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SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF SOME BISPHENOL DERRIVATIVES, POLYMERS AND COMPOSITES

A

THESIS

SUBMITTED TO THE SAURASHTRA UNIVERSITY

FOR

THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

THE FACULTY OF SCIENCE (CHEMISTRY)

BY

POOJA P. ADROJA

UNDER THE GUIDANCE

OF

Dr. P. H. PARSANIA

DEPARTMENT OF CHEMISTRY
SAURASHTRA UNIVERSITY
RAJKOT- 360 005
INDIA

May-2011

Gram: UNIVERSITY
Fax: 0281-2577633

Phone: (R) 2581097
(O) 2578512

SAURASHTRA UNIVERSITY

Dr. P. H. PARSANIA
M.Sc., Ph.D.
Professor & Head
Department of Chemistry

Residence
"Maulik"
20-A/1, University
Karmachari Co. Hsg. Society
University Road,
Rajkot – 360 005
Gujarat – (INDIA)

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

The work incorporated in the thesis is my own work under the supervision of **Dr. P. H. Parsania** and leads to some contribution in the field of Polymer Chemistry and supported by number of references.

Date: -5-2011
Place: Rajkot.

(Pooja P. Adroja)

This is to certify that the present work submitted for the Ph. D. Degree of Saurashtra University by **Pooja P. Adroja** is her own work and leads to some advancement in the knowledge of Polymer Chemistry. The thesis has been prepared under my supervision.

Date : -5-2011
Place : Rajkot

Dr. P. H. PARSANIA
Professor & Head
Department of Chemistry,
Saurashtra University
Rajkot - 360 005

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CONTENTS

General introduction

Modern era is a polymer era in which new materials are constantly replacing older ones with the advent of new technologies in which natural fibers have assumed great importance. The potential and future benefits of polymers to mankind are unlimited. In India natural fibers such as jute, coir, sisal, pineapple, ramie, bamboo, banana, etc are available in abundant. Natural fibers based composites are well suited as wood substitutes for housing and construction applications. They prevent depletion of forest resources and ensure good returns to the cultivators. During natural calamities like earthquakes, floods, cyclones, etc light weight building materials are very important in saving life and house hold commodities.

Natural fiber reinforced polymeric composites offer many potential advantages over the traditional construction materials namely steel and aluminum [1-3].

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1. Drzal1, L.T.; Mohanty, A. K.; Burgueño, R.; Misra, M., "Biobased Structural Composite Materials for Housing and Infrastructure Applications: Opportunities and Challenges" *NSF-PATH Housing Research Agenda Workshop, Proceedings and Recommendations*, 2004, 129-140.
2. "Handbook of Engineering Polymeric Materials," edited by N. P. Cheremisinoff, Marcel Dekker, New York, 1997.
3. A.S. Singha and Vijay Kumar Thakur, *Grewia optiva* Fiber Reinforced Novel, Low Cost Polymer Composites E-Journal of Chemistry, 6(1), 71-76,2009.

The advantages of polymeric composites are low density, low thermal conductivity, excellent corrosion and chemical resistance, high strength to weight ratio, better design flexibility, excellent fatigue and impact properties, improved acoustical performance, low maintenance, etc. Composites materials find their applications in car, aircraft, railway and truck industries, road construction, irrigation systems, furniture industries, sport products, electrical industries.

Epoxy resins are useful resins known for their outstanding properties. Epoxy resins are found very useful in casting, coating, molding, electric components, high strength composites and hardware applications for aircraft missiles and space structures due to the formation of three dimensional infusible, hard thermoset network via curing process [4,5]. Modification of epoxy resin is feasible due to highly reactive epoxy ring, which can also undergo ring opening reaction in the presence of acids to yield polyester polyol containing a free hydroxyl functional group that can be utilized to produce polyurethanes [4,5]. Polyurethanes are well known for their excellent adhesion, flexibility, high cohesive strength and amenable curing speed. The main advantage of polyurethanes is that they can be tailor-made as the applications require. Polyester polyols are more effective than the polyether polyols for synthesizing polyurethane adhesives. [6]

