5	2.3
	96	3.6	2.3	1.8	3.0	3.0
	120	4.3	3.0	2.6	3.7	4.1
	144	5.0	3.6	3.3	4.5	4.1
	168	5.3	4.0	4.5	5.2	4.1
	192	5.8	4.0	4.9	6.0	4.1
	216	6.2	4.0	5.1	6.2	4.1
	240	6.8	4.0	5.1	6.2	4.1
	264	7.0	4.0	5.3	6.2	4.1
	288	7.0	4.0	5.3	6.2	4.1
	312	7.0	4.0	5.3	6.2	4.1
	336	7.0	4.0	5.3	6.2	4.1
	360	7.0	4.0	5.3	6.2	4.1

Table 4.11: The % weight gain data of RERPU-2, RERPU-3, RAER-3- 20%PEG and RAER-3-30% PEG polyurethanes coated copper plates in 10% HCl solutions with time at room temperature

Chemical	Time (h)	% Weight gain			
		RERPU-2	RERPU-3	RAER-3-20%PEG	RAER-3-30% PEG
HCl	24	0.4	0.0	0.0	0.2
	48	0.8	0.0	0.6	0.8
	72	1.6	0.0	1.4	1.6
	96	2.2	0.0	2.0	2.6
	120	2.7	0.0	2.9	3.4
	144	3.1	0.5	3.3	3.6
	168	3.7	1.1	3.7	3.8
	192	4.4	1.4	4.1	3.9
	216	4.7	1.4	4.9	4.1
	240	4.8	1.4	5.2	4.1
	264	4.8	1.4	5.4	4.1
	288	4.8	1.4	5.6	4.1
	312	4.8	1.4	5.6	4.1
	336	4.8	1.4	5.6	4.1
	360	4.8	1.4	5.6	4.1

Table 4.12: The % weight gain data of RERPU-2, RERPU-3, RAER-3- 20%PEG and RAER-3-30% PEG polyurethanes coated steel plates in 10% HCl solutions with time at room temperature

Chemical	Time (h)	% Weight gain			
		RERPU-2	RERPU-3	RAER-3-20%PEG	RAER-3-30% PEG
HCl	24	0.6	0.0	0.6	0.0
	48	1.0	0.0	1.3	0.0
	72	1.7	0.0	1.8	0.9
	96	2.5	0.0	2.6	1.5
	120	3.3	0.0	3.5	2.2
	144	3.7	1.2	3.9	2.2
	168	4.2	1.6	4.6	2.2
	192	4.8	1.9	5.1	2.2
	216	5.3	2.5	5.6	2.2
	240	5.5	2.8	6.0	2.2
	264	5.6	2.8	6.3	2.2
	288	5.6	2.8	6.0	2.2
	312	5.6	2.8	6.0	2.2
	336	5.6	2.8	6.0	2.2
	360	5.6	2.8	6.0	2.2

Table 4.13: The % weight gain data of RERPU-2, RERPU-3, RAER-3- 20%PEG and RAER-3-30% PEG polyurethanes coated aluminium plates in 10% HCl solutions with time at room temperature

Chemical	**Time (h)**	**% Weight gain**			
		RERPU-2	**RERPU-3**	**RAER-3-20%PEG**	**RAER-3-30% PEG**
HCl	24	0.0	0.0	0.2	0.4
	48	1.2	0.0	0.5	0.5
	72	2.1	0.0	1.3	1.4
	96	2.6	0.0	2.1	1.5
	120	3.0	0.0	2.8	2.1
	144	3.2	0.9	3.5	2.4
	168	3.4	1.4	3.9	2.7
	192	3.5	1.6	4.4	3.0
	216	3.5	1.6	4.7	3.3
	240	3.5	1.6	4.7	3.3
	264	3.5	1.6	4.7	3.3
	288	3.5	1.6	4.7	3.3
	312	3.5	1.6	4.7	3.3
	336	3.5	1.6	4.7	3.3
	360	3.5	1.6	4.7	3.3

Table-4.14: The % equilibrium weight gain and equilibrium time data for different resin coated plates in acidic environment at room temperature

Resin system	The % equilibrium weight gain			Equilibrium time, h		
	Copper	Steel	Aluminium	Copper	Steel	Aluminium
RAERPU-1	5.0	5.5	4.1	192	192	192
RAERPU-2	3.0	2.9	2.0	192	192	168
RAERPU-3	0.3	6.1	3.4	168	216	120
RAERPU-4	4.3	4.4	2.5	192	144	120
RAERPU-5	3.1	4.0	3.4	168	168	120
OAERPU-1	8.5	7.3	7.0	288	288	264
OAERPU-2	5.4	6.9	4.0	240	216	168
OAERPU-3	4.7	7.0	5.1	216	264	216
OAERPU-4	7.8	8.2	6.2	240	264	216
OAERPU-5	6.0	4.8	4.1	264	240	120
RERPU-2	4.8	5.6	3.5	264	264	192
RERPU-3	1.4	2.8	1.6	192	240	192
RAER-3-20% PEG	5.6	6.0	4.7	288	240	216
RAER-3-30% PEG	4.1	2.2	3.3	216	120	216

From Table-4.14, it is clear that water absorption in acidic environment by different resins is dependent on nature of PU resins as well as the nature of the substrates. The gain in weight is mainly due to H-bond formation with polar groups of the PU resins. From the experimental observations, it is concluded that coated films possess excellent hydrolytic stability against pure water and 10% aq. NaCl solution but they possess water absorption (0.3–8.2%) tendency in acidic environment indicating usefulness of the resins as coating materials.

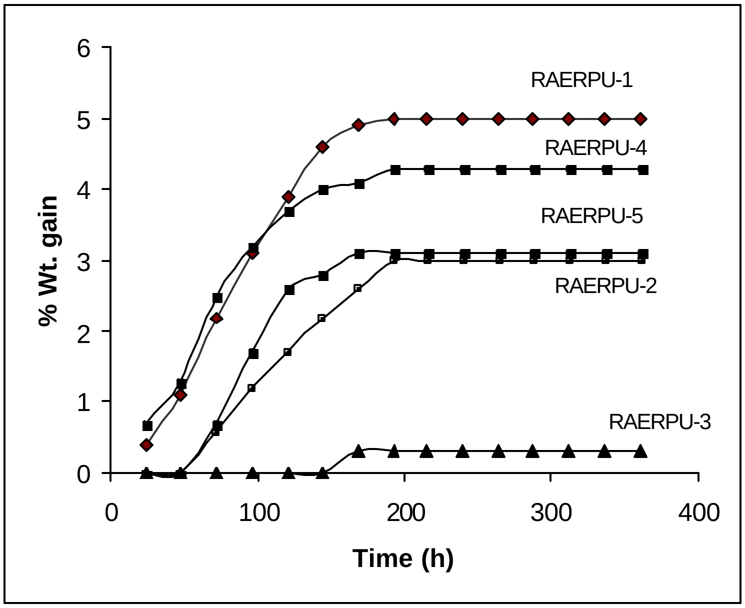


Figure-4.1: The % weight gain data of RAERPU-1 to RAERPU-5 coated copper plates in 10% HCl solutions at room temperature

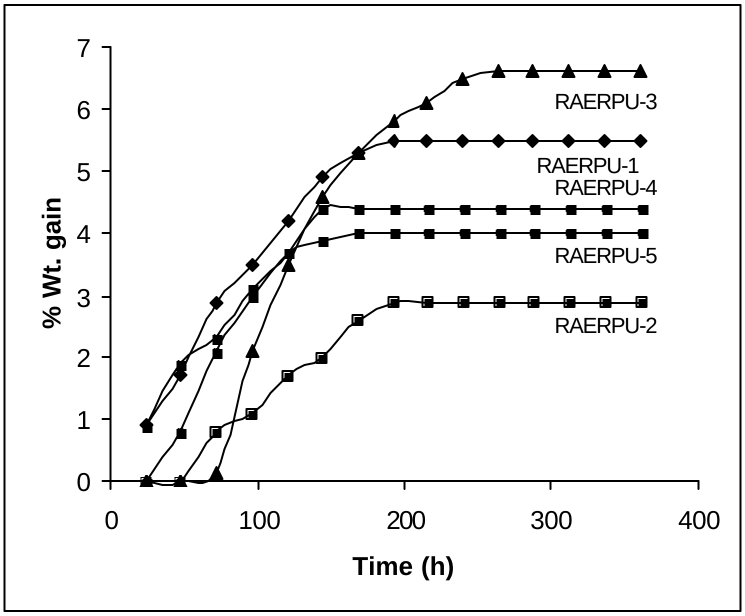


Figure-4.2: The % weight gain data of RAERPU-1 to RAERPU-5 coated steel plates in 10% HCl solutions at room temperature

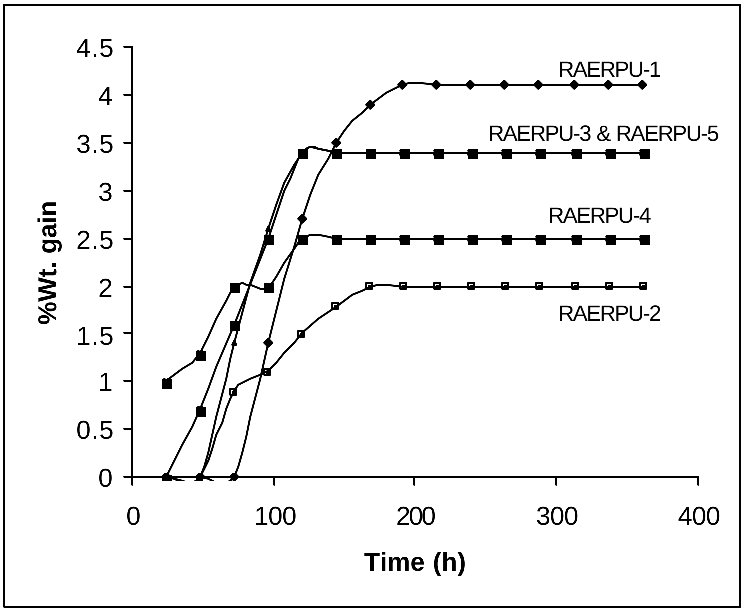


Figure-4.3: The % weight gain data of RAERPU-1 to RAERPU-5 coated aluminium plates in 10% HCl solutions at room temperature

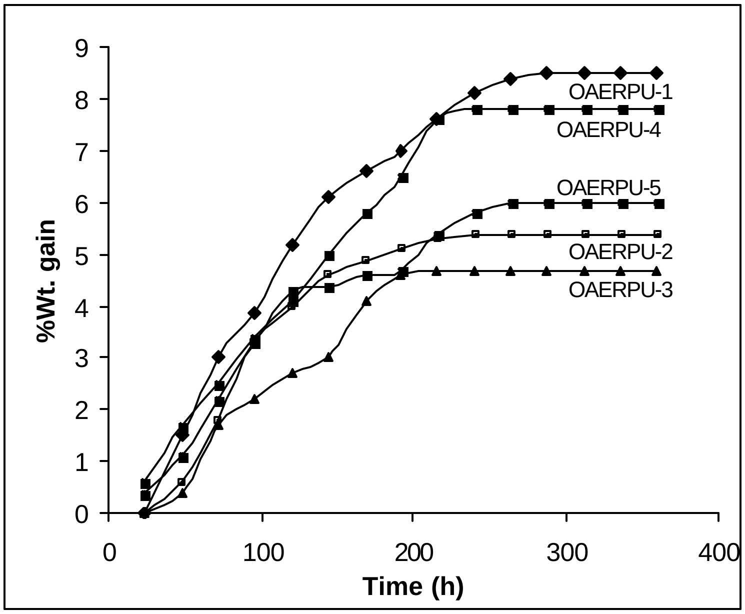


Figure-4.4: The % weight gain data of OAERPU-1 to OAERPU-5 coated copper plates in 10% HCl solutions at room temperature

