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SYNTHESIS AND PHYSICO-CHEMICAL INVESTIGATION OF SOME THERMOSETS AND THEIR COMPOSITES

A
THESIS
SUBMITTED TO THE SAURASHTRA UNIVERSITY
FOR
THE DEGREE OF
DOCTOR OF PHILOSOPHY

IN

THE FACULTY OF SCIENCE (CHEMISTRY)

BY

Pankaj K. Mer

UNDER THE GUIDANCE

OF

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

Date: -04-2010
Place: Rajkot.

(Mr. Pankaj K. Mer)

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

Date : -04-2010
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Dedicated to

my

Beloved Family…

ACKNOWLEDGEMENTS

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

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The never ending process of unsurpassable devotion, love and affection, which was showered upon me by my father Kishorbhai, mother Jayshreeben, brothers, sister in law, who have enlightened my path and always boosted me to go ahead to reach the goal.

Pankaj K. Mer

CONTENTS

SYNOPSIS

SYNTHESIS AND PHYSICO-CHEMICAL INVESTIGATION OF SOME THERMOSETS AND THEIR COMPOSITES

Mr. Pankaj K. Mer

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

FACULTY : **SCIENCE**
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INVESTIGATION OF SOME
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GENERAL INTRODUCTION

The use of renewable starting materials in the preparation of polymers has been stimulated over the years by researchers and governmental agencies all over the world as a 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].

Vinyl ester (VE) resins are well-known for their outstanding corrosion resistance and satisfy a critical requirement in fiber reinforced plastic applications. VE resins are brittle in nature and therefore, toughening properties is essential for both scientific and engineering purposes. Several techniques have been developed to improve the toughness of VE resins including (1) modifications of network structure via manipulation of VE molecular weight and styrene content, (2) use of reactive and nonreactive rubber modifiers designed for phase separation upon cure, and (3) use of nanostructured thermoplastic fiber mats for interlaminar toughening [4].

Vinyl ester resins are thermosetting resins [5] that consist of a polymer backbone (usually epoxy resins) with an acrylate or methacrylate termination. The combination of excellent chemical resistance and mechanical properties [6, 7] of epoxies and handling properties comparable to those of unsaturated

---

1. Jeevananda, T. and Siddaramaiah, “Synthesis and characterization of polyaniline filled PU/PMMA interpenetrating polymer networks.” Eur. Polym. J. **39,**569, 2003.
2. Kendagannaswamy, B. K., and Siddaramaiah, “Chain extended polyurethane-synthesis and characterization.” J Appl. Polym. Sci. 84, 359, 2002.
3. Gandini, A, Comprehensive Polym. Sci., Suppl.1, 1992.
4. Robinette, E. J.; Ziaee, S. and Palmese, G. in International SAMPE Symposium and Exhibition (Proceedings) 47(II), 1339, 2002
5. Launikitis, M. B. Vinyl ester resins. In Hand Book of Composities; Lubin, G., Ed.; Van Nostran Reinhold Company: New York, 38–49 1982.

polyesters has made them a viable product for various industrial applications such as coatings, varnishes, radiation curable inks, laser video discs, spherical lens materials and specialty coatings for optical fibers, printed circuit boards, composites, etc. [8–14].

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6. Poland, D. E.; Martineau, R. R. FRP in the bottle against acid rain, part-3. Epoxy based vinyl ester resins as materials of construction. Mater. Process. Tech. Environ. Prot. Min. Metall. Proc. Ibnt. Symp. 1993; Godbehev, P. W., Eds.; Chem. Abstr. 181350z, 15–163, 121, 1993.
7. Peng, L.; Xiaoping, Y.; Yunhua, Y.; Dingshing, Y. Cure kinetics, microheterogeneity, and mechanical properties of the high temperature cure of vinyl ester resins. J. Appl. Polym. Sci., 92 (2), 1124–1133, 2004.
8. Amendola, E.; Giamberini, M.; Carfagna, C.; Ambrogi, V. Self-toughening liquid crystalline vinyl ester adhesives. Macromole. Symp., 180 (1), 153–168, 2002.
9. Yamada, K.; Yamane, H.; Kumada, K.; Tanabe, S.; Kajiyama, T. Plasma-graft polymerization of a monomer with double bonds onto the surface of carbon fiber and its adhesion to a vinyl ester resin. J. Appl. Polym. Sci., 90 (9), 2415–2419, 2003.
10. Howell, B. F.; De Realf, Pigmented coatings cured with visible light. Polym. Mater Sci. & Engg., 74, 387–388, 1996.
11. Masujiro, S.; and Kazuyoshi, I. Thermosetting Printing Inks. JP 74, 67, 709. esterification of monoepoxies 327, July 01, 1974.
12. Macinally, A.; and Miller, A. The Use of epoxy VER system in the marine, offshore, chemical and construction industries. Proc. Int. Conf. Fiber Reinf. Compos. 7th 1998.
13. Henne, M.; Breyer, C.; Niedermeier, M.; and Ermanni, P.A. New kinetic and viscosity model for liquid composite molding simulations in an industrial environment. Polym. Comp., 25 (3), 255–269, 2004.
14. da-Silva, A.L.; Teixcira, S.C.S.; Widal, A.C.C.; Coutinho, F.M.B. Mechanical properties of polymer composites based on commercial epoxy vinyl ester resin and glass fiber. Polym. Test., 20 (8), 895–899, 2001.

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

CHAPTER-1:	**Introduction**
CHAPTER-2:	**Syntheses of monomers, epoxy and epoxy esters**
CHAPTER-3:	**Curing of resins and their characterization**
CHAPTER-4:	**Fabrication and physico-chemical characterization of the composites**
CHAPTER-5:	**A comprehensive summary of the work done**

CHAPTER-1: Introduction

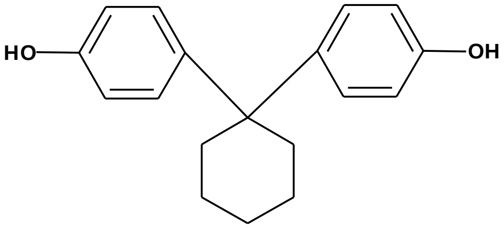
This chapter of the thesis describes the up to date literature survey on synthesis, applications and characterization of epoxy resins, epoxy esters (polyester polyols), vinyl ester resins and their composites in various fields of science.

CHAPTER-2: Syntheses of monomers, epoxy and epoxy esters

This chapter is further subdivided into six sections:

Section-1: Synthesis of 1, 1'- bis (4-hydroxy phenyl) cyclohexane [Bisphenol – C]

Bisphenol–C was synthesized by Friedel–Crafts condensation of phenol with cyclohexanone by using a mixture of HCl:CH_3COOH (2:1 v/v) as a catalyst at 50-55^oC for 4h and were repeatedly recrystallized from methanol-water system prior to their use.

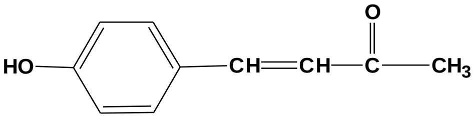


BC

Section-2: Synthesis of bis-phenol of chalcone

[A] Synthesis of 4-(4-Hydroxyphenyl)but-3-en-2-one

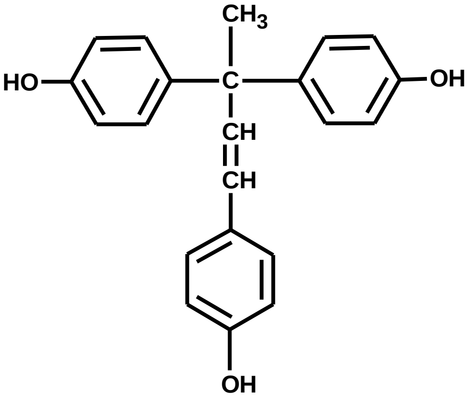
4-(4-Hydroxyphenyl)but-3-en-2-one was synthesized by condensing p-hydroxy benzaldehyde and acetone in basic condition for 4 h at 30°C. The structure of the chalcone is as under.



CN

[B] Synthesis of 4,4',4''-but-1-ene-1,3,3-triyltriphenol

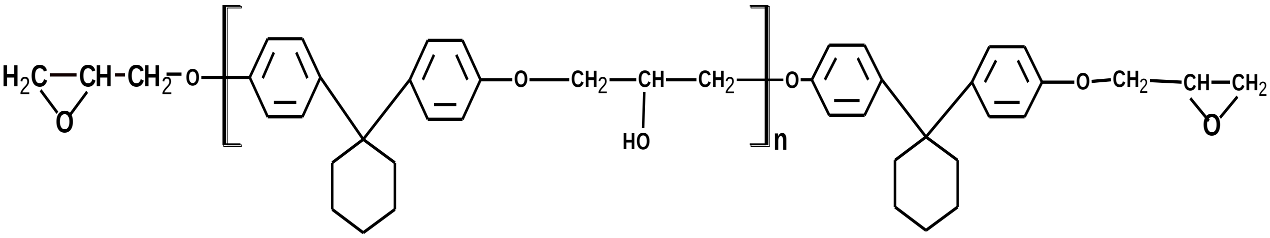
4,4',4''-but-1-ene-1,3,3-triyltriphenol was synthesized by Friedel–Crafts condensation of phenol with chalcone by using a mixture of HCl:CH_3COOH (2:1 v/v) as a catalyst at 50-55°C for 2h and was repeatedly recrystallized from methanol-water.



BCN

Section-3: Synthesis of epoxy resin of Bisphenol-C

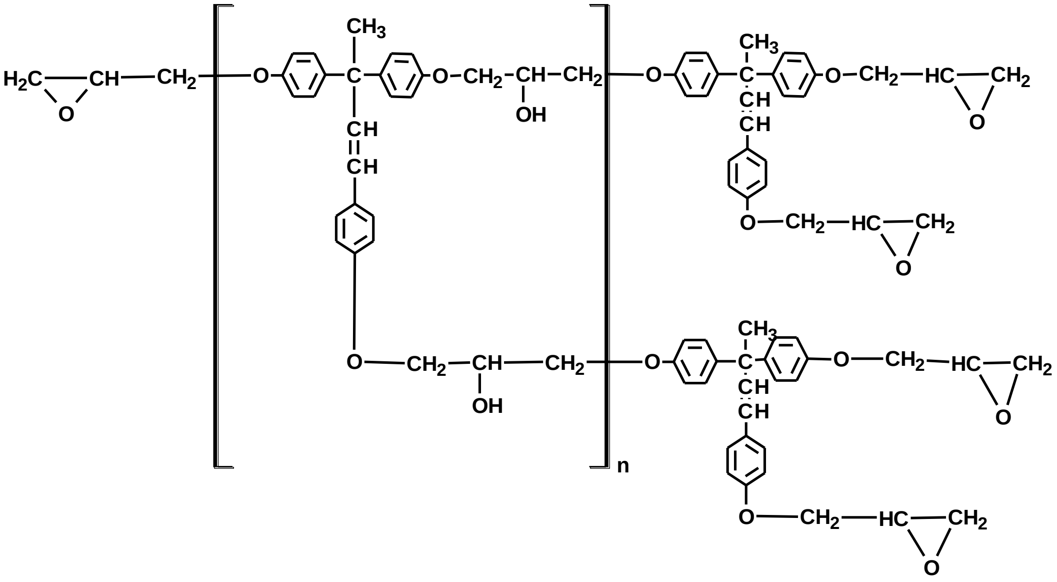
Epoxy resin of BC was synthesized by condensing BC with epichlorohydrin by using isopropanol as a solvent and alkali as a catalyst at reflux temperature for 3 h. The resin was isolated from chloroform.



EBCA

Section-4: Synthesis of epoxy resin of BCN

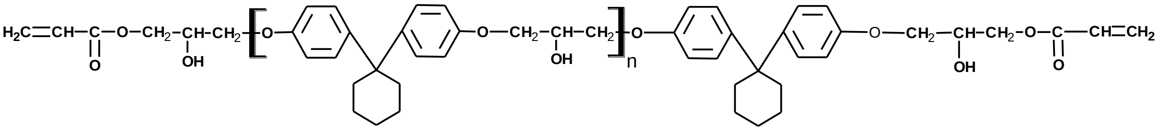
Epoxy resin of bisphenol of chalcone was synthesized by condensing bisphenol of chalcone with epichlorohydrin by using isopropanol as a solvent and alkali as a catalyst at reflux temperature for 3 h. The resin was isolated from chloroform.



ECN

Section-5: Synthesis of epoxy acrylate

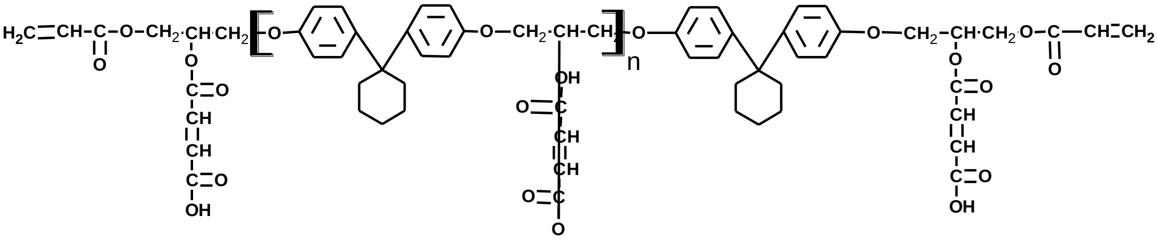
The epoxy acrylate was synthesized by condensing EBC with acrylic acid (1:2 mole ratio) by using 1, 4- dioxane as a solvent and tri ethyl amine as a catalyst at reflux temperature for 4-6h to get acid value < 10. The structure of the epoxy acrylate is as under



EBCA

Section-6: Synthesis of vinyl ester resin by using maleic anhydride

The polyester polyols were synthesized by condensing EBC with acrylic acid (1:2 mole ratio) by using 1, 4- dioxane as a solvent and tri ethyl amine as a catalyst at reflux temperature for 4-6h to get acid value < 10. The resultant VE was reacted with maleic anhydride (1:2 mole ratios) to get comb type polymeric structure. The general structure of the polyester polyols is as under.



ECAM

Section-7: Syntheses of polyurethane resins

[A] Synthesis of polyurethane of EBCAAM

Polyurethane of EBCAAM was prepared by reacting polyester polyol with 2, 4-toluene diisocyanate by using $CHCl_3$ as a solvent at room temperature for 15 min.

[B] Synthesis of copolyurethane resin

Copolyurethane resin of PU was synthesized by reacting corresponding polyol, TDI and PEG-200 (30% of polyester polyol) at room temperature.

CHAPTER-3: Curing of resins and their characterization

This chapter is further subdivided into five 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 by 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 vinyl ester & unsaturated poly ester resins in varying compositions were investigated by TG method at the heating rate of 10 ^{0}C/min in an N_2 atmosphere

CHAPTER-4: Fabrication and physico-chemical characterization of the composites

This chapter is further subdivided into three sections.

Section-I: Fabrication of composites

Composite materials are formed by combination of two or more materials that retain their respective characteristic properties when combined together but they are superior to those of individual constituents. Main constituents of the composites are matrix materials i.e. resins and reinforcing materials (synthetic/natural fibers).

Composite of jute fibers were prepared by hand lay up compression molding under pressure of 30.4 MPa and at appropriate temperature.

Section-II: Mechanical and electrical properties of composites

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

Section-III: Chemical resistance and boiling water study of composites

The composites of the 50mm x 50mm dimensions were prepared and the edges of composites were sealed with the resins. The chemical resistance of the composites was determined at room temperature and at the interval of 24 h against water, 10% each of aqueous solutions of HCl and NaCl at room temperature by change in mass method till equilibrium was established. The moisture uptake data are interpreted in light of medium and fiber modification.

In order to study effect of moisture absorption in boiling water, preweighed composites of 50mm x 50mm were placed into a 250 ml beaker containing boiling water. The samples were taken out of boiling water at the interval of 1h, cooled, wiped the surfaces with tissue papers, reweighed and reimmersed in boiling water till equilibrium was established. The data are interpreted in light of effect of temperature on moisture uptake.

CHAPTER-5: A brief summary of the work done

A brief review of the work incorporated in the thesis is described in this chapter.

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CHAPTER – 1

Introduction

General Introduction

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

Historians frequently classify the early ages of man according to the materials that he used for making his implements and other basic necessities. The 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 he was employing a range of materials such as stones, woods, ceramics, glasses, skins and fibers. Until the 19th century man's inanimate possessions, his home, his tools, his furniture, were made from varieties of these classes of materials.

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

The most ancient polymeric materials, 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. This in modern times became of great importance in the vulcanization of rubber and production of thermosetting plastics.

[A] LITERATURE SURVEY ON BISPHENOLS

Bisphenols are the important constituents or intermediates in dyes, drugs, paints and varnishes, coatings, pesticides, plasticizers, fertilizers, bactericides and in other applications. They are widely applied in manufacturing thermally stable polymers, epoxy resins and polyester resins.

Farbenind [1, 2] has studied the condensation of phenols and ketones in the presence of acetic acid, hydrochloric acid at 50°C and also reported the melting points of 1,1'-bis(4-hydroxy phenyl) cyclohexane (186°C). 1,1'-bis(3-methyl-4- hydroxyl phenyl) cyclohexane (186°C) and 1,1'-bis(4-hydroxy phenyl)-4-methyl cyclohexane (179°C). The products are useful as inter- mediates for dyes and drugs.

McGreal et al [3] have reported the condensation of ketones (0.5 mol) and phenols (1.0 mol) in acetic acid. The solutions were saturated with dry HCl for 3-4 h and the mixture was kept up to 4 weeks until the mass 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

   $PhOH + R_2CO \rightarrow R_2C(OH)C_6H_4OH$
2. $R_2C(OH)C_6H_4OH + PhOH \rightarrow R_2C(C_6H_4OH)_2 + H_2O$

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1. I. G. Farbenind. Condensation of ketones with phenols. Fr. Patent 647,454; C.A. 23, 2540, 1929.
2. I. G. Farbenind. Ger. Patent 467,728 1927; C.A. 23, 1929.
3. M. E. McGreal, V. Niedert and J. B. Niedert. Condensation of ketones with phenols. J. Am. Chem. Soc., 61, 345-348, 1939.

Johnson and Musell [4, 5] have reported synthesis of 1,1'-bis(4-hydroxy phenyl) cyclohexane (I) using 5 mol of phenol, 1 mol of a cyclohexanone, H_2S or BuSH below 40°C with 0.1-0.3 mol dry HCl gave (I) m.p.186-187°C; 4-Me-I 178°C; 1,1'-bis(4-hydroxy-3-methyl phenyl) cyclohexane m.p. 187°C and 1,1'-bis(4-hydroxy-3-isopropyl phenyl) cyclohexane, m.p. 109-111.5°C. Mash containing small quantities of bisphenol (I) protect chickens from coccidiosis better than does a sulfaguanidine.

Bender et al. [6] have reported preparation of various bisphenols by reacting phenol, NaOH and acetone. The mixture was refluxed for 16 h and acidified to p^H 2-3 with 6N HCl. The yield was 47.5%. Similarly they have also synthesized 1,1'-bis(4-hydroxy phenyl) cyclohexane (m.p. 187°C), 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane (m.p.186-9°C) and 1,1'-bis(3-chloro-4-hydroxy phenyl) 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 ultraviolet in the presence of 37% aq. HCl or 70% H_2SO_4 as condensing agent and stirring at 30-37°C. 1,1'-Bis(4-hydroxy phenyl) cyclohexane (m.p. 186-189° C) was obtained in 93% yield from 1 mol cyclohexanone and 4 mol 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 as a catalyst at room temperature for 6 days.

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4. J. E. Johnson and D. R. Musell. Bis (hydroxy phenyl) cyclohexane compositions. U.S. 2,538,725 1951; C.A. 45, 4412, 1951.
5. J. E. Johnson and D. R. Musell. Diphenol compound composition for coccidiosis, U.S. 2,535,014 1950., C.A. 45, 2635, 1951.
6. H. L. Bender, L. B. Conte and F. N. Apel. Bisphenols. U.S. 2,858,342 1958; C.A. 53, 6165, 1959.
7. H.L.Bender, L.B.Conte and F.N.Apel. Diphenol compound composition for coccidiosis control. U.S. 936,272 1960; C.A. 45, 2635, 1951.
8. Farbenfabriken. Bisphenols. Ger. 1,031,788 1958; C.A. 54, 19603, 1960.

Alexandru [9] 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.

Freudewald et al. [10] have reported the condensation of phenol (94 g) with cyclohexanone (98 g) in the presence of 2 g EtSH and anhydrous HCl (4.7 g) and heating at 70^oC in closed system for 3 h to give 97% yield of 1,1'-bis(4-hydroxy phenyl) cyclohexane.

Rao et al. [11] have reported a convenient method for the preparation of bisphenols. Cyclohexanone was treated with PhOH at 40^oC and with o-cresol at room temperature in the presence of HCl and AcOH to give 1,1'-bis(4-hydroxy phenyl) cyclohexane and 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane, respectively.

Garchar et al. [12-15] have studied optimization reaction conditions for the synthesis of 1,1'-bis(R, R'-4-hydroxy phenyl) cyclohexane by condensing cyclohexanone (0.05 mol) and phenol, o-cresol, and 2,6-dimethyl phenol (0.1 mol) 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, 70^oC.

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9. B.S. Alexandru, U.S. Patent 4,766,255 1988; *C.A.* 110, 38,737, 1989.
10. Freudewald, E. Joachim, Konarad and M. Frederic. p-Phenylphenol. Fr. 1,537,574, 1968; C.A. 71, 21868, 1969.
11. M. V. Rao, A. J. Rojivadiya, P. H. Parsania and H. H. Parekh. Convenient method for the preparation of the bisphenols. J. Indian Chem. Soc., 64, 758-759, 1987.
12. H. H. Garchar, H. N. Shukla and P. H. Parsania. Kinetics of formation of 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane, Indian Acad. Sci. (Chem. Sci)., 103, 149-153, 1991.
13. 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, 340-347, 1993.
14. H. H. Garchar and P. H. Parsania. Optimization reaction conditions for synthesis of 1,1'-bis(3,5-dimethyl-4-hydroxy phenyl) cyclohexane. Asian J. Chemistry, 6, 87-91, 1994.
15. H. H. Garchar and P. H. Parsania. Optimization reaction conditions for synthesis of 1,1'-bis(4-hydroxy phenyl) cyclohexane. Asian J. Chemistry, 6, 135-137, 1994.

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 different 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 antifungal agents.

[B] LITERATURE SURVEY ON EPOXY RESINS, EPOXY ESTERS (POLY ESTER POLYOLS)

Epoxy resins are the most versatile class of contemporary plastics. Due to tendency of undergoing variety of chemical reactions and became material of choice for researchers for several years. By the help of reactions like co-polymerization, chain extension by reactive diluents, side chain modification, incorporation of variety of fillers and structure modifiers, the resin structure can be modified. The capabilities of undergoing vast chemical reactions of the resins the desire properties can be achieved.

Epoxy resins are widely used as a matrix in composites in different applications where chemical, mechanical, thermal, and dielectric properties are necessary. In addition, epoxy resins are versatile crosslinked thermosetting polymers with an excellent chemical resistance and good adhesion properties to different substrates. Due to these properties, they are used as adhesives and coatings [16]. Epoxy is best for laminates in combination with glass fiber to achieve excellent electrical insulators.

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16. Hackman, and L. Hollaway. Composites Part A, 37, 1161–1170, 2006.

Use of epoxy resins in composite matrix in high technology areas is limited, as these areas require material with inherent low thermal expansion coefficients and high toughness [17,18] and better heat and moisture stability. Recently, a lot of research work has been done to improve the required parameters of epoxy resins through modifications in both the backbone and pendant groups. Urea-formaldehyde and silicon resins have been reported to have excellent properties as modifiers for the epoxy resins. The first commercial attempts to prepare resins from epichlorohydrin were made in 1927 in the United States. Credit for the first synthesis of bisphenol-A-based epoxy resins is shared by Dr. Pierre Castan of Switzerland and Dr. S.O. Greenlee of the United States in 1936. Dr. Castan's work was licensed by Ciba, Ltd. of Switzerland, which went on to become one of the three major epoxy resin producers worldwide. Ciba's epoxy business was spun off and later sold in the late 1990s and is now the advanced materials business unit of Huntsman Corporation of the United States. Dr. Greenlee's work was for the firm of Devoe-Reynolds of the United States. Devoe-Reynolds, which was active in the early days of the epoxy resin industry, was sold to Shell Chemical (now hexion, formerly Resolution Polymers and others).

Desai et. al [19] 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 as studied for the bond strength improvement

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17. D. Puglia, L. B. Manfredi, A. Vazquez and J. M. Kenny. Thermal degradation and fire resistance of epoxy-amine phenolic blends. Polym. Degr. and Stab., 73(3), 521–527, 2001.
18. K. E. L. Gersifi, N. Destais-Orvoe¨n, and G. Tersac. Glycolysis of epoxid–amine hardened networks. 1. diglycidylether/aliphatic amines model networks. Polymer, 44(14), 3795–3801, 2003.
19. 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.

via an increase in wettability of the rubber surface. Wettability was found by measuring the contact angle using Goniometer.Bond strength was evaluated by a 1800 T-peel strength test. The surface modification and mode of bond failure were studied by scanning electron microscopy (SEM).

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 [20]. Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes [21], 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 [22] 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.

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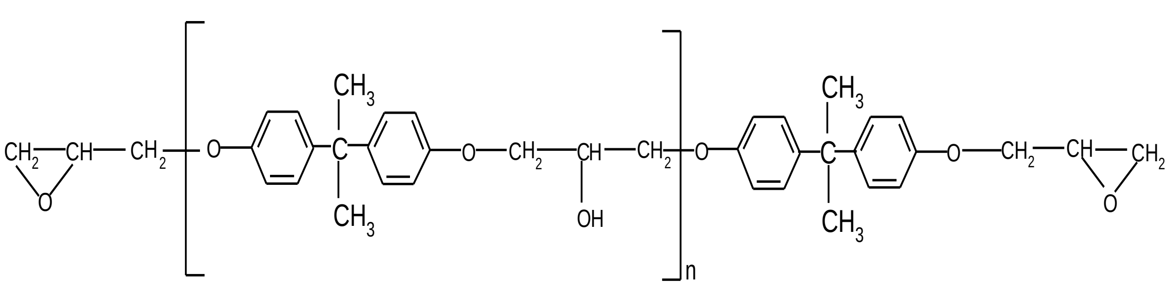
20. A. F. Yee, and R. A. Pearson, Toughening mechanisms in elastomer modified epoxies: Part-1 mechanical studies, J. Mater. Sci., 21, 2462-2474, 1986.
21. A. V. Cunliffe, M. B. Huglin, P. J. Pearce and D. H. Richards, An anionically prepared flexible adhesive: 1: Synthesis. Polymer, 16, 654-658, 1975.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

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). 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

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) (I).



(I)

The resin can be obtained with different degrees of polymerization ranging from low viscosity liquids to high melting solids [23] 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 bisphenol-A in the presence of a suitable polymerization catalyst such that the reaction takes place without evolution of byproduct [24].

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23. I. A. Brydson. Plastics materials VIth edition, Butterworth Heinemann Ltd., Oxford, 722, 1995.
24. H. Lee and K. Neville. 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 (^{o}C)	Molecular Weight	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

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

- Resin viscosity (of liquid resin)
- Epoxide equivalent
- Hydroxyl equivalent
- Average molecular weight
- Melting point (of solid resin)
- Heat distortion temperature (of cured resin)

The epoxy resin can be converted into three dimensional infusible networks together by covalent bonds. This conversion from a liquid or a friable brittle solid into tough cross-linked polymer is called curing or hardening in epoxy technology. Mainly amine hardening and acid hardening systems are employed for curing of epoxy resins.

Epoxy resins are widely used for land, marine and space transportation, automobile and electrical components, rehabilitations products and pollution control equipments. The characteristic properties of epoxy resins make them suitable for an increasing number of engineering applications, such as high strength and stiffness, good dielectric behavior, resistance to chemicals, low shrinkage during cure, etc. Despite of excellent properties their brittle behavior with low elongation restricts their use for high performance applications [25].

Chemie Produkte [26] has reported the sealing composition for pipe joints and building materials. A typical composition consists of a mixture of an epoxy resin, a hardener and tar, which polymerized rapidly.

Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes[27], acrylates, etc. This

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25. A. F. Yee, and R. A. Pearson. Toughening mechanisms in elastomer modified epoxies: Part-1 mechanical studies. J. Mater. Sci., 21, 2462-2474, 1986.
26. Chemie Produkte. Epoxy resins containing sealing compositions. Ger. 1,020,140, 1957., C.A. 54, 179704, 1957.

modification of epoxy resin is feasible due to highly reactive epoxy ring, which can also undergo ring opening reaction in the presence of acids [28] to yield polyester polyol containing a free hydroxyl group that can be utilized to produce polyurethanes. To make an economic production of polyurethanes, efforts have been made to prepare polyester polyols from the low cost natural oils and their derivatives.

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

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

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27. A. V. Cunliffe, M. B. Huglin, P. J. Pearce and D. H. Richards. An anionically prepared flexible adhesive, Polymer, 16, 654-658, 1975.
28. C. A. May. Epoxy resins- chemistry and technology. Marcel Dekker, New York, 1988.

Table-1.2 Fatty acids and properties of epoxy esters

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 baking.

Greenlee [29] has prepared the rapid drying composition from diphenols and epichlorohydrin and esterified this product with Tall–oil.

Chemie Produkte [30] 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 [31] 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. [32] have prepared epoxy resin foams from aqueous dispersions. Epoxy resin based on bisphenol-A, benzsulfohydrazide, dipropylene triamine were dispersed in water by 2,3-dibromopropyl phosphate as a dispersing medium. Rigid foam was obtained by this composition, which is suitable for architectural uses.

CIBA Ltd. [33] has reported coating composition for floors, roofs, walkers and walls based on bisphenol–A epoxy resin. The composition was room temperature hardenable having quartz sand, epoxy resin, dibutyl phthalate together with triethylene tetramine. This composition has consistency of mortar and a pot life of 2.0 – 2.5h. It is spread on a concrete floor to a depth of 4mm. hardening required 24-48h. The composition shows excellent adhesion in non-cracking and is highly resistance to chemical.

Union Carbide Co. [34] has reported curing of polyepoxides with liquid glycol diamines ($H_2N(CH_2)_3O(C_nH_{2n}O)_x\ (CH_2)_3NH_2$), where n is 2-5 and x is 1-11.

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29. S. O. Greenlee. Tall-oil esters, U.S. 2,493,486, 1949; C.A. 44 2770, 1950.
30. Chemie Produkte. Epoxy resins containing sealing compositions. Ger. 1,020,140 1957; C.A. 54, 179704, 1957.
31. B. E. Lederman (Midland Chemical Co.). Bisphenol-modified wrinkle varnish. C.A. 53, 1779, 1959.
32. R. Petri, H. Reinhard and L. Keller. Epoxy resin foams from aqueous dispersions Ger. 1,080,774, 1960; C.A. 55, 14,982, 1961.
33. CIBA Ltd. Epoxy resin containing coatings. Brit. 883,521, 1961 C.A. 56, 11746, 1962.