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4. H. Lee and K. Neville, *Handbook of Epoxy Resins*. Mc Graw Hill, New York, 1967.
5. C. A. May, *Epoxy Resins-Chemistry and Technology*. Marcel Dekker, New York, 1988.
6. Ying-Ling Liu, Yu-Lo Lin, Chih-Ping Chen, Ru-Jong Jeng. Preparation of epoxy resin/silica hybrid composites for epoxy molding compounds. J Appl Polym Sci 90: 4047–4053, 2003

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

CHAPTER -1: Literature survey

CHAPTER -2: Syntheses of Bisphenol-C derivatives, epoxy resins, polyester polyols, and polyurethanes

CHAPTER-3: Analyses of monomers and resins

CHAPTER-4: Thermal analysis

CHAPTER-5: Fiber Reinforced composites

CHAPTER-6: Surface coating and chemical resistance

CHAPTER-7: Comprehensive summery

CHAPTER -1: Literature survey

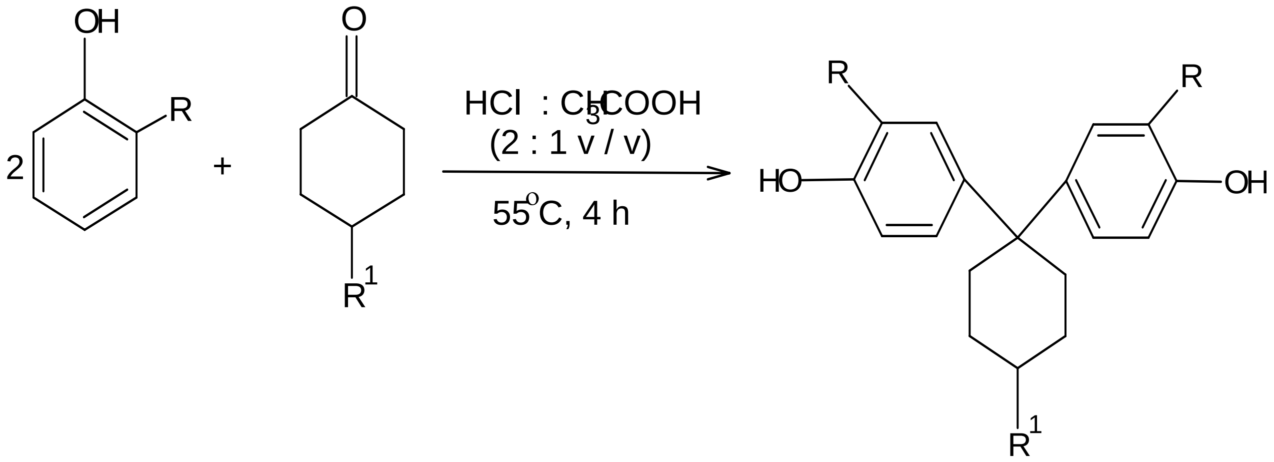
This chapter of the thesis describes up to date literature survey on syntheses, characterization and applications of aromatic cardo bisphenols, polyesters, epoxy resins, polyester polyols, polyurethane based coating materials and fiber reinforced composites.

CHAPTER-2: Syntheses of bisphenol-C derivatives, epoxy resins, polyester polyols, and polyurethanes

This chapter is further subdivided into five sections:

Section-1: Synthesis of 1, 1’-bis (3-R-4- hydroxy phenyl) cyclohexane and 1,1’-bis(4-hydroxy phenyl)4-methyl cyclohexane

1,1’-Bis(4-hydroxy phenyl)cyclohexane, 1,1’-bis(3-methyl-4-hydroxyphenyl) cyclohexane and 1,1’-bis(4-hydroxy phenyl) 4-methylcyclohexane are synthesized by reacting cyclohexanone/ 4-methyl cyclohexanone (0.5 mol,) with phenol/ o-cresol (1.0 mol,) and mixture of HCl:CH_3COOH (2:1 v/v, 100:50 ml) as a Friedel-Crafts catalyst at 55^{o}C for 4 h.