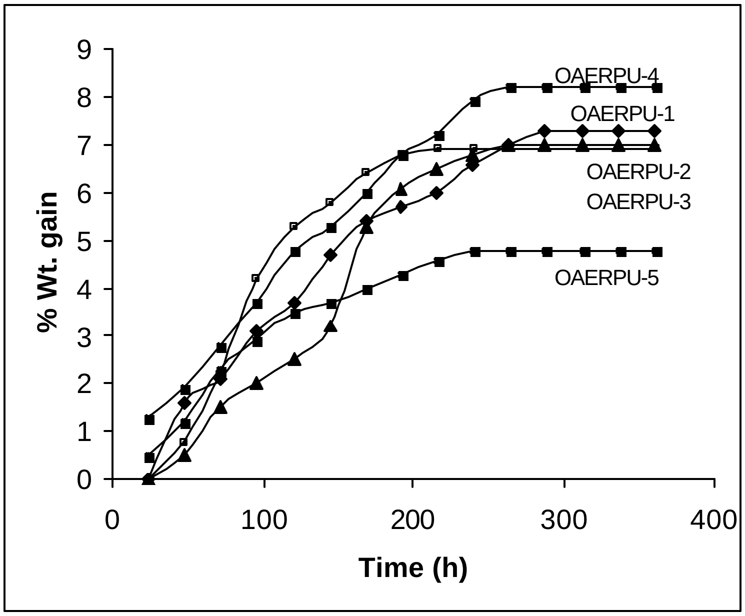


Figure-4.5: The % weight gain data of OAERPU-1 to OAERPU-5 coated steel plates in 10% HCl solutions at room temperature

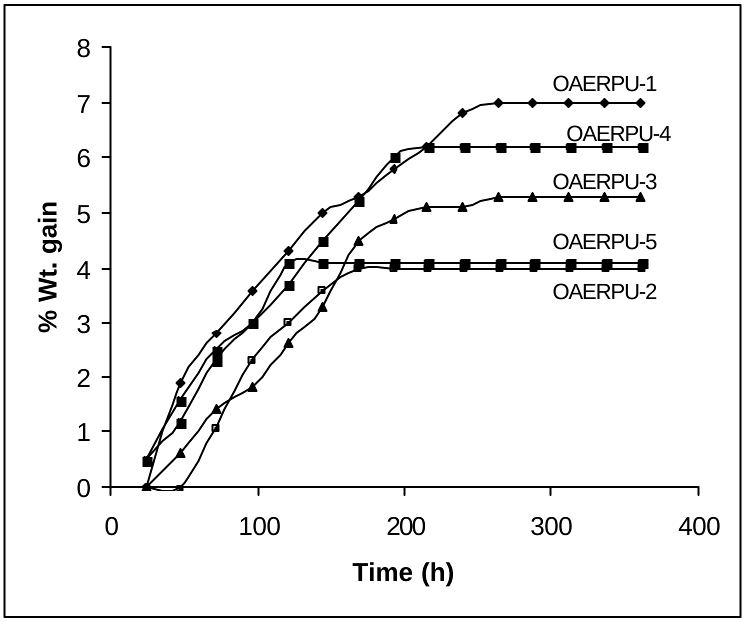


Figure-4.6: The % weight gain data of OAERPU-1 to OAERPU-5 coated aluminium plates in 10% HCl solutions at room temperature

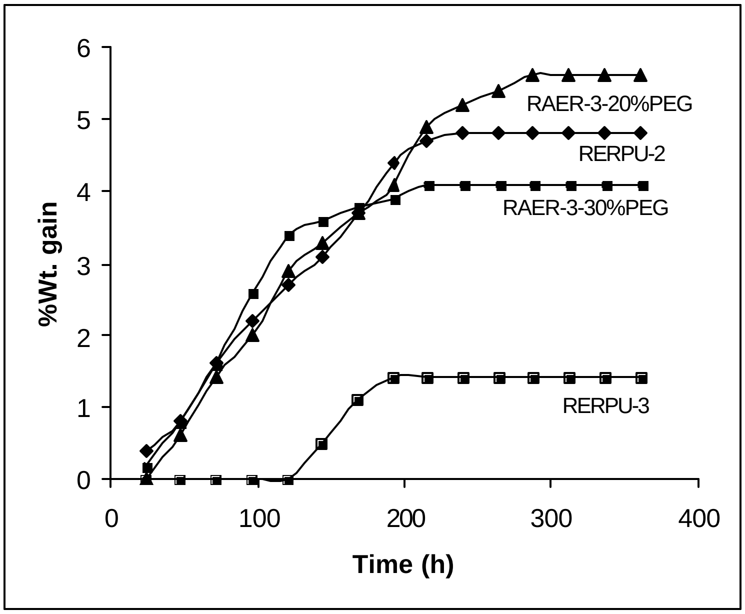


Figure-4.7: The % weight gain data of RERPU-2, RERPU-3, RAER-3-20%PEG and RAER-3-30% PEG polyurethanes coated copper plates in 10% HCl solutions at room temperature

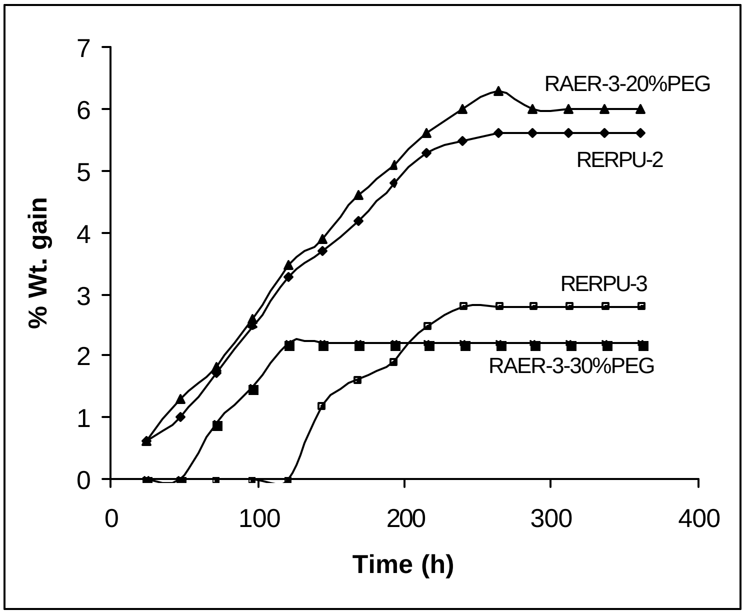


Figure-4.8: The % weight gain data of RERPU-2, RERPU-3, RAER-3-20%PEG and RAER-3-30% PEG polyurethanes coated steel plates in 10% HCl solutions at room temperature

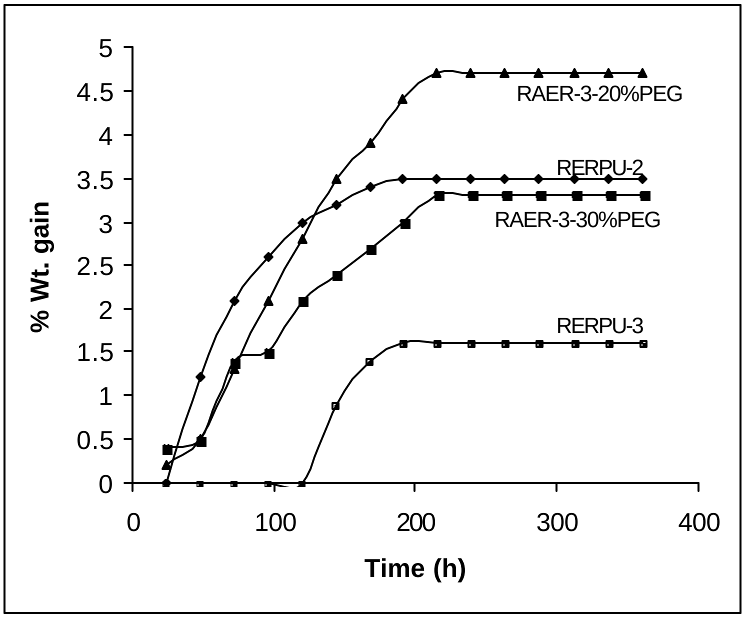


Figure-4.9: The % weight gain data of RERPU-2, RERPU-3, RAER-3-20%PEG and RAER-3-30% PEG polyurethanes coated aluminium plates in 10% HCl solutions at room temperature

This chapter of the thesis elaborates the fabrication, mechanical, electrical and chemical resistance studies of the polyurethane composites. This chapter is further subdivided into three sections:

SECTION-1: FABRICATION OF DIFFERENT TYPES OF COMPOSITES

SECTION-2: MECHANICAL AND ELECTRICAL PROPERTIES OF THE COMPOSITES

SECTION-3: CHEMICAL RESISTANCE STUDY OF COMPOSITES

GENERAL INTRODUCTION

Composite the wonder material is defined as "An anisotropic, heterogeneous medium, made by combining two or more materials with different properties. Properties of the composites are different do not merge completely into each other and can be physically identified along with the interface between them. The properties of the interface also contribute to the properties of the composite".

Over the last forty years, composites, plastics and ceramics have been the dominant emerging materials. The volume and number of applications of composite materials have grown steadily, penetrating and conquering new market relentlessly. Modern composite material constitutes a significant proportion of the engineered materials market ranging from every day products to sophisticated niche applications.

Composite the wonder material with light weight, low density, high strength to weight ratio, stiffness property and corrosion resistance have come a long way in replacing the conventional materials such as steel, aluminium, timber, etc. Now a day composites are being used for the manufacturing of prefabricated, portable and modular buildings as well as for exterior cladding panels, which can simulate masonry or stone. In exterior applications composites are used in the manufacturing of the shower enclosures, trays, bath, sinks and troughs. Cast composites products are widely used for the production of vanity units, bench tops and basins. Owing to their good combination of properties, recently composites are widely used in automotive and aircraft industries in the manufacturing of spaceships, sea vehicles, etc.

Composite consists of two major ingredients viz: reinforcing fibers (dispersed phase) responsible for stress resistance and matrix materials (continuous phase) responsible for stress propagation.

Reinforcing fibers

The base of the composite is fibers. It is often called reinforcing materials. A strength of composite is mainly depends upon the nature of reinforcing fibers. There is a broad classification of reinforcing fibers but mainly they are classified according to their origin i.e. synthetic or natural fibers. They are available in different forms such as woven, non-woven or randomly oriented in more than one direction.