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. [35] have reported synthesis of flexible adhesive film having honeycomb structure. Thus, an epoxy resin mixture was prepared by heating 100 parts of glycidyl ether of bisphenol–A at 121^oC, adding 2-parts fine SiO_2 and stirring at 149^oC 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^oC and the resulting mixture was milled at 77^oC to complete dispersion.

Bremmer [36] 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^oC under an N_2 atmosphere with stirring. The composition was cured by triethyl amine.

Taft [37] has reported new polymeric coating agents with improved properties. Such composition consists of a reaction product of hydroxy or epoxy containing compound capped with the bisphenol acid, 4-4'-bis(4-hydroxy phenyl) valeric acid (II) with a poly isocyanate and cross linked with an amine.

Thus (II) reacts with 1,6-hexanediol and the reaction product was treated with Mondur HC (poly isocyanate) to give a composition, which was sprayed to a

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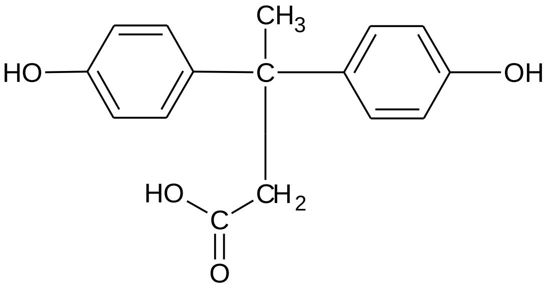
34. Union Carbide Co. (by Norman H. Reinking.). Liquid glycol diamine curing agent for polyepoxides. Brit. 904, 403, 1962; C.A. 58, 1643, 1963.
35. Minnesta (Mining and Manufacturing Co.). Flexible adhesive film, Ger. 1,100,213, 1961; C.A. 58, 11551, 1963.
36. B. J. Bremmer (Dow Chemicals Co.). Flame retardant epoxy resin. U.S.3, 294,742, 1966; C.A. 66, 38487, 1967.
37. D. D. Taft. (Ashland Oil Inc.). Polymeric coating agents. U.S. 2,203,594, 1971; C.A. 77, 154099, 1972.

10-75 μ thick film on glass, metal or wood and cured for 5-15 sec in triethylamine. On heating 200g (I) and 50 g nonyl phenol for 1h at 66°C gave the blocked curing agent. A mixture of this compound, bisphenol-A-epichlorohydrin copolymer (epoxy equivalent ~190) and 2,2-bis(o-hydroxy phenyl) propane-propylene oxide copolymer epoxide equivalent ~ 345) were cooked together. The composition has self-life of about 4 h and 70 min at 0°C.



(II)

Castan and Gandillon [38] 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. [39] have reported coatings of polyepoxy resin and dimeric fatty acids. Aliphatic polyepoxides or dihydric phenol react at 150° 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 baking in the presence of amine catalysts and optically together with phenol or urea HCHO resins.

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38. P. Castan and C. Gandillon (to Stella S.A.,). U.S. 3,028, 348, 1958; C.A., 57, 11,338, 1962.
39. Devoe and Raynolds Co. Inc. (by John E. Masters). Ger. 1,130, 598, 1953; C.A., 57, 12,660, 1962.

Kinck and Ditrych [40] had synthesized epoxy resin ester of Bisphenol-C 1, epichlorohydrin 1.16, and NaOH 1.25 moles in organic solvents at 80-100º until the softening point was 100ºC. The resin obtained had an ester equivalent of 180 content of epoxy groups 0.11 mole/100 g, and no. of -OH groups 0.33 mole/100 g. Fatty acid (1600 parts) isolated from a soyabean oil was treated with 400 parts dicyclopentadiene at 280ºC during 3h.Volatile and unreacted components were distilled in vacuum. The prepared resin (900 parts) was mixed in a stainless steel vessel with the prepared acids (950 parts) and heated to 140^{o}C, and stirred under CO_2. When the mixture was homogenized, the product was heated to 230^{o}C during 2 h and kept at the temperature until the acid no was 10 mg KOH /g, then the mixture was cooled to 170^{o}C and dissolved 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. [41] has reported salt spray resistant coating composition of alkyd resin, drying oil (soyabean oil), and liquid epoxy resin (condensation) product of epichlorohydrin and diphenyl isoporpane. These compositions exhibit good adhesion and corrosion resistance under topcoats of acrylic enamel.

Shimizu et al. [42] 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 [43] 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

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40. J. Kinck and Z. Ditrych, Czech. 101,431, 1961; C.A., 58, 674, 1963.
41. Nemours and Co. (by Ralph G. Swanson) Belg. 632, 997, 1963; C.A., 59, 14,734, 1964.
42. Shimizu Shigeo, Tachibana Akihiro, Aritomi Michio, Mori Akitshi, Suzuki Tsotoma (Toko Chemical Industry Co., Ltd). Japan Kokai 4,90,14,600, 1974; C.A. 81, 1,53,510, 1974.

group. For example bisphenol-F and styrene were reacted in presence of catalyst at 120°C, and equivalent weight 670-690 g/mol and viscosity at 25°C in 40% butyl diglycol solutions 480-510 mPas.

Nakahara et al. [44] 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′-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 than that of glass.

Liu et al. [45] have prepared simultaneous interpenetrating polymer networks (IPNs) based on epoxy (diglycidyl ether of bisphenol-A) and unsaturated polyester resin (UP) using m-xylene diamine and benzoyl peroxide as curing agents. A single glass transition temperature for each IPN was observed with differential scanning calorimetry (DSC), which suggested good compatibility of epoxy and UP. This compatibility was further confirmed by the single damping peak of the rheometric dynamic spectroscopy. Curing behaviors were studied with dynamic differential scanning calorimetry and the curing rates were measured with a Brookfield RTV viscometer. It was noted that an interlock

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43. U. Neumann and M. Hoenel, Can. Pat. Appl. CA 95, 2,152,427, 1995; C.A. 124, 234985, 1996.
44. 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.
45. 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.

between the two growing networks did exist and led to a retarded viscosity increase. However, the hydroxyl end groups in UP catalyzed the curing reaction of epoxy; in some IPNs where the hydroxyl concentration was high enough, such catalytic effect predominated the network interlock effect, leading to fast viscosity increase. In addition, the entanglement of the two interlocked networks played an important role in cracking energy absorption and reflected in a toughness improvement.

Sanariya et al. [46] have reported a convenient method for the preparation of epoxy resins based on bisphenols-C. The epoxy resins of bisphenols-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mol in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was 75-80 %.

Kagathara et al. [47] 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 %.

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46. 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.
47. 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, 1-8, 2001.

Liu et al. [48] have reported combination of epoxy and novolac resins. In a typical study, a novel phosphorus-containing Ar-alkyl novolac (Ar-DoPo-N) was prepared. The Ar-DoPo-N blended with novolac and used as a curing agent for o-cresol formaldehyde novolac epoxy, resulting in cured epoxy resins with various phosphorus contents. The epoxy resins exhibited high glass-transition temperatures (159-176^{o}C), good thermal stability (>320^{o}C).

Polyesters

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

Polyester resins are produced by different reactions such as the esterification of acids or 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. Polyester resin is used for casting, auto body repair, wood

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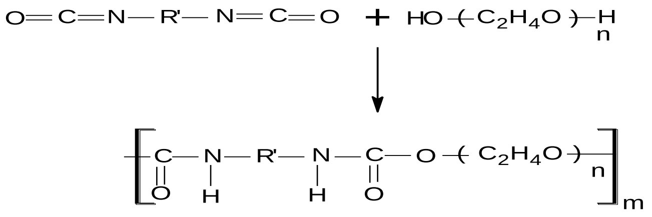
48. Y. L. Liu, C. S. Wu and K. Y. Hsu. Flame retardant epoxy resins from o-cresol novolac epoxy cured with a phosphorus containing aralkyl novolac. J. Polym. Sci. Part A, 40, 2329-2339, 2002.

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

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.

[C] LITERATURE SURVEY ON POLYURETHANE RESINS

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



$$O{=}C{=}N{-}R'{-}N{=}C{=}O + HO{-}\left(C_2H_4O\right)_n{-}H \longrightarrow \left[\underset{\overset{\|}{O}}{C}{-}\underset{\overset{|}{H}}{N}{-}R'{-}\underset{\overset{|}{H}}{N}{-}\underset{\overset{\|}{O}}{C}{-}O{-}\left(C_2H_4O\right)_n \right]_m$$

The urethane reaction is catalyzed in a strict technical sense, i.e. the catalysts increase the rate of reaction without themselves being consumed. The most commonly used catalysts are organo tin compound for example dibutyl tindilaurate (DBTDL) and tertiary amines for example 1,4-diazobicyclo(2,2,2)-octane (DABCO), and tetramethyl butane diamine (TMBDA). Polyurethane resins are characterized by a segmented structure, consisting of flexible segment, the polyol chains, and hard segments, crystallizability of segment, segmental length, intra and inter segment interactions such as H-bonding, overall compositions and molecular weight.

Polyurethanes possess a unique combination of performance and application properties with excellent abrasion resistance, flexibility, hardness, chemical resistance, UV light resistance and anti-microbial characteristics [49]. 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 [50, 51]

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 [52, 53].

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

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49. 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.
50. J. M. Buist. Development in polyurethane-1. Applied Science Publishers Ltd. London, 1978.
51. I. S. Lin, J. Biranowski and D. H. Lorenz. Urethane chemistry and applications. K.N. Edwards, Ed; ACS Symposium Series, 172, 34, p. 523, 1981.

the diversified demands of modern technologies such as coatings, adhesives, foams, rubbers, reaction molding plastics, thermoplastic elastomers and composites. The pioneering work on polyurethane polymers was conducted by Otto Bayer and his coworkers in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany [54]. They recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities, especially when compared to already existing plastics that were made by polymerizing olefins, or by polycondensation. The new monomer combination also circumvented existing patents obtained by Wallace Carothers on polyesters [55].

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

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

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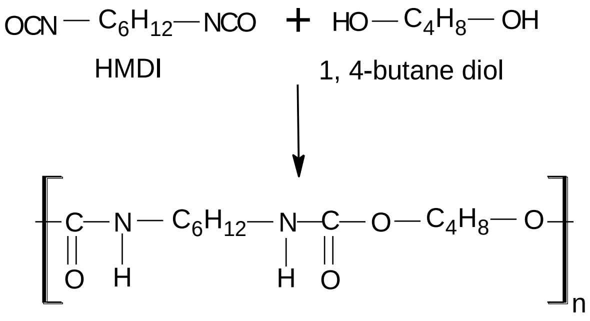
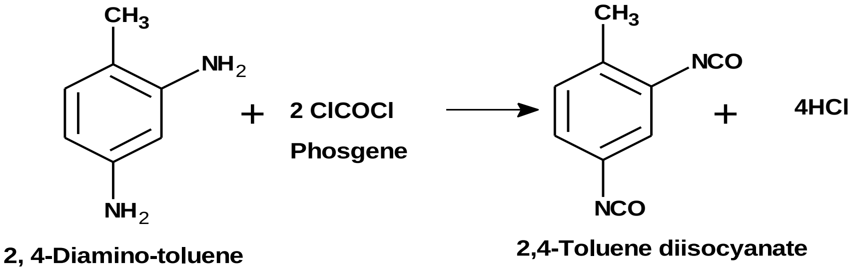
52. J. A. Grapski and S. L. Cooper. Synthesis and characterization of biocidal polyurethanes Biomaterials. 22, 2239-2246, 2001.
53. A. Z. Okeema and S. L. Cooper. Effect of carboxylate and/or sulphone ion incorporation on the physical and blood contacting properties of polyetherurethane. Biomaterials, 12, 668-676, 1991.
54. I. G. Farben. German Patent 728.981, 1937.
55. B. Raymond, Seymour George, B. Kauffman. Polyurethanes: A class of modern versatile materials. J. Chem. Ed., 69, 909, 1992.



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

Full scale commercial isocyanate manufacture began in the United 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-1.3. The other component in the production of polyurethane is polyol. Polyols are hydroxyl terminated polyesters, polyethers, acrylic polyols and polyols based on natural oils. Applications of polyurethanes in various fields are listed in Table 1.4.

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 [56].

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 cheap and renewable resources such as natural oils [57]. 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 [58, 59].

Table-1.3 The common diisocyanates used for the production of polyurethanes

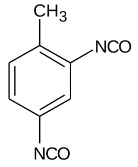
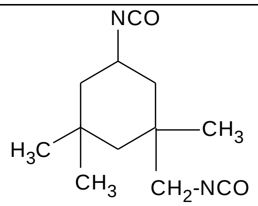
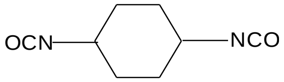
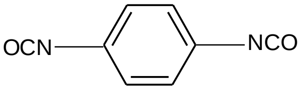
Sr. No.	Chemical Name	Abbreviation	Structure
1	Toluene-2,4-diisocyanate	TDI	
2	Hexamethylene diisocyanate	HMDI	$OCN-C_6H_{12}-NCO$
3	Isophorone diisocyanate	IPDI	
4	4,4’-Methylene bis phenylene diisocyanates	MDI	$OCN-Ph-CH_2-Ph-NCO$
5	Cyclohexane-1,4-diisocyanate	CHDI	
6	p-Phenylene-1,4-diisocyanate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

Table-1.4 Applications of polyurethanes in various fields

Application	Amount of polyurethane used (millions of pounds)	Percentage of total
Building & Construction	1,459	26.8
Transportation	1,298	23.8
Furniture & Bedding	1,127	20.7
Appliances	278	5.1
Packaging	251	4.6
Textiles, Fibers & Apparel	181	3.3
Machinery & Foundry	178	3.3
Electronics	75	1.4
Footwear	39	0.7
Other uses	558	10.2

- 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

Schoener et al. [60] have synthesized moisture curable polyurethane coating compositions with improved pot life. Such enhancement is accomplished by blending with said coating composition a stabilized amount of stabilizing agent from the group of a mercapto compound, a polyphenol characterized by being reactable with an isocyanate group in the presence of a tertiary amine catalyst, and mixtures thereof. The amounts of stabilizing agents ranged from about 1% to 10% by weight. The enhanced pot life is realized even in the presence of significant quantities of water.

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56. 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.
57. G. Scott. Polymer and environment. Cambridge: Royal Society of Chemistry, 27, 1999.
58. 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.
59. 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.
60. S. E. Thomas, B. A. Blakely and G. M. Carlson. Stabilized moisture curable PU coatings. EP 0,276,667, 1988.

Ashraf et al. [61] 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 [62] have studied the damping properties of epoxy resin / PU (EP/PU) semi interpenetrating polymer networks (IPNs) by dynamic mechanical analysis (DMA) method. It showed that the semi IPNs have excellent damping properties at ordinary temperature. The maximum value of tanδ is about 1 when the weight composition of EP/PU is 70/30. Tensile tests also indicate that the system has good tensile strength and elongation at break at this ratio. The effect of structures on the properties of semi-IPNs is discussed. Applied to the cavitation corrosion resistant coating, the semi-IPNs showed good cavitation corrosion resistance.

Opera [63] 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.

Kolekar and Athawale [64] have synthesized interpenetrating networks composed of glycerol modified castor oil based polyurethane (CG-PU) and

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61. S. Ahmad, S. M. Ashraf, E. Sharmin, F. Zafar and A. Hasant. Studies on ambient cured PU modified epoxy coatings synthesized from sustainable resource. Prog. Cryst. Grow. Chara. Mater., 45, 83-88, 2002.
62. 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.
63. S. Opera. Epoxy-urethane acrylate. Eur. Polym. J., 36, 373-378, 2000.

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

Prabu and Alagar [66] 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 γ-amino propyl triethoxysilane and vinyl triethoxysilane as silane crosslinker and dibutyltindilaurate as a catalyst. The coating materials were obtained in the form of tough films and characterized for their ASTM

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64. S. Kolekar and V. Athawale. Interpenetrating polymer networks based on polyol modified castor oil polyurethane and PMMA. Eur. Polym. J., 34, 1447-1451, 1998.

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 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 interested ification reactions at high temperature.

Keun et al. [67] 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

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65. 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.
66. 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.
67. 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.

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.

Jimenez et al. [68] 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. [69] have synthesized two parts adhesive having superior strength at cryogenic temperatures, which contains a urethane resin composition part and a hardner part. The urethane resin composition part comprises 50-99% by weight of a modified polyurethane prepolymer having an epoxy group at each of its respective end and 1-50% by weight of a modified urethane compound having substantially no ether cyanate (NCO) groups and at least two epoxy groups per molecule and a molecular weight less than 800 daltons. The hardener part is a polyamine containing primary or secondary amine groups. The equivalent ratio of the amine groups of the polyamine to the epoxy groups of the urethane resin composition part is 0.5-2.0.

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68. 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.
69. 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.

Somani et al. [70] have synthesized polyurethane adhesives from different polyester polyols. The polyester polyols were synthesized by reacting castor oil derivatives with glycols (diols), while adhesives have been synthesized by reacting different polyester polyols with diisocyanate adducts in different NCO/OH ratios. The polyols and polyurethanes were characterized by FTIR spectroscopy. The effect of NCO/OH ratios, types of isocyanate adducts, and chain length of glycols were studied by determining wood to wood adhesion strength, i.e. by lap shear strength measurements and the change in lap shear strength after being placed in cold water, hot water, acid or alkali solutions was tested. Thermal stability of PU adhesives was determined by TGA.

Papon et al. [71] have synthesized the thermoplastic polyurethane elastomers (TPUs) of constant composition by prepolymer method and studied the influence of synthesis condition (pre polymerization and chain-extension time) on the final properties of TPUs. The TPUs were characterized by gel permeation chromatography, differential scanning calorimeter, stress-strain measurements and contact angle measurements. The adhesion properties of the TPUs were determined by measuring the T-peel strength and found that above the threshold value the pre polymerization time influenced the final properties of the TPUs (viscosity of solutions, molecular weight, mechanical and adhesive behavior), whereas chain extension time does not. Therefore this is possible to prepare TPUs with specific properties by changing the polymerization conditions.

Papon et al. [72] 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

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70. 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.
71. 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.
72. 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.

synthesis. The properties of the materials are studied using solution viscosity measurements, size exclusion chromatography, stress controlled rheometry, differential scanning calorimetry (DSC), wide angle X-ray diffraction and contact angle measurements. Rosin as a chain extender led to increase the viscosity and molecular mass as well as improvements of rheological properties and changes in morphology. The crystalline regions are more affected (variations in the softening temperature and enthalpy) than the amorphous ones (quite constant glass transition temperature). The rosin act as actual chain extender and modified the organizations of both soft and hard segments of the polymers. The adhesive properties of the TPUs were determined by measuring the T- peel strength of the PVC/TPUs adhesive joints.

Kim et al. [73] 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. [74] 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.

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73. 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.
74. 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.

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. [75] have synthesized the polyurethane networks (PUNs) using polyols derived from soybean oil, petroleum, or a blend of the two in the conjunction with diisocyanate. The soybean-based polyols (SBPs) were prepared using air oxidation, or by hydroxylating epoxidized soybean oil. Some of the networks were subjected to several solvents to determine their respective swelling behavior and solubility parameters. Sol-fractions were also determined, and DMA experiments were utilized to monitor the changes in storage modulus and tan δ with temperature for networks with sol and with the sol extracted. A linear relationship was noted between the hydroxyl number of a SBP and the glass transition temperature of its corresponding unextracted PU network within the range of hydroxyl numbers (i.e., 55-237 mg KOH/g) and glass transition temperatures (i.e., -21 to +83°C) encountered in this work. This same linear relationship was realized between the weighted hydroxyl number of soy and petroleum-based polyol blends and the glass transition temperature of the resulting unextracted and extracted network PUs within the ranges utilized in this study (i.e., 44-57 mg KOH/g, -54-19°C).

Kumar et al. [76] 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

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75. T. W. Pechar, S. Sohn, S. Ghosh, C. E. Frazie, 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.
76. 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.

mechanical properties. The microcrystalline parameters such as crystal size ($\langle N\rangle$,lattice disorder (g), surface (Ds) and volume (Dv) 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.

[C] NATURAL FIBER REINFORCED COMPOSITES

Composite materials are formed by the combination of two or more materials, which retain their respective characteristics when combined together, but their chemical and mechanical properties are improved upon combination. “Two or more dissimilar materials when combined are stronger than that of individual materials.”

Today, where in world market demands for product performance are ever increases, composite materials have proven to be effective in reducing cost and improve in performance. Composites solve problems; raise performance levels by development of many new materials.

History

The use of natural composite materials has been a part of man’s technology; the first ancient builder used straw to reinforce mud bricks.

The 12th century Mongols made the advance weapons of their day with bows that were smaller and more powerful than their rivals. These bows were composite structures made by combining cattle tendons, horn, bamboo, which bonded with natural pine resin. The tendons were placed on the tense of the bow, the bamboo was used as a core, and sheets of horn were laminated the compression side of the bow. The entire structure was tightly wrapped using the rosin adhesive. The 12th century weapons designers certainly understood the principles of composite design. In the recent time some of the old museum pieces were strung and tested.

They were about 80% as some modern composite bows [77].

In the late 1800s Canoe builders were experimenting with gluing together 1st graft paper with shellac to form paper laminates. While the concept was such the materials did not perform well.

In the year between 1870 and 1890, revolution was occurring in chemistry, first synthetic (man made) resins were developed, which could be converted liquid to solid polymerization. These polymer resins are transformed from liquid state to solid state by crosslinking the molecules. Early synthetic resin included cellulose, melamine and Bakelite.

In the early 1930s two chemical companies that were working on the development of polymer resins were American Cyanamid and DuPont. In the course of the experimentation, both the companies independently formulated polyester resin first time. In the same time period, Owens-Illinois Glass Company began the glass fiber into a textile fabric on commercial bases.

During the time between 1934 and 1936, experimenter Ray Green, in Ohio combined these two new products and began molding small boats. This was the beginning of modern composites. During World War II the development of required non-metallic housings and the US military advanced fledgling composites technology with many research projects. Immediately following war II composite materials immersed as major engineering material.

First composites industry began in earnest in the late 1940s and developed in 1950s. Most of the composites processing methods used today like molding, filament winding, hand lay-up technique, resin transfer molding, vacuum bagging were all developed and used in production between 1946 and 1950. Some products manufactured from composites during this period included: boats bodies (corvette), truck parts, aircrafts component, underground storage tank, buildings and many familiar products. Composites typically use thermoset resins, which begin as liquid polymers converted to solid during the molding process. This process known as crosslinking is irreversible. Because of this, these

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77. W. Doppler. Farmer’s Business and Participation for Sustainable Agriculture. Proc. of SATHLA International Conference, Rio de Janeiro, Brazil, March-1998.

polymers are known as thermosets and can not be melted and reshaped. The benefit of composite materials have fueled growth of new application markets such as transportation, constructions, corrosion resistance, marine infrastructure, consumer products, electrical, aircraft and aerospace application and business equipments.

The benefits of using composites materials include:

- High strength: Composite materials can be designed to meet the specific requirements of an application. A distinct advantage of composites over other materials is ability to use many combinations of resins and reinforcement.
- Light weight: Composites are materials that can be designed for both light weight and high strength. In fact composites are used to produce the highest strength to weight ratio structures known to man.
- Corrosion resistance: Composites products provide long-term resistance from severe chemical and temperature environments. Composites are the materials choice for outdoor exposure, chemical handling application and severe environments service.
- Design flexibility: Composites have an advantage over other materials because they can mold into complex shapes at relatively low cost. The flexibility creating complex shapes offers designers a freedom that hallmarks composites achievement.
- Durability: Composite structures have an exceedingly along life span with low maintenance requirements, the longevity of composite is a beneficial critical applications. In a half–century of composite development, well-desired composite structures have yet to wear out.

Compare a ¼ inch diameter steel rod to a ¼ inch diameter glass fiber composites rod. The steel rod will have higher tensile strength and compressive strength, but weight is more. If the fiber glass rod were increased in diameter to the same weight as steel rod, it would be stronger [78].

Automotive industries in Europe show large interest in NFC (Natural Fiber Composite) that can be used in load bearing elements of cars. Some of the

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78. Composites Fabricators Association–The Composites Industry Overview-2003.

beneficial points for using composites over conventional ones are below [79].

- Tensile strength of composites is four to six times greater than that of steel or aluminium
- Improved torsional stiffness and impact properties
- Composite have higher fatigue endurance limit (up to 60% of ultimate tensile strength)
- Composite materials are 30-45% lighter than aluminium structures designed to the same functional requirements
- Lower embedded energy compared to other structure materials like steel, aluminium, etc.
- Composites are more versatile than metals and can be tailored to meet performance needs and complex design requirements
- Long life offers, excellent fatigue, impact, environmental resistance and reduced maintenance
- Composites enjoy reduced life cycle cost compare to metals
- Composite exhibit excellent corrosion resistance and fire retardancy
- Improved appearance with smooth surfaces and readily incorporable integral decorative melamine are other characteristics of composites
- Composite parts can eliminate joints/ fasteners, providing part by simplification and integrated design compared to conventional metallic parts.

Different types of fibers for reinforcement and study of their properties. Natural cellulose based fibers are gaining attention as their application is diversified into engineering end uses such as building materials and structural parts for motor vehicles [80, 81], where light weight is required. There are at least 1000 types of plant that bear usable fibers [82].

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79. U. Gayer and Th. Schuh. Automotive applications of Natural Fiber Composites. First International Symposium on ligno-cellulosic Composites –UNESP- Sao Paulo State, 1999.
80. A. Maguno. 2nd International Wood and Natural Fiber Composites Symposium. Kassel, Germany, 29-1, June 28-29, 1999.

Khan et al. [83] have fabricated jute reinforced polyurethane composites under gamma irradiation. Thick polymer film was prepared under gamma irradiation using urethane acrylate in the presence of N-vinyl pyrrolidone, ethyl hexyl acrylate, and trimethylol propane triacrylate. Both jute dust and hessain cloth (jute fabric) were used to constitute composites based on the prepared resin matrix. Some of their mechanical and physical properties were studied.

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

Tay et al. [84] 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

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81. H. A. Al-Qureshi. 2^{nd} International wood and natural fiber composites symposium, Kassel, Germany, 32-1, June 28-29, 1999.
82. J. Robson, J. Hague, G. Newman, G. Jeronimidis and M. P. Ansell. Report No. EC/ 431/ 92 to DTI LINK, Structural Composites Committee. January 1993.
83. 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.
84. 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.

behavior of the composites made from the glycol mixture was predominantly influenced by the PPG -400.

Tay et al. [85] have fabricated the oil palm EFB-PU composites and investigated the effect of isocyanate (NCO)/ glycol (OH) ratio, glycol type and mixtures [polyethylene glycol PEG-400 (MW- 400) and polypropylene glycol PPG (MW-400)] on the flexural properties. Composites made with PEG-200 exhibited higher flexural properties than with PEG-400 and PPG-400. The flexural properties were also found to be influenced by the PPG-400/ PEG-400 ratio.

Wolcott et al. [86] 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. In order to save a crop from extinction and to ensure a reasonable return to the farmers, non-traditional outlets have to be explored for the fiber. One such avenue is in the area of fiber-reinforced composites. Such composites can be used as a substitute for timber as well as in number of less demanding applications [87].

In order to save a crop from extinction and to ensure a reasonable return to the farmers, non-traditional outlets have to be explored for the fiber. One such avenue is in the area of fiber-reinforced composites. Such composites can be

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85. 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, 249-260, 2003.
86. 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.

used as a substitute for timber as well as in number of less demanding applications [87].

The estimated global tonnage of fibrous raw material from agricultural crops is provided in Table 1.5 [88]. Jute, sisal, banana and coir, the major sources of natural fibers are grown in many parts of the world. Some of them have aspect ratios (ratio of length to diameters) > 1000 and can be woven easily. These fibers are extensively used for cordage, sacks, fishnets, matting and rope and as filling for mattresses and cushions. Cellulosic fibers are obtained from different parts of plants, e. g. Jute are obtained from stem; sisal, banana and pineapple from the leaf; cotton from seeds; coir from fruit, vegetables. The properties of some of the natural fibers are compared in Table-1.6 [89]. The comparison of mechanical properties for jute and glass fibers [90] is given in Table-1.7. Jane L. O'Dell has reported the comparative properties of lingo cellulosic fibers with glass and carbon fibers [91]. The comparisons of properties of different fibers are given in Table-1.8.

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87. S. Biswas, G. Srikanth and S. Nangia. Development of Natural Fiber Composites in India-Composites 2001 convention and Trade show, Composites Fabricators Association. October 3- 6, 2001, Tampa – FL, USA.
88. R. Kozlowski. A report on Green Fibers and Their Potential in Diversified Application, Institute of Natural Fibers, Poland, 2003.
89. S. Nangia and S. Biswas. Jute composite: Technology and business Opportunities in News and Views, 2003.
90. Jane L. O'Dell. Natural fibers in Resin Transfer Molded Composites. The fourth International Conference on Wood Fiber-Plastic Composites, Forest Products Society, Madison, 1997.
91. M. K. Sridhar, G. Basavarappa, S. G. Kasturi and N. Balasubramaniam. Mechanical properties of jute / polyester composites. Indian J. Tech., 22, 213-218, 1984.

Table-1.5 Estimated global tonnage of fibrous raw materials from agricultural crops

Crops	Plant component	Availability in 10^3 tones
Rice	Straw	465.2
Wheat	Straw	739.7
Oats	Straw	50.8
Corn	Straw	727.3
Bast fibrous plant	Straw	25.0
Sugarcane	Baggasse	100.2

Table-1.6 Properties of selected natural fibers and glass fiber

Property	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	---	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 Content (%)	61	65	67	81	43	---
Lignin Content (%)	12	5	12	12	45	---
Elastic Modulus(GN/m^2)	---	8-20	9-16	34-82	4-6	85.5
Tenacity (MN/m^2)	440-553	529-754	568-640	413-1627	131-175	4585
Elongation (%)	1-1.2	1.0-3.5	3-7	0.8-1.6	15-40	5.7

Table-1.7 Mechanical properties of glass and jute fibers

Property	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	28.8	42.7

Table-1.8 Comparison of properties of different fibers

Fiber	Specific gravity	Specific tensile strength (GPa)	Cost (US $ / ton)	Energy to Produce (GJ / ton)
Lignocellulosic	0.6-1.2	1.6-2.95	200 - 1000	4
Glass	2.6	1.35	1,200 – 1,800	30
Carbon	1.8	1.71	12,500	130

The attractive features of natural fibers like jute [92-93], sisal [94], coir [95, 96], and banana [97] are their low cost, light weight, high specific modulus, renewability and biodegradability. Many plant fibers have lots of applicable part as commercialized materials are concerned. One of the common and very critical environmental solutions is biodegradable nature of all these natural fibers, which increases their demand in world composite manufacture markets. Plant fibers are composed of cellulose, hemicellulose and lignin. Other components, usually regarded as surface impurities, are pectin and wax substances (Table-1.9) [98].