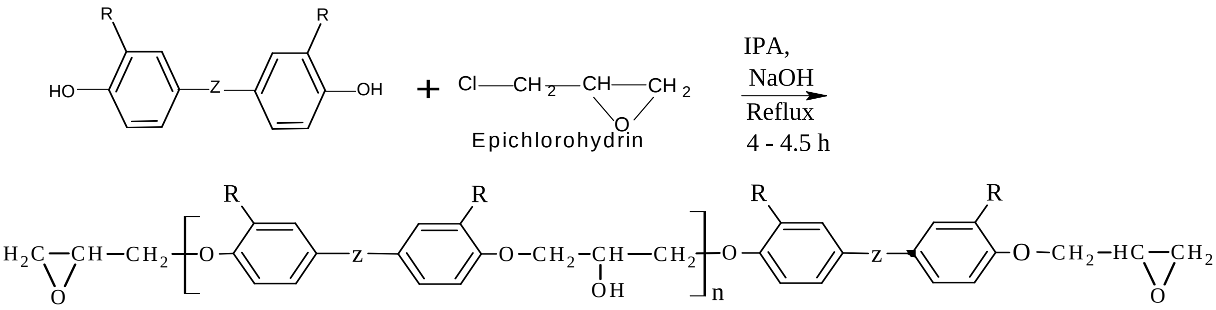
BC: R=H and R^1=H

MeBC: R-CH_3 and R^1=H

BMC: R=CH_3 and R^1=CH_3

Section-2 Synthesis of epoxy resins and curing study

Epoxy resins were synthesized by condensing BC/MeBC/BMC(0.5mol) with epichlorohydrin (1.1 mol) and using isopropanol (250 mol) as a solvent and 1.25 mol sodium hydroxide in 50 ml water as a catalyst at reflux temperature for 4- 4.5 h. The separated solid resin was isolated by distillation of excess of isopropanol. The solid and liquid resins were washed well with water and extracted in chloroform and evaporated to dryness. Highly transparent yellowish colored resins was formed, which are soluble in $CHCl_3$, acetone, 1,4-dioxane, DMF, 1,2-dichloroethane, dichloromethane, and DMSO and partially soluble in ethanol and isopropanol. Epoxy resins are cured using phthalic anhydride and triethyl amine at different temperature and concentrations.