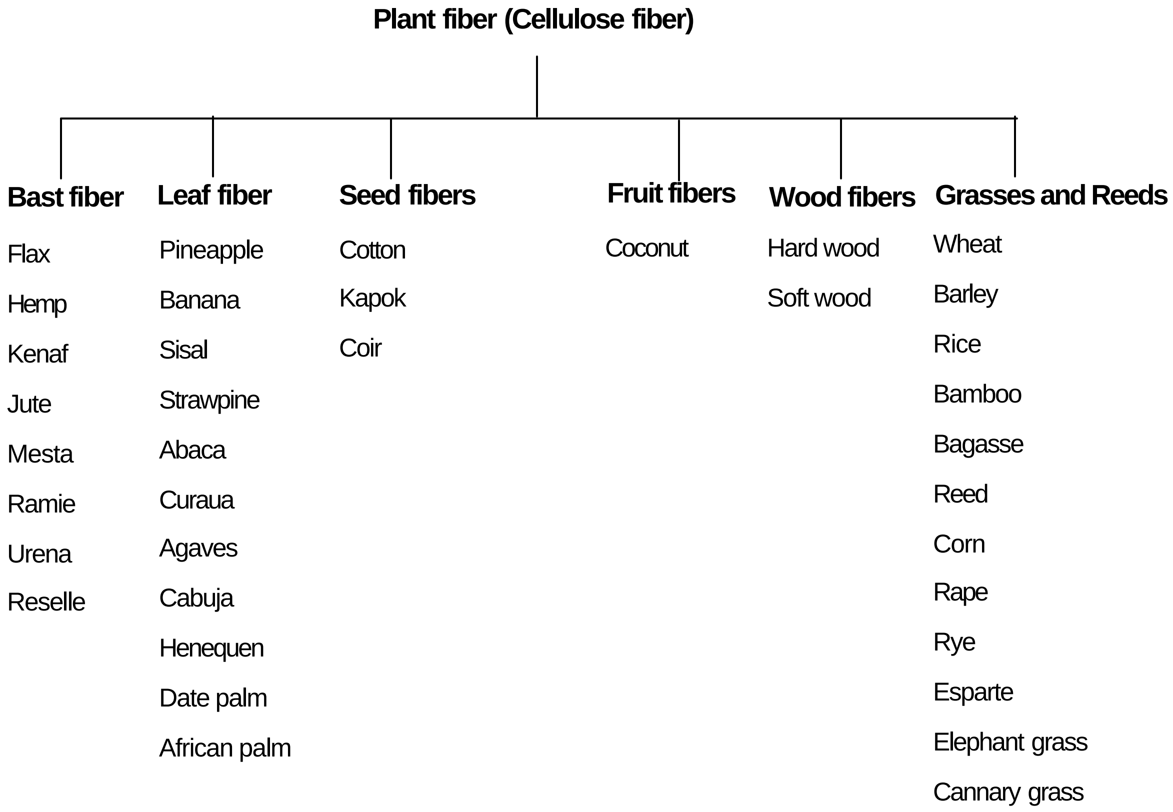
Different job calls different fibers, depending upon the mode of application, selection of fibers are made. Especially for engineering and high performance applications, synthetic fibers are called for the job. The fibers like glass, aramid, Kevlar, carbon, spectra (PE-fibers), etc are popular for load bearing applications. Each fiber has specific features that suit the requirement. The glass fiber is most popular due to low price and suitable for engineering applications. Where cost is no factor, one can use strong fibers like Kevlar, aramid, carbon and spectra fibers.

The other cheap option for composite application is natural fibers in its raw form, originated directly from nature. Natural fibers have been used as reinforcement in composite materials since the beginning of our civilization, when grass, straw and animal hair were used to reinforce mud bricks also known as adobe. Recent years have seen a growing interest in the development of natural fiber reinforced composites in terms of both industrial applications and fundamental research. The natural fibers are incorporated into a matrix material such as thermosetting plastics, thermoplastics or rubber. The significant weight savings and the ease of low cost of the raw constituent materials make these composites an attractive alternative material to glass and carbon. The most commonly used natural fibers are shown in the chart. The properties of some natural fibers are shown in Table-5.1

The advantages of natural fibers over the synthetic fibers are:

- Low cost

- Light weight, Low density
- Easy availability
- Enhanced energy recovery and biodegradability
- High strength to weight ratio
- High specific strength
- Reduced tool wear and safer handling
- Reduced dermal and respiratory irritation
- Easy surface modification



Classification of natural fibers

Table 5.1: Properties of selected natural fibers

Properties	Jute	Banana	Sisal	Pineapple	Coir	Glass
Width or Diameter, mm	-	80-250	50-200	20-80	100-450	7-8
Density (g/cc)	1.3	1.35	1.45	1.44	1.15	2.5
Volume Resistivity at 100 volts cm X10^5	-	6.5-7	0.4-0.5	0.7-0.8	9-14	9-10
Micro-Fibrillar Angle (degree)	8.1	11	10-22	14-18	30-49	-
Cellulose/lignin content (%)	61/12	65/5	67/12	81/12	43/45	-
Elastic Modudlus GN/m^2	-	8-20	9-16	34-82	4-6	85.5
Tenacity (MN/m^2)	440-533	529-754	568-640	413-1627	131-175	4585
Elongation (%)	6-9	-	-	-	12	0.5

Amongst all the natural fibers, jute fibers have received considerable attention for its diversified used as a potential reinforcement in the production of the polymer composites [1, 2]. The jute is an attractive natural fiber for the reinforcement due to its low cost, renewable nature and much lower energy requirement for processing. Jute fiber contains high proportion of stiff natural cellulose. Rated fibers of jute have three main chemical constituents, namely α- cellulose, hemicellulose and lignin. In addition, they contain minor constituents such as fats and waxes, minerals, nitrogenous matter and trace of pigments like β-carotene and xanthophylls. Several studies of fiber composition and morphology have found that cellulose content and micro fibril angle tend to control the mechanical properties of the cellulosic fibers. The specific mechanical properties of the composites are comparable to those of the glass fiber reinforced plastics (GRP). Comparison of mechanical properties of E-glass with jute is listed in Table-5.2. Various items such as school buildings, food grain silos, wood substitutes, low cost housing units, roofing, pipes [3], etc. have been fabricated from the jute fiber reinforced composites.

Modern technology can not be satisfied with a single structured material to fulfill the needs of the mankind. To make an economic production of desired articles with desired combination of properties often necessary to use complex structured material. Recently research is being directed in producing low cost hybrid composites. Hybrid composites are the materials made by combining two or more different types of fibers in a common matrix. They offer a range of properties that can not be obtained

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1. J. Gassan and V.S. Gutowski, “Effects of corona discharge and UV treatment on the properties of jute-fiber epoxy composites”, Compos. Sci. and Technol., **60**, 2857-2863, 2000.
2. A.K. Bledzki, S. Reimance and J. Gassan, “Properties and modification methods for vegetable fibers for natural fiber composites”, J. Appl. Polym. Sci., **59**, 1329-1336, 1996.
3. M.A. Semsarzadesh, “Fiber matrix interactions in jute reinforced polyester resin polymer composites”, Polym. Compos., **7**, 23-25, 1986.

Table 5.2: Mechanical properties of E-Glass and Jute

Properties	**E-glass**	**Jute**
Specific gravity	2.5	1.3
Tensile strength (MN/m^2)	3400	442
Young's modulus (MN/m^2)	72	55.5
Specific strength (MN/m^2)	1360	340
Specific modulus (GN/m^2)	28.8	42.7

with a single kind of reinforcement. By careful selection of reinforcing fibers, the material cost can be reduced substantially [4].

Low cost hybrid composites are produced by the use of biomass or agro waste in combination with jute. In India rice husk (RH) and wheat husk (WH) are the biomass materials, which are byproducts from the crops. Considerable work has been carried out on the utilization of biomass for particle board, medium density board, pulp and composites [5, 6]. The incentives of utilizing agro waste in the fabrication of composites are greater deformability, low density, less abrasiveness to equipments, low cost, etc. The characteristics of NFC boards are as follow:

- Attractive natural look as it can be painted, polished or laminated.
- Water proof with minimum surface absorption
- Economical, strong and rigid
- Environmental friendly
- It can be nailed, screwed and cut sharply.

Matrices

The role of matrix (resin) is to hold reinforcement together. A loose bundle of fibers would not be of much use. In addition, though the fibers are strong, they can be brittle but matrix can absorb energy by deforming under stress. Thus, matrix adds toughness to the composites. Depending upon the properties required, different matrix materials are being used viz:

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4. S.V. Joshi, L.T. Drzal, A.K. Mohanty and S. Arora, “Are natural fiber composites environmentally superior to glass fiber reinforced composites”, Compos. Part-A, **35**, 371-376, 2004.
5. H. Hatakeyama, S. Hirose, K. Nakamura and T. Hatakeyama, “New type of polyurethane derived from lignocellulose and saccharides. Cellulose: chemical, biochemical and material aspects”. In: J.F. Kennedy, G.O. Philips, P.A. Wiliams, Horwood, Elis. New York, London, Toronto, Sydney, Tokyo, Singapore, 525-536, 1993.
6. A. Khalil, H. Ismail, M.N. Ahmed, A. Ariffrin and K. Hassan, “The effect of various anhydride modifications on mechanical properties and water absorption of oil palm empty fruit bunches reinforced polyester composites”, Polym. Inter. **50**, 395-402, 2001.

epoxy, phenolic, unsaturated polyester, polyurethane, polyimide, etc. When going for cheaper application, phenolic and epoxy systems are used in combination with glass fibers with decent properties. Unsaturated polyester resin is being used in combination with glass woven cloth for composite fabrication, but restricts their use due to high shrinkage when cured, more moisture absorption, lower impact strength and low chemical resistance.

Another specialized matrix system is polyurethane, which possesses three dimensional network structures. The unique feature of polyurethane is that it can be tailor made to fit the application requires. Today, polyurethanes are finding a growing interest for the applications as composites virtually in all the sectors especially in the automotive market because of their flexibility, excellent adhesion, high cohesive strength, excellent hardness, impact resistance, high scratch and abrasion resistance and excellent chemical resistance [7].

Another low cost system is vinyl ester resin derived from esterification of diepoxide with acrylic and methacrylic acids results in vinyl ester epoxy resin that is curable with vinyl monomers like styrene and divinyl benzene by free radical mechanism. Such a low cost system is advantageous over unsaturated polyester resin due to low shrinkage, low moisture absorption and good chemical resistance.

For real high temperature applications such as space shuttles, vehicles, etc. traveling beyond the velocity of sound, a great deal of air friction is produced on the surface of the object that generates extreme heat. Special kinds of matrix system, namely, polyimide, bismaleimide or polybenzoxazole are being widely used.

The selection of resin that depends on property required in a final composites. Since a single resin system may not satisfy all the requirements of designer, a certain amount of compromise has to be carried out.

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7. J.P.L. Dwanisa, A.K. Mohanty, M. Misra, M. Kazemizadeh and L.T. Drzal, “Novel soy oil based polyurethane composites: Fabrication and dynamic mechanical properties evaluation”, J. Mater. Sci. 39, 1887-1890, 2004.

Fabrication of composites

Hybrid composites of glass with different natural fibers like jute, coir, hemp, flex, sisal, etc. can be fabricated initially by hand lay out technique for making the sheet-molding compounds. Jute composites are being used in India in various commercial sectors. However, as use of jute alone as reinforcing fiber is not suitable for high strength applications, jute-glass fiber combination can be well suited for such applications. Incorporation of glass with jute brings about large increase in mechanical properties of composites.

Phenolic resin is one of the first synthetic resin exploited commercially for fabrication of jute-composites products mainly because of its high heat resistance, low smoke emission, excellent fire retardancy and compatibility with jute fibers. Even though new resin systems like epoxy, unsaturated polyester and polyurethanes have also come into picture for composite applications. Designers to fabricate composites adopt many techniques. Some of them are listed below:

- **Compression molding**

In this process, reinforcing fibers are impregnated with the appropriate resin. The prepregs are allowed drying under hot air. These pre-impregnated layers are stacked one over other and arranged to desire thickness. They are subjected to hydraulic pressure of 1.5 to 2 tons at temperature about 120-150^0 C. The composite fabricated by this technique have good mechanical properties and good compactness.

- **Pultrusion**

Another unique process converts primary raw materials directly into finished products continuously. The technique serves good for thermoplastic as well as thermosetting. Natural fibers available in continuous form such as mat, roving, woven cloth, yarn, etc. is impregnated with resin and passed through hot die to complete curing reaction. The speed of pultrusion ranges from 0.4 to 1.0 m/min depending upon complexity of the products. For high speed manufacturing of articles, pultrusion is successfully implemented.

- **Resin Transfer Molding (RTM)**

A quick and cost effective process for the production of quality volume composites, this technique is commonly employed. By the help of RTM technique variety of articles can be molded ranging from simple sheets to complex shape.