Diversified uses of green fibers

Global trends towards sustainable development have brought to light natural, renewable, biodegradable raw materials. Science and technology continue in extending their use in textile and other industries. Recent achievements and new applications of green fibers and associated products, bast fibrous

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92. P. Kumar. Mechanical behavior of jute fiber and their composites. Indian J. Tech., 24, 29-32, 1986.
93. A. N. Shah and S. C. Lakkad. Mechanical properties of jute reinforced plastics. Fiber Sci. Tech., 15, 41-45, 1981.
94. E. T. N. Bisanda and M. P. Ansell. The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites. Compos. Sci. Tech., 41, 165-78, 1991.
95. S. V. Prasad, C. Pavithran and P. K. Rohatgi. Alkali treatments of coir fibers for coir-polyester composites. J. Mater. Sci., 18, 1443-1449, 1983.
96. J. Rout, M. Mishra, S. K. Nayak, S. S. Tripathy and A. K. Mohanty. Effect of surface modification of coir fiber on physico-mechanical behavior of coir-polyester composites In: A. K. Ghosh, editor. Polymers beyond AD 2000, P. 489-91, 1999
97. L. A. Pothan, S. Thomas and N. R. Neelakantan. Short banana fiber reinforced polyester composites: Mechanical, failure ageing characteristics. J. Reinforced Plastics, 16, 744-751, 1997.
98. L. Y. Mwaikambo and Martin P. Ansell. Chemical modification of hemp, sisal, jute and kapok fibers by alkalization. J. Appl. Polym. Sci., 84, 2222-2236, 2002.

Table-1.9 Important chemical composition (%) of some selected fibers

Fiber type	Cellulose	Hemi cellulose	Lignin	Pectin
Cotton	92	6	---	<1
Jute	72	13	13	---
Flax	81	14	3	4
Sisal	73	13	11	2
Hemp	74	18	4	1
Coir	43	<1	45	4
Ramie	76	15	1	2
Straw	40	28	17	8
Kapok	13	---	---	---

plants can provide from the background for following conclusions:

1. Fast growing population, eco and health awareness creates large space for future expansion of other than cottons, natural cellulosic fibers.
2. Present achievements in breading/production/ processing extended the use of bast fibers in textiles. To make the way for these, difficult in processing fibers, into textile production being beyond their reach for centuries, it was necessary to develop : new, softer, finer 100 percent bast or bast blended yarns, amongst them knitting yarns; new crease- resistant finishing treatments; new products, which could meet the needs of demanding apparel sector.
3. All the textile goods made on the basis of green fibers can boast high comfort / health properties and are ecological items. They can be labeled as “NATURAL”. This is the key to market success.
4. Green fibers / bast fibrous plants will also be used in growing amounts in wide spectrum of biocomposites materials. Being lignocellulosic they can be combined with man-made or natural polymers to provide a wide range of useful composites in textiles.

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.

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

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

III. To fabricate jute composites and evaluate their mechanical and electrical properties.

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

CHAPTER – 2

Syntheses of monomers, epoxy and epoxy esters

This chapter is further subdivided into seven sections:

SECTION-I: **Synthesis of 1,1'-bis (4-hydroxy phenyl)cyclohexane [Bisphenol – C]**

SECTION-II: **Synthesis of bisphenol of 4-(4-hydroxyphenyl)but-3-en-2-one**

SECTION-III: **Synthesis of epoxy resin of bisphenol-C**

SECTION-IV: **Synthesis of epoxy resin of bisphenol of 4-(4-hydroxyphenyl)but-3-en-2-one**

SECTION-V: **Synthesis of epoxy acrylate**

SECTION-VI: **Synthesis of epoxy-acrylate-maleate resin by using maleic anhydride**

SECTION-VII: **Syntheses of polyurethane resins**

SECTION-I: Synthesis of 1, 1'- bis (4-hydroxy phenyl) cyclohexane [Bisphenol – C]

1, 1'- Bis (4-hydroxy phenyl) cyclohexane (I) here after designated as BC was synthesized according to reported methods [1, 2]. Thus, 0.5 mol (49 g) cyclohexanone was treated with 1.0 mol (94 g) phenol in the presence of mixture of HCl :CH_3COOH (2:1 v/v, 100:50 ml) as a Friedel-Craft catalyst at 55^oC for 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution.

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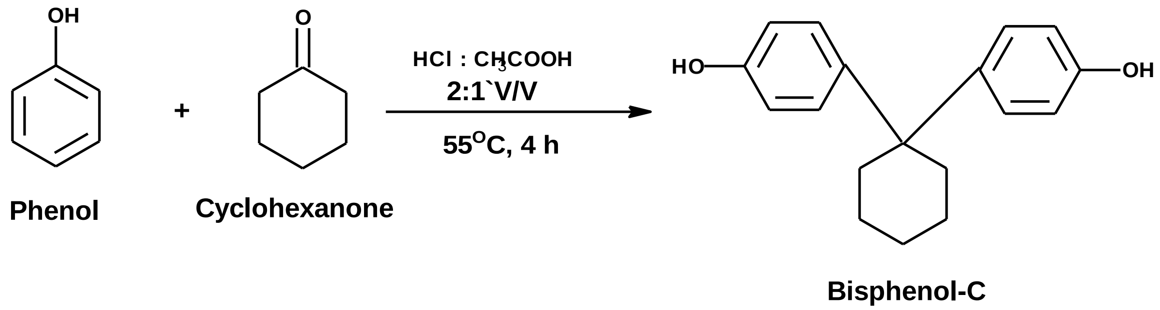
1. M. V. Rao, A. J. Rojivadia, P. H. Parsania and H. H. Parekh. A convenient method for the preparation of bisphenols. J. Ind. Chem. Soc.,64, 758-759, 1987.
2. H. H. Garchar, H. N. Shukla and P. H. Parsania. Kinetics of formation of 1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane. Indian Acad. Sci. (Chem. Sci.), 103, 149-153, 1991.

The resinous material was removed by filtration through cotton plug. The yellowish solution so obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50°C. BC was further crystallized repeatedly from benzene and methanol-water systems. The process was repeated to get pure, white, shining crystals of ~81% yield, and m. p. of BC was 186°C

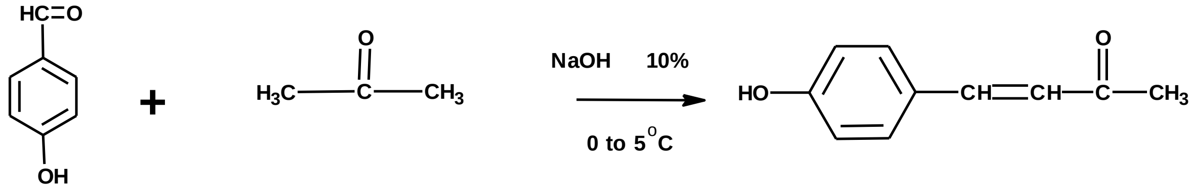


(I)

Section-2: Synthesis of bisphenol of 4-(4-hydroxyphenyl)but-3-en-2-one

[A] Synthesis of 4-(4-hydroxyphenyl)but-3-en-2-one monomer (CN)

4-(4-Hydroxyphenyl)but-3-en-2-one (II) was synthesized according to reported method [3]. Thus, 0.5 mol (29 ml) acetone was treated with 1.0 mol (122 g) p-hydroxy benzaldehyde in the presence of 10% NaOH (20 ml) at 0-5°C for 4 h. The off white colored product was filtered, washed well with water and dried. CN was crystallized repeatedly from $CHCl_3$ and n-hexane systems. The process was repeated to get pure, white, shining crystals of ~93% yield.



CN (II)

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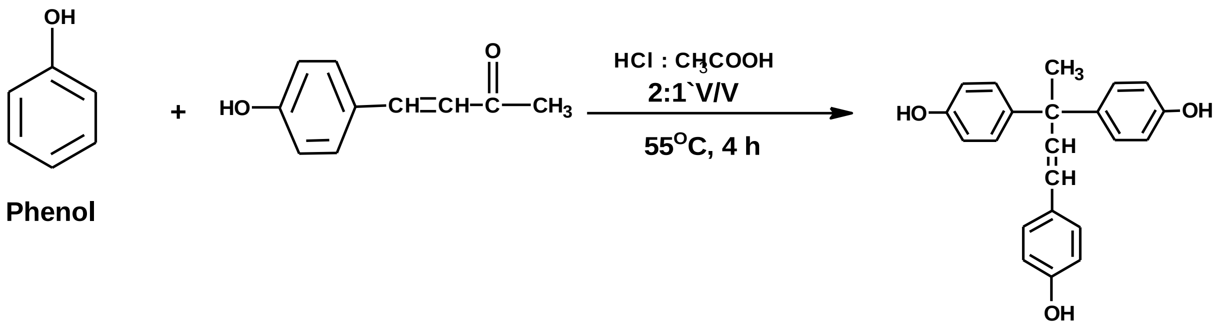
3. Xin-Hua Cui, Pin Song, Bao-An Bhadury, Pinaki S. Zhu, Hai-Liang Wang, Shi-Fan. Synthesis, structure and antibacterial activity of novel 1-(5-substituted-3-substituted-4,5-dihydropyrazol-1-yl)ethanone oxime ester derivatives. Bioorganic & Medicinal Chemistry, 16(7), 4075-4082, 2008.

[B] Synthesis of 4,4',4''-but-1-ene-1,3,3-triyltriphenol (BCN)

0.5 mol (81 g) 4-(4-hydroxyphenyl)but-3-en-2-one was condensed with 1.0 mol (94 g) phenol in the presence of 100:50 ml mixture of HCl:CH_3COOH (2:1 v/v) as a Friedel-Craft catalyst at 55^oC for 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution. The resinous material was removed by filtration through cotton plug. The yellowish solution so obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50^oC. BCN was further crystallized repeatedly from benzene and methanol-water systems. The process was repeated to get pure, white, shining crystals of ~84% yield.



(BCN) (III)

Section-3: Synthesis of epoxy resin of bisphenol-C

Epoxy resin of bisphenol-C (IV), here after designated as EBC, was synthesized according to the reported method [4]. Thus, 0.5 mol (134 g) BC, 1.1 mol (138.8 g) epichlorohydrin and isopropanol (250 ml) were placed in a round bottomed flask equipped with a condenser. The mixture was brought to reflux with stirring and 1.25 mol NaOH in 50 ml water was slowly added to the solution and the refluxed for 4.5 h. The separated solid resin was isolated by filtration and liquid resin by distillation of excess of isopropanol.

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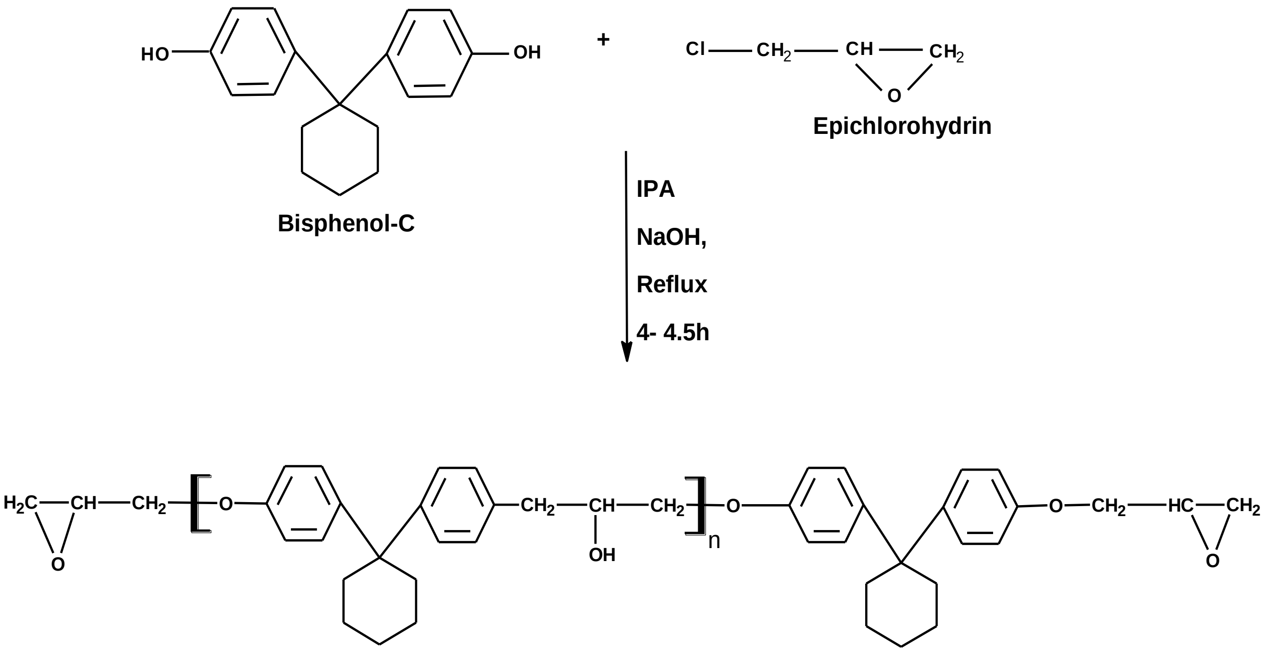
4. M. R. Sanariya, D. R. Godhani, S. Baluja and P. H. Parsania. Synthesis and characterization of epoxy resins based on 1,1'-bis(4-hydroxy phenyl)cyclohexane and 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane. J. Polym. Mater., 15, 45-49, 1998

The solid and liquid resins were washed well with water and extracted in chloroform and evaporated to dryness. Highly transparent yellowish color resin was formed, which is soluble in $CHCl_3$, acetone, 1, 4-dioxane, DMF, 1, 2-dichloroethane and DMSO; and partially soluble in ethanol and isopropanol.

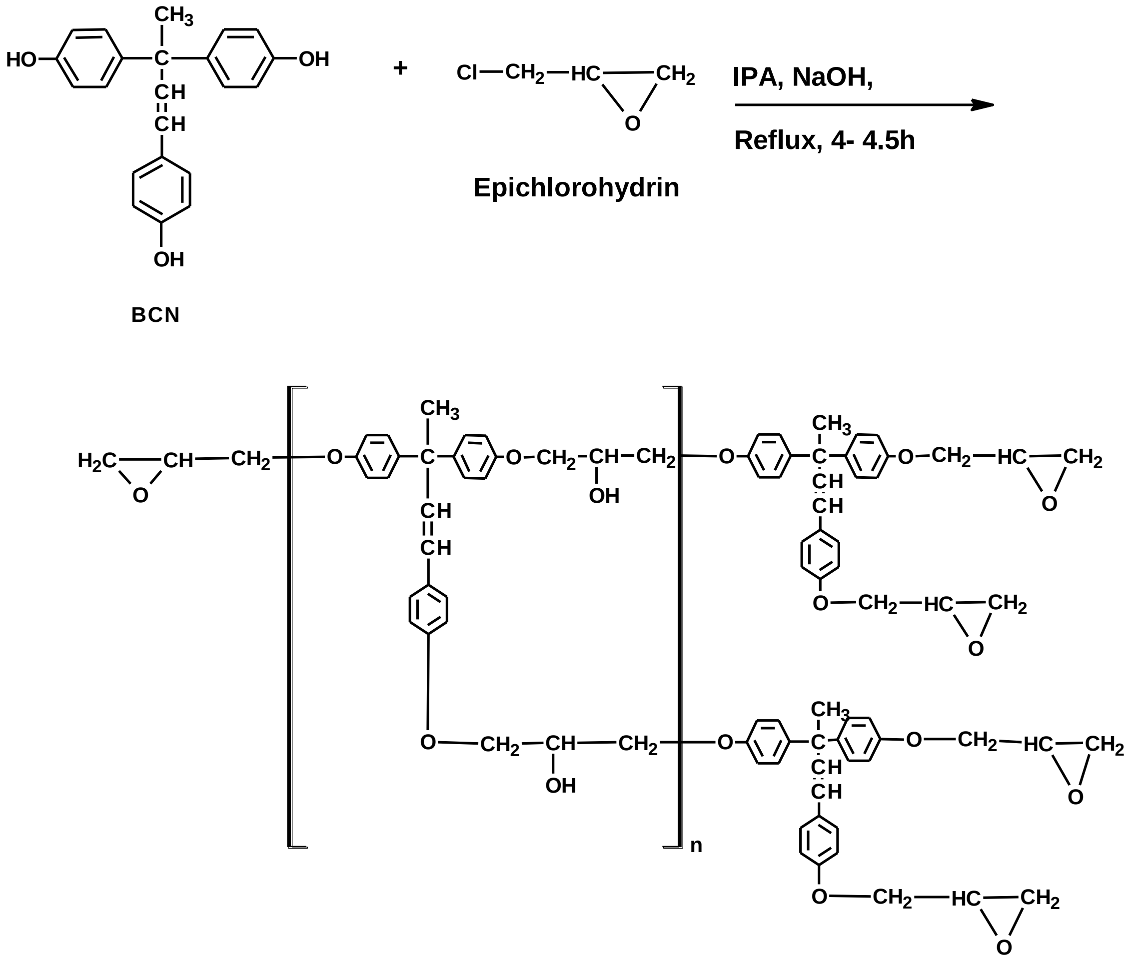


IV

Section-4 Synthesis of epoxy resin of bisphenol of 4-(4-hydroxy phenyl)but-3-en-2-one

Epoxy resin of BCN (V), here after designated as EBCN, was synthesized as follows.

Thus, 0.5 mol (166 g) BCN, 1.1 mol (138.8 g) epichlorohydrin and 250 ml isopropanol were placed in a round bottomed flask equipped with a condenser. The mixture was brought to reflux with stirring and 1.25 mol NaOH in 50 ml water was slowly added to the solution and the refluxed for 4.5 h. The separated solid resin was isolated by filtration and liquid resin by distillation of excess of isopropanol. The solid resin was filtered, washed well with water and extracted in chloroform and evaporated to dryness. Yellowish color resin was formed which is soluble in $CHCl_3$, acetone, 1, 4-dioxane, DMF, 1, 2-dichloroethane and DMSO; and partially soluble in ethanol and isopropanol.



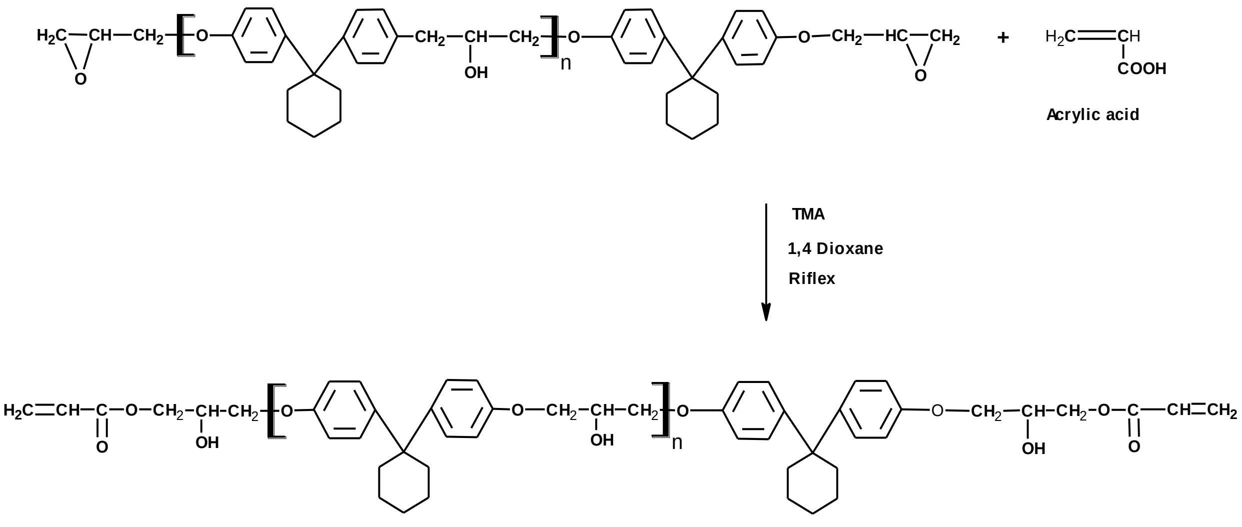
(V) (EBCN)

Section-5: Synthesis of epoxy acrylate

Epoxy acrylate resin of EBC (VI), here after designated as EBCA, was synthesized according to reported method [5].

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

Esterification reactions are favored by removing water of reaction. Generally xylene is used as a solvent to remove water azeotropically. EBCA was synthesized by condensing 0.01 mol (11.52 g) EBC with 0.02 mol (1.44 ml) acrylic acid by using 100 ml 1, 4- dioxane as a solvent and 2 ml triethylamine as a catalyst at reflux temperature for 6h to get acid value < 10. The reaction time was set in such a way that the acid value was decreased below 10 mg KOH/g of the resin. The resin is 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.



E B C A (VI)

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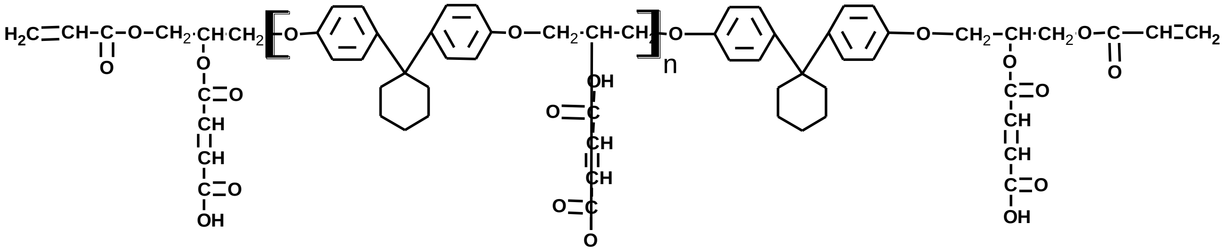
5. V. M. Kagathara and P. H. Parsania. Thermal analysis of cured chloro epoxy resin and epoxy acrylates-styrene copolymers. Polymer Testing, 21(6), 659-663, 2002.

Section-6: Synthesis of epoxy-acrylate-maleate resin

Epoxy-acrylate-maleate resin of (VII) of EBCA, here after designated as ECAM, was synthesized as follows.

To a 500 ml three necked flask equipped with a mechanical stirrer, a condenser and a thermometer was placed in a thermostat and were added 0.01 mol (5.76 g) epoxy acrylate resin in 30 ml 1,4-dioxane, 0.02 mol (1.96 g) maleic anhydride. The reaction mixture was refluxed with stirring for 4h and excess solvent was distilled off. The resin was purified three times from acetone–chloroform. Yellowish viscous liquid was stored in air tight bottle.



ECAM

(VII)

Synthesis of unsaturated polyester resin

Unsaturated polyester resin (VIII) of phthalic anhydride, malieic anhydride and propylene glycol here after designated as PMP, was synthesized according to the reported method [6].

To a 500 ml three necked flask equipped with a mechanical stirrer, a condenser and a thermometer was placed in a thermostat and were added 0.1 mol (16.6 g) phthalic anhydride, 0.2 mol (15.2 ml) propylene glycol, 0.1 mol (9.8 g) maleic anhydride in presence of xylene (15 ml) for azeotropic distillation. The

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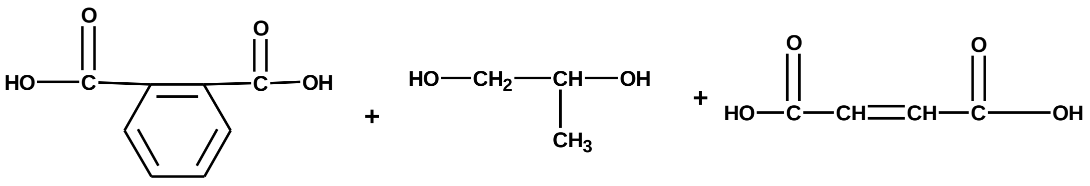
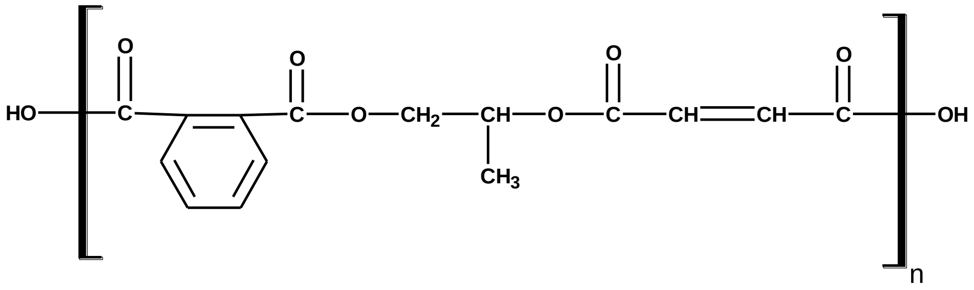
6. Tong S. N. and Wu P. T. K.; Super tough Unsaturated Polyester and Its SMC. J. Reinf. Plast. Comp. 9, 299-311, 1990.

reaction mixture was heated up to 220°C till 0.2 mol (3.6 ml) water was distilled off to get acid value ~50-60. The resin was purified three times from acetone–chloroform. Transparent viscous liquid was stored in air tight bottle.



Phthalic anhydride **Propylene glycole** **Melieic anhydride**



PMP (VIII)

Curing study of epoxy-acrylate-maleate, unsaturated polyester resin and their mixed matrix materials

Curing behavior of ECAM, PMP and their varying compositions (25-75 wt %) was studied using methyl ethyl ketone peroxide (MEKP) as an initiator and cobalt naphthenate as an accelerator. Thus 5 g of ECAM/PMP was dissolved in 10 ml acetone in a corning test tube and were added 0.5 ml (10%) MEKP and 0.5 ml (10%) cobalt naphthenate and solvent were evaporated at 35°C. The test tube containing a thermometer was placed in a thermostat bath at 35°C and gel time and peak exotherm temperature were monitored and recorded in table 1. Similarly curing behavior of mixed matrix materials of varying composition was performed. The numerical digits indicate the composition of PMP in the mixed matrix materials. After post curing for 30 min, samples were collected by breaking of tubes and removing of glass species if any adhered to the samples. All samples are found to be insoluble in common solvents.

Table 1 Gel time and peak exotherm temperature of ECAM, PMP and their mixed matrix materials

Composition code	Gel time, Sec.	Peak exotherm, ^{o}C
ECAM	121	48
ECAM -PMP -25	182	51
ECAM-PMP-50	189	56
ECAM-PMP-75	243	67
PMP	300	71

Section-7: Syntheses of polyurethane resins

[A] Synthesis of polyurethane resin

Polyurethane resin (IX) of ECAM and 2, 4-toluene diisocyanate here after designated as ECAMT, was synthesized as follows.

To a 100 ml beaker were added 0.005 mol (13.19g) ECAM in 15 ml $CHCl_3$ and 0.01 mol (1.85g) TDI in 15 ml $CHCl_3$ at room temperature. The reaction was stirred manually for about 25-30 min. The separated solid resin was filtered and liquid resin was isolated by distillation of excess of $CHCl_3$. Orange colored resin was formed which is soluble in $CHCl_3$, MEK, acetone, 1, 4-dioxane, DMF, DMSO and not soluble in ethanol and isopropanol.

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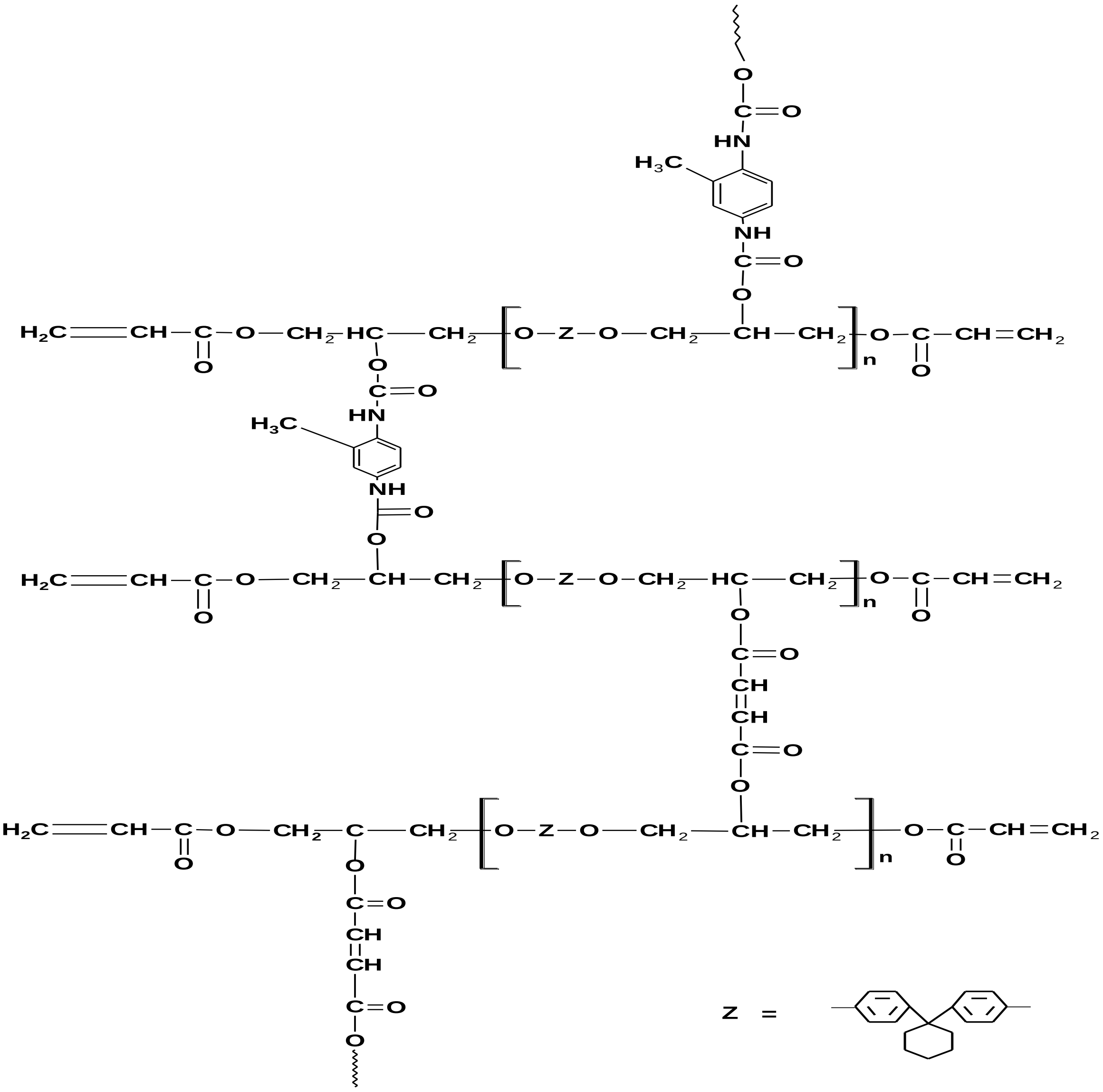
6. Bilibin A. Y., Zuev V. V., and Skorokhodov S. S. Synthesis of liquid crystalline poly(oxyfumaroyloxy-1,4-phenylenecarbonyloxyaleneoxy carbonyl-1,4-phenylene)s. Markromol. Chem. Rapid. Commun., 6(9):601-606,1985

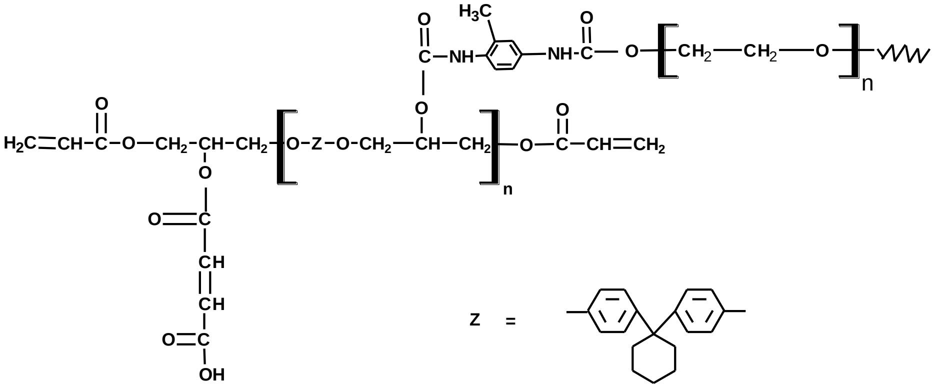


Polyurethane resin of ECAM (IX)

[B] Synthesis of copolyurethane resin

In order to improve flexibility of PU an attempt has been made to use of PEG-400. Copolyurethane resin (X) of ECAM, 2, 4-toluene diisocyanate and PEG-400 here after designated as ECAMPT, was synthesized as follows.