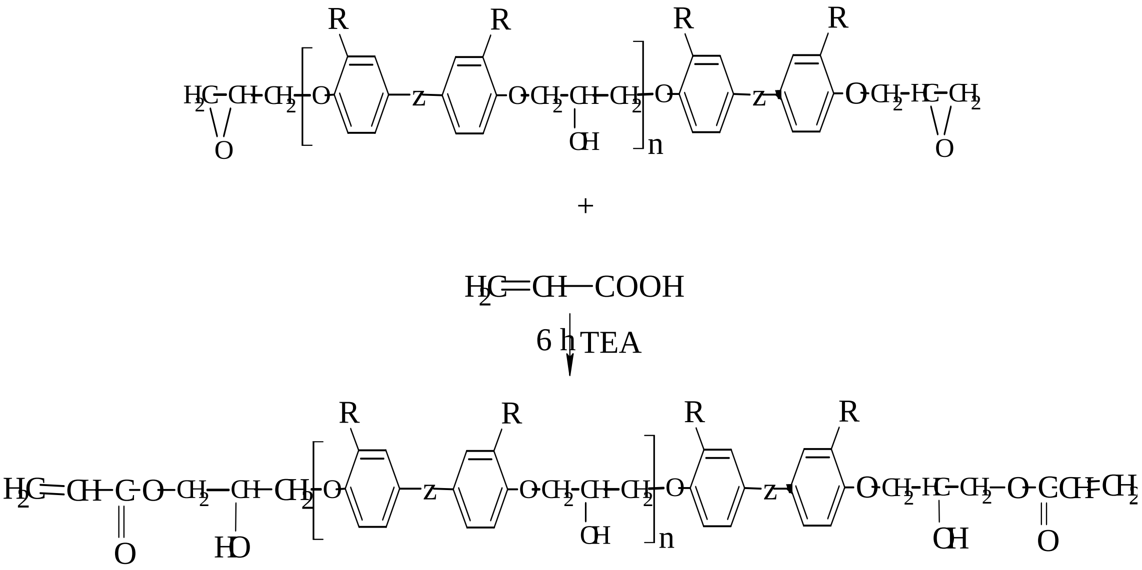
EBC: Z = Cyclohexyl and R=H

EMBC: Z = Cyclohexyl and R=CH_3

EBMC: Z= 4-methyl cyclohexyl

Section-3 Syntheses of epoxy acrylates

Epoxy acrylates of required acid value(‹ 30) were synthesized by condensing EBC/EMBC/EBMC with acrylic acid by using 1,4-dioxane/xylene as a solvent and triethyl amine/phenothiazine as a catalyst at reflux temperature for 5- 6h.

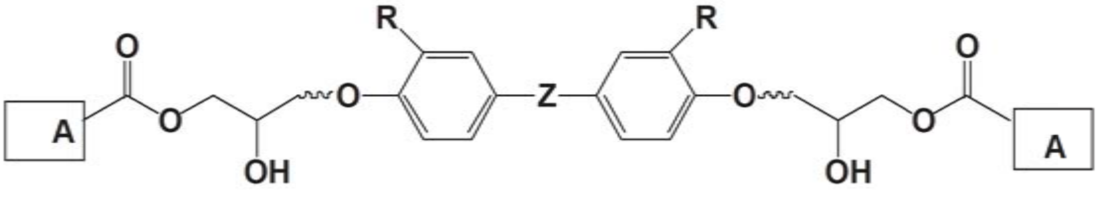


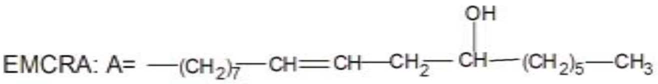
EMBCT: Z= Cyclohexyl and R=CH_3

EBMCT: Z= 4-Methyl cyclohexyl and R= $-CH_3$

Section-4: Syntheses of polyester polyols

The polyester polyols of required acid value (‹30) were synthesized by condensing EMBC with ricinoleic acid/oleic acid/rosin/linoleic acid/terephthalic acid/isophthalic acid by using 1, 4- dioxane as a solvent and triethyl amine as a catalyst at reflux temperature for 1-6h. The resins are soluble in common organic solvents.

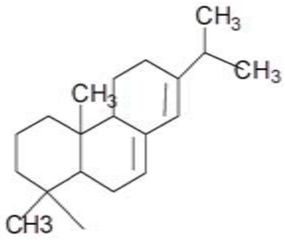



EMCRA: A= $-(CH_2)_7-CH{=}CH-CH_2-\overset{OH}{\overset{|}{CH}}-(CH_2)_5-CH_3$

EMCLA :A= $-(CH_2)_7-CH{=}CH-CH_2-CH{=}CH-(CH_2)_4-CH_3$

EMCOA :A= $-(CH_2)_7-CH{=}CH-(CH_2)_7-CH_3$

EMCR: A=



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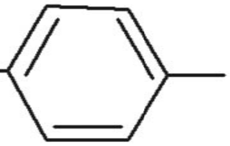

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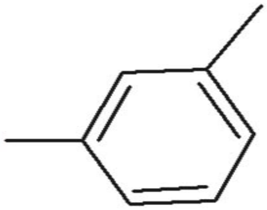