Applications of composites

- **Composites for structural applications**

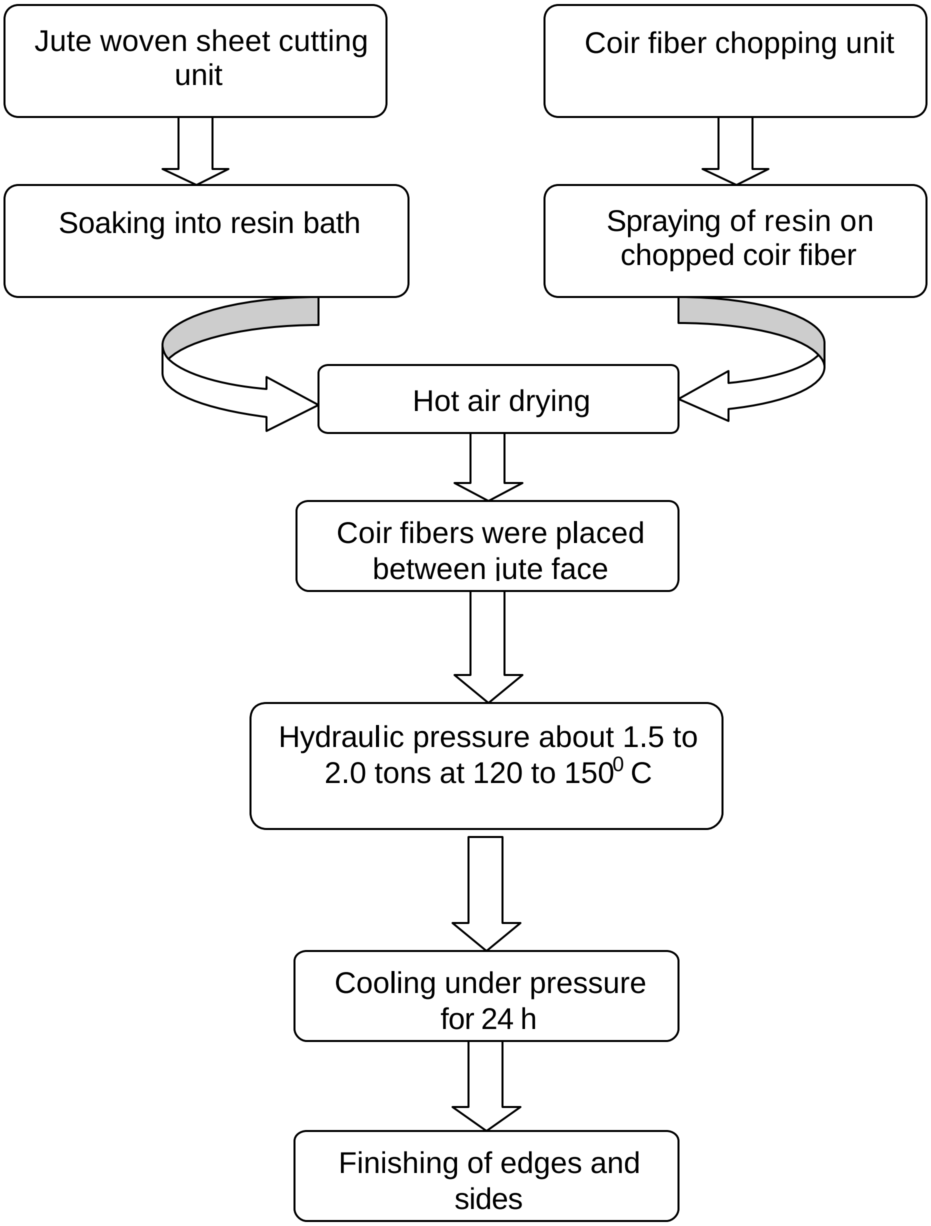
Such a wonder material has been used in construction industries ranging from structural gratings to full structural systems for industrial support, buildings, long span roof, tanks, bridges, and buildings. Composite represents immense opportunity to play increasing role as alternative material to replace timber, wood, steel, aluminium and concrete buildings.

- **Road and bridges**

Bridges account for a major sector of the construction industries and have attracted strong interest for the utilization of high performance FRP. It is found quite suitable for repair, seismic retrofitting and up gradation of concrete bridges as a way to extend the service life of existing structures. It is also being considered as an economic solution for new bridges structure. The commercial validity for repairs has been proven in Europe, Japan and North America. The composite bridge decks are fairly suitable for replacing conventional/old bridge decks having super structure intact. The replacement can save time without disturbance of traffic.

- **Pultruded profiles**

Among the wide array of composite products, pultruded profiles such as gratings, ladders, cable trays, solid rods and other sections are used in many structural applications. With class I flame retardancy, pultruded sections are well-established alternatives to steel, wood and other metals. Structural sections have ready market in oil exploration rings, chemical industries, etc. The pultruded profiles are already being recognized as a commodity in the international market for construction.



Flow Chart to fabricate jute-coir composites

Power transmission

High voltage electrical transmission towers are now being constructed from pultruded composite section, which eliminates the use of fasteners and adhesives. Due to its lightweight and easy transportations to required places to remote areas permits easy accessibility.

Composite as a building material

Composite is an ideal material for the manufacture of prefabricated modular buildings as well as for exterior cladding panels. In interior applications, composites are used in the manufacture of shower enclosures and trays, baths, sinks, etc. Composite plates are successfully used to repair masonry beams, columns, buildings and other structural damages by natural calamities like flood, earthquake and cyclones.

Composite reinforced bars may be used to replace steel in conventional reinforced concrete in order to prevent “concrete cancer” problems resulting from internal corrosion of reinforcement. Now a days epoxy mortars have replaced heavy weight cement mortars due to lightweight, corrosion resistance and good moisture protection to structures.

Composites in bio medical applications

Since portion of human body is a part of composite structure, the use of composite materials to mimic the human body structure is needed. The use of composite and related advance technology gives the possibility to design biomaterials and implants having physical properties similar to the natural structure. Composites as a biomedical application need to be explored in the following fields:

- Composite materials for orthopedics application (hip joints, plates and nails)
- Composite dental implants
- Tissue engineering and polymers for surgery applications

Comparative mechanical properties of FRP Vs other conventional materials are listed in Table-5.3.

Table -5.3: Comparative mechanical properties of FRP Vs other conventional materials

Mechanical Properties	**Pultruded FRP**		**Rigid PVC**	**Mild Steel**	**Stainless Steel**	**Wood**
	Polyester	**Vinyl Ester**				
Tensile Strength (N/mm^2)	382	401	44	340	340	80
Flexural strength (N/mm^2)	468	508	70	380	380	12
Izod impact strength (Kg-m/cm)	1.36	1.63	0.09	1.5	0.53	-
Specific gravity	1.80	1.80	1.38	7.8	7.92	0.52
Safe working Temp. (^{0}C)	120	170	55	600	600	160

The history of composites traced us back before three thousand years ago, when in an ancient Egypt pharaoh mummies were wrapped in a linen cloth impregnated with dead sea salts, natural resins and honey in order to protect and reinforce them. These were most likely the first known man made composites in human history [8].

Ash et al. [9] have reported building boards from phenolic resin and cellulosic material coated with petroleum hydrocarbons. They have prepared hard boards/chip boards from cellulosic waste material, bounded in PhOH-HCHO resin (100:160 parts). The boards were prepared by spraying a resin on the mass of wood chips previously mixed with approx 1.5% by weight of petroleum based on the weight of dry wood chips. The prepregs was subjected to compression press at 350^0F for 150-250 lb/sq. in. The modulus of rupture of this board is 1860 lb/sq. in., water absorption is 18% and swelling is 3.2%.

Razera et al. [10] have prepared untreated and alkali treated phenolic composites. Different fiber lengths and fiber content were used to reinforce the phenolic matrices. The untreated and treated jute fiber-reinforced composites were characterized by water absorption, mechanical property and morphological aspects of the composites were evaluated by SEM. The results indicated that the alkali treated composites possessed excellent mechanical properties and lower water absorption as compared to untreated composites.

8. R. Kozlowski and P.M Wladyka, "Natural fiber reinforced composites-Recent advances" F.T. Wallenberger, P.V. Kandachar (Eds.), Kluwer Academic Publishers, Boston, Dordrecht, London (In press)
9. J.R. Ash, G.E. Brocon and C.R. Cox, "Building boards from phenolic resin and cellulosic material coated with petroleum hydrocarbon", U.S. 2,962,459 (1960); C.A. **55**, 5908, 1961.
10. I. A.T. Razera and E. Frollini, "Composites based on jute fibers and phenolic matrices: Properties of fibers and composites", J. Appl. Polym. Sci. **91**, 1077-1085, 2004

Winfield and Barbara [11] have prepared low cost housing that can withstand cyclic winds in countries like Bangladesh. A house constructed from jute-reinforced polyester with 1-inch thickness and exterior layers of glass reinforced polyester. Such composite boards can withstand windblast from jet aircraft of 230 mph and exposure of 750 gallons/min of water and 200^0F for maximum wall deflection of 2 -3 inch.

Ray et al. [12] have reported impact fatigue behavior of vinyl ester resin matrix composites reinforced with alkali treated jute fibers. An impact fatigue study has been made for the first time on 35% jute vinyl ester composite containing both untreated and alkali treated composite followed by the untreated and 4h treated composites. The flexural strength of treated fibers composites was superior.

Cichocki and Thomason [13] have studied the thermoplastic anisotropy of jute fibers with epoxy resin as a matrix system. The dynamic mechanical and thermal mechanical techniques have been employed to measure the elastic and thermal expansion characteristic of model composite system containing jute fibers over a broad temperature range. The jute fibers investigated in this study exhibits considerable elastic and thermal expansion anisotropy. The fibers longitudinal young's modulus was estimated to range between 5 to 10 times that of its transverse modulus over a temperature range of -50 to 50^0C.

Singh et al. [14] have fabricated jute fiber reinforced phenolic composites for the study of durability and degradation due to out door exposure. The physical and mechanical properties of jute composites have

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11. A.G. Winfield and L. Barbara, "Reinforced plastics in low cost housing", Adv. Chem. Ser. 134, 207-218, (1973); C.A. **82**, 32,004, 1975.
12. D. Ray, B.K. Sarkar and N.R. Bose, "Impact fatigue behavior of vinyl ester resin matrix reinforced with alkali treated jute fibers", Compos. Part-A, **33**, 233-241, 2002.
13. F.R. Cichocki, and J.L. Thomason, "Thermoplastic anisotropy of natural fiber", Composite Sci. and Tech. **62**, 669-678, 2002.
14. B. Shing, M. Gupta and A. Verma "The durability of jute fiber reinforced phenolic composites", Composite Sci. and Tech., **60**, 581-589, 2000.

been studied under various humidity, hydrothermal and weathering conditions. The ageing induced deterioration effect of their conditions on the dimensional stability, surface topology and mechanical properties of the composite was observed.

Ray et al. [15] have studied dynamic mechanical and thermal analysis of vinyl ester resin composites reinforced with untreated and alkali treated jute fibers. The dynamic modulus E*, storage modulus E', loss modulus E" and damping parameter tanδ were calculated from thermograms of 23, 30 and 35 volume% untreated jute composites and 35 volume% alkali treated (5% NaOH treated for 4 and 8h) jute composites.

Biswas et al. [16] 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.

Dash et al. [17] have fabricated jute-polyester composites with untreated (control) and bleached slivers with 60% loading of fibers by weight and were designated as JPH(C) and JPH(B), respectively. Both types of composite specimens were subjected to water absorption, out door weathering tests, tensile and flexural strengths and thermal analyses (TGA/ DTG and DSC). Both the composites show low water absorption, JPH(B) showed lesser water absorption (8.48%) than JPH (C) (12.25%).