To a 100 ml beaker were added 0.005 mol (13.19g) ECAM in 15 ml $CHCl_3$ and 0.01 mol (1.85g) TDI in 15 ml $CHCl_3$ at room temperature. The reaction was stirred manually for about 25-30 min. Then to this prepolyurethane 30% PEG-400 in 5 ml $CHCl_3$ was added dropwise and the reaction mixture was stirred for further 10 min. The structure of copolyurethane is shown in Schemes X. The separated solid resin was filtered and liquid resin by distillation of excess of $CHCl_3$. Orange colored resin was formed which is soluble in $CHCl_3$, MEK, acetone, 1, 4-dioxane, DMF, DMSO and not soluble in ethanol and isopropanol.



Copolyurethane resins of ECAM (X)

CHAPTER – 3

Curing of resins and their characterization

This chapter of the thesis describes the determination of epoxy equivalent of the epoxy resins, acid and hydroxyl values of the polyester polyols, thermal, and spectral characterization of the resins. This chapter is subdivided into five subsections.

Section-I: Spectral characterization of monomers and resins

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

Section-III: Determination of acid values of polyester resins

Section-IV: Determination of hydroxyl values of polyester resins

Section-V: Thermal analysis of polyester and polyurethane resins

Section-I: Spectral characterization of monomers and resins

This section of the thesis includes the IR, Mass and NMR spectral characterization of the monomers, epoxy resin, epoxy ester, unsaturated polyester, epoxy-acylate-maleate and polyurethane resins:

[A] IR spectral characterization

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

The intensity of an absorption band depends on the size of dipole moment change associated with the vibration. In other words, depends on polarity of the vibrating bond. Intensity of the absorption band also depends on number of bonds responsible for the absorption. The concentration of the sample used to obtain an IR spectrum also affects the intensity of absorption bands.

The IR spectra of resins and polymers were scanned on a Shimadzu-8400 FTIR spectrometer over the frequency range from 4000-400 cm-1. The IR spectra of resins and polymers are shown in Figs. 3.1 to 3.10. The characteristic IR absorption frequencies (cm^{-1}) are reported in Tables-3.1 and 3.3.

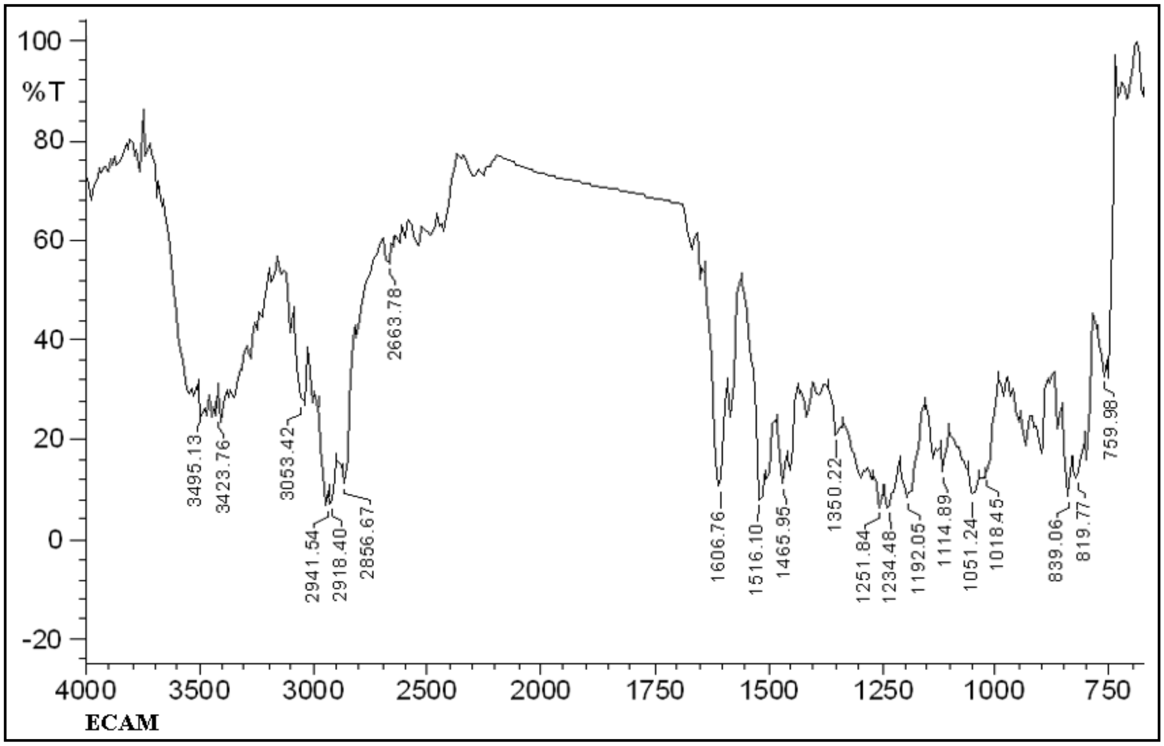


Fig. 3.1 IR (KBr) spectrum of ECAM

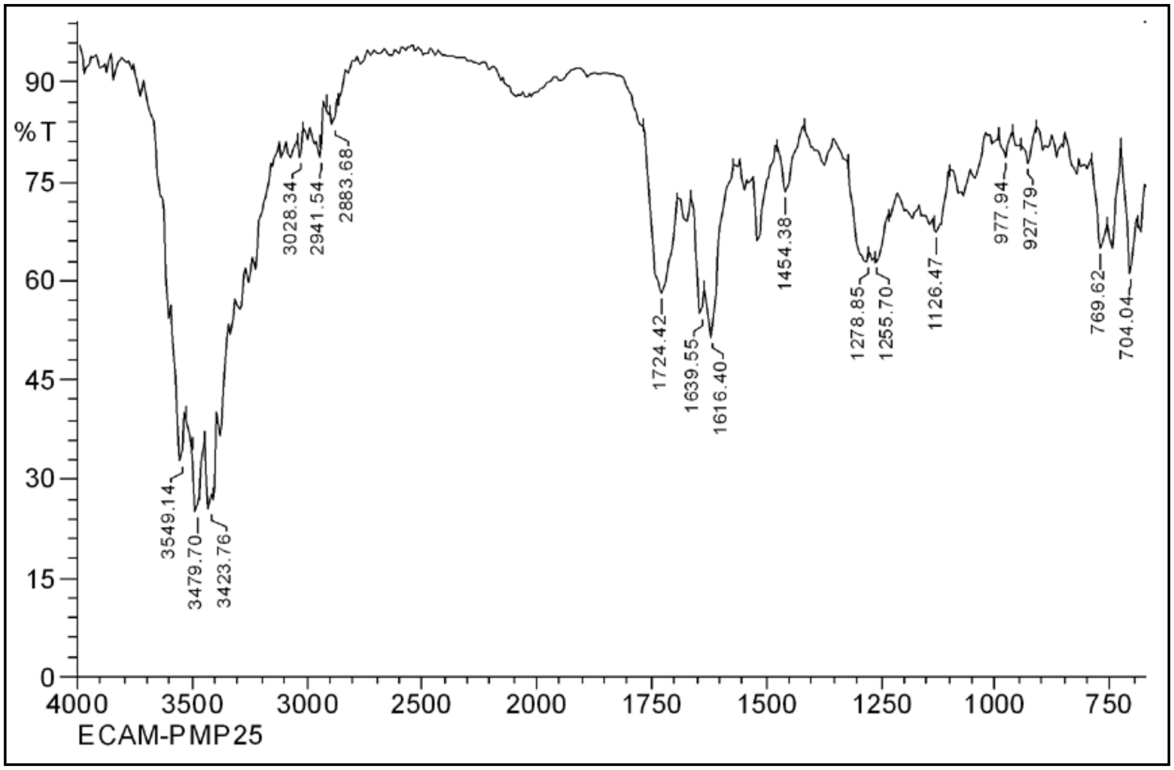


Fig. 3.2 IR (KBr) spectrum of ECAM-PMP-25

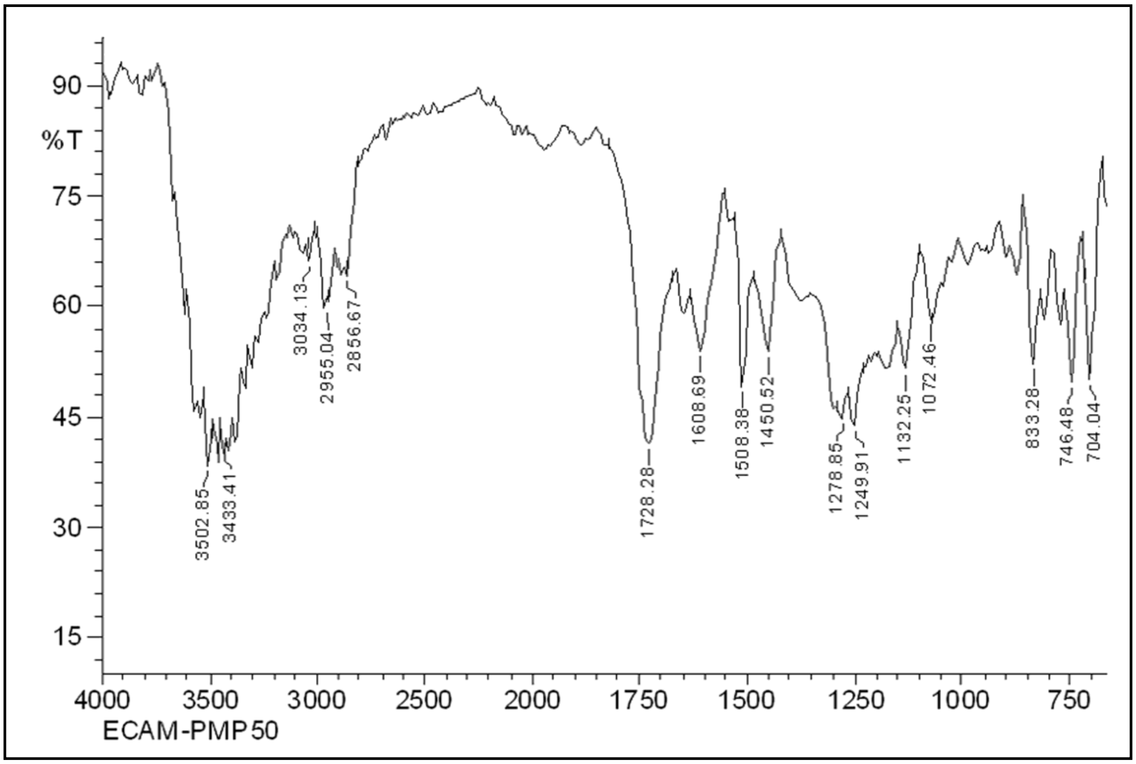


Fig. 3.3 IR (KBr) spectrum of ECAM-PMP-50

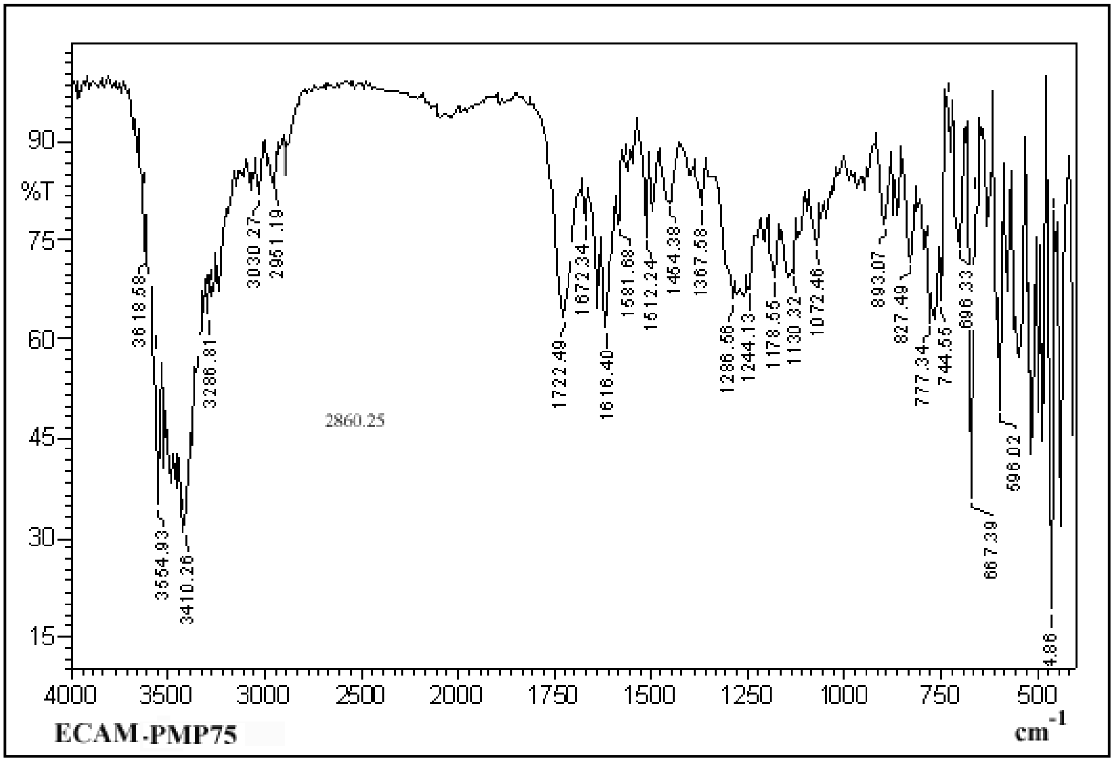


Fig. 3.4 IR (KBr) spectrum of ECAM-PMP-75

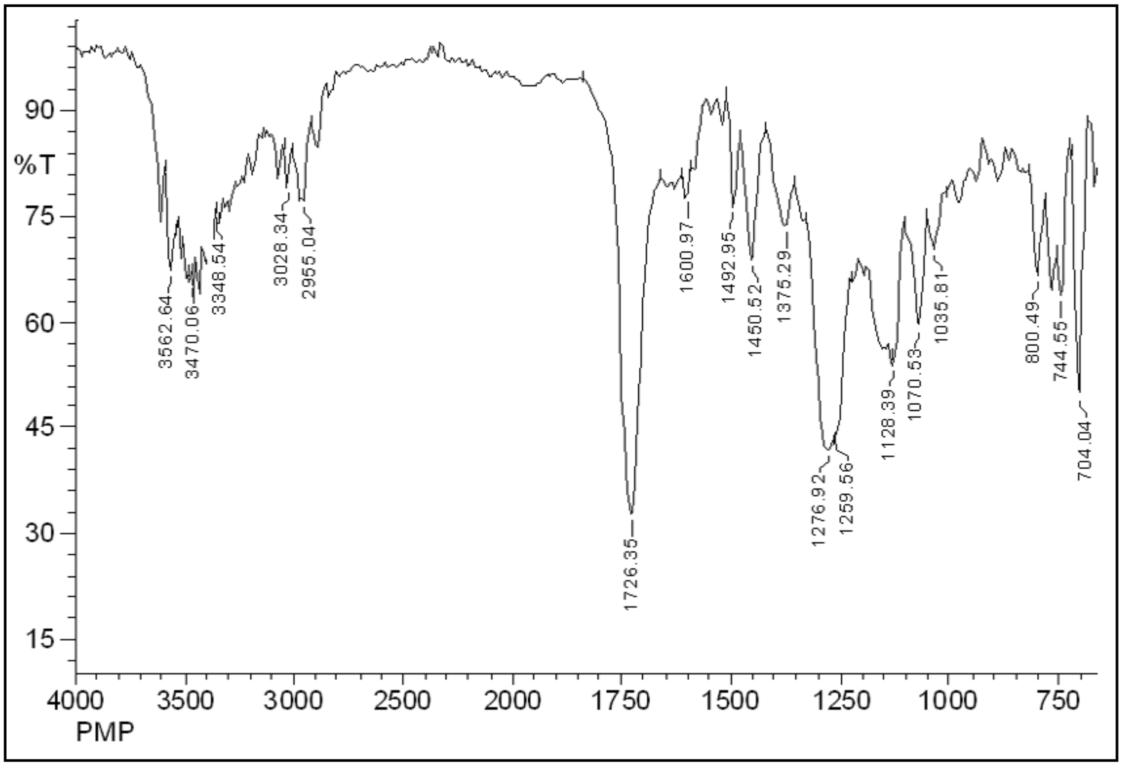


Fig. 3.5 IR (KBr) spectrum of PMP

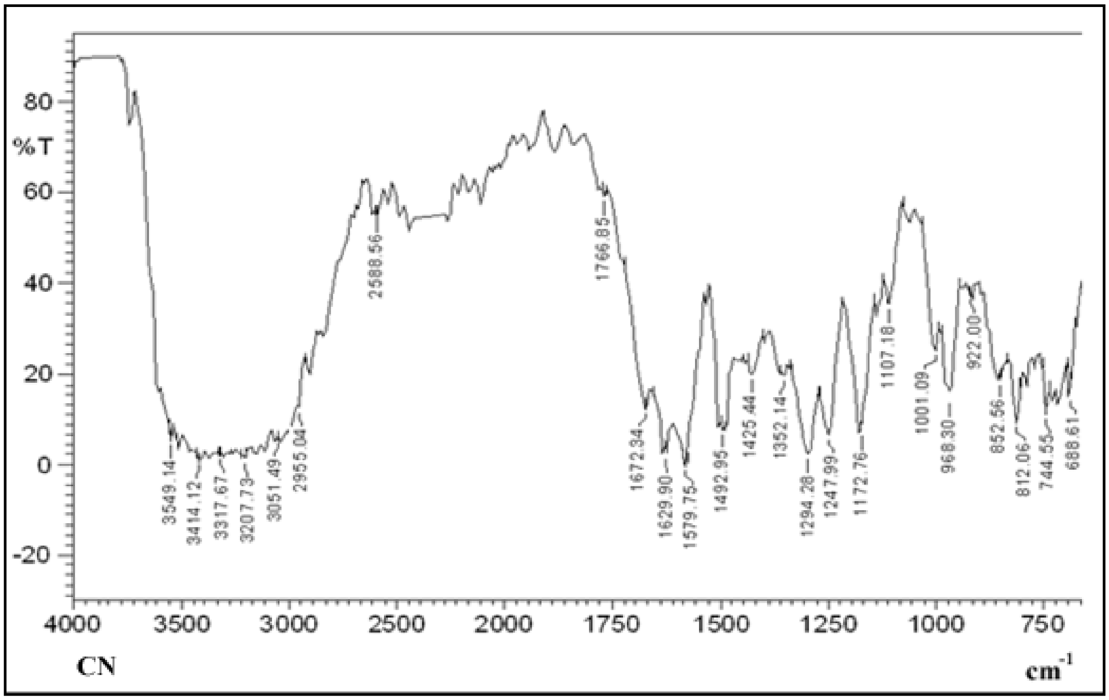


Fig. 3.6 IR (KBr) spectrum of CN

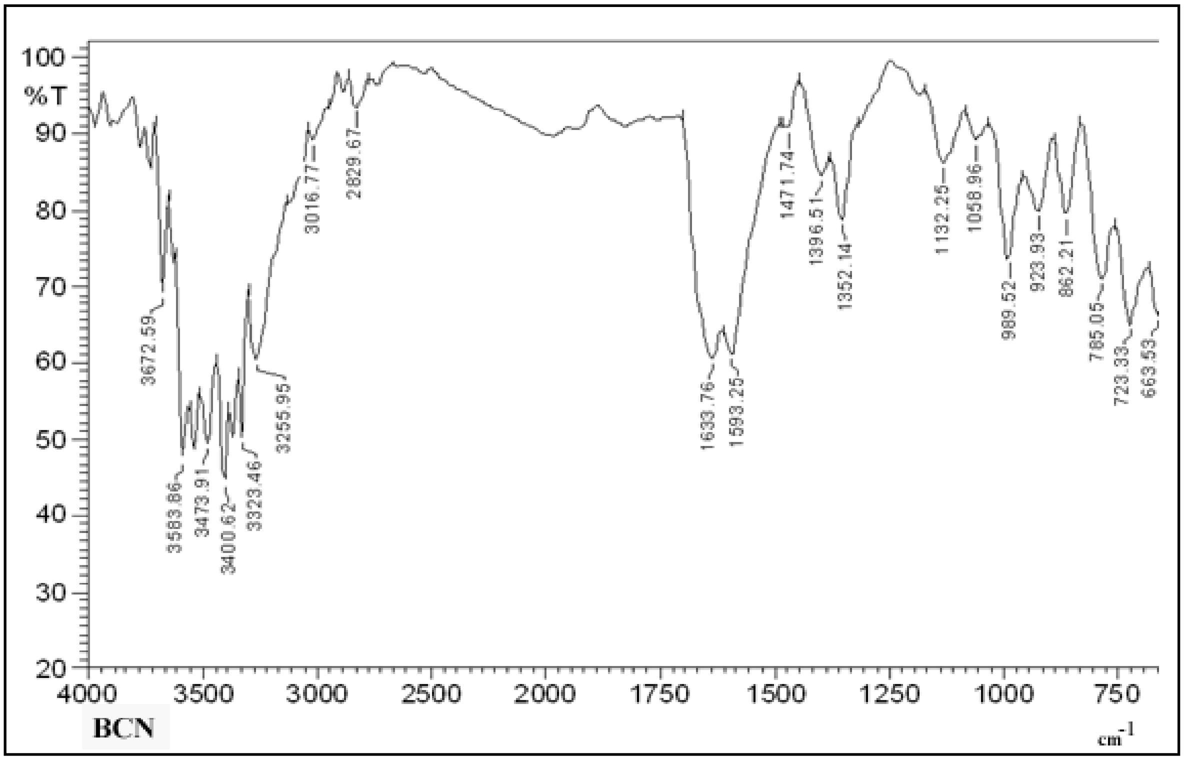


Fig. 3.7 IR (KBr) spectrum of BCN

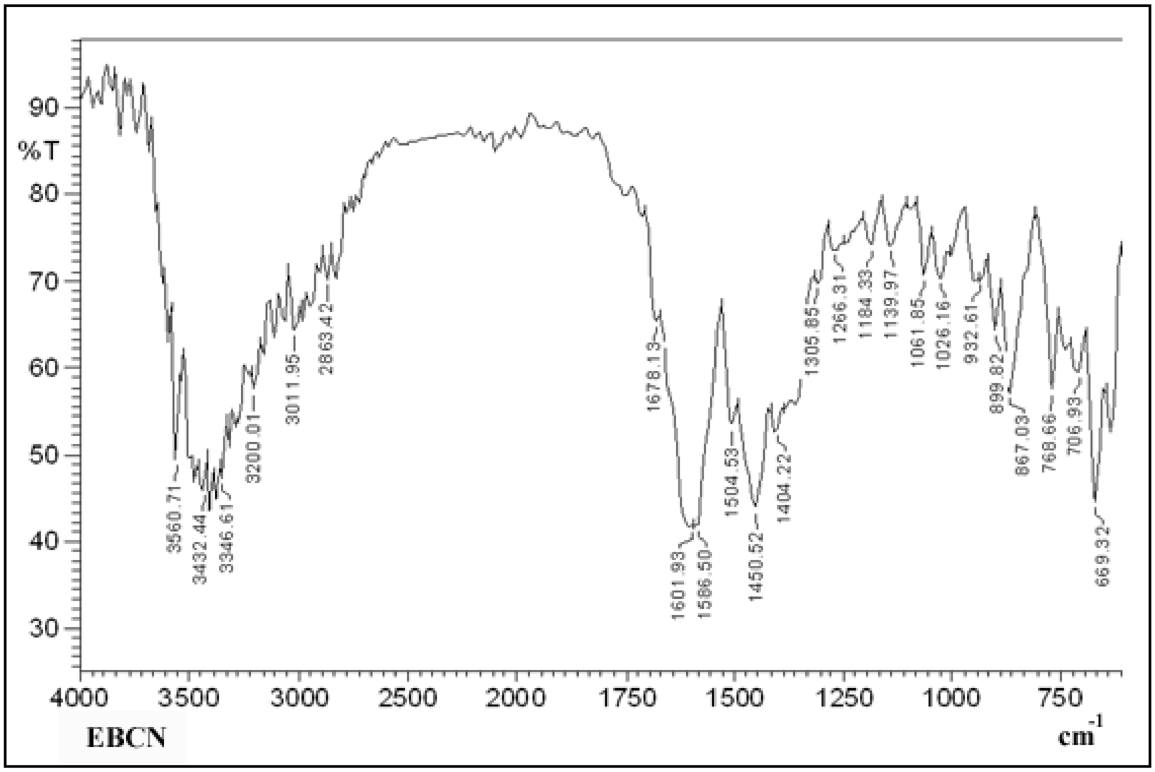


Fig. 3.8 IR (KBr) spectrum of EBCN

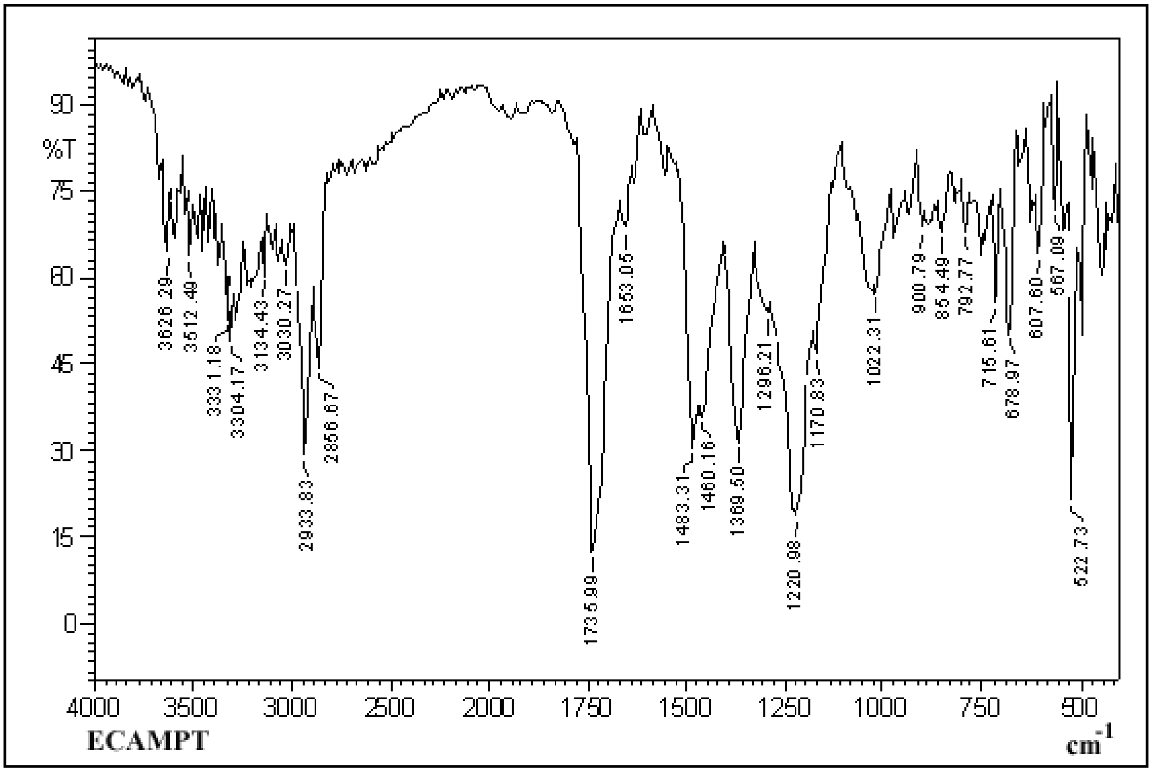


Fig. 3.9 IR (KBr) spectrum of ECAMT

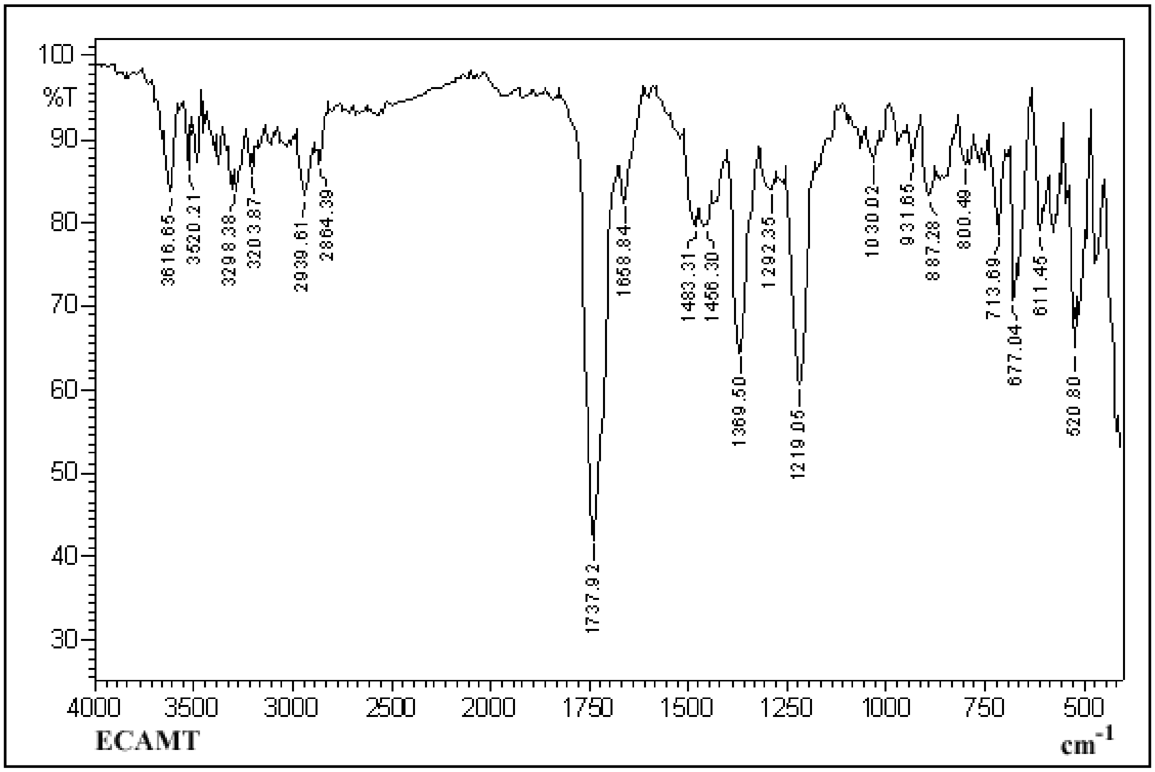


Fig. 3.10 IR (KBr) spectrum of ECAMPT

Table 3.1 The characteristic IR absorption frequencies of ECAM, PMP and their cured mixed matrix materials