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15. D. Ray, B.K. Sarkar, S. Das and A.K. Rana "Dynamic mechanical and thermal analysis of vinyl ester resin matrix composites reinforced with untreated and alkali treated jute fibers", Composite Sci. and Tech., **62**, 911-917, 2002.
16. S. Biswas, G. Shrikanth and S. Nangia, "Development of natural fiber composites in India", Composite 2001 Convention and Trade Show, composite fabrication association, Oct. 3-6, 2001, Tampa, FL, USA.
17. B.N. Dash, A.K. Rana, H.K. Mishra, S.K. Nayak and S.S. Tripathy, "Novel low cost jute polyester composites III Weathering and thermal behavior", J. Appl. Polym. Sci. **78**, 1671-1679, 2000.

The tensile and flexural strengths of both the composites were measured for both the weathered and unweathered specimens and was found that the tensile strength of JPH (C) and JPH (B) decreased, while tensile modulus increased after weathering. The flexural strength, modulus and ILSS of the weathered specimens were less than those of unweathered ones. Also the thermal stability of JPH (C) was found to be better than that of JPH (B).

Zarate et al. [18] have fabricated vegetable fibers like cotton, sisal, sugarcane bagasse reinforced phenol formaldehyde-resole composites and studied the influence of fiber volume V_f in flexural properties and density of the composites. The results revealed that as the fiber volume fraction increased the flexural strength and density was also increased in case of sisal fiber reinforced composites, while the sugarcane bagasse possessed maximum strength value at maximum fiber volume friction. A good fiber matrix adhesion was confirmed by the scanning electron microscopy.

Bruce et al. [19] have fabricated high volume fraction hemp and flex fiber epoxy and phenolic composites and studied the effect of fiber treatment on the properties. The epoxy composites with 80% volume fraction of flax fibers showed mean stiffness of 26GPa and mean strength of 378MPa, while phenol formaldehyde composites with 40% volume fraction showed mean stiffness of 3.7GPa and mean strength of 27MPa. Both the fibers were pretreated to improve adhesion with resins. The first treatment was of 6M urea and second was 50% PVA solution. The results revealed that the PVA treatment improved the stiffness and strength of both the composites.

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18. C.N. Zarate, M.I. Aranguren and M.M. Reboredo,“Resole-vegetable fibers composites”, J. Appl. Polym. Sci. **77**, 1832-1840, 2000.
19. D.M. Bruce, J.F.V. Vincent, G. Jeronimidis and D.G. Hepworth, “The manufacturing and mechanical testing of thermosetting natural fiber composites”, J. Mater. Sci., **35**, 293-298, 2000.

Paulmer et al. [20] have studied the effect of crosslinking agents on the structure and properties of the millable polyurethane (PU) elastomers. Effects of the conventionally used dicumyl peroxide (DCP) and toluene diisocyanate dimer (TDID) on the curing characteristics, mechanical properties, and relative thermal stabilities of the PU composites have been compared. The mixture of DCP and TDID is also evaluated as crosslinking agents. A dramatic improvement in the mechanical properties and thermal stability is observed because of the mixed type of crosslinking obtained by the combined use of DCP and TDID.

Chen and Ma [21] have developed a process manufacture of polyurethane (PU) pultruded composites. The PU used in this study was prepared from ε-caprolactam blocked blends of toluene diisocyanate and branched polyester. The static mechanical and thermal properties of various fibers (glass, carbon and Kevlar-49 aramid fiber) reinforced blocked PU composites have been studied. Results showed that the static mechanical properties (i.e. tensile strength, specific tensile strength, flexural strength, specific flexural strength, flexural modulus and impact strength) and thermal properties (heat deflection temperature (HDT) increased with fiber content. Kevlar-fiber blocked-PU composites possess the highest impact strength, specific tensile strength and HDT, whereas carbon-fiber blocked-PU composites show the highest tensile strength, flexural strength, specific flexural strength and flexural modulus. The glass-transition temperature (T_g) increased slightly and the damping peak (tan d) was broadened as a consequence of fiber reinforcement.

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20. R.D.A. Paulmer, C.S. Shah, M.J. Patni and M.V. Pandya, "Effect of crosslinking agents on the structure and properties of polyurethane millable elastomer composites", J. Appl. Polym. Sci., **43**, 1953-1959, 1991.
21. C.H. Chen and C.C. Ma, "Pultruded fiber-reinforced polyurethane composites III Static mechanical, thermal, and dynamic mechanical properties", Compos. Sci Tech., **52**,427-432, 1994.

Melo and Pasa [22] have fabricated eucalyptus tar pitch polyurethane (PU) composites. Polyurethane samples were prepared with 4,4′-diphenylmethane diisocyanate (NCO/OH = 1), eucalyptus tar pitch (biopitch), castor oil as a polyol, and dibutyltin dilaurate as a catalyst. These materials were reinforced with different contents of short sisal fibers (0, 2.5, 5.0, 7.5, and 10.0%) and were prepared by resin-transfer molding. The composites were characterized by IR absorption spectroscopy, thermal analysis [thermogravimetry (TGA) and differential scanning calorimetry (DSC)], impact resistance, scanning electron microscopy (SEM), and water absorption resistance. The composites showed hydrophobic characteristics, despite the addition of sisal fibers.

Mothe et al. [23] have prepared sisal and the sugarcane waste reinforced polyurethane composites. The composites of these fibers with polyurethanes were obtained by processing these materials in a Haake plastograph, and their homogeneity was characterized by nuclear magnetic resonance (NMR) measurements. The results are discussed in terms of composites interaction, homogeneity, and compatibility.

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22. B.N. Melo and V.M.D. Pasa, “Composites based on eucalyptus tar pitch/castor oil polyurethane and short sisal fibers”, J. Appl. Polym. Sci. **89**, 3797-3802, 2003.
23. C.G. Mothé, C.R. Araújo and M.B. Tavares, “Solid-state nuclear magnetic resonance study of polyurethane (PU)/natural fibers composites”, J. Appl. Polym. Sci. **85**,1465-1468, 2002.

SECTION-1: FABRICATION OF DIFFERENT TYPES OF COMPOSITES

This section of the thesis describes the detailed procedure of the fabrication of polyurethane jute and hybrid (jute-RH and jute-WH) composites.

Woven jute fibers (Brown jute, **Corchorus Capsularis** 61-64% cellulose, 21-23% hemicellulose and 13-14% lignin) used in the present study was obtained from Indian Jute Industries' Research Association (IJIRA), Kolkata, India. The agro wastes rice husk **[Oryza sativa]** (RH, 2-3mm size: 35% cellulose, 25% hemicellulose and 20% lignin) and wheat husk **[Triticum aestivum]** (WH, 6-8 mm size; 33-39% cellulose, and 16-23% lignin) were obtained from the local market. Epoxy resin of bisphenol-C (ER-2) and bisphenol-C- formaldehyde resin (BCF) were synthesized according to our recent work.

[A] Fabrication of jute fiber reinforced polyurethane composites

The composites of BCFPU and ER-2PU were prepared by hand lay up technique. The detailed procedure of synthesis of BCFPU and ER-2PU and the fabrication procedure of the composites is described as under.

To a 250ml beaker 0.023mol (9g)/0.007mol (3g) BCF was dissolved in 100/30ml methyl ethyl ketone (MEK) at room temperature. To this solution 0.155 mol (27g)/0.051 mol (9g) toluene diisocyanate (TDI) in 50/20 ml MEK was added drop wise over a period of 10 min. The reaction mixture was stirred manually for about 15-30 min. at room temperature.

Polyurethane resin of ER-2 (ER-2 PU) was prepared by reacting 0.018 mol (22g) /0.005 mol (6.5g) ER-2 in 70/15 ml MEK with 0.035mol (6.26g)/0.0106 mol (1.85g) TDI in 30/15 ml MEK at room temperature. The reaction was stirred manually for about 25-30 min. at room temperature. The prepared polyurethane resins were used in the manufacturing of the composites.

Woven jute matrices (15cm X 15cm and 5cm X 5cm) were kept ready for the impregnation of polyurethane solutions. A 62.6% (BCF-PU) / 45% (ER-2PU) solution (total weight of jute fibers) was prepared in methyl ethyl ketone (MEK) and applied with the help of a smooth brush by hand lay up technique. The 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 heated stainless steel plates under the hydraulic pressure of 30.4MPa at room temperature / 135^0C (BCF-PU / ER-2PU) for 2.5h under heating and 12h at room temperature. Silicone spray was used as a mold releasing agent. The type of composites, weight of jute matrix and weight of resin used in the fabrication of Jute-PU composites are reported in Table-5.4. The arrangement of woven fibers is shown in the Fig.5.1.

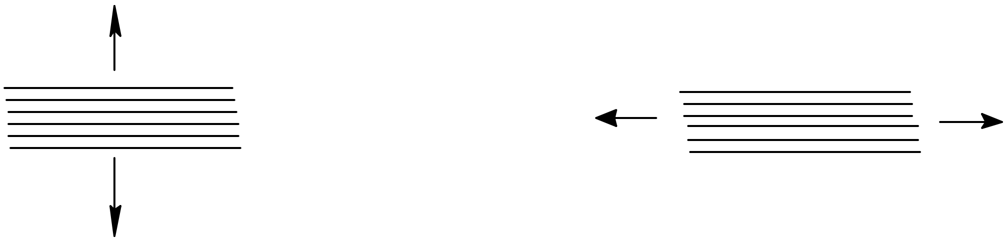

Figure-5.1: The arrangement of woven fibers in the composites

[B] Fabrication of hybrid polyurethane composites

The hybrid composites are made by one shot method. An ordinary sieve was used to separate the different sizes of rice husk (RH) /wheat husk (WH) fillers. The average filler size used in the present study was 2-3 mm (RH) and 6-8mm (WH). Polyurethane resin used for the preparation of hybrid composites was prepared according to method discussed above. Polyurethane resin (total weight of jute and filler material) BCF-PU (70.6%) / ER-2 PU (54%)solution was applied to two 15cmx15cm woven jute fiber sheets with the help of a smooth brush and remaining resin was mixed with 40g RH/WH at room temperature.

Resin coated jute sheets and RH/WH filler were allowed to dry at room temperature for about 15 min. Resin coated RH/WH filler was uniformly sandwiched between two resin coated jute sheets and placed between two preheated stainless steel plates and pressed under hydraulic pressure of 30.4 MPa at 110^0C (BCF-PU) / 135^oC (ER-2PU) for 2.5 h and 12h at room temperature by using silicone spray as a mold releasing agent. The arrangement of biomass with jute in the composites is shown in Fig. 5.2.

Table -5.4: The type of composites, weight of jute matrix and weight of resin used in the fabrication of Jute -PU composites.

Polyurethane resin	Type of composites	Weight of jute matrix, g	Weight of resin in %
BCF-PU	Jute (15cm X 5cm)	57.5	62.6
	Jute (5cm X5cm)	19	63
ER-2 PU	Jute (15cm X 15cm)	62.3	45
	Jute (5cm X5cm)	19	44

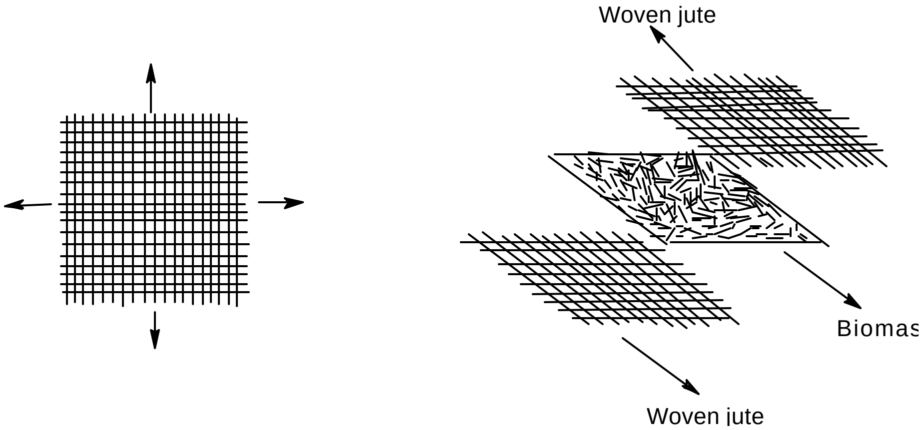

Figure-5.2: Arrangement of Jute-Biomass composite

The type of composites, weight of jute matrix and fillers (RHWH) and weight of resins used in the fabrication of polyurethane composites are reported in Table-5.5.

SECTION-2: MECHANICAL AND ELECTRICAL PROPERTIES OF THE 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 the service, composite has to suffer the cyclic stress, tensile, flexural, impact forces, bending, friction, wear and different type 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
- Type of curing mechanism and density of curing

Table -5.5: The type of composites, weight of jute matrix and fillers (RH/WH) and weight of resins used in the fabrication of hybrid composites

Polyurethane resin	**Type of composites (15cm X 15cm)**	**Weight of Jute-matrix and fillers (RH/WH), g**		**Weight of resin, %**
		Jute	**RH/WH**	
BCF-PU	Jute- RH	11	40	70.6%
	Jute-WH			
ER-2 PU	Jute- RH	12.3	40	54%
	Jute- WH			

- 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

Depending on the property to be measured, a large number of 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 punching technique as per prescribed standard tests for tensile and flexural testing.

The tensile strength (σ) of the composites was determined according to Eqn.5.1:

$$s = \frac{W}{A}$$ **… 5.1**

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.5.2:

$$\text{Flexural strength} = \frac{1.5FL}{wt^2}$$ **… 5.2**

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 bestbe 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. [24] 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.

Vajrasthira et al. [25] 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.

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24. R. Joffe, L. Wallstrom and L.A. Berflund, "Natural fiber composites based on flax matrix affects", Proceedings of International Scientific Colloquium, Modeling for Saving Resources, Riga, May 17, 2001.

25 C. Vajrasthira, T. Amornsakchai and S.B Limcharoen, 'Fiber-matrix interactions in aramid-short-fiber-reinforced thermoplastic polyurethane composites", J. Appl. Polym. Sci., **87**, 1059-1067, 2003.

Reboredo et al. [26] have fabricated the composites of unsaturated polyester using saw dust and Eucaliptus saligna 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. [27] have fabricated the empty fruit bunch–polyurethane (EFB–PU) composites reacting EFB and polyethylene glycol (PEG) with diphenylmethane 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. [28] 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

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26. M.M. Reboredo, M.I. Aranguren and N.E. Marcovich, "Composites from saw dust and unsaturated polyester", J. Appl. Polym. Sci., **61**,119-124,1996.
27. G.S. Tay, A. Abubakar, R.N. Kumar and H.D. Rozman, "Tensile properties of oil palm empty fruit bunch–polyurethane composites", Eur. Polym. J., **37**, 1759-1765, 2001
28. K.R. Ahmadhilmi, A. Abubakar and H.D. Rozman, "Polyurethane (PU)—oil palm empty fruit bunch (EFB) composites: the effect of FBG reinforcement in mat form and isocyanate treatment on the mechanical properties", Polym. Testing, **23**, 559-565, 2004.

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. [29] have fabricated the flex 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. [30] have evaluated the tensile and impact behavior of jute fabrics—polyester composites as a function of the fabric style (knitted or weaved cloths), 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 results obtained 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

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29. J. Gassan, T. Dietz and A.K. Bledzki, "Effect of silicone interphase on the mechanical properties of flax-polyurethane composites",Compos Interfaces, **7**, 103-115, 2000.
30. L.H.de Carvalho, J.M.F. Cavalcante, J.R.M.d' Almeida, "Comparison of the mechanical behavior of plain weave and plain weft knit jute fabric-polyester-reinforced composites", Polym. Plast. Technol. Eng. **45**, 791-797, 2006.

compared with that of the knit fabric. The impact strengths of both composites were higher than that of the matrix and were shown to increase with fiber content. WKT-reinforced composites showed better impact absorption capacity than PWF composites.

Sastra et al. [31] 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 results above 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. [32] have fabricated waterborne polyurethane (WPU) composites and have studied the effect of crosslinking agent on the different properties. Water bone 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

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31. H.Y. Sastra, J.P. Siregar, S.M. Sapuan and M.M. Hamdan, “Tensile properties of arenga pinnata fiber-reinforced epoxy composites”, Polym. Plast. Technol. Eng. **45,** 149-155, 2006.

32. N. Wang, Y. Lu, Y. Du and L. Zhang, “Properties of crosslinked casein/waterborne polyurethane composites” J. Appl. Polym. Sci. **91**, 332-338, 2004

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. [33] 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 [34] 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

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33. X. Cao, J. Huang, G. Yang, Y. Wang and L. Zhang, "Structure-properties relationship of starch/waterborne polyurethane composites", J. Appl. Polym. Sci. **90**, 3325-3332, 2003
34. Z. Fengchang and H. Weibo, "Studies on the dynamic mechanical and vibration damping properties of polyether-urethane and epoxy composites", J. Appl. Polym. Sci. **50**, 277-283, 1993.

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 [35] 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. [36] 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.

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35. H. Kumar and Siddaramaiah, “Studies on bamboosa balcooa bamboo fiber for green composites with polyurethane and polyurethane / poly (methyl methacrylate) semi-interpenetrating polymer network”, J. Bamboo and Rattan, **3**, 237-243, 2004.
36. L. Musa, A. Abubakar and H.D. Rozman, “The mechanical and dimensional properties of rice husk (RH)-unsaturated polyester composites”, Polym. Plast. Technol. Eng., **44**, 489-500, 2005.

Hazlan et al. [37] have produced rice husk (RH)–glass fiber (GF) hybrid polyester 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. [38] have fabricated polyurethane composites with rice husk (RH) with polypropylene glycol, molecular weight (M_w) of 400 (PPG400) 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

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37. A. Hazlan, A. Abubakar and H.D. Rozman, "Preliminary study on mechanical and dimensional stability of rice husk–glass fiber hybrid polyester composites", Polym. Plast. Technol. Eng., **43**, 1129-1140, 2004.
38. L.G. Ang, G.S. Tay, A. Abubakar and H.D. Rozman, "The mechanical properties of rice husk-polyurethane composites", Polym. Plast. Technol. Eng. **42**,327-343, 2003.

was attributed to the ability of RH OH groups to absorb water, causing the cell wall to swell.

Tay et al. [39] have fabricated empty fruit bunch-polyurethane (EFB-PU) composites by reacting EFB and polyethylene glycol (PEG) with diphenylmethane diisocyanate (MDI) and have investigated their mechanical properties. From the results of flexural and impact properties, it was found that these 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.

Fujii et al. [40] 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

The tensile strength (IS: 11298-Pt-2-87) and flexural strength (ASTM D-790-92) measurements were made on a Universal Tensile Testing Machine, Model No. 1185 at a speed of 50mm/min.

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39. G.S. Tay, A. Abubakar, R.N. Kumar and H.D. Rozman, “A preliminary study on the oil palm empty fruit bunch-polyurethane (EFB-PU) composites”, Inter. J. Polym. Mater. **51**, 1087-1194, 2002.
40. T. Fujii, Y. Yamamoto and K. Okubo, “Development of bamboo-based polymer composites and their mechanical properties”, Compos. Part-A: Appl. Sci. and Manf., **35**, 377-383, 2004.

Comparative tensile and flexural strengths of Jute, Jute-RH and Jute-WH PU composites are reported in Table-5.6, from which it is clear that upon hybridization tensile strength of Jute-RH-BCFPU (79%) and Jute-WH-BCFPU (83%) has decreased to a great extent mainly due to random orientation of sandwiched biomass fillers supporting discontinuous stress transfer from matrix to fiber. Flexural strength of Jute-RH-BCFPU (38%) and Jute- WH-BCFPU (70%) has decreased considerably upon hybridization due to decrease in stiffness of the hybrid composites. Similarly tensile strength of Jute-RH-ER-2PU (9.5MPa) and Jute-WH-ER-2PU (14.7MPa) and the flexural strength of Jute-RH-ER-2PU (12.9MPa) and Jute-WH-ER-2PU (21.3MPa) have decreased upon hybridization. From the Table-5.6, it is also observed that, Jute-WH-ER-2PU has 1.65 times more flexural strength than Jute-RH-ER-2PU indicating better stiffness of Jute-WH-ER-2PU.

There are two types of interfacial interactions namely covalent and H-bonding. Hydroxyl groups of lingo celluloses serve as reaction sites with various functional groups present in the resin. Thus RH and WH both can be used as fillers as well as reactive components (Polyols). It is interesting to note that Jute composites of both types of polyurethane resins have almost same tensile strength and flexural strength but they are different for hybrid composites. In hybrid 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.

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 hybrid 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/WH fibers and hence resulted in improved

Table -5.6: Mechanical properties of the BCF-PU and ER-2 PU composites

Resin	Type of composites	Thickness (mm)	Tensile strength (MPa)	Flexural strength (MPa)
BCF-PU	Jute	4.05	53	50
	Jute-RH	3.15	11	31
	Jute-WH	4.05	9	15
ER-2 PU	Jute	3.95	37.4	39.6
	Jute-RH	3.65	9.5	12.9
	Jute-WH	3.15	14.7	21.3

interfacial adhesion. Urethane segments are hard and brittle in nature and therefore they cause lowering in mechanical strength.

In present case Jute composite possesses good tensile and flexural properties but hybrid 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 in its newer applications. 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 O cm or O m)
- Surface resistivity (usually measured in O 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 5.7.

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} [41]. 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

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41. O.M. Kazarnovasky, B.M. Tareev, I.O. Forsilova and L.I. Lybimov "Testing of electrical insulating materials", Mir Publishers, Moscow, 1982.

Table -5.7: Typical electrical properties of some selected plastic materials

Polymer	Volume resistivity (O cm)	Dielectric strength (KV/cm)	Dielectric constant		Power factor	
			60 Hz	10^6 Hz	60 Hz	10^6 Hz
PTFE	$>10^{20}$	180	2.1	2.1	<3 x 10^{-4}	<3 x 10^{-4}
PE	10^{20}	180	2.3	2.3	<3 x 10^{-4}	<3 x 10^{-4}
PS	10^{20}	240	2.55	2.55	<3 x 10^{-4}	<3 x 10^{-4}
PP	$>10^{19}$	320	2.15	2.15	8 x 10^{-4}	4 x 10^{-4}
PMMA	10^{16}	140	3.7	3.0	6 x 10^{-2}	2 x 10^{-2}
PVC	10^{17}	240	3.2	2.9	1.3 x 10^{-2}	1.6 x 10^{-2}
Nylon 66	10^{15}	145	4.0	3.4	1.4 x 10^{-2}	4 x 10^{-2}
PC	10^{18}	160	3.17	2.96	9 x 10^{-4}	1 x 10^{-2}
Phenolic	10^{13}	100	5.0-9.0	5.0	8 x 10^{-2}	4 x 10^{-2}
Urea Formaldehyde	10^{14}	120	4.0	4.5	4 x 10^{-2}	0.3

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 [41].

$$E_{br} = \frac{U_{br}}{t} \qquad \textbf{… 5.3}$$

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 [42].

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

$$\text{Dielectric strength} = \frac{V}{t} \qquad \textbf{… 5.4}$$

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

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42. A.B. Mathur and I.S. Bhardwaj “Testing and Evaluation of Plastics”, Allied Publishers Pvt. Ltd., 2003.

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.

The volume resistivity of the material can be determined by the following equation:

$$\text{Volume resistivity} = \frac{R_v A}{t} \qquad \textbf{… 5.5}$$

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

Naik and Mishra [43] have fabricated wood polymer composites from agro-waste (banana, hemp, and agave fibers) and novalac resin and determined their electrical properties. Banana, hemp, and agave fibers were treated with novalac 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.