Types	Group vibration mode	Observed IR frequencies, (cm^{-1})					Expected frequencies, (cm^{-1})
		ECAM	ECAM-PMP25	ECAM-PMP50	ECAM-PMP75	PMP	
Alkane -CH_3 and -CH_2-	C-H (υ_{as})	2941.54	2941.54	2955.04	2953.12	2955.04	3010-2950
	C-H (υ_{s})	2856.67	2883.68	2856.67	2860.25	--	2880-2853
	C-H def, -CH_3		1454.38	1450.52	1452.45	1450.52	1470-1435
	C-H def, -CH_2-	1465.95	-	-	-	1492.95	1485-1445
	Twistiing & Wagging	1251.84	1255.70	1278.85	1286.56	1259.56	~1250
	Skeletal CH_2 4 or >	759.98	769.62	746.48	766.77	744.55	750-720
-OH	O-H (str.)	3423.76	3423.76	3433.41	3414.12	3470.06	3400-3200
Arom-atic	C-H (i.p.d.)	1114.89	1126.47	1072.46	1072.46	1070.53	1258±11, 1175±6, 1117±7, 1073±5 (1,4 sub.)
	C-H (o.o.p.d.)	819.77	821.70	833.28	827.49	800.49	900-860, 860-800 (1,2,4 sub.)
	C=C (str.)	1606.76	1616.40	1608.69	1616.40	1600.97	1600±6, 1579±6
Ester	C=O (str.)	--	1724.42	1728.28	1722.49	1726.35	1780-1710
	C-O(str.)	1251.84	1278.85	1249.91	1286.56	1276.92	1300-1250

Table 3.2 The characteristic IR absorption frequencies of CN, BCN and EBCN

Types	Group vibration mode	Observed IR frequencies, (cm^{-1})			Expected frequencies, (cm^{-1})
		CN	BCN	EBCN	
Alkane $-CH_3$ and $-CH_2-$	C-H (υ_{as})	2955.04	3016.77	3011.95	3010-2950
	C-H (υ_s)	-	2829.67	2863.42	2880-2853
	C-H def, $-CH_3$	1425.44	1396.51	1450.52	1470-1435
	C-H def, $-CH_2-$	1492.95	1471.74	1504.53	1485-1445
	Twistiing & Wagging	1247.99	-	-	~1250
-OH	O-H (str.)	3317.67	3323.46	3432.44	3400-3200
Arom-atic	C-H (i.p.d.)	1172.76	1132.25	1139.97	1258±11, 1175±6, 1117±7, 1073±5 (1,4 sub.)
	C-H (o.o.p.d.)	852.56	862.93	867.03	900-860, 860-800 (1,2,4 sub.)
	C=C (str.)	1629.90	1633.76	1601.93	1600±6, 1579±6
Ester	C=O (str.)	1672.34	-	-	1780-1710
	C-O(str.)	1294.28	-	1266.31	1300-1250

Table 3.3 The characteristic IR absorption frequencies of ECAMT and ECAMPT

Type	Absorption frequencies, cm^{-1}	
	ECAMT	**ECAMPT**
-N-H Str.	3616.65	3626.29
$-CH_2$Str. (sym.) $-CH_2$Str. (asym.)	2864.39	2856.67
Urethane -C=O Str.	1737.92	1735.99

[B] NMR spectral characterization

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

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

The decrease in intensity of incident radiation owing to absorption during a particular transition is related to the number of nuclei in the sample that undergo the transition and can be used for quantitative analysis. NMR spectrometer was

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1. V. M. Parikh. Absorption Spectroscopy of Organic Molecules. Addission Wesley Pub., 243-258, 1978.
2. D. L. Pavia, G. M. Lampan and G. S. Kriz. Introduction to Spectroscopy. Saunders Publisher, Philadelphia, 46, 1979.
3. R. M. Silverstein, G. C. Bassler and T. C. Morrill. Spectrometric Identification of Organic Compounds. 6th Ed. John Willey and Sons, New York, 1996.
4. C. N. R. Rao. Chemical Applications of Infrared Spectroscopy. Academic Press, New York, 317-333, 1963.
5. D. W. Thomson and G. F. L. Ehlers. J Polym. Sci. Part- A, 3, 1051-1056, 1964.

invented in 1945 by Falix Bloch (Stanford University) and Edward Purcell. They shared the Nobel Prize (1952) in Physics for their work.

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

The NMR spectra of ECAM, CN and BCN were scanned on a Bruker AVANCE II (400MHz) spectrometer by using $CDCl_3$ as a solvent and TMS as an internal standard and are presented in Figs. 3.11 to 3.13. ECAM showed complex NMR splitting pattern due to internal $-OCH_2CH(OH)CH_2O-$(4.3 to 3.32 ppm) and terminal $–OC(=O)-CH=CH_2$ groups. Observed chemical shifts (ppm) are 1.17 (α-CH_2-), 2.197 (β +γ- CH_2-), 6.8(ArH attached to cyclohexane ring) and 7.14 (ArH attached to oxygen). Olephinc protons overlapped with aromatic protons. Residual chloroform and acetone appeared at 7.26 and 1.52ppm, respectively. In case of CN olephinic protons showed very diffuse signals (Fig.3.12). Similarly olephinic protons of BCN merged with phenolic protons (7.26-7.05 and 6.74-6.72ppm). Methyl protons appeared at 2.16ppm and residual $CHCl_3$ at 7.264ppm. Mass spectral data clearly indicated molecular ion peaks confirming formation of CN and BCN.

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6. J. R. Ebdon. 220 MHz proton magnetic resonance analysis of some methyl methacrylate-chloroprene copolymers. Polymer, 15, 782-786, 1974.
7. V. S. Nithianandan, K. Kaleem, K. V. S. Sreenivasan and K. T. Joseph. Estimation of reactivity ratios of acrylate copolymer by ^{1}H NMR. J. Polym. Sci. Polym. Chem., 21, 761-765, 1983.
8. A. Rudian, F. F. O'Driscoll and M. S. Rumack. Use of n.m.r. data to calculate copolymer reactivity ratios. Polymer, 22, 740-747, 1981
9. G. V. S. Shashidhar, K. Ranga Rao, N. Satyanarayana and E.V. Sundaram, Spectroscopic methods for the determination of composition in styrene-methacrylate copolymers. Polym. Sci. Part-C Polym. Lett., 28, 157-161, 1990.
10. R.Ulku and M.B.Bhahatti, J. Appl. Polym. Sci., 32, 58-65, (1986).

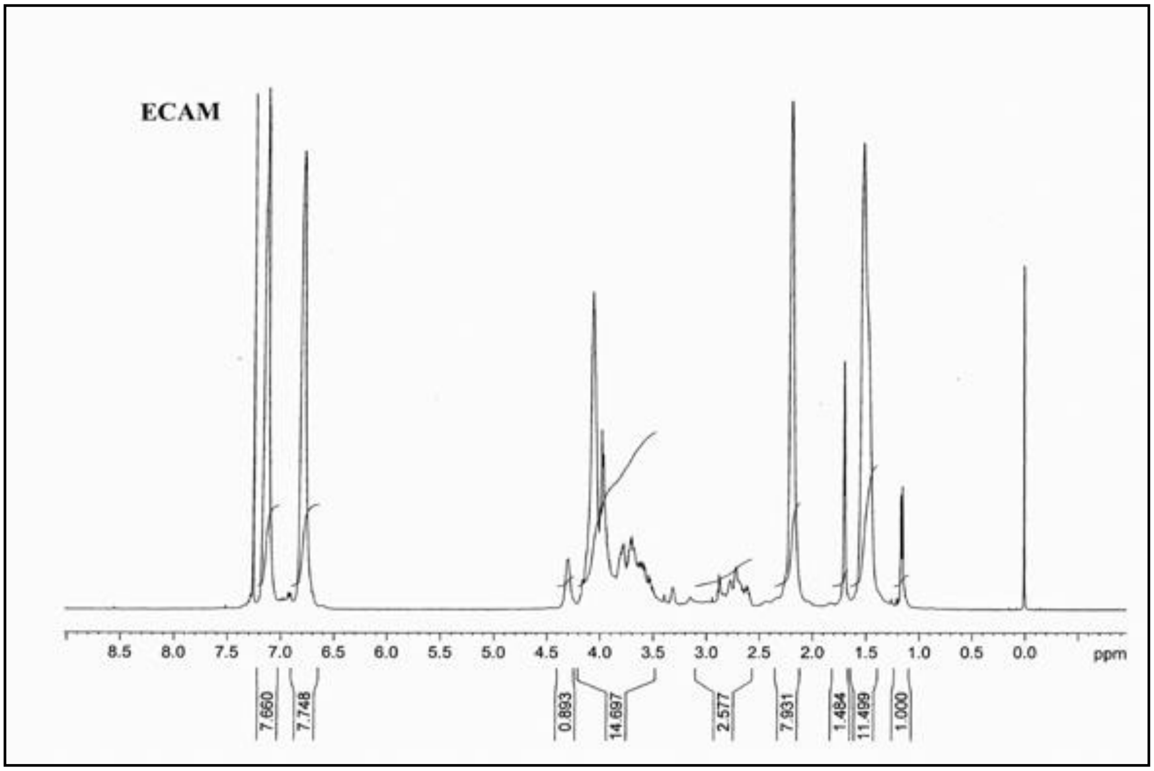


Fig. 3.11 NMR (400MHZ) spectrum of ECAM

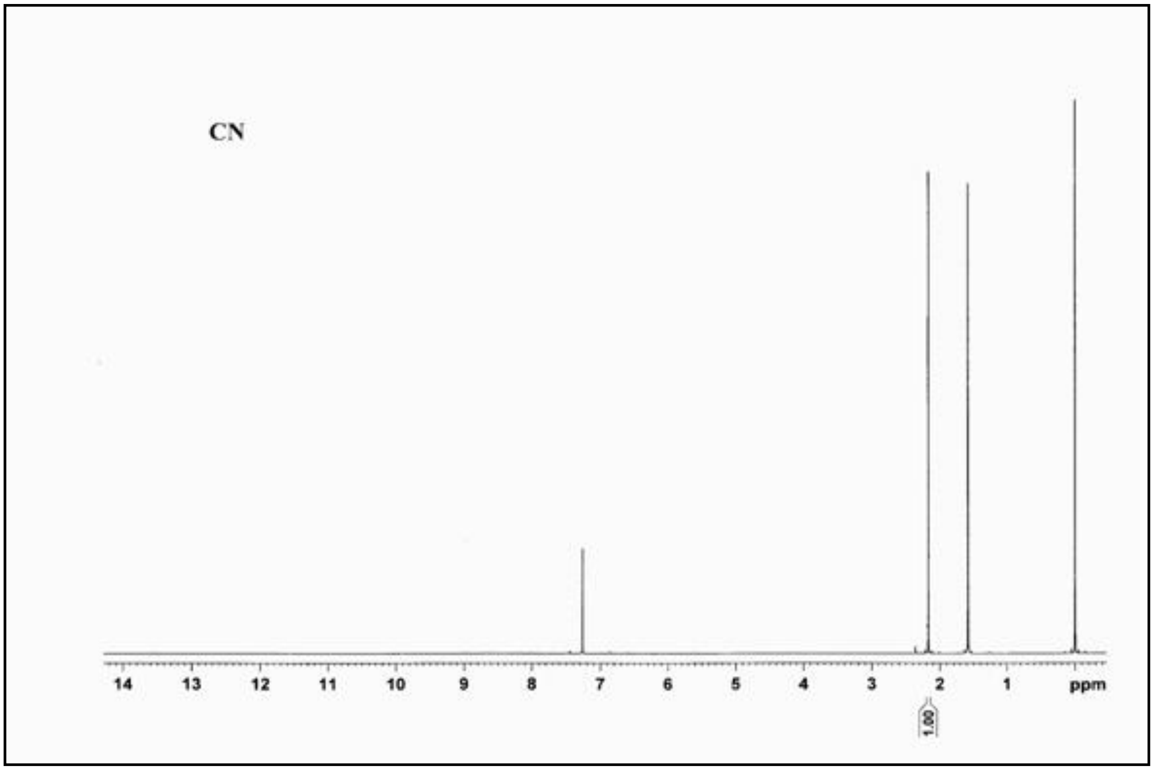


Fig. 3.12 NMR (400MHZ) spectrum of CN

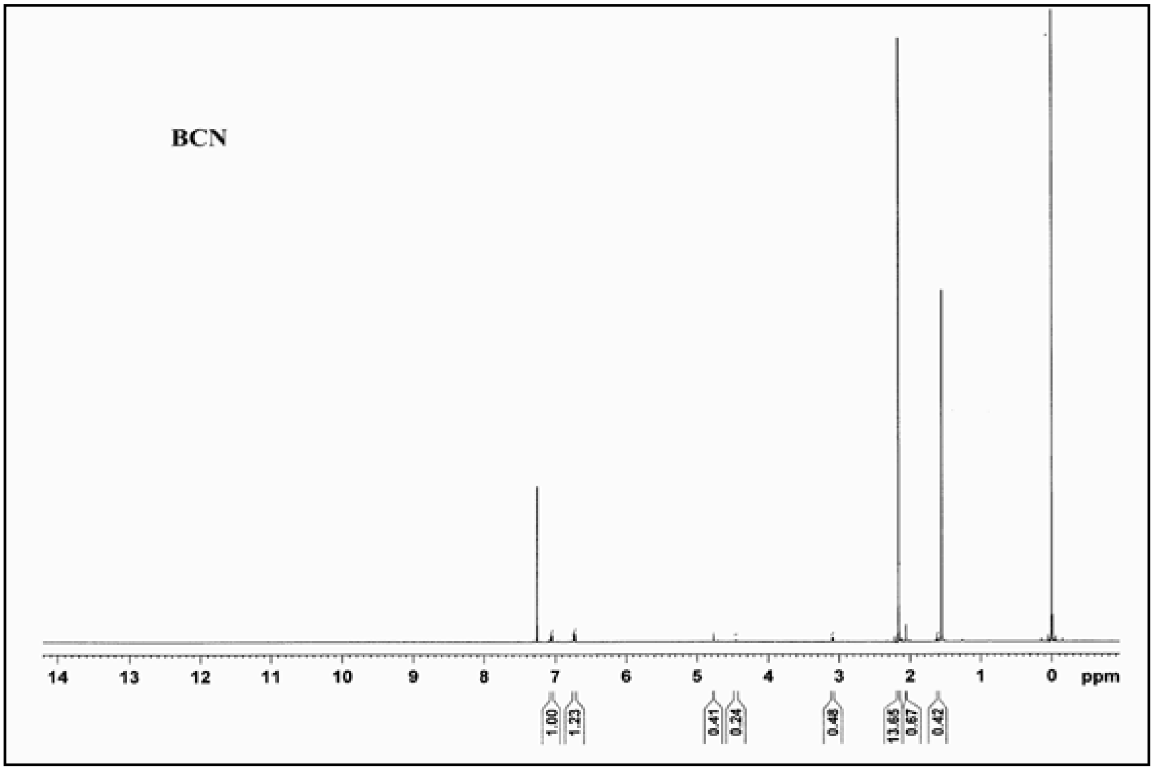


Fig. 3.13 NMR (400MHZ) spectrum of BCN

[C] Mass spectral study

Mass spectra were recorded on a Shimadzu GC-MS-QP-2010 model using Direct Injection Probe technique. Mass spectra of Chalcone and BCN are shown in Figs. 3.14 and 3.15. Molecular ion peak was observed in agreement with molecular weight of respective compound. Mass fragmentation pattern for CN and BCN is shown in Figs.3.16 and 3.17.

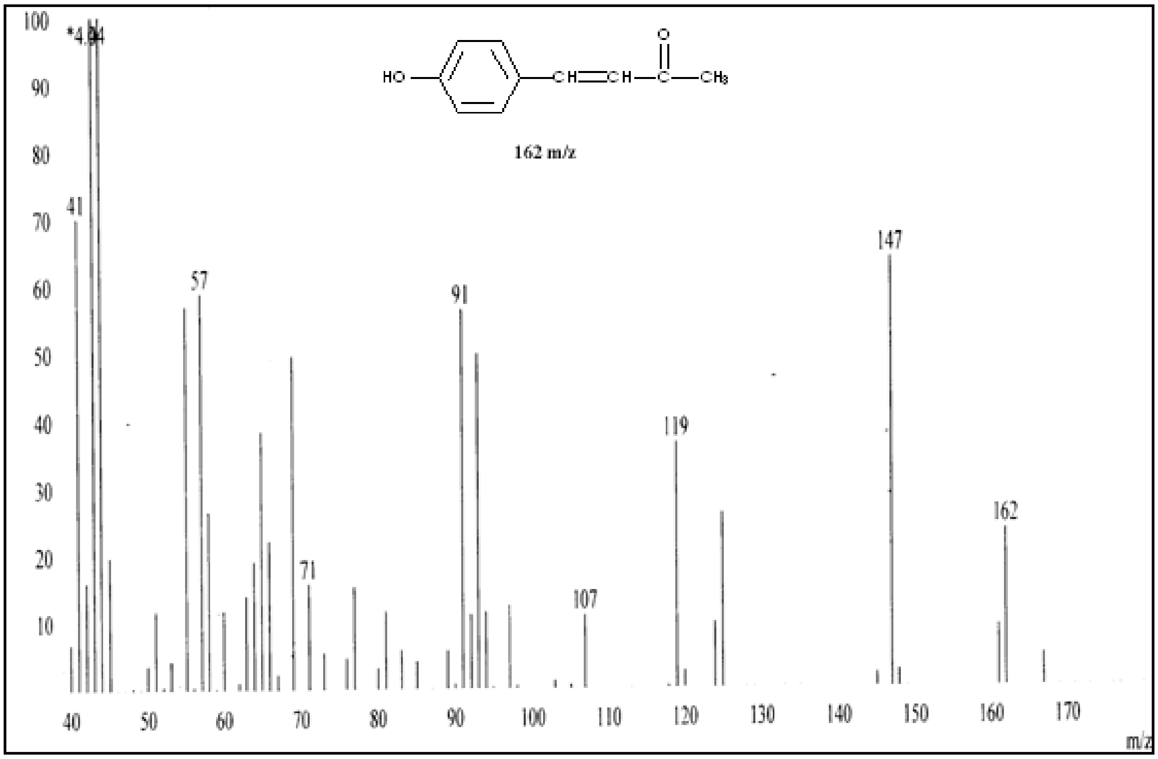


Fig. 3.14 Mass spectrum of 4-(4-hydroxyphenyl)but-3-en-2-one

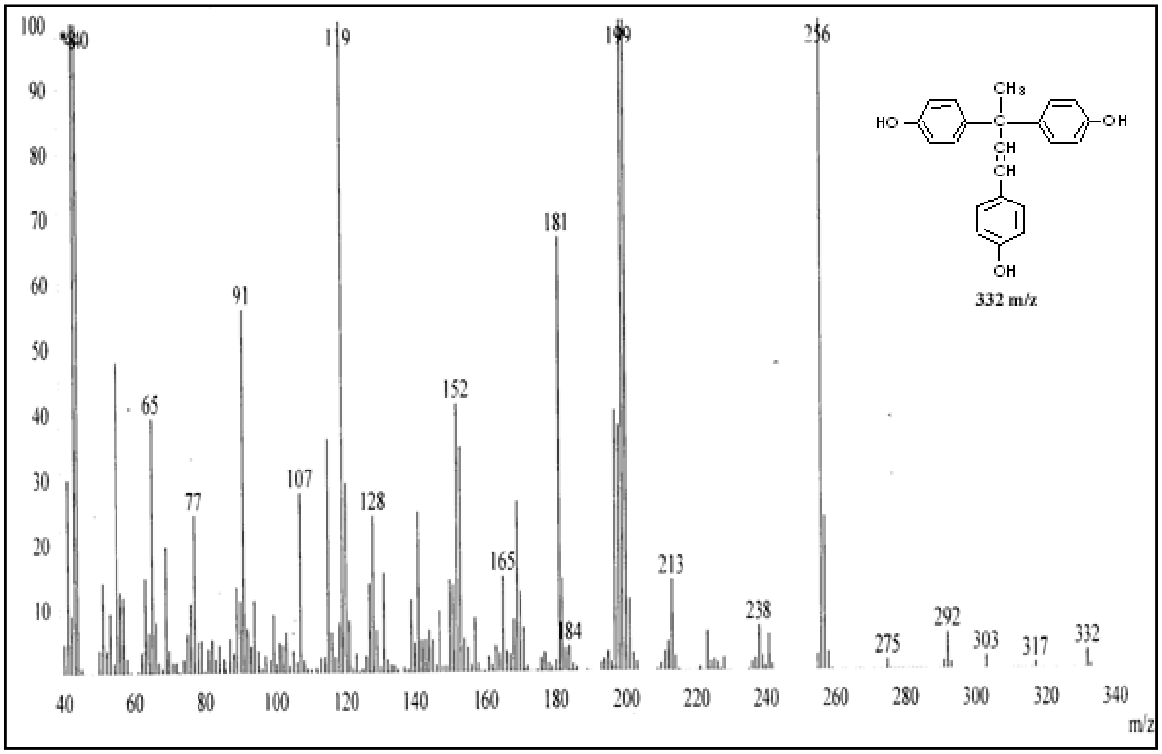


Fig. 3.15 Mass spectrum of 4,4',4''-but-1-ene-1,3,3-triyltriphenol

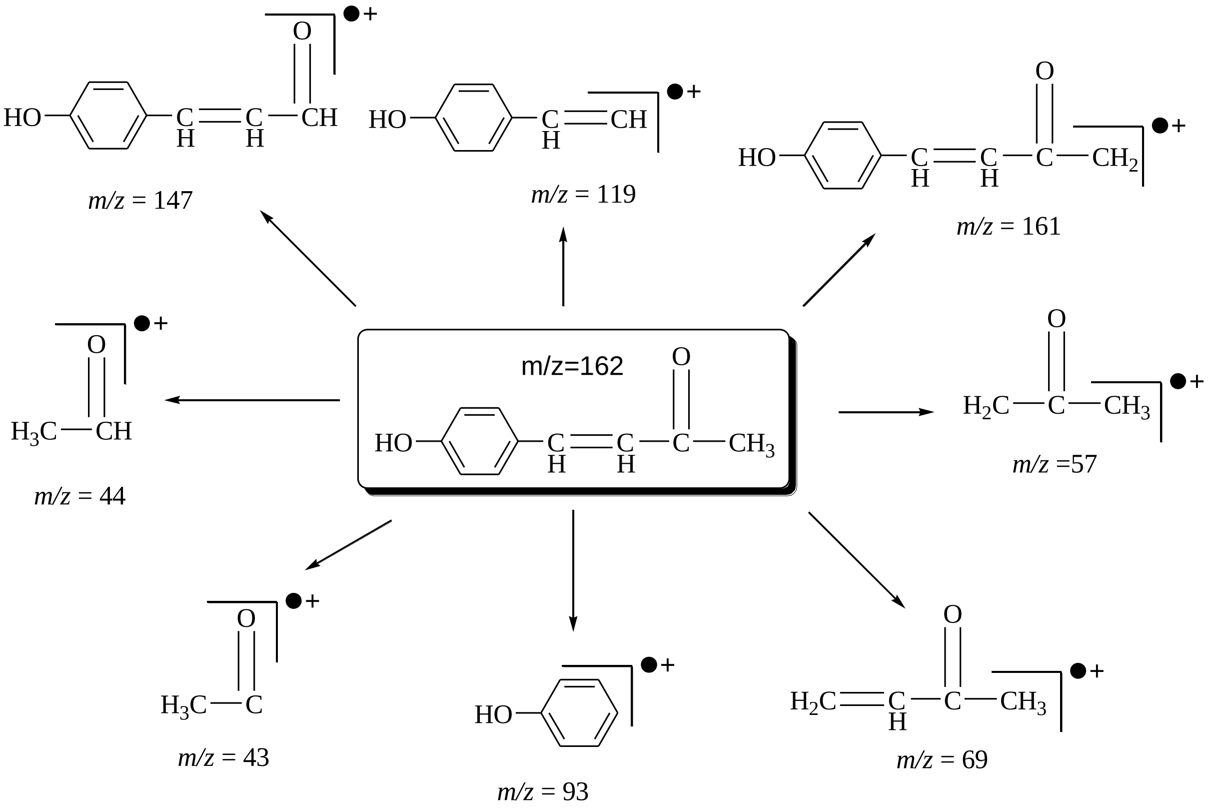


Fig. 3.16 Mass fragmentation of 4-(4-hydroxyphenyl)but-3-en-2-one

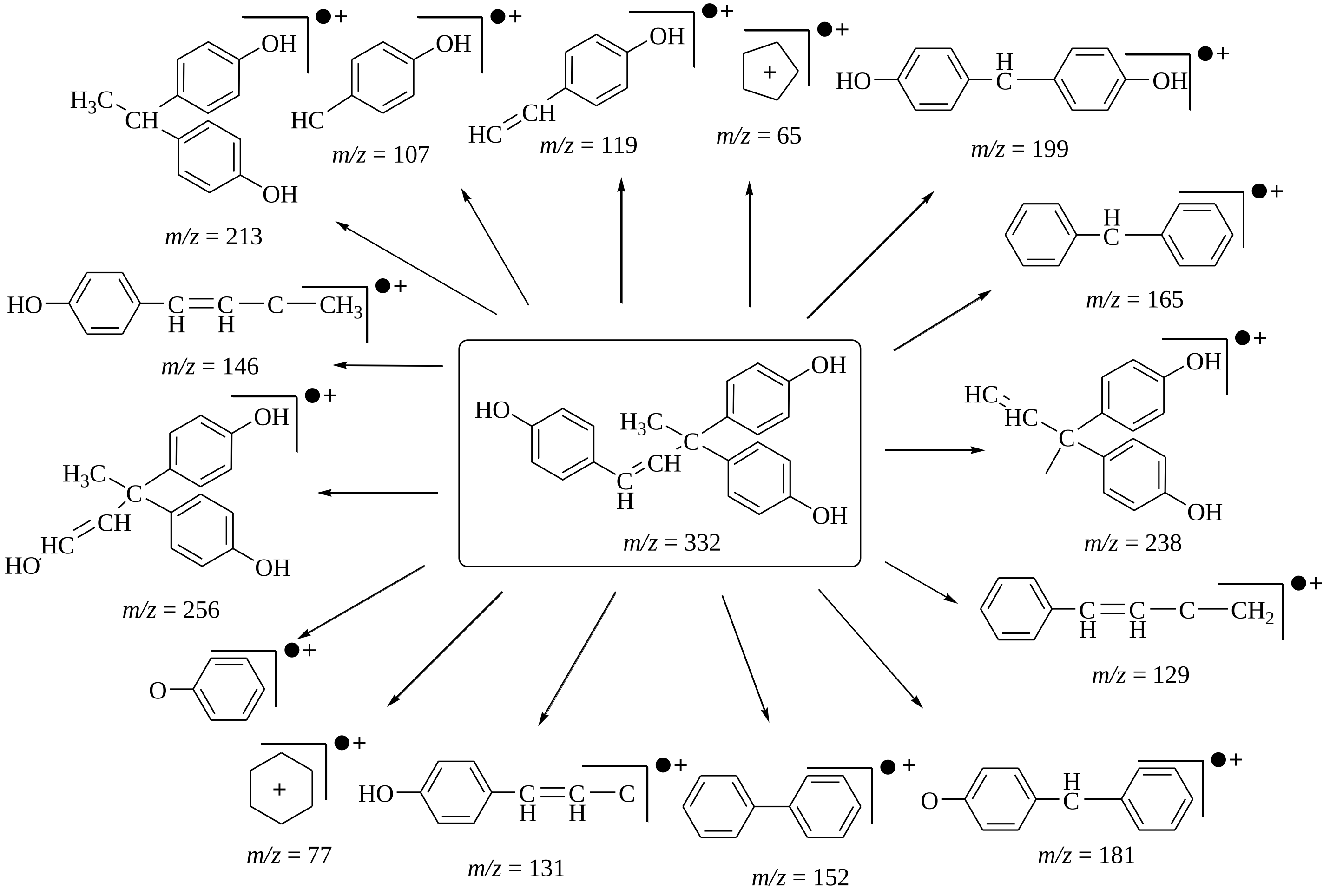


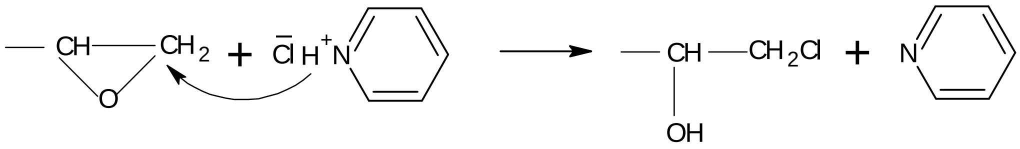
Fig. 3.17 Mass fragmentation of 4,4',4''-but-1-ene-1,3,3-triyltriphenol

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

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

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

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



$$HCl + NaOH \longrightarrow NaCl + H_2O$$

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11. J. Bomstein. Infrared Spectra of Oxirane Compounds. Correlations with Structure. Anal. Chem., 30, 544-546, 1958.

12. 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).

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

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

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

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

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13. J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss. Organic Analysis (J. Mitchell Jr., ed.). 1, 127, Interscience, New York, 1953.

14. R. E. Burge, Jr. and B. P. Geyer. Analytical Chemistry of Polymers. (G. M. Hline, ed.) Vol. XII/1, Interscience New York, 1959.

The number 0.016 is the mili equivalent weight of oxygen in grams. The epoxide equivalent of the epoxy resin of bisphenol-C and epoxy resin of bisphenol of 4-(4-hydroxyphenyl)but-3-en-2-one resin used was found to be 576 and 889, respectively.

Section-III: Determination of acid values of the epoxy ester and epoxy-acrylate-maleate

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

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

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

Where N = Normality of KOH

A = Sample burette reading

B = Blank burette reading

W = Weight of sample in grams

The average of three measurements of each of epoxy ester and epoxy-acrylate-maleate are reported in Table-3.7.

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15. ASTM-D-1639-61

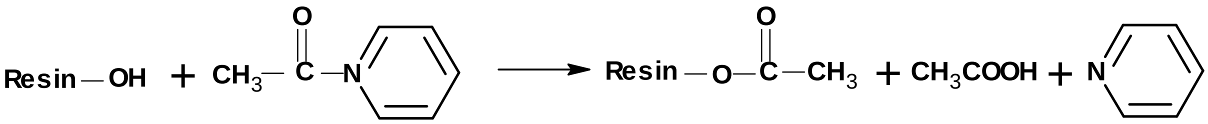
Table 3.8 Acid values of EBCA, ECAM and PMP

Type of resin	Acid value, mg KOH/g
EBCA	5.58
ECAM	32
PMP	56.4

Section-IV: Determination of hydroxyl values of polyester polyols

Hydroxyl value is a measure of free hydroxyl groups present in the epoxy ester and epoxy-acrylate-maleate, it is expressed as number of milligrams of potassium hydroxide equivalent to the quantity of acetic acid that binds with 1 g of hydroxyl containing substances.

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



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

Hydroxyl values of epoxy ester and epoxy-acrylate-maleate were determined according to standard reported method. Epoxy ester was exactly weighed (1- 2 g) in a small capsule and placed carefully in a 250 ml RBF and to it 20 ml of acetylating mixture (1 volume of acetic anhydride and 3 volume of pyridine) was added. The flask was swirled for some time and heated gently to dissolve sample completely. The content was refluxed on a boiling water bath for 30 min. The solution was cooled to room temperature and was added 50 ml cold water slowly down to the condenser and was titrated the free acetic acid with standard 1N NaOH using phenolphthalein as an indicator. The procedure was repeated for blank titration under similar condition. The average of three measurements was used to determine the hydroxyl value of given sample according to following relationship.

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

Where N = Normality of KOH

A = Sample burette reading

B = Blank burette reading

W = Weight of sample in grams

Observed Hydroxyl values of EBCA and ECAM are 124.2 and 58.7 mg KOH/g

Section-V: Thermal analysis of cured ECAM, PMP and their mixed matrix materials

Synthetic polymers are highly useful in the rapidly developing fields such as space exploration, terrestrial, transportation, modern communications, energy saving, environmental protection, public health, microbiology, medicine, etc. A major driving force for the growth and interest in the studies of thermally stable polymers is attributed to their extensive applications in aeronautics and in supersonic appliances. Considerable research work has been undertaken [16] on the thermal stability of polymers to derive the polymers, which may be useful for high temperature applications.

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

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

Kinetic study of thermal decomposition of epoxy resins containing flame retardant components was reported by Wang and Shi [17]. Hyperbranched polyphosphate ester (HPPE) and phenolic melamine (PM) were blended in different ratios with a commercial epoxy resin to obtain a series of flame retardant resins. The thermal decomposition mechanism of cured ester was studied by thermogravimetric analysis and in situ Fourier-transform infrared spectroscopy. The degradation behaviors of epoxy resins containing various flame retardant components were found to be greatly changed.

Laza et al. [18] have studied the dynamic-mechanical properties of different mixtures formed by an epoxy resin (DGEBA type) and a phenolic resin (resole type) cured by triethylene tetramine and/or p-toluene sulphonic acid at different concentrations by means of dynamic mechanical thermal analysis (DMTA). All samples were cured by pressing at 90°C during 6h.

The mechanical studies were performed between -100 to 300 °C at a heating rate of 2°C/min. Thermal degradation and decomposition products of

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16. R. T. Conley. Thermal Stability of Polymers. Marcell Dekker, New York, 1973.
17. Q. Wang and W. Shi. Kinetics study of thermal decomposition of epoxy resins containing flame retardant components. Polym. Deg. and Stab., 91, 1747-1754, 2006.
18. J. M. Laza, J. L. Vilas, M. T. Garay, M. Rodríguez and L. M. León. Dynamic mechanical properties of epoxy-phenolic mixtures. J. Polym. Sci., Part B: Polym. Physics, 43, 1548-1557, 2005.

electronic boards containing BFRs have been studied by the Barontini et al. [19]. They have investigated the thermal degradation behavior of electronic boards manufactured using tetrabromobispheno-A and diglycidyl ether of bisphenol-A epoxy resins. Qualitative and quantitative information was obtained on the products formed in the thermal degradation process, and the bromine distribution in the different product fractions was determined. The more important decomposition products included hydrogen bromide, phenol, polybrominated phenols, and polybrominated bisphenol-A species.

Wang et al. [20] have reported the cure study of addition-cure-type and condensation-addition-type phenolic resins by the incorporation of propargyl and methylol groups on to novolac backbone, a series of addition-curable phenolic resins and condensation-addition dual-cure type phenolic resins (novolac modified by propargyl groups referred as PN, and novolac modified by propargyl and methylol groups simultaneously referred as MPN) were synthesized.

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

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19. F. Barontini, K. Marsanich, L. Petarca and V. Cozzani. Thermal degradation and decomposition products of electronic boards containing BFRs. Ind. and Eng. Chem. Res., 44, 4186-4193, 2005.
20. M. Wang, L. Wei and T. Zhao. Cure study of addition-cure-type and condensation-addition type phenolic resins. Eur. Polym., J., 41, 903-917, 2005.

have a bright prospect of application as matrix for thermal-structural composite materials.

Nair et al. [21] have reported the thermal characteristics of addition-cure phenolic resins. The thermal and pyrolysis characteristics of four different types of addition-cure phenolic resins were compared as a function of their structure. Whereas the propargyl ether resins and phenyl azo functional phenolics underwent easy curing, the phenyl ethynyl and maleimide-functional required higher thermal activation to achieve cure. All addition-cure phenolics exhibited improved thermal stability and char-yielding properties in comparison to conventional phenolic resole resin. The maleimide-functional resins exhibited lowest thermal stability and those crosslinked via ethynyl phenyl azo groups were the most thermally stable systems. Propargylated novolac and phenyl ethynyl functional phenolics showed intermediate thermal stability. The maximum char yield was also given by ethynyl phenyl azo system. Non-isothermal kinetic analysis of the degradation reaction implied that all the polymers undergo degradation in at least two steps, except in the case of ethynyl phenyl azo resin, which showed apparent single step degradation.

Effect of various operating parameters

1. Atmosphere

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

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21. C. P. Reghunadhan Nair, R. L. Bindu and K. N. Ninan. Thermal characteristics of addition-cure phenolic resins. Poly. Deg. and Stab., 73, 251-263, 2001.

homogeneous reactions or may be reflected back to the sample surface and react there.

2. Container geometry

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

3. Container material

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

4. Sample size

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

5. Rate of heating

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

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

Physical transformation [22] such as glass transition, cold crystallization and crystallization from melts, crystalline disorientation, and melting can be studied by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Glass transition involves the motion of short segments in the amorphous region and is related to the brittleness of the polymer. Crystallization from the melt is of great practical importance. A number of properties of polymers like melting range, heat of fusion and melting point depression, degree of crystallinity, random copolymer structure and stereo regularity and identification of composition of a mixture may be studied through melting. DSC is a method where by the energy necessary to establish a zero temperature difference between a substance and a reference material is recorded as a function of temperature or time. The energy input to the sample is compensated by an increased energy input to the sample in order to maintain a zero temperature difference because this energy input is precisely equivalent in magnitude to the energy absorbed during the transition in direct calorimetric measurement. The combination of programmed and isothermal techniques has been used for characterizing unresolved multistep reactions in polymers [23]. DSC provides useful information about crystallinity, stability of crystallites, glass transition temperature, cross linking, kinetic parameters such as the activation energy, the kinetic order, frequency factor, entropy change and heat of polymerization.

Thermo Gravimetric Analysis (TGA)

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

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

Most of the studies of polymers are generally carried out with dynamic thermogravimetry. Normally sample starts losing weight at a very slow rate up to a particular temperature and thereafter, the rate of loss becomes large over narrow range of temperature. After this temperature the loss in weight levels off.

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22. E. Heisenberg. Cellulose Chemie, 12,159, 1931; C.A. 25, 59, 823, 1931.
23. A. A. Duswalt. The practice of obtaining kinetic data by differential scanning calorimetry. Thermochemica Acta, 8, 57-68, 1974.

TGA curves are characteristic for given polymers because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at the rates that are function of the polymer structures.

The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evaluation of volatile products in the formation of heavier reaction products. Pyrolysis of many polymers yields TG curves, which follow relatively simple sigmoidal curves. In such a case weight of sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction gets completed. The shape of the curve depends on the kinetic parameters: reaction order (n), frequency factor (A) and activation energy (Ea). The values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation [24, 25].

Reich and Levi [26] have described several temperature characteristics for qualitative assessment of relative thermal stability of polymers:

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

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

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24. D. W. Levi, L. Reich and H. T. Lee. Degradation of polymers by thermal gravimetric techniques. Polym. Engg. Sci., 5, 135-141, 1965.
25. H. L. Friedman, U. S. Dept. Com., Office. Tech. 24 pp, (1959); C.A. 55, 26, 511, 1961.
26. L. Reich and D. W. Levi, Macromol. Rev.Eds. Peterlin Goodman Willey Interscience, New York, 173, 1968.

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

$$\frac{dC}{dt} = k\,f\,(C) \qquad \ldots 3.1$$

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

f (C) = temperature independent function of C

The constant k is generally assumed to have the Arrhenius form

$$k = A\,e^{-Ea/RT} \qquad \ldots 3.2$$

C is defined as the conversion with respect to initial material

$$C = 1 - \frac{W}{W_o} \qquad \ldots 3.3$$

Where W_o= Initial weight of the material and W= weight of the material at any time.

The residual weight fraction is given by

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

and the rate of conversion is given by

$$\frac{dC}{dt} = -\left(\frac{1}{W_O}\right)\frac{dW}{dt} \qquad \ldots 3.4$$

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

$$f\,(C) = (1-C)^n \qquad \ldots 3.5$$

Where n = order of the reaction

Upon substituting Eqns. 3.2 and 3.5 into Eqn. 3.1

$$\frac{dC}{dt} = A\,e^{-Ea/RT}\,(1-C)^n$$

OR

$$\frac{dC}{dT} = \left(\frac{A}{\beta}\right)(e^{-Ea/RT)}\,(1\text{-}C)^n \qquad \ldots 3.6$$

Where β= Rate of heating

Methods of single heating rate

1. Freeman-Carroll [27] and Anderson-Freeman methods [28]

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

$$\frac{\Delta \ln\ dC/dt}{\Delta \ln\ 1-C} = n - \frac{E_a}{R}\left[\frac{\Delta(1/T)}{\Delta \ln(1-C)}\right] \qquad \ldots\ 3.7$$

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

$$\Delta\ln\left(\frac{dC}{dt}\right) = n\ \Delta\ \ln\ (1-C) - \frac{E_a}{R}\ \Delta\left(\frac{1}{T}\right) \qquad \ldots 3.8$$

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

2. Sharp-Wentworth method [29]

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

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

---

27. E. S. Freeman and B. Carroll. The application of thermoanalytical techniques to reaction kinetics: the thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. J. Phys. Chem., 62, 394, 1958.
28. D. A. Anderson and E. S. Freeman. The kinetics of the thermal degradation of polystyrene and polyethylene. J. Polym. Sci., 54, 253, 1961.
29. J. H. Sharp and S.A. Wentworth. Kinetic analysis of thermogravimetric data. Anal. Chem., 41, 2060-2062, 1969.

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

3. Chatterjee method [30]

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

$$n = \frac{\log\left(\frac{dW}{dt}\right)_1 - \log\left(\frac{dW}{dt}\right)_2}{\log W_1 - \log W_2} \qquad \ldots\ 3.10$$

Where W_1 and W_2 are the sample weights.

4. Horowitz -Metzger method [31]

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

$$\ln\left[\ln(1-C)^{-1}\right] = \frac{Ea}{RTs^2}\theta \qquad \ldots\ 3.11$$

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

The frequency factor A and entropy change ΔS can be determined respectively according to Eqns. 4.12 and 4.13.

$$\ln E - \ln\left(RTs^2\right) = \ln A - \ln \beta - \frac{E}{RTs^2} \qquad \ldots.\ 3.12$$

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

Where k_b is Boltzmann constant.

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30. P. K. Chatterjee. Application of thermogravimetric techniques to reaction kinetics J. Polym. Sci., A-3, 4253-4262, 1965.

31. H. H. Horowitz and G. Metzger. A new analysis of thermogravimetric traces. Ana. Chem., 35, 1464-1468, 1963.

Experimental

TGA and DSC thermograms of ECAM, PMP and their mixed matrix material were scanned on Perkin Elmer DSC-TGA (Model Pyris-I) at the heating rate of 10^{o}C/min in nitrogen atmosphere.

Results and Discussion

DSC thermograms of ECAM, PMP and mixed matrix material are presented in Figs. 3.18 to 3.22. The DSC transitions are summarized in Table 3.10. Endothermic transitions (69-91^{o}C) below 100^{o}C are due to melting of uncured ECAM and mixed matrices. Endothermic transition at 122^{o}C for ECAM due to some chemical change in is further supported by weight loss over the temperature range 100-200^{o}C in the TG thermogram (Fig.3.23) and other endothermic transition at 225^{o}C is due to some physical change (glass transition temperature) is supported by partially no loss over the temperature range 200-300^{o}C. Endothermic transition at 415.7^{o}C for ECAM-PMP-25 is due to some physical change. A small but broad endothermic transition at 172.8^{o}C for ECAM-PMP-75 is probably due to glass transition temperature and other endothermic transition at 388.7^{o}C is due to some physical change. Again a small but broad endothermic transition at 226.8^{o}C for PMP is probably due to glass transition temperature and other endothermic transition is due to some physical change. Thus, physical/chemical change for each sample is supported in corresponding TG curves (Fig.3.23) of the samples.

From Fig.3.23, it is evident that all samples apparently followed single step degradation leaving 10-25% residue above 400^{o}C except ECAM. The initial decomposition temperature (T_o), decomposition range and temperature of maximum decomposition along with % weight loss involved and % residue for each sample are presented in table 3.10. ECAM is more thermally stable than that of PMP, while mixed matrix materials possess intermediate thermal stability of ECAM and PMP. Similar trend is also for observed in T_{max}. High magnitude % residue for ECAM above 400^{o}C indicated formation of high cross-linked product as a consequence of primary decomposition.

The plots of $\Delta \ln \frac{dW}{dt}$ against $\Delta \ln W$ are presented in Figs. 3.24-3.28 Associated kinetic parameters and detail calculation schemes are presented in Table 3.11to 3.15. The energy of activation (Ea), frequency factor (A), temperature of maximum weight loss (Tmax) and entropy change (ΔS*) are determined according to Anderson-Freeman method [28] (Eqn. 3.8) and are reported in Table 3.16 from which, it is clear that cured samples followed fractional (0.6-2.4) order degradation kinetics. Upon comparing kinetic parameters of ECAM and PMP, it is observed that PMP is somewhat more rigid than that of ECAM and this may be due to more cross-linking density. Maleate branching courses low degree of cross-linking due to comparatively a large distance between to branches and vinyl ester. In case of mixed matrix materials both E & A are lower than parent materials indicated improvement in flexibility mainly due to flexible maleate linkages. The entropy change ΔS* was determined at their respective Tmax according to equation 3 and is also reported in Table 3. The large and negative magnitudes of ΔS* confirmed highly ordered transition state than individual polymer molecules.

Degradation process is a complex process and involves a variety of reactions such as chain cleavage, branching, rearrangement, cross-linking, etc. Selective degradation occurs from weak points in the chains and consequently formation of free radials result, which further undergo a variety of reactions and degrade at higher temperature (>4000C) to form low molecular weight substances.

Ether and ester groups (main chain and side chain) in ECAM and ester and pendent methyl groups in PMP are thermally weak points in the resin molecules and therefore selective degradation is likely from these points.

Table 3.10 DSC and TGA data of resins

Resin	T_0, °C	T_f, °C	T_{max}, °C	Decompn. Range, °C	%wt. loss	% Residue	DSC Transitions (Endo), °C
ECAM	**300**	**400**	**370**	**307.6-400**	**59.36**	**24.68**	**91** **122** **225**
ECAM-PMP-25	**240.9**	**390.9**	**335**	**201.5-390.9**	**79.37**	**11.29**	**71** **415.7**
ECAM-PMP-50	**225.8**	**378.3**	**305**	**219.2-378.3**	**76.7**	**10.01**	**70.5**
ECAM-PMP-75	**231.8**	**355.6**	**320**	**225.3-355.6**	**70.37**	**11.67**	**69.8** **172.8** **388.7**
PMP	**227**	**371.5**	**335**	**228.3-371.5**	**78.70**	**10.00**	**226.8** **390.8**

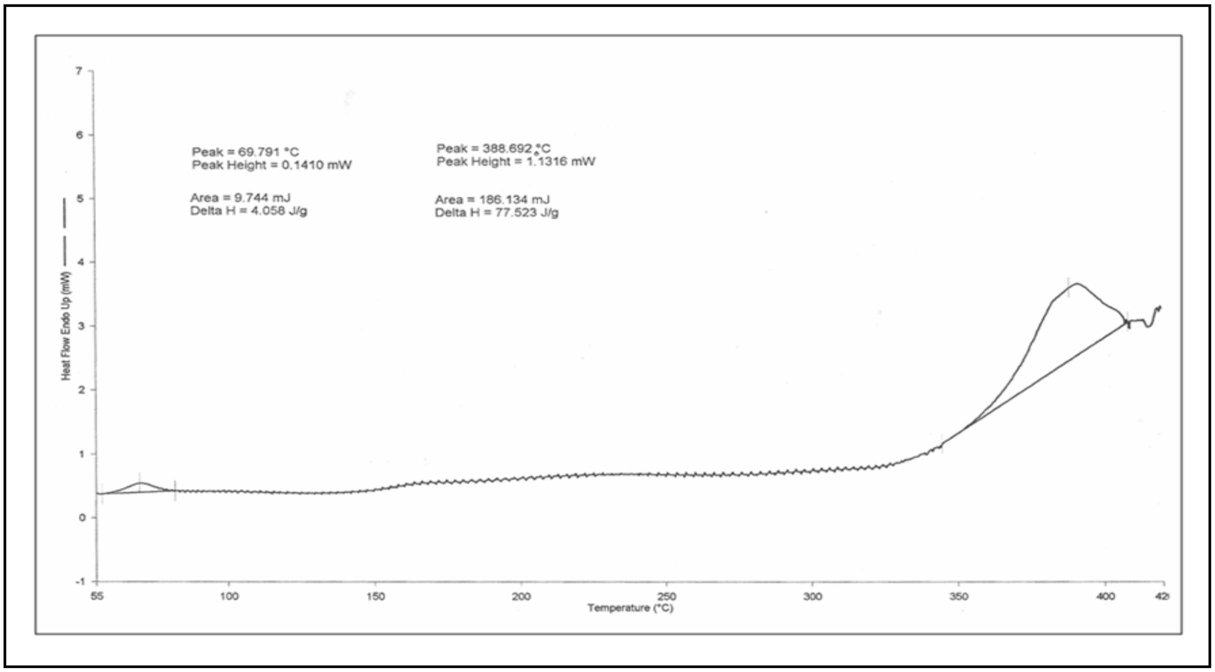

Fig. 3.18 DSC thermogram of ECAM at the heating rate of 10^{o}C/min in an N_2 atmosphere

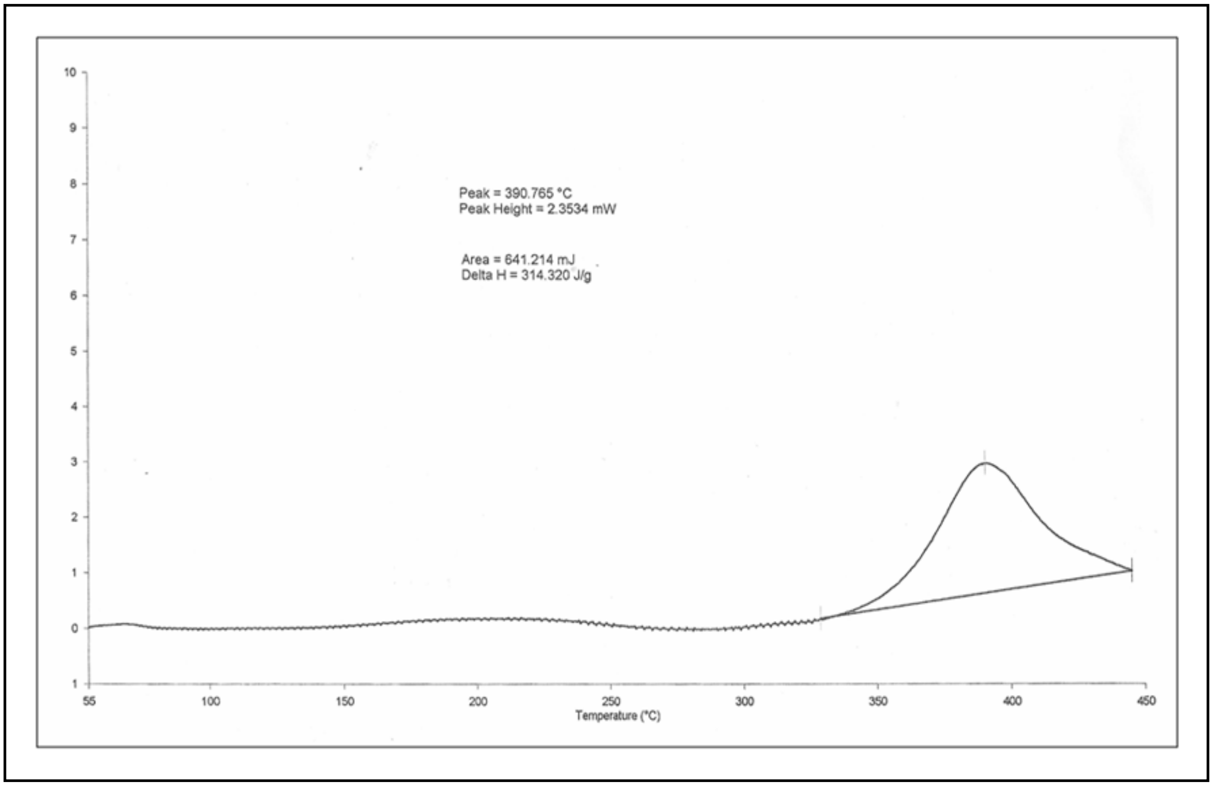

Fig. 3.19 DSC thermogram of ECAM-PMP25 at the heating rate of 10^{o}C/min in an N_2 atmosphere

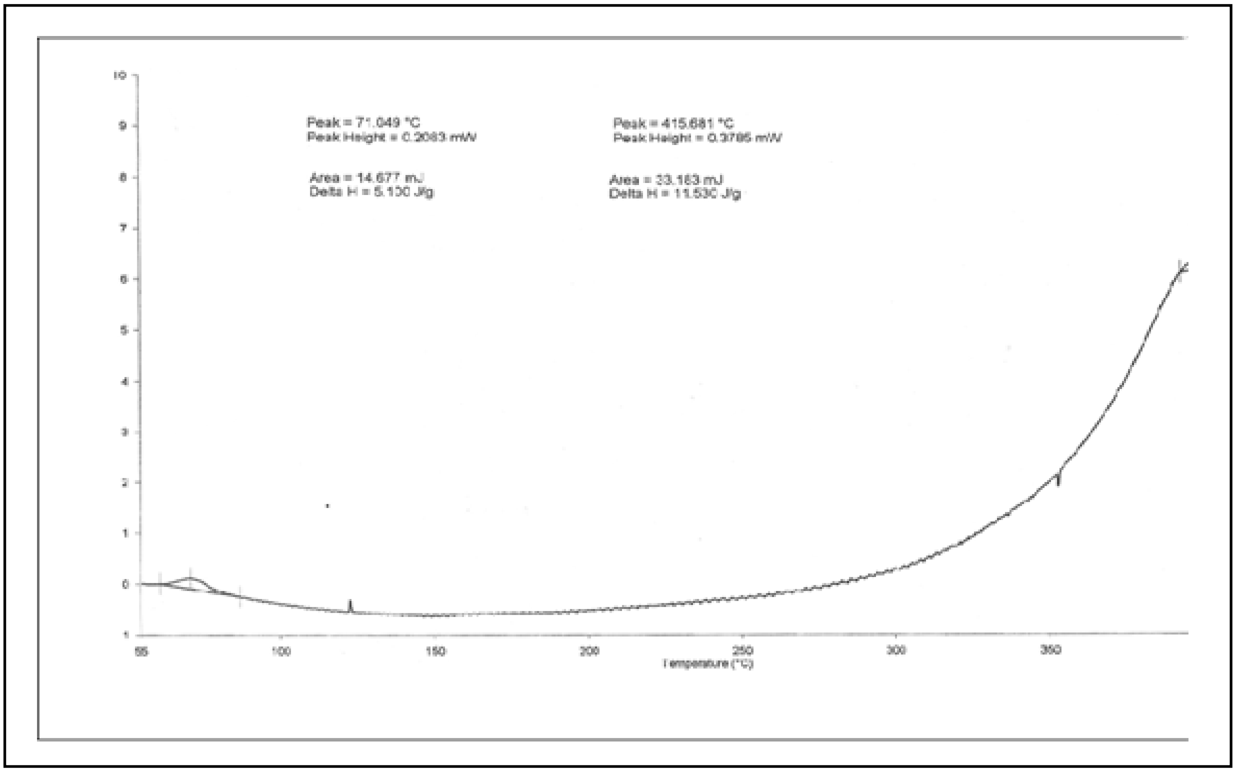

Fig. 3.20 DSC thermogram of ECAM-PMP50 at the heating rate of 10^{o}C/min in an N_2 atmosphere

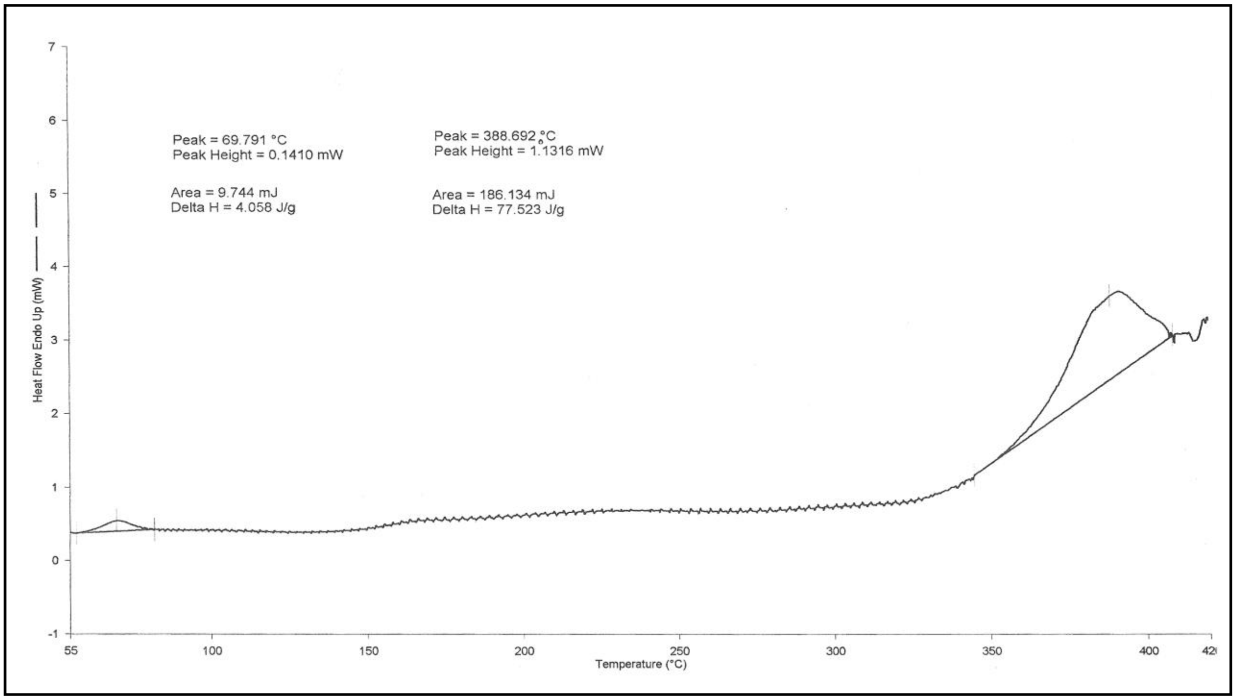

Fig. 3.21 DSC thermogram of ECAM-PMP75 at the heating rate of 10^{o}C/min in an N_2 atmosphere

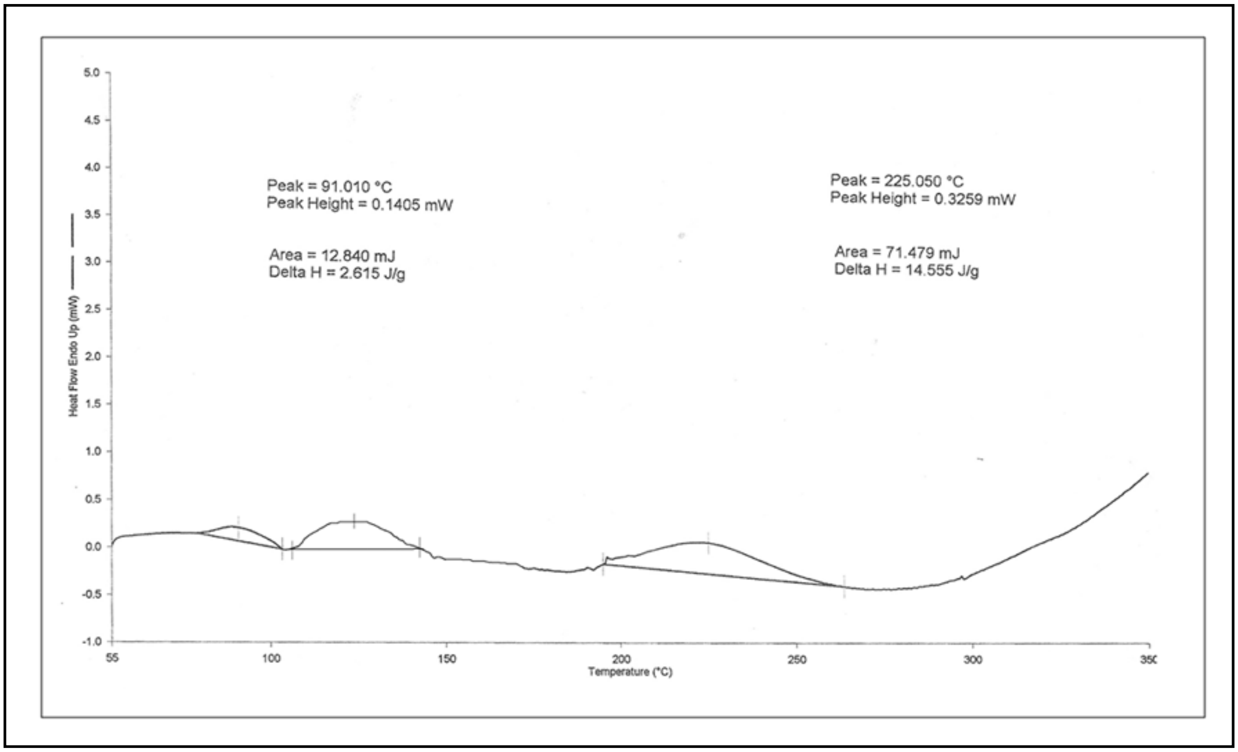

Fig. 3.22 DSC thermogram of PMP at the heating rate of 10^{o}C/min in an N_2 atmosphere