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[43] J.B. Naik and S. Mishra, "Studies on electrical properties of wood polymer composites based on agro-waste and novolac", Polym. Plast. Technol. Eng. **43**, 1085-1091, 2004.

Jain and Chand [44] have fabricated different directionally oriented sisal fiber reinforced epoxy resin composites and studied the effect of temperature and frequency variation on dielectric constant (e'), dielectric dissipation factor (tan d) and on A.C. conductivity ($s_{a.c.}$) 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 d and A.C. conductivity increased with increasing temperature. The dependence of dielectric constant, tan d and A.C. conductivity with frequency have also been studied and it was found that e' and tan d of the epoxy and 0 and 90° 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 d and A.C. conductivity were observed. Clear relaxation peaks for tan d 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° 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 °C.

Paul et al. [45] 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

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44. D. Jain and N. Chand, “Effect of sisal fiber orientation on electrical properties of sisal fiber reinforced epoxy composites”, Compos. Part-A, **36**, 594-602, 2005.
45. A. Paul, K. Joseph and S. Thomas, “Effect of surface treatments on the electrical properties of low-density polyethylene composites reinforced with short sisal fibers”, Compos. Sci and Technol. **57**, 67-79, 1997.

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, reaches 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

Electric strength (IEC-243-Pt-1-88) and volume resistivity (ASTM D-257-92) measurements were made on a high voltage tester (Automatic Electric-Mumbai) in air at 27^{O}C by using 25/75mm brass electrodes and a Hewlett Packard high resistance meter at 500 V DC after charging for 60 sec, respectively.

The comparative electric strength and volume resistivity of the polyurethane composites are reported in Table-5.8, from which it is evident that evident that the electric strength of Jute-BCFPU (1.82 kV/mm) and Jute-RH-BCFPU (2.1 kV/mm) is comparable but for Jute-WH-BCFPU (1.11 kV/mm) it is almost half of later composites. Similarly volume resistivity of Jute-BCFPU (9.38×10^{11} ohmcm), Jute-RH-BCFPU (1.14×10^{12} ohmcm) and Jute-WH-BCFPU (1.26×10^{12} ohmcm) is comparable and upon hybridization it is improved 22-34%.

Both electric strength and volume resistivity of Jute-ER-2PU, Jute-RH-ER-2PU and Jute-WH-ER-2PU are improved 1.3 to 1.5 times upon hybridization. The improvement in the electrical properties is due to the lone pairs of electrons of urethane linkages, which form H-bonds with unreacted OH groups resulting in neutralization of partial charges present

Table -5.8: The comparative electric strength and volume resistivity of the polyurethane composites

Resin	Type of composites	Thickness (mm)	Electric strength, kV/mm	Volume resistivity, ohmcm
BCF-PU	Jute	4.05	1.82	9.38×10^{11}
	Jute-RH	3.15	2.1	1.14×10^{12}
	Jute-WH	4.05	1.11	1.26×10^{12}
ER-2 PU	Jute	3.95	1.3	$1.40 X 10^{13}$
	Jute-RH	3.65	1.8	$1.84 X 10^{13}$
	Jute-WH	3.15	1.9	$1.91 X 10^{13}$

on polar groups and hence increase in electric strength and volume resistivity. Thus composites possess fairly good electric strength and volume resistivity signifying their importance as insulating materials and can be used in electrical industries.

SECTION-3: CHEMICAL RESISTANCE 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 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 [46-48]. 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 [49].

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.

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46 J. Gassan and A.K. Bledzky, “The influence of fiber surface treatment on the mechanical properties of jute-polypropylene composites”, Composites, **28**, 1001-1005,1997.

47 S. Das, A.K. Saha, P.K. Choudhary, R.K. Basak, B.C. Mitra, T. Todd and S. Lang, “Effect of steam pretreatment of jute fiber on dimensional stability of jute composite”, J. Appl. Polym. Sci., **76**, 1652-1661, 2000.

48 S. Pavlidou and C.D. Papaspyrides, “The effect of hygrothermal history on water sorption and inter laminar shear strength of glass/polyester composites with different interfacial strength”, Composites Part-A, 34, 1117-1124, 2003.

49. S.L.Gibson, V. Baranauskas, J.S. Riffle and U. Sorathia, “Cresol-novalac epoxy networks: properties and processability”, Polymer, **43**, 7389-7398, 2002.

Absorbed water causes hydrolytic degradation of both matrix and interface during service [50]. Water absorption in polymeric composites is shown to be Fickian as well as non-Fickian in character [51, 52]. 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. 5.6:

$$G = 1 - \frac{8}{p^2} \sum_{J=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left[- \frac{(2j+1)^2 p^2 D_x t}{h^2} \right] \quad \textbf{… 5.6}$$

Where Dx = diffusivity, t = time (second) and h = sample thickness (m)

The water content in the sample can be determined according to Eqn. 5.7:

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50. C.S. Tyberg, K.M. Bergeron, Sankarapandian, P. Singh, A.C. Loss, D.A. Dillard, J.E. McGrath and J.S. Riffle, “Structure–property relationships of void-free phenolic–epoxy matrix materials”, Polymer, **41**, 5053-5062, 2000.
51. G. Pritchard and S.S. Speake, “The use of water absorption kinetic data to predict laminate property changes”, Composites, **18**, 227-232, 1987.
52. G. Camino, M.P. Luda, A.Y. Polishchuk, M. Revellino, R. Blancon G. Merle and V.J. Mattinez, “Kinetic aspects of water sorption in polyester-resin/glass-fiber composites”,Compo. Sci. and Technol., **57**, 1469-1482, 1997.

$$M = \frac{W_m - W_d}{W_d} X100 \qquad \textbf{… 5.7}$$

Where M = % water absorbed, W_m = weight of moist sample and W_d = weight of dry sample.

The solution of diffusion equation in terms of % water absorption is given by eqn.5.8:

$$M = \frac{4M_m}{h}\sqrt{\frac{t}{p}}\sqrt{D_x} \qquad \textbf{… 5.8}$$

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. 5.8:

$$D_x = p\left(\frac{h}{4M_m}\right)^2 (slope)^2 \qquad \textbf{…5.9}$$

In present case assuming one dimensional Fickian diffusion water absorption by Jute-BCFPU/Jute-ER-2PU in pure water, 10% HCl and 10% NaCl is carried out at room temperature.

Moisture absorption study of Jute- BCFPU / Jute-ER-2 PU composite was 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 % water absorbed by Jute-BCFPU in different environments (water, 10% HCl and 10% NaCl) and diffusivity at room temperature with the passage of time are presented in Table-5.9 from which, it is evident that water absorption behavior is quite different in different environments supporting different diffusion behavior. Equilibrium water content and equilibrium time data are also reported in Table-5.9 from which, it is clear that equilibrium time (96h) and equilibrium water content (6.05%) in salt environment is almost half of water (192h and 9.75%) and acid (192h and 12.14%) environments. The observed trend in absorbed water in Jute-BCFPU is HCl > Water> NaCl. Water penetration into composite is due to

Table -5.9: Moisture uptake and diffusivity data of Jute- BCFPU composite at room temperature

Properties	**Water**	**10% NaCl**	**10%HCl**
Equilibrium time, h	192	96	192
Equilibrium water content,%	9.75	6.05	12.14
Diffusivity D_x,10^{-12} ,m^2/s	0.47	1.24	2.64

mainly by diffusion mechanism. The penetration of water in composites also occurs through capillary flow along the fiber/matrix interface followed by diffusion from the interface into the bulk resin and transported by micro cracks. Absorbed water may induce irreversible changes like chemical degradation, cracking and debonding. Cracking and blistering cause high water absorption, while leaching of small molecules results in decrease in weight.

The diffusivity in Jute-BCFPU composite in water, 10% HCl and 10% NaCl solutions was determined using Eqn.8 and it is reported in Table-5.9 from which, it is clear that diffusivity is different in different environments. The diffusivity is 2.64 times higher in salt solution and 5.62 times in acidic solution. The presence of electrolyte in water breaks water structure and hence increases diffusivity. High diffusivity in acid solution supports more structure breaking tendency as compared to salt solution. 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 due to 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 Jute-BCFPU composite. Ionic size has also affected water structure in diffusion process. H^+ ions have high tendency to break water structure as compared to Na^+ ions. The size of the hydrated Na^+ ions is greater than that of H_3O^+ ions leading to low diffusivity. Thus, smaller is the size greater is the diffusivity.

The % moisture uptake by Jute-ER-2 PU in pure water, 10% HCl and 10% NaCl as a function of time at room temperature is shown in Table-5.10, from which, it is evident that the moisture uptake behavior is quite different in water, acidic and saline environments supporting different diffusion processes.

The % equilibrium moisture uptake and equilibrium time are reported in Table-5.10, from which, it is evident that no much difference in equilibrium water uptake is observed in pure water (11.3%) and acidic (13.6%) environments but in saline (5.5%) atmosphere it is almost half of

Table - 5.10: Moisture uptake and diffusivity data of Jute-ER-2 PU composites at room temperature

Property	**Water**	**10% HCl**	**10%NaCl**
Equilibrium time, h	120	144	92
Equilibrium water content,%	11.3	13.6	5.5
Diffusivity $D_{x,10^{-12}}$ m^2/s	2.36	1.33	9.31

water and acidic environments. The equilibrium time is considerably longer in water and acidic environments than that in saline atmosphere. The observed trend in water uptake is acid > water> salt. Thus, substantially low moisture absorption tendency of Jute-ER-2PU in 10% NaCl supports its utility in marine applications. The moisture absorption study of hybrid composites was not done due to delamination in the above media.

The diffusivity of Jute-ER-2PU in different environments at room temperature is reported in Table-5.10, from which it is clear that the diffusivity in saline environment is about 3.94 times more than that in water environment and almost half in acidic environment. The different magnitudes of diffusivity in different environments indicate ionic effect on the diffusion rate. High diffusivity in saline atmosphere is probably due to electrostatic interactions between hydrated ions and polar groups present in composites. A decrease in D_x in 10% HCl is due to apparent increase in hydrated ionic size, which restricts the diffusion in cell walls. Saline solutions affect the water structure and from the present observations, it is concluded that NaCl causes breaking of water structure and hence increases the diffusivity. The moisture uptake by Jute-ER-2PU is mainly due to presence of hydroxyl groups in jute fibers and to some extent due to salvation phenomena. The π- electrons of benzene ring form weak H-bonds in aqueous environment. The lone pairs of electrons of ether oxygen and urethane linkages also form H-bonds in water and ionic media. Hydrated ions play an important role in moisture uptake behavior.