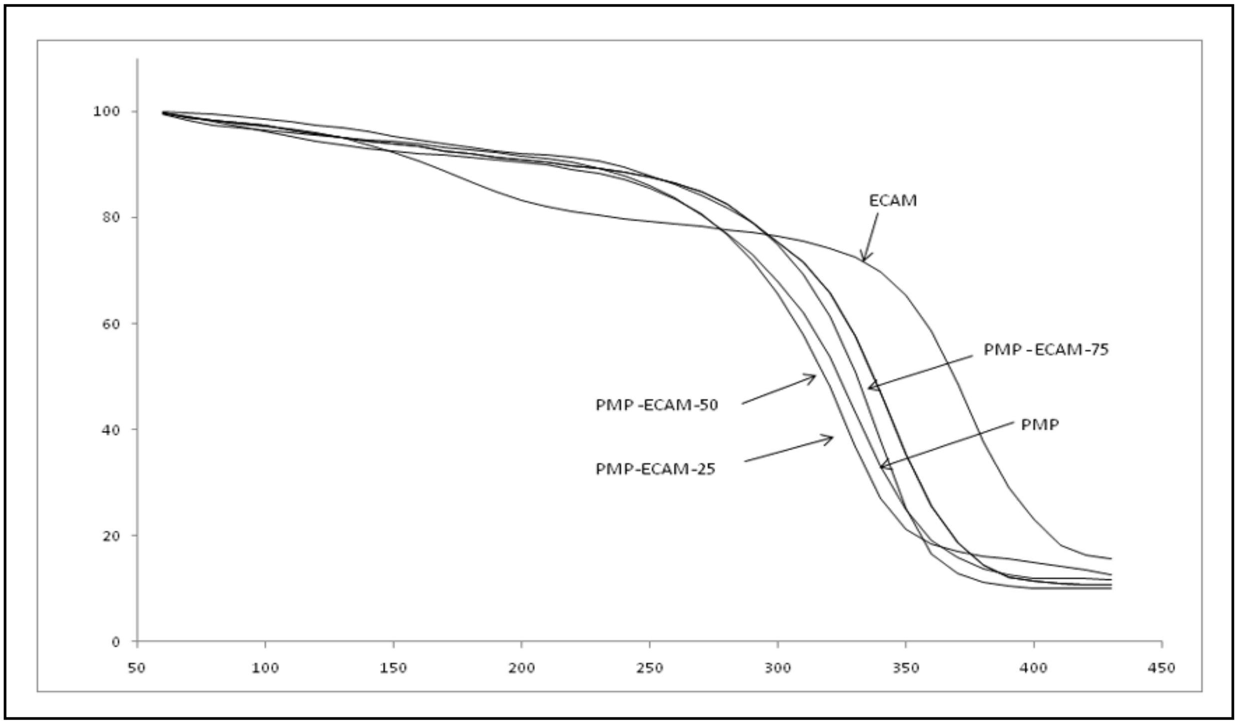

Fig. 3.23 TG thermograms of cured ECAM, PMP and their mixed matrix materials at the heating rate of 10^{o}C/min in an N_2 atmosphere

Table 3.11 The calculation scheme for ECAM by Anderson-Freeman method

10^3/T	% Wt. loss	dw\dt	W	lnW	lndw/dt	ΔlnW	Δlndw/dt
ECAM							
1.54	62.36	9.735	12.23	2.5038	2.2757	0.2788	0.0428
1.55	58.43	10.161	16.16	2.7826	2.3186	0.2170	0.0167
1.56	54.51	10.332	20.08	2.9996	2.3352	0.1747	-0.0088
1.57	50.68	10.241	23.91	3.1743	2.3264	0.1435	-0.0347
1.58	46.99	9.892	27.60	3.3178	2.2917	0.1192	-0.0618
1.59	43.49	9.299	31.10	3.4371	2.2299	0.0996	-0.0914

Table 3.12 The calculation scheme for ECAM-PMP25 by Anderson-Freeman method

$10^3/T$	% Wt. loss	dw\dt	W	lnW	lndw/dt	ΔlnW	Δlndw/dt
				ECAM-PMP25			
1.62	63.00	9.30	16.38	2.7958	2.2301	0.2081	0.0552
1.63	59.21	9.83	20.17	3.0040	2.2853	0.1716	0.0392
1.64	55.43	10.22	23.94	3.1756	2.3245	0.1443	0.0265
1.65	51.72	10.50	27.66	3.3199	2.3510	0.1230	0.0146
1.66	48.10	10.65	31.28	3.4429	2.3656	0.1057	0.0028
1.67	44.61	10.68	34.76	3.5486	2.3684	0.0913	-0.0075
1.68	41.29	10.60	38.09	3.6398	2.3609	0.0791	-0.0189
1.69	38.15	10.40	41.22	3.7189	2.3420	0.0685	-0.0301

Table 3.13 The calculation scheme for ECAM-PMP50 by Anderson-Freeman method

103/T	% wt. loss	dw/dt	W	lnW	ln dw/dt	ΔlnW	Δlndw/dt
ECAM-PMP50							
1.66	59.95	5.37	16.76	2.8188	1.6802	0.1692	0.2638
1.67	56.86	6.99	19.85	2.9880	1.9440	0.1434	0.1872
1.68	53.80	8.42	22.91	3.1314	2.1312	0.1235	0.1373
1.69	50.79	9.66	25.92	3.2549	2.2685	0.1075	0.1012
1.7	47.85	10.69	28.86	3.3624	2.3696	0.0943	0.0730
1.71	45.00	11.50	31.71	3.4566	2.4426	0.0832	0.0496
1.72	42.25	12.09	34.46	3.5398	2.4922	0.0736	0.0294
1.73	39.62	12.45	37.09	3.6134	2.5216	0.0653	0.0112
1.74	37.11	12.59	39.60	3.6788	2.5328	0.0581	-0.0059
1.75	34.75	12.51	41.96	3.7368	2.5269	0.0516	-0.0223
1.76	32.52	12.24	44.19	3.7884	2.5046	0.0458	-0.0386
1.77	30.45	11.78	46.26	3.8342	2.4660	0.0406	-0.0550
1.78	28.53	11.15	48.18	3.8749	2.4110	0.0359	-0.0720
1.79	26.77	10.37	49.94	3.9108	2.3390	0.0317	-0.0898
1.66	59.95	5.37	16.76	2.8188	1.6802	0.1692	0.2638

Table 3.14 The calculation scheme for ECAM-PMP75 by Anderson-Freeman method

103/T	% wt. loss	dw/dt	W	lnW	ln dw/dt	ΔlnW	Δlndw/dt
ECAM-PMP75							
1.68	58.84	5.37	11.52	2.4444	1.6802	0.2279	0.2638
1.69	55.90	6.99	14.47	2.6723	1.9440	0.1848	0.1872
1.7	52.96	8.42	17.41	2.8571	2.1312	0.1545	0.1373
1.71	50.05	9.66	20.32	3.0117	2.2685	0.1318	0.1012
1.72	47.18	10.69	23.18	3.1434	2.3696	0.1140	0.0730
1.73	44.38	11.50	25.98	3.2575	2.4426	0.0997	0.0496
1.74	41.66	12.09	28.71	3.3571	2.4922	0.0877	0.0294
1.75	39.03	12.45	31.34	3.4449	2.5216	0.0777	0.0112
1.76	36.50	12.59	33.87	3.5225	2.5328	0.0690	-0.0059
1.77	34.08	12.51	36.29	3.5915	2.5269	0.0614	-0.0223
1.78	31.78	12.24	38.59	3.6529	2.5046	0.0547	-0.0386
1.79	29.61	11.78	40.75	3.7076	2.4660	0.0487	-0.0550

Table 3.15 The calculation scheme for PMP by Anderson-Freeman method

103/T	% wt. loss	dw/dt	W	lnW	ln dw/dt	ΔlnW	Δlndw/dt
PMP							
1.65	60.10	12.49	18.610	2.92370	2.5246	0.1977	-0.0011
1.66	56.03	12.47	22.677	3.12136	2.5235	0.1647	-0.0208
1.67	51.97	12.21	26.737	3.28605	2.5027	0.1394	-0.0395
1.68	47.97	11.74	30.738	3.42548	2.4632	0.1192	-0.0577
1.69	44.08	11.08	34.629	3.54470	2.4055	0.1025	-0.0756
1.7	40.34	10.28	38.366	3.64716	2.3299	0.0882	-0.0937
1.71	36.81	9.36	41.903	3.73536	2.2362	0.0758	-0.1120

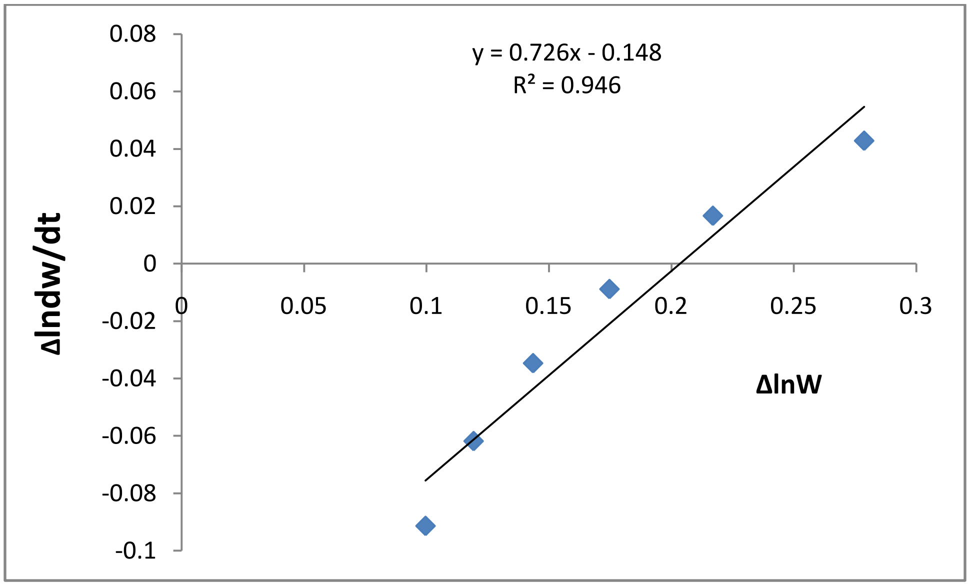

Fig. 3.24 The Anderson-Freeman plots for ECAM

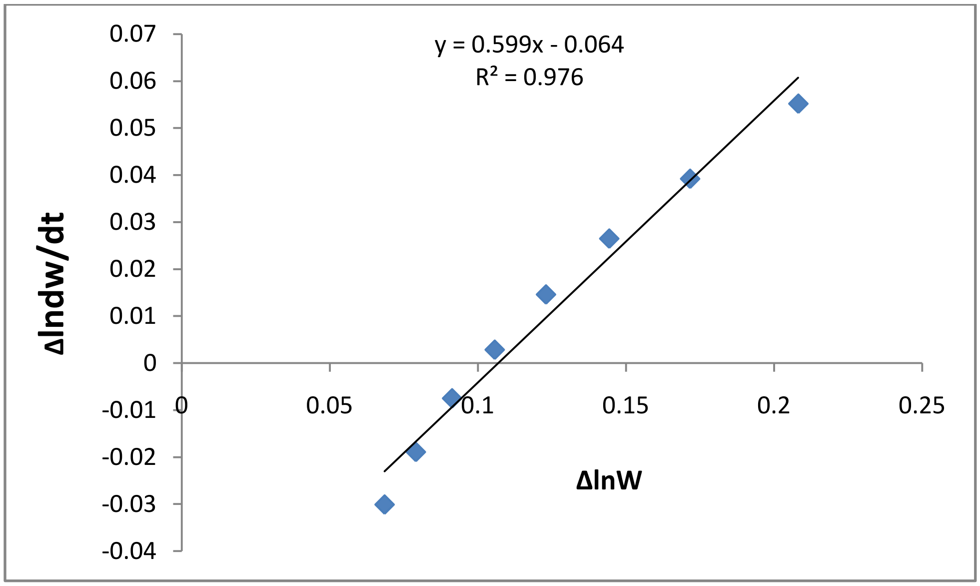

Fig. 3.25 The Anderson-Freeman plots for ECAM-PMP25

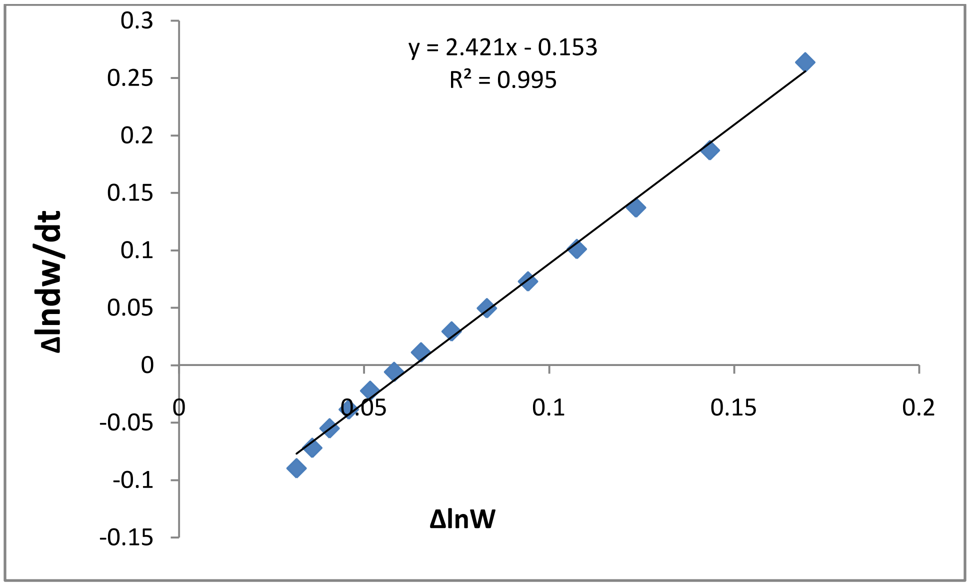

Fig. 3.26 The Anderson-Freeman plots for ECAM-PMP50

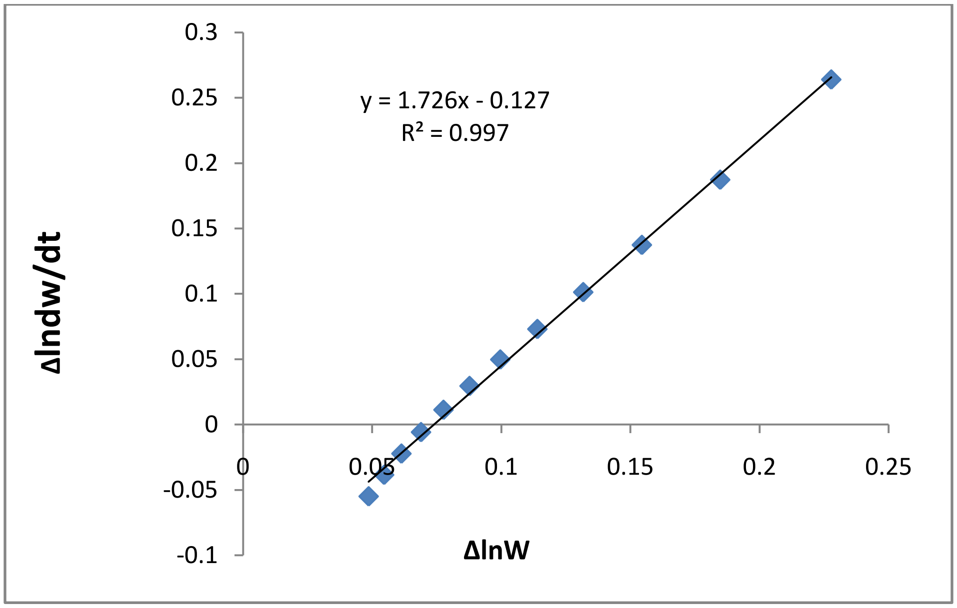

Fig. 3.27 The Anderson-Freeman plots for ECAM-PMP75

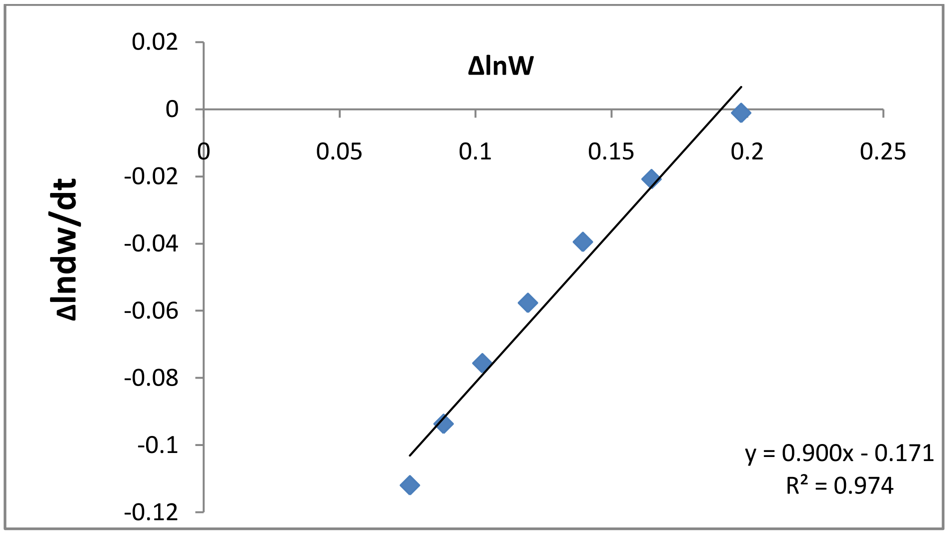

Fig. 3.28 The Anderson-Freeman plots for BCFMPT

Table 3.16 Kinetic parameters of resins

Sample	n	E, kJ	A, s^{-1}	ΔS^*, JK^{-1}	Regression coefficient, R^2
ECAM	**0.7**	**123**	**5.87×10^7**	**-102.6**	**0.946**
ECAM- PMP - 25	**0.6**	**53**	**1.07×10^2**	**-211.98**	**0.976**
ECAM- PMP -50	**2.4**	**127**	**2.37×10^9**	**-70.9**	**0.995**
ECAM- PMP-75	**1.7**	**106**	**1.2×10^7**	**-115.1**	**0.997**
PMP	**0.9**	**142**	**1.25×10^{10}**	**-57.5**	**0.974**

CHAPTER – 4

Fabrication and physico-chemical characterization of the composites

This chapter of the thesis describes the composites based on jute fibers.

This chapter is further subdivided into three sections:

Section-I: Fabrication of composites

Section-II: Mechanical and electrical properties of composites

Section-III: Water uptake study of composites

Section-I: Fabrication of composites

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

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

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

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

Woven jute fibers (Brown jute, Corchorus Capsularis) used in present study was collected from the local market. ECAM resin was synthesized and purified according to section 6 of Chapter 2.

Fabrication of Mixed matrix materials of epoxy-acrylate-maleate and Unsaturated polyester resin composites

ECAM and unsaturated polyester resin (PMP) used for the preparation of hybrid composite were prepared as under.

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1. Carignani and Giancarlo. GRP expanded plastic composites. Kunstat. Ger. Plast., 68, 8-17, 1978.
2. P. K. Pal. Jute reinforced plastics: A low cost composite material. Plast. and Rubber Proc. and Appl., 4, 215-222, 1984.
3. Mc Cormack and E. William. Fabrication and joining of polymer-matrix composites: Flight-vehicle materials, structures, and dynamics–assessment and future directions. J. Appl. Polym. Sci., 1, 348-356, 1994.
4. M. A. Hayat and S. M. A. Suliman. Mechanical and structural properties of glass reinforced phenolic laminates. Polym. Test., 17, 79-85, 1998.
5. J. Sinke. Manufacturing of GLARE parts and structures. App. Compos. Mater., 10, 293-305, 2003.
6. S. R. Dyer, L. V. J. Lassila, M. Jokinen and P. K. Vallittu. Effect of cross-sectional design on the modulus of elasticity and toughness of fiber-reinforced composite materials. J. Prosthetic Dentistry, 94, 219-226, 2005.
7. P. Thomas, K. Dwarkanath, P. Sampathkumaran, S. Seetharamu and Kishore. Influence of moisture absorption on electrical characteristics of glass-epoxy polymer composite system. Proceedings of the International Symposium on Electrical Insulating Materials, 3, 605, 2005.

Mixed matrix materials (ECAM and PMP of varying compositions) used for the composite preparation were 50 wt. % of jute fabric (15 cm x 15 cm and 5 cm x 5 cm). Required matrix materials (Table-4.1) were dissolved in 100/10 ml acetone and then were added 5 ml cobalt naphthenate and 5 ml MEKP as an initiator. The solution was applied to jute sheets with a smooth brush. Ten such prepregs were dried in sunlight for 15 min, staked one over other and pressed between two preheated stainless steel plates under 15.4 MPa pressure at 150^{o}C for 2 h and at room temperature for 12 h. Silicone spray was used as a mold releasing agent. The edges of 5 cm x 5 cm composites were sealed using same matrix materials.

Table-4.1 Experimental details required matrix materials of composite preparation

Composite	For 15cm X 15cm composite			For 5cm X 5cm composite		
	ECAM, g	PMP, g	Jute g	ECAM, g	PMP, g	Jute, g
J- ECAM	50.5	0	101	17.5	0	35
J- ECAM- PMP-25	38.6	12.9	103	12.4	4.1	33
J- ECAM-PMP--50	27	27	108	9	9	36
J-ECAM-PMP--75	13.4	40.1	107	4	12	32
J- PMP	0	52.5	105	0	16.5	33

Section-II: Mechanical and electrical properties of composites

Mechanical properties

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

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

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

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

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

- **Short-term mechanical properties**

They are measured at a constant rate of stress or strain in different modes

- Tensile strength

- Flexural strength
- Compression strength
- Shear strength

❖ **Long-term mechanical properties**

They are the measurements of deformation or stress decay with respect to time in static conditions

- Visco-elasticity
- Creep
- Stress relaxation

❖ **Surface properties**

The mechanical properties of the surface include

- Hardness
- Scratch resistance
- Friction
- Abrasion resistance

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

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

$$\sigma = \frac{W}{A} \qquad \ldots \mathbf{4.1}$$

Where W= the load value at break and A=original cross sectional area of the sample

Flexural strength is the resistance of material under the bending mode. Flexural properties are useful for quality control and classification of materials with respect to bending strength and stiffness. They depend upon various factors namely

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

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

$$\text{Flexural strength} = \frac{1.5FL}{wt^2} \qquad \textbf{… 4.2}$$

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

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

The mechanical properties may best be divided into three sections:

(1) Reversible rigidity/flexibility or modulus, which measures the stiffness of the polymer

(2) Mechanical failure by yielding (Permanent deformation) or breaking at low or high rates of test or under a multiple cyclic stress

(3) Complex mechanical properties involving a combination of these simpler processes

Joffe et al. [8] have studied the composites based on 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

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8. 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.

some cases. They have concluded that such a good mechanical properties in combination with lightweight makes use of NFC very attractive for automotive industries.

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

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

Gassan [11] have fabricated the composite of jute-polypropylene and apply fiber-surface treatment and studied the effect of filler concentration and surface treatment on the ultimate strength, elongation, modulus and dynamic mechanical properties.

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9. 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.
10. 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.
11. J. Gassan and A. K Bledzki. The influence of fiber-surface treatment on the mechanical properties of jute-polypropylene composites. Composites Part-A. 28, 1001-1005, 1997.

Tay et al. [12] have fabricated the empty fruit bunch–polyurethane (EFB–PU) composites reacting EFB and polyethylene glycol (PEG) with diphenyl methane diisocyanate (MDI) and determined their tensile properties. The results revealed that the tensile properties were influenced by the percentage of -OH groups of EFB, coupled with the reinforcing effect of EFB filler. In addition to that, the formation of PU matrix from PEG and isocyanate proved to be crucial in producing good stress transfer from the matrix to the filler. SEM study showed that surface area of the filler also contributed towards the strength of the composites.

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

Carvalho et al. [14] have evaluated the tensile and impact behavior of jute fabrics-polyester composites as a function of the fabric style (knitted or weaved clothes), fiber weight fraction, and direction of the applied load. The tensile properties of plain-weave-fabric-reinforced composites (PWF) were higher than ethane diol to prepare a series of sheets. Their structure and properties were

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12. 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.
13. 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.
14. L. H. de Carvalho, J. M. F. Cavalcante and J. R. Md.’ 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.

those of plain weft knit cloth composites (WKT) and were dependent on fiber content and test direction. The properties of the WKT, however, were independent of these variables. The obtained results indicate that the orthogonal fiber alignment of weaved cloths favors anisotropy, while the interconnected loops in knit fabrics favors isotropy. The results also indicated weak fiber-matrix interactions in both fabrics and a better fabric impregnation for the plain weave fabric, if compared with that of the knit fabric. The impact strength of both composites was higher than that of the matrix and was shown to increase with fiber content. WKT-reinforced composites showed better impact absorption capacity than PWF composites.

Sastra et al. [15] have determined the tensile strength of arenga pinnata fiber as a natural fiber and epoxy resin as a matrix. For this the arenga pinnata fibers were mixed with epoxy resin at the various fiber weight percentages of 10%, 15%, and 20% arenga pinnata fiber and with different fiber orientations such as long random, chopped random, and woven roving. Results from the tensile tests of arenga pinnata fiber reinforced epoxy composite were that the 10 wt% woven roving arenga pinnata fiber showed the highest value for maximum tensile properties. The tensile strength and Young's modulus values for 10 wt. % of woven roving arenga pinnata fiber composite are 51.7 MPa and 1255.8 MPa, respectively. The above results indicated that the woven roving arenga pinnata fiber has a better bonding between its fiber and matrix compared to long random arenga pinnata fiber and chopped random arenga pinnata fiber. Scanning electron microscopy (SEM) tests were also carried out after tensile tests to observe the interface of fiber and matrix adhesion.

Wang et al. [16] have fabricated waterborne polyurethane (WPU) composites and have studied the effect of crosslinking agent on the different properties. Waterborne polyurethane (WPU) and casein (1:1 by weight) were blended at 90°C for 30 min, and then were crosslinked by adding 1-10 wt % ethane diol to prepare a series of sheets. Their structure and properties were

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15. 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.

characterized by using infrared spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), dynamic mechanical analysis, and tensile testing. The results indicated that crosslinked blend sheets exhibited a certain degree of miscibility, and exhibited much higher tensile strength and water resistivity than did the WPU, casein, and the uncrosslinked blend from WPU and casein. When the ethane diol content was 2 wt %, the tensile strength and elongation at break of crosslinked sheets achieved 19.5 MPa and 148% in the dry state, and 5.0 MPa and 175% in the wet state, respectively. A 2 wt % content of ethane diol played an important role in the enhancement of mechanical properties, thermal stability, and water resistivity of the blends of WPU and casein.

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

Fengchang and Weibo [18] have studied the dynamic mechanical and vibration damping properties of polyether urethane and epoxy composites. The

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16. N. Wang, Y. Lu, Y. Du and L. Zhang. Properties of crosslinked casein/waterborne polyurethane composites. J. Appl. Polym. Sci. 91, 332-338, 2004.
17. 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.

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

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

Musa et al. [20] have produced rice husk (RH)-unsaturated polyester (USP) composites and investigated their tensile, flexural, impact and dimensional properties. From the results, it was observed that the tensile, flexural and impact properties decreased as the percentage of filler was increased. The composites with smaller filler size displayed higher tensile, flexural and impact properties

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18. 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.
19. 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.
20. 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.

than those with larger filler size. This might be attributed to the higher surface area of the RH, which resulted in more interaction between the -OH groups of RH of the polyester matrix. The water absorption and thickness swelling of the composites showed an increasing trend as the immersion time was increased. However, samples with smaller filler size showed lower water absorption and thickness swelling than those with larger filler size.

Hazlan et al. [21] have produced rice husk (RH)–glass fiber (GF) hybrid polyester composites 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.

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

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21. 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.
22. 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.

electron microscope (SEM) analysis. The increased in water absorption and thickness swelling as the percentage of RH was increased was attributed to the ability of RH -OH groups to absorb water, causing the cell wall to swell.

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

Nakamura R, [24] have fabricated the composite of fully green composite laminates and natural fibers at high temperatures and studied the effect of filler concentration and surface treatment on the Tensile properties, r-values, deep drawing, modulus and dynamic mechanical properties.

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23. T. Fujii, Y. Yamamoto and K. Okubo. Development of bamboo-based polymer composites and their mechanical properties. Composites: Part-A: Appl. Sci. and Manuf., 35, 377-383, 2004.
24. R. Nakamura, K. Goda, J. Noda ang J. Ohgi. High temperature tensile properties and deep drawing of fully green composites. eXPRESS Polymer Letters, 3, 19-24, 2009.

MEASUREMENTS

Tensile strength and flexural strength (IS 6748:1994) measurements were made on a Shanta Engineering Tensile Testing Machine, Model No. SET/T/50 at a speed of 50 mm/min. Tensile strength and flexural strength of J-ECAM, J-PMP and their hybrid composites are shown in Table-4.2 from which it is clear that tensile and flexural strengths are intermediate of the parent matrix-jute composites. ECAM composite is 1.8 times stiffer than that of PMP composite. Similarly ECAM composite is 2.2 times stronger than PMP composite. Comparatively good tensile and flexural properties of ECAM composite are due to better matrix–fiber interfacial bonding. Thus, moderate tensile and flexural properties of the composites signify their importance for low load bearing applications especially for housing units. The mechanical properties of the composites depend on number of factors namely fiber content, fiber orientation (Figure 1), nature of fibers, fiber modification, interfacial bonding, additives like fillers, compatibilizer and impact modifier, humidity and mode of testing, etc[25].

Mechanical performance and durability of the composites are governed by reinforcement, matrix material and interfacial bond strength. Strength, stiffness and stability of fibers and matrix are very important for long term service of composites. Natural fibers are hygroscopic and possess low wettability with hydrophobic matrix material and therefore it is necessary to modify fibers and improve resin compatibility. Good interfacial bond strength is necessary for effective stress transfer from matrix to fiber in the composites. There are two types of interfacial interactions namely covalent and H-bonding. Hydroxyl groups of jute serve as reaction sites with various functional groups present in the mixed material (hydroxyl, ester and carboxyl groups). Jute fibers serve as filler as well as a reactive component. Comparatively good tensile and flexural strengths of the composites indicated their usefulness as low load bearing housing units.

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25. D. Ray, B. K. Sarkar, S. Das and A. K. Rana. Dynamic mechanical and thermal analysis of vinylester-resin-matrix composites reinforced with untreated and alkali-treated jute fibres. Compos. Sci. Technol., 62, 911-917, 2002.