Water absorption in boiling water

Water absorption in composites mainly depends on temperature and it is independent on water content. The effect of boiling water on water absorption in Jute-BCFPU / Jute-ER-2PU composite with time is shown in Table-5.11 and Fig.5.3 and 5.4, from which, it is evident that in case of Jute-BCFPU composite water absorption is the maximum (23.5%) within an hour and then it decreased to 21.7% and reached in equilibrium within 3h, while in case of Jute-ER-2PU composite the equilibrium (6h) moisture uptake is 20.8% and after 6h it remained almost constant. The decrease in

Table -5.11: The effect of boiling water on water absorption in Jute-BCFPU /Jute- ER-2PU composite with time

Time (h)	**% Weight change**	
	Jute-BCFPU	**Jute-ER-2PU**
0	0.00	0.00
1	23.47	19.37
2	22.39	20.22
3	22.02	20.51
4	21.82	20.65
5	21.75	20.76
6	21.67	20.83
7	21.67	20.83
8	21.67	20.83
9	21.67	20.83
10	21.67	20.83

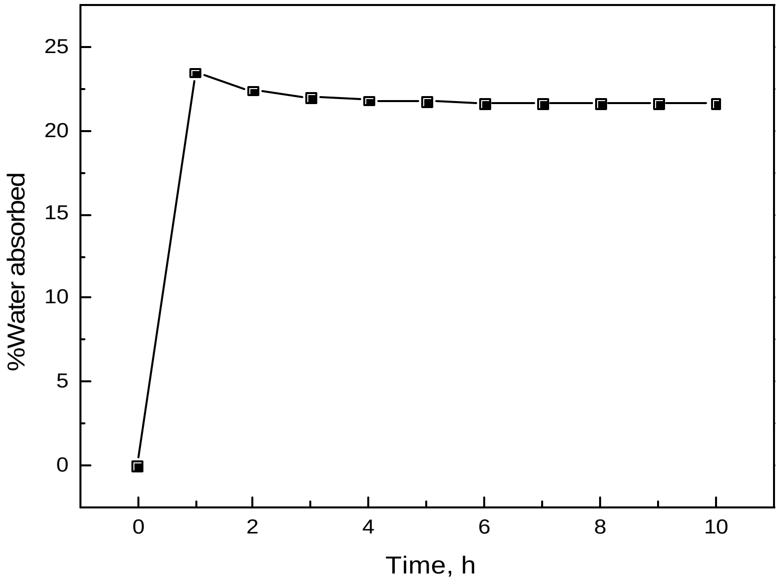

Figure-5.3: The plot of % water absorbed against time for Jute-BCFPU in boiling water

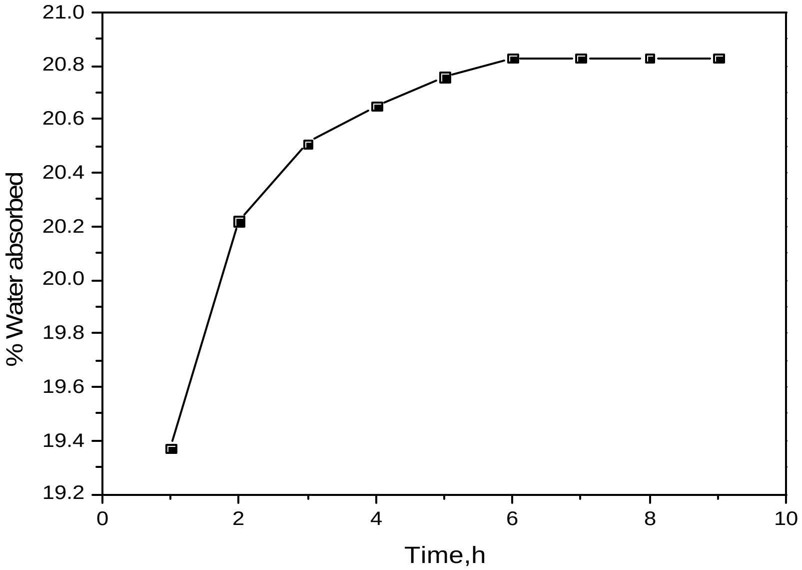

Figure-5.4: The plot of % water absorbed against time for Jute-ER-2PU in boiling water

water uptake in case of Jute-BCFPU composite after 1h is due to leaching of small components.

Equilibrium water absorption in Jute-BCFPU composite in boiling water is increased 2.2 times, but equilibrium time is reduced 64 times, while in case of Jute-ER-2PU composite equilibrium time is reduced 15.3 times and % equilibrium moisture content is increased 1.8 times compared to room temperature process supporting powerful hydrolytic stability without damaging the composites, indicating their usefulness in humid environment.

This chapter of the thesis deals with the brief summary of the work done.

CHAPTER-1

This chapter describes the general introduction and up to date literature survey on phenolic and epoxy resins, epoxy esters (polyester polyols) and polyurethane resins and their composites and their characterization.

CHAPTER-2

This chapter of the thesis deals with the synthesis of bisphenol-C (BC) and its derivatives, epoxy resins based bisphenol-C and its derivatives, bisphenol-C-formaldehyde resin, polyester polyols (epoxy esters) and polyurethane resins.

CHAPTER-3

This chapter deals with the determination of epoxy equivalent, acid values, and hydroxyl values of the epoxy resins and polyester polyols. The structures of the resins are supported by IR spectral data. This chapter also describes physico-chemical characterization of the polyurethane resins. The epoxy equivalents of the epoxy resins ER-1 to ER-5 are found to be 475, 442, 436, 389 and 500, respectively. The acid values of the polyester polyols, RAER-1 to RAER-5 were found to be 3.0, 2.03, 2.14, 9.36 and 7.025 mg KOH/g, while for OAER-1 to OAER-5 they are 3.57, 2.79, 2.49, 6.25 and 9.34 mg KOH/g and those of RER-2 and RER-3 they are 15.83 and 11.14 mg KOH/g, respectively. The hydroxyl values of the polyester polyols RAER-1 to RAER-5 are found to be 882, 867, 911, 1020 and 805 mg KOH/g, respectively and for OAER-1 to OAER-5 they are 790, 626, 848, 878, 770 mg KOH/g, while those of RER-2 and RER-3 they are 626 and 870 mg KOH/g, respectively. Thermal analysis of the RAER-1, RAER-2, RAER-3-20% PEG, RAER-3-30% PEG, BCFPU and ER-2PU were scanned at the heating rate of 10^0C/ min in the nitrogen atmosphere. All the resins have followed three step degradation kinetics. RAER-1 and RAER-2 are thermally stable up to about $182\text{-}188^0$C and are completely degraded above 600^0C into low molecular weight mass substances. Thus, incorporation of cardo group in polyurethane chains did not impart any change in thermal properties. RAER-3-20% PEG and RAER-3-30% PEG are thermally stable up to about 190-

198^0C and involved three step degradation kinetics. It is found that no effect of PEG-400 content is observed on thermal properties of co polyurethanes. For RAER-3-20% PEG, T_0, T_{10} and T_{50} are 190, 225.1 and 362.6^0C, while for RAER-3-30% PEG they are 198, 235.5 and 369.0^0C, respectively. The decomposition ranges are 190-304, 342-440 and 472-540; and 198-307, 350-430, and 448-590^0C, respectively for RAER-3-20% PEG and RAER-3-30% PEG. In case of BCFPU the first step weight loss(8.1%) in the temperature range 247-287^0C is due to decomposition of urethane linkage and moisture content leading to the formation of CO_2, alcohols, amines, aldehydes, CO, etc. The second step weight loss (42.7%) in the temperature range 459-600^0C is due to the complete decomposition of the polyurethane. In case of ER-2PU the first, second and third step weight losses are 21.1%, 27.8% and 16.2%, respectively. The ER-2PU is completely degraded in the temperature range 465-530^0C.

The densities of RAERPU-1, RAERPU-2, RAER-3-20% PEG and RAER-3-30% PEG films were determined by a floatation method at room temperature (~ 30^0C) by using CCl_4-n- hexane system. The observed densities of RAER-1 and RAER-2 are 1.2190±0.0004 g/cm^3 and 1.2308 ± 0.0002 g/cm^3, respectively, while for RAER-3-20% PEG and RAER-3-30% PEG they are 1.2379±0.0006 and 1.2016 ± 0.0006 g/cm^3, respectively. The density has decreased with increasing amount of PEG.

The tensile strength, electric strength and volume resistivity of the RAERPU-1 and RAERPU-2 are 34.7, 18.7 MPa; 80.7, 44.4 kV/mm and 1.7×10^{15}, 2.2×10^{15} ohm cm, respectively, while for RAER-3-20% PEG and RAER-3-30% PEG it is 33.0, 4.5 MPa; 57.2, 43.1 kV/mm and 4.6×10^{12}, 2.7×10^{12} ohm cm, respectively. The lower tensile and electrical properties in case of RAERPU-2 is due to the restricted rotation of the bulky cyclohexyl group. The lowering of mechanical and electrical properties in case of RAER-3-30% PEG is due to the higher inter chain distances in the networks, which imparts higher flexibility to the resin.

Chemical resistance of RAERPU-1, RAERPU-2, RAER-3-20% PEG and RAER-3-30% PEG films was tested against various reagents such as pure water, 10% each of aqueous HCl, HNO_3, H_2SO_4, NaOH, KOH and NaCl at room temperature and at the interval of 24h for 30 days by change in weight method. RAERPU-1 and RAERPU-2 have remained unaffected in pure water. In HCl solution RAERPU-1 has remained unaffected up to 24h but after that it has shown water absorption tendency. It gained weight up to 72h and then remained constant (6.4%). In H_2S0_4 solution it remained unaffected throughout but in HNO_3 solution it showed weight gain tendency up to 72 h and then remained constant (8.3%) and the film became yellowish after 6 days indicating nitration of aromatic rings. In NaCl solution, the film remained unaffected up to 48 h and then it showed weight gain tendency up to next 24 h and gained maximum weight (8.3%). Similarly in NaOH and KOH solutions, it remained unaffected up to 24h and then weight gain increased up to 72h and then remained constant. The equilibrium weight gain in NaOH solution is 6.6%, while it is 13% in KOH solution.

The RAER-3-20% PEG and RAER-3-30% PEG remained unaffected in pure water and 10% NaCl solution and showed moisture uptake tendency in acidic and alkaline atmosphere. The maximum moisture uptake is observed within 24-48h and it is 4.7-15% in 10% each of HCl, H_2SO_4 and HNO_3 and 8.7-14.2 % in 10% each of NaOH and KOH solutions. RAER-3-30% PEG has much low water absorption tendency as compared to RAER-3-20% PEG due to increasing hydrophobic PEG-400 concentration.

CHAPTER-4

This chapter of the thesis describes the coating application of the polyurethane resins on different substrates such as glass, copper, steel and aluminium. The coated plates were tested for their water, salt and acid resistance. Coated films possess excellent hydrolytic stability against pure water and 10% aq. NaCl solution but they possess water absorption (0.3–8.2%) tendency in acidic environment.

CHAPTER-5

This chapter of the thesis elaborates the fabrication, mechanical, electrical and chemical resistance studies of the composites. Jute, Jute-RH and Jute-WH composites were prepared by hand-lay-up technique under 30.4MPa pressure.

Similarly Jute-ER-2PU and Jute-RH/WH-ER-2PU composites were fabricated. Jute-BCFPU composite possesses good tensile strength and flexural strength (50-53MPa), while Jute-RH/WH-BCFPU hybrid composites possess moderate tensile strength (9-11MPa) and a fairly good flexural strength (15-31MPa). Composites possess 1.1-2.2 kV electric strength and 0.94 -1.26x10^{12} ohmcm volume resistivities. Jute-ER-2PU, Jute-RH-ER-2PU and Jute-WH-ER-2PU possess respectively 37.4, 9.5 and 14.7 MPa tensile strength; and 39.6, 12.9 and 21.3MPa flexural strength, 1.3, 1.8 and 1.9kV/mm electric strength and 1.40x 10^{13}, 1.84x10^{13} and 1.91x10^{13} ohm cm volume resistivity.

Moisture uptake behavior in Jute-BCFPU composite is different in water (9.75%), 10%HCl (12.14%) and 10%NaCl (6.05%). Equilibrium water uptake time in salt environment is observed 96h, while in pure water and acidic environments it is 192h. In boiling water equilibrium moisture uptake and equilibrium time are found to be 21.7% and 3h, respectively. The moisture uptake behavior of Jute-ER-2PU in water, 10% HCl and 10% NaCl at room temperature is quite different. Equilibrium moisture content of Jute-ER-2PU in 10% NaCl (5.5%) is almost half of those in water (11.3%) and 10% HCl (13.6%) environments. Comparatively equilibrium time for saline environment is also low. Equilibrium moisture uptake and equilibrium time in boiling water are 20.83% and 6h, respectively.