Figure-4.1: Arrangement of Jute composite

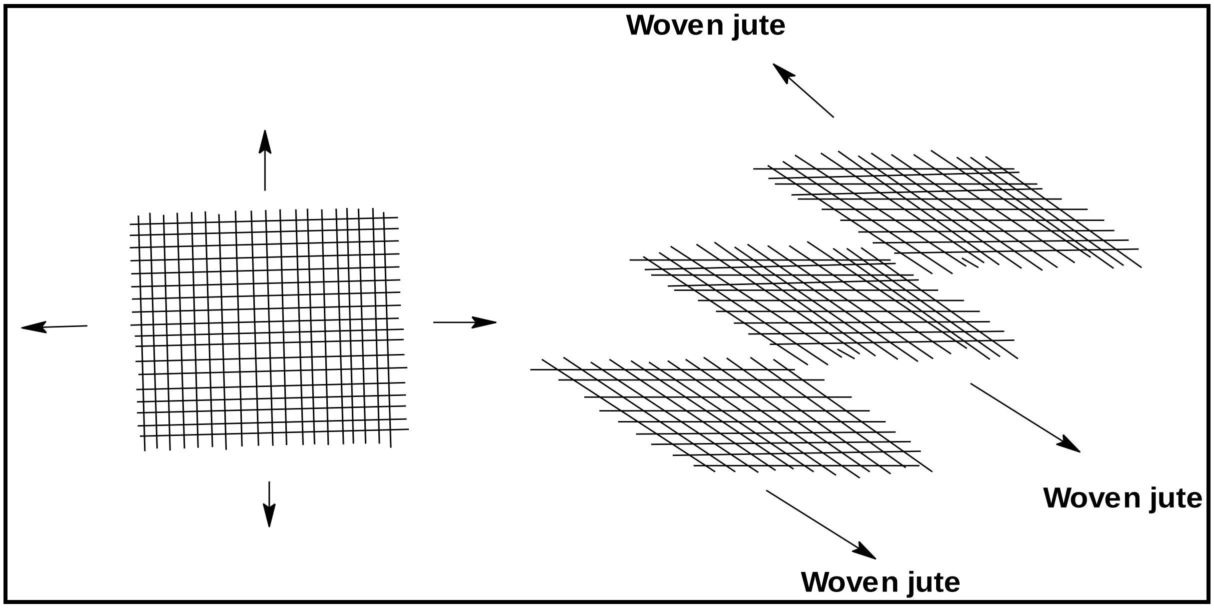

Table-4.2 Mechanical properties of J-ECAM, J-PMP and their hybrid composites

Composite	Tensile strength, MPa	Flexural strength, MPa
J-ECAM	92	89
J -ECAM-PMP-25	61	64
J -ECAM-PMP-50	57	42
J -ECAM-PMP-75	49	52
J-PMP	41	50

Electrical properties

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

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

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

Typical electrical properties of some selected plastic materials are reported in Table-4.3. 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 –OH m'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} [26]. In some cases voltage lower than the break down voltage gives rise to a surface discharge that dose not penetrate deep into the bulk of a material. This is a surface or creeping, breakdown occurring at a surface break down voltage. The basic characteristic of an electrical insulating material is its breakdown or dielectric strength E_{br} (also called electric strength), which is a minimum strength of the uniform electric field that causes dielectric breakdown. The calculation of breakdown strength calls for measuring the breakdown voltage of the material under test. The breakdown voltage (U_{br}) is proportional to the electric field strength (E_{br}) only if the field is uniform. Such a field exists between two electrodes, which have the shape of the bodies of revolution; the surface of these electrodes may be described by Rogovsky equation [26].

$$E_{br} = \frac{U_{br}}{t} \qquad \text{… 4.3}$$

Where, t is the thickness of the material

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

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

Table-4.3 Electrical properties of some selected plastic materials

Polymer	Volume resistivity (Ω cm)	Dielectric strength (kV/mm)	Dielectric constant		Power factor	
			60 Hz	10^6 Hz	60 Hz	10^6 Hz
PTFE	$>10^{20}$	18	2.1	2.1	$<3 \times 10^{-4}$	$<3 \times 10^{-4}$
PE	10^{20}	18	2.3	2.3	$<3 \times 10^{-4}$	$<3 \times 10^{-4}$
PS	10^{20}	24	2.55	2.55	$<3 \times 10^{-4}$	$<3 \times 10^{-4}$
PP	$>10^{19}$	32	2.15	2.15	8×10^{-4}	4×10^{-4}
PMMA	10^{16}	14	3.7	3.0	6×10^{-2}	2×10^{-2}
PVC	10^{17}	24	3.2	2.9	1.3×10^{-2}	1.6×10^{-2}
Nylon 66	10^{15}	14.5	4.0	3.4	1.4×10^{-2}	4×10^{-2}
PC	10^{18}	16	3.17	2.96	9×10^{-4}	1×10^{-2}
Phenolic	10^{13}	10	5.0-9.0	5.0	8×10^{-2}	4×10^{-2}
Urea Formaldehyde	10^{14}	12	4.0	4.5	4×10^{-2}	0.3

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 [27].

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

$$\text{Dielectric strength} = \frac{V}{t} \qquad \textbf{... 4.4}$$

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

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

$$\text{Volume resistivity} = \frac{R_v A}{t} \qquad \textbf{... 4.5}$$

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

Naik and Mishra [28] 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

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

resin for the formation of their composites in the different ratios of 60:40, 55:45, 50:50, 45:55, and 40:60 (wt/wt). These fibers were also treated with maleic anhydride and the effect of maleic anhydride was studied on surface resistivity and volume resistivity of wood polymer composites. The maximum surface and volume resistivities were found in maleic anhydride treated and untreated banana fiber composites, respectively. The treatment of maleic anhydride improved the surface resistivity of respective fiber composites. Maleic anhydride treated banana fiber composites showed maximum surface resistivity, while untreated agave fiber composites showed minimum surface resistivity.

Jain and Chand [29] have fabricated different directionally oriented sisal fiber reinforced epoxy resin composites and studied the effect of temperature and frequency variation on dielectric constant (ε'), dielectric dissipation factor (tan δ) and on A.C. conductivity ($\sigma_{\text{a.c.}}$) 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 δ and A.C. conductivity increased with increasing temperature. The dependence of dielectric constant, tan δ and A.C. conductivity with frequency have also been studied and it was found that ε' and tan δ of the epoxy and 0 and 90^0C oriented sisal fiber epoxy composites decreased with increasing frequency and A.C. conductivity increased with increasing frequency. Near the transition temperature of theepoxy the observed properties showed anomalous behavior. Peaks for dielectric constant, tan δ and A.C. conductivity were observed. Clear relaxation peaks for tan δ around 169 °C were observed in epoxy resin, shifting to the lower temperature side with increasing frequency. The relaxation time of epoxy and 0 and 90^0

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28. 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.
29. 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.

oriented sisal fiber epoxy composites has been calculated and it was found that $\tau_{(s)}$ was 4.09×10^{-5}, 5.52×10^{-5} and 5.47×10^{-5}, respectively at 100^{0}C.

Paul et al. [30] have investigated the electrical properties of short-sisal-fiber-reinforced low-density polyethylene (LDPE) composites. Various surface treatments such as alkali, CTDIC, stearic acid, peroxide, permanganate and acetylation were carried out on the sisal fibers to improve interfacial bonding. The treated surfaces were characterized by infrared spectroscopy. The dielectric constant increased progressively with increase in fiber loading and decreased with increase in frequency for all composites. The dielectric constant values of the composites were found to have decreased as a result of chemical treatments. This is due to the fact that the hydrophilic nature of natural fiber decreased with treatment. Volume resistivity values of treated-sisal fiber/LDPE composites were found to be greater than those of raw-sisal-fiber/LDPE composites. Volume resistivity values of permanganate treated sisal fiber reinforced LDPE composites depended on the concentration of $KMnO_4$ solution used for treatment. The value of volume resistivity increased, reached a maximum and then decreased with increase in concentration of potassium permanganate solution. The dielectric loss factors of treated-sisal-fiber-reinforced/LDPE composites were found to be lower than that of untreated-sisal fiber/LDPE composites. The relaxation peak was found to be in the same region for all composites.

MEASUREMENTS

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

Volume resistivity and dielectric strength of ECAM, PMP and their matrix jute composites are summarized in Table-4.4 from which it is clear that all the

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30. 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 possess moderate volume resistivity and low dielectric strength in comparison to PFR and UFR materials (Table-4.3). 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. In conclusion composites possess good mechanical and moderate electrical properties signifying their importance for low load bearing applications in housing units and electrical electronic appliances.

Table- 4.4 Volume resistivity and dielectric strength data of ECAM, PMP and their mixed matrix material jute composites

Composite	**Volume resistivity, Ω cm**	**Dielectric Strength, kV/mm**
J-ECAM	$3.3X10^{9}$	0.8
J-ECAM-PMP-25	$9.8X10^{10}$	1.2
J-ECAM-PMP-50	$8.9X10^{9}$	1.1
J-ECAM-PMP-75	$5.4X10^{10}$	0.9
J-PMP	$2.7X10^{11}$	1.0

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 [31-34]. 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 [35].

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

Absorbed water causes hydrolytic degradation of both matrix and interface during service [36].

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31. B. N. Das, 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.
32. 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.
33. 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.
34. S. Pavlidou and C. D. Papaspyrides. The effect of hygrothermal history on water sorption and interlaminar shear strength of glass/polyester composites with different interfacial strength. Composite Part-A, 34, 1117-1124, 2003.
35. S. L.Gibson, V. Baranauskas, J. S. Riffle and U. Sorathia. Cresol-novalac epoxy networks: properties and processability. Polymer, 43, 7389-7398, 2002.

Water absorption in polymeric composites is shown to be Fickian as well as non-Fickian in character [37, 38]. The visco-elastic nature of polymers and cracks are responsible for non-Fickian diffusion. Water absorption in composites depend upon fraction of fibers, void volume, additives, humidity and temperature.

Diffusivity

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

$$G = 1 - \frac{8}{\pi^2}\sum_{J=0}^{\infty}\frac{1}{(2j+1)^2}\exp\left[-\frac{(2j+1)^2\pi^2 D_x t}{h^2}\right] \qquad \textbf{… 4.6}$$

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

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

$$M = \frac{W_m - W_d}{W_d} X100 \qquad \textbf{… 4.7}$$

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36. 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.
37. G. Pritchard and S. S. Speake. The use of water absorption kinetic data to predict laminate property changes. Composites, 18, 227-232, 1987.
38. G. Camino, M. P. Luda, A. Y. Polishchuk, M. Revellino, R. Bla-NCOn 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.

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.4.8:

$$M = \frac{4M_m}{h}\sqrt{\frac{t}{\pi}}\sqrt{D_x} \qquad \text{...4.8}$$

Where M_m = equilibrium water content.

Diffusivity in a given environment can be determined from the initial slope of the plot of %M against $\sqrt{t}$ according to Eqn. 4.9:

$$D_x = \pi\left(\frac{h}{4M_m}\right)^2 \ slope^{\ 2} \qquad \text{...4.9}$$

In present case assuming one dimensional Fickian diffusion, water absorption by J-ECAM, J-PMP and their mix matrix material in pure water, 10% HCl and 10% NaCl is carried out at 30°C. Moisture absorption study of J-ECAM, J-PMP and their mix matrix material composites 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 percentage weight gained by the composites in water, 10 % aq. HCl and 10 % aq. NaCl solutions with the passage of time ($t^{1/2}$) is shown in Figs. 4.2-4.4. The % weight gained by each composite increased, reached maximum and then practically remained constant when equilibrium was established in each of the environment. The equilibrium time and equilibrium water content for composites in water, 10 % aq. NaCl, 10 % aq. HCl environments are recorded in Table-4.5. It is observed that the % water uptake increased linearly with the passage of time and remained practically constant till the equilibrium was established (96h) in each of the environment. Table-4.5 summarizes equilibrium water content of the composites in three different environments. It is clear from Table-4.5 that practically almost constant equilibrium water content is observed in all the three environments. In water and saline environment, water uptake is almost the same and somewhat less than in acidic environment. The presence of strong electrolytes in water affects the structure of water and hence diffusion in fiber through capillary action. Water absorption 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 blistering.

Diffusivity in different environments was determined according to Eqns. 4.8 and 4.9 and is reported in Table-4.5 from which it is observed that diffusion coefficient of J-ECAM and J-PMP and it is somewhat varied for hybrid composites and J-PMP in three different environments but for J-ECAM it is quite different. Thus, little electrolyte effect on diffusion behavior in hybrid composites and J-PMP is observed.

Absorption of water in composites causes swelling of fibers till the cell walls are saturated with water and beyond that water exists as free water in the void structure leading to composites delamination or void formation. Absorbed water causes weakening of interfacial adhesion and hydrolytic degradation of both matrix and fibers [39]. Cracking and blistering of fibers cause high water absorption, while degradation causes leaching of small molecules [40].

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39. S. Lin-Gibson, V. Baranauskas, J. S. Riffle and U. Sorathia. Cresol novolac-epoxy networks: Processability and properties. Polymer, 43, 7389-7398, 2002.

40. L. R. Bao and A. F. Yee. Effect of temperature on moisture absorption in a bismaleimide resin and its carbon fiber composites. Polymer, 43, 3987-3997, 2002.

Figure 4.2 The plots of % weight gain against $t^{1/2}$ for J-ECAM, J-PMP and their hybrid composites in water at 30°C

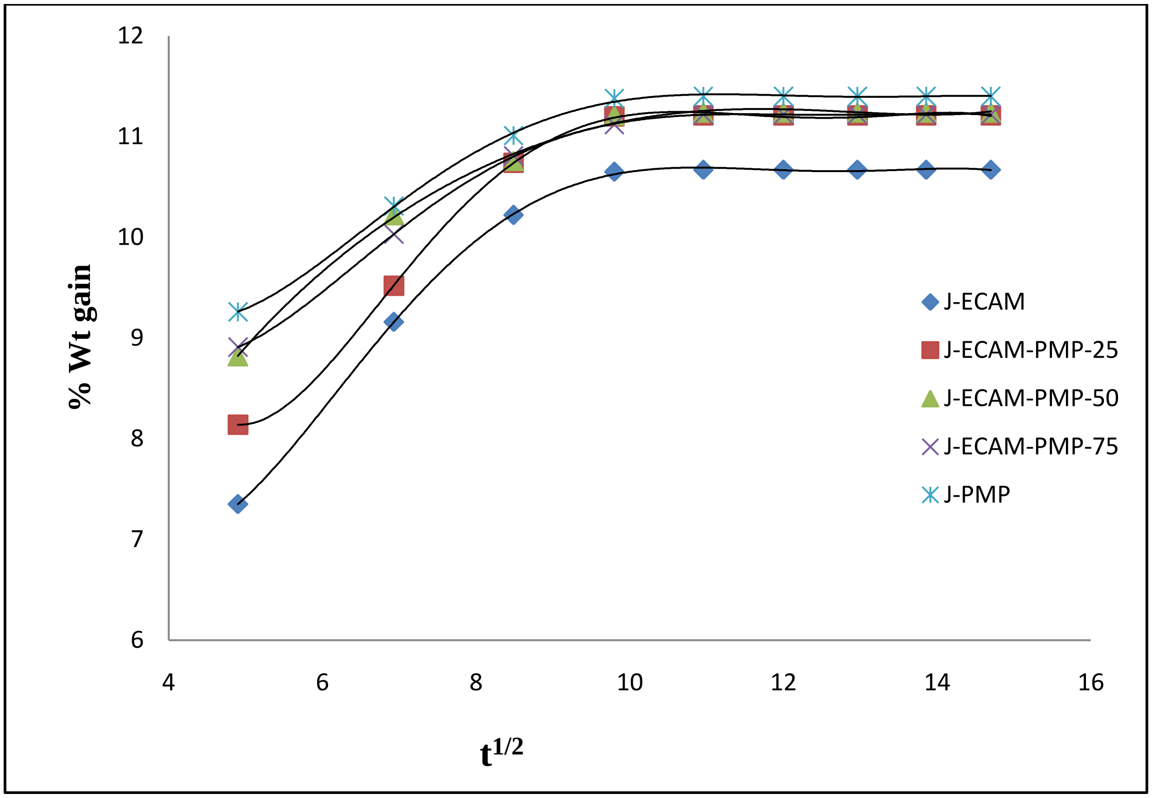

Figure 4.3 The plots of % weight gain against $t^{1/2}$ for J-ECAM, J-PMP and their hybrid composites in 10% HCl at 30°C

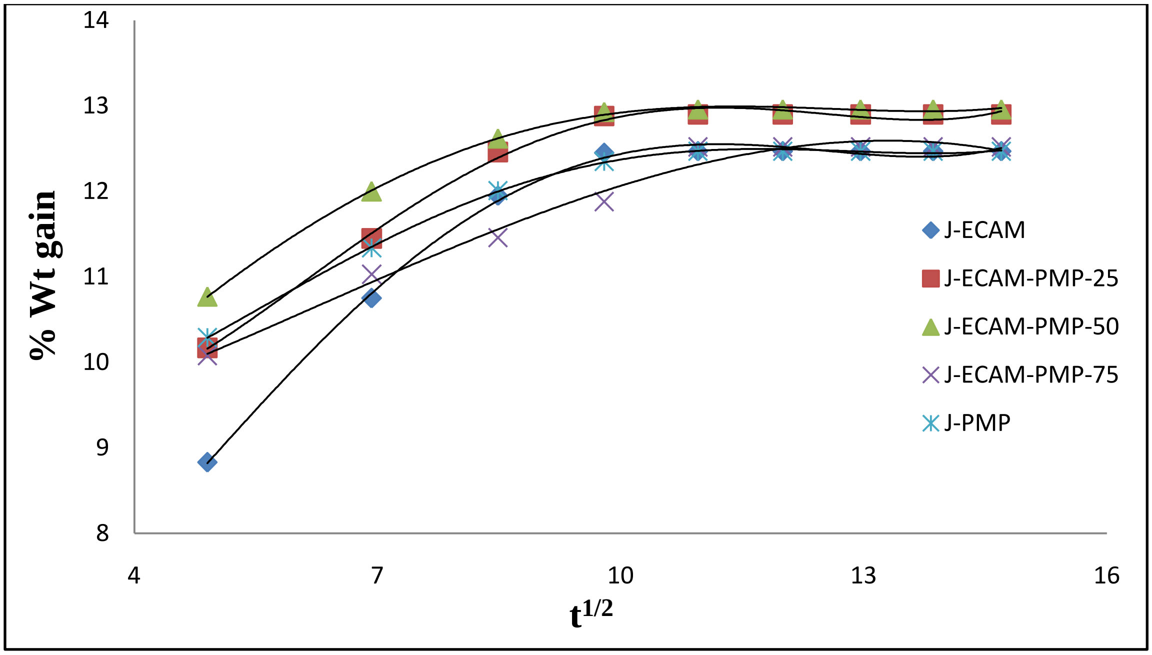

Figure 4.4 The plots of % weight gain against $t^{1/2}$ for J-ECAM, J-PMP and their hybrid composites in 10% NaCl at 30°C

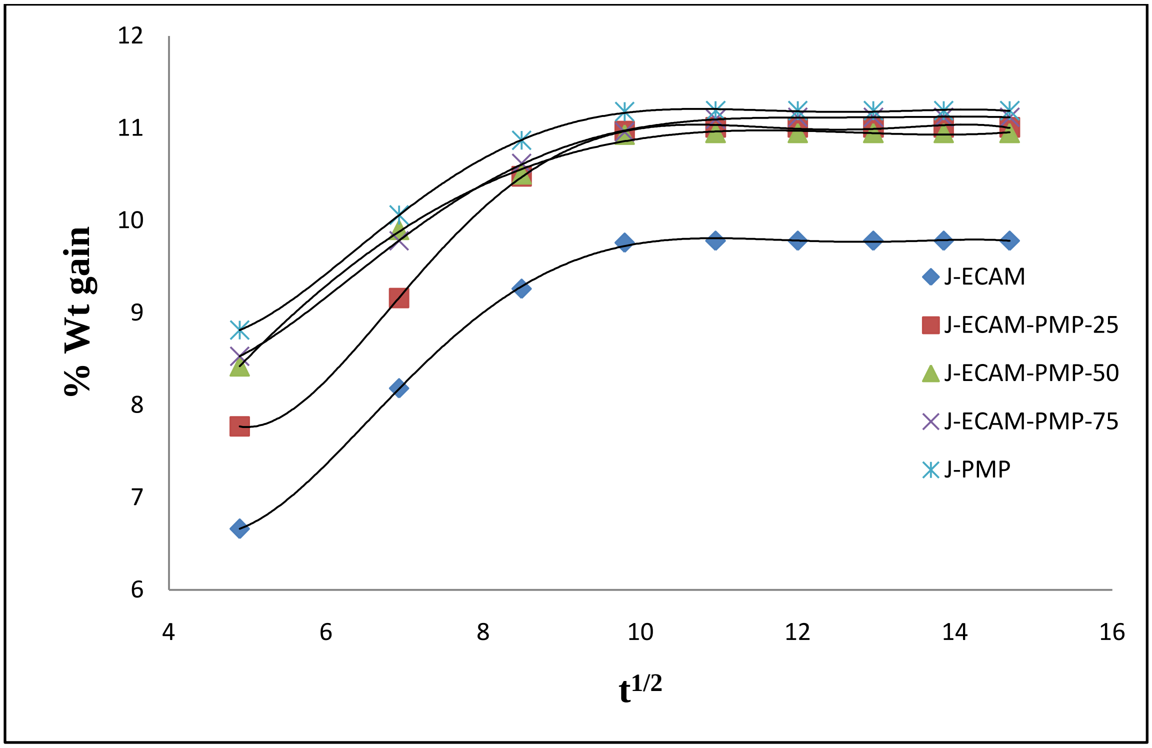

Table-4.5 Moisture uptake and diffusivity data of composite at 30^{o}C

Composite	%, Equilibrium water content at 30^{o}C			Diffusivity(D_x), 10^{-12}, m^2/s		
	H_20	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl
J-ECAM	10.7	9.8	12.5	12.1	12.5	10.6
J-ECAM -PMP-25	11.2	11.0	12.9	9.9	12.1	6.7
J-ECAM -PMP-50	11.2	11.0	13.0	6.5	7.7	4.2
J-ECAM -PMP-75	11.2	11.1	12.5	5. 6	6.8	3.8
J-PMP	11.4	11.2	12.5	4.3	5.7	3.4

Water absorption in boiling water

Water absorption in composites mainly depends on temperature besides presence of hydrophilic groups in composites. The effect of boiling water on % water absorption with time is shown in Fig. 4.5 and Table-4.6 from which it is evident that the water absorption in composites is the maximum after 6h and remained almost constant, it is evident that equilibrium water absorption time is reduced drastically without any damage to the composites. Thus, composites possess excellent hydrolytic stability against boiling water and even in harsh acidic and saline environments.

From experimental data it is clear that composites possess fairly good mechanical and electrical properties and excellent hydrolytic stability against harsh environmental conditions, which signify their usage as low load bearing housing units and in electrical and electronics and in marine field.

Figure 4.6 The plots of % weight gain against time for J-ECAM, J-PMP and their hybrid composites in boiling water

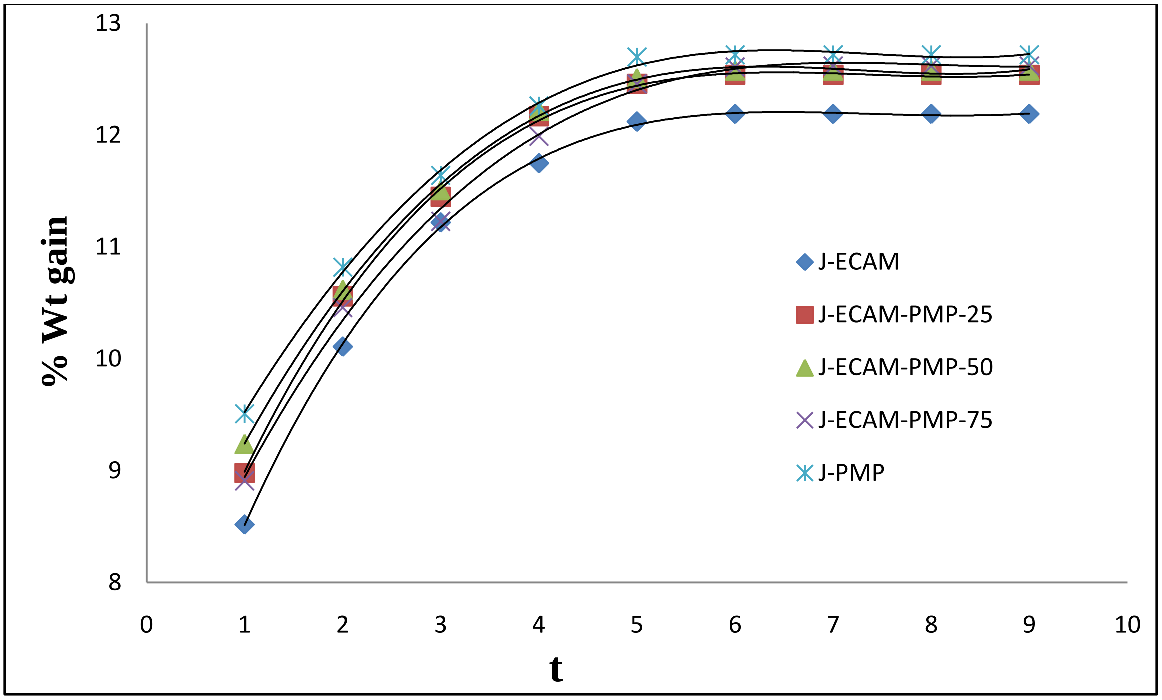

Table-4.4 The effect of temperature on water absorption in J-ECAM, J-PMP and their hybrid composites

Time, h	**% Weight change**				
	J-ECAM	**J-ECAM-PMP-25**	**J-ECAM-PMP-50**	**J-ECAM-PMP-75**	**J-PMP**
0	0.00	0.00	0.00	0.00	0.00
1	8.52	8.98	9.24	8.91	9.51
2	10.11	10.56	10.62	10.46	10.82
3	11.22	11.45	11.51	11.23	11.64
4	11.75	12.17	12.22	11.99	12.26
5	12.12	12.46	12.51	12.46	12.70
6	12.19	12.54	12.58	12.61	12.72
7	12.19	12.54	12.58	12.62	12.72
8	12.19	12.54	12.58	12.62	12.72
9	12.19	12.54	12.58	12.62	12.72
10	12.19	12.54	12.58	12.62	12.72

CHAPTER – 5

A brief review of the work done

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

CHAPTER-1

This chapter of the thesis describes up to date literature survey on bisphenols, epoxy, epoxy esters, epoxy-acrylate-maleate resin, polyurethane resins, properties, applications of natural fibers and composites in diverse fields.

CHAPTER-2

This chapter deals with the synthesis of 1,1'-bis (4-hydroxy phenyl) cyclohexane, 4-(4-hdroxyphenyl)but-3-en-2-one, 4,4',4''-but-1-ene-1,3,3-triyl triphenol, its epoxy resin, epoxy ester based on acrylic acid, epoxy-acrylate-maleate resin and their polyurethane resins, resin and its epoxy resin.

CHAPTER-3

This chapter describes the characterization of the resins by IR, 1HNMR, Mass spectral data, epoxy equivalent, acid values, and hydroxyl values of the epoxy resins and epoxy ester resin, DSC and TGA. The epoxy equivalent of the EBC and EBCN are found to be 576, 889, respectively. The acid values of the EBCA, PMP and ECAM were found to be 5.58, 56.4 and 32 mg KOH/g, respectively. The hydroxyl values of the EBCA and ECAM were found to be 124.2 and 58.7 mg KOH/g, respectively. TG thermograms of the ECAM, PMP and their mixed matrix materials were scanned at the heating rate of 10oC/ min in the nitrogen atmosphere. Endothermic transitions (69-91oC) below 100oC are due to melting of uncured ECAM and mixed matrices. Endothermic transition at 122oC for ECAM due to some chemical change in is further supported by weight loss over the temperature range 100-200oC in the TG thermogram and other endothermic transition at 225oC is due to some physical change (glass transition temperature) is supported by partially no loss over the temperature range 200-300oC. Endothermic transition at 415.7oC for ECAM-PMP-25 is due to some physical change. A small but broad endothermic transition at 172.8oC for ECAM-PMP-75 is probably due to glass transition temperature and other endothermic transition at 388.7oC is due to some physical change. Again a small but broad endothermic transition at 226.8oC for PMP is probably due to glass transition temperature and other endothermic transition is due to some physical change. it is evident that all samples apparently followed single step degradation leaving 10-25% residue above 400oC except ECAM.

ECAM is more thermally stable than that of PMP, while mixed matrix materials possess intermediate thermal stability of ECAM and PMP. Similar trend is also for observed in $T_{max.}$ High magnitude % residue for ECAM above 400oC indicated formation of high cross-linked product as a consequence of primary decomposition. It is clear that cured samples followed fractional (0.6-2.4) order degradation kinetics. Upon comparing kinetic parameters of ECAM and PMP, it is observed that PMP is somewhat more rigid than that of ECAM and this may be due to more cross-linking density. Maleate branching courses low degree of cross-linking due to comparatively a large distance between to branches and vinyl ester. In case of mixed matrix materials both E & A are lower than parent materials indicated improvement in flexibility mainly due to flexible maleate linkages. The entropy change ∆S* was determined at their respective Tmax according to equation 3 and is also reported in Table 3. The large and negative magnitudes of ∆S* confirmed highly ordered transition state than individual polymer molecules.

Degradation process is a complex process and involves a variety of reactions such as chain cleavage, branching, rearrangement, cross-linking, etc. Selective degradation occurs from weak points in the chains and consequently formation of free radials result, which further undergo a variety of reactions and degrade at higher temperature (>4000C) to form low molecular weight substances. Ether and ester groups (main chain and side chain) in ECAM and ester and pendent methyl groups in PMP are thermally weak points in the resin molecules and therefore selective degradation is likely from these points.

CHAPTER-4

This chapter of the thesis elaborates fabrication and evaluation of mechanical, electrical and chemical resistance of the composites. Jute composites were prepared by hand-lay-up technique under 15.4 MPa pressure.

ECAM composite is 1.8 times stiffer than that of PMP composite. Similarly ECAM composite is 2.2 times stronger than PMP composite. Comparatively good tensile and flexural properties of ECAM composite are due to better matrix–fiber interfacial bonding. Comparatively good tensile and flexural strengths of the composites indicated their usefulness for low load bearing housing units.

It is observed that the % water uptake increased linearly with the passage of time and remained practically constant till the equilibrium was established (96h) in each of the environment. In water and saline environment, water uptake is almost the same and somewhat less than in acidic environment. The presence of strong electrolytes in water affects the structure of water and hence diffusion in fiber through capillary action. Water absorption continues till the cell walls are saturated with water.

The diffusion coefficient of J-ECAM and J-PMP and it is somewhat varied for hybrid composites and J-PMP in three different environments but for J-ECAM it is quite different. Thus, little electrolyte effect on diffusion behavior in hybrid composites and J-PMP is observed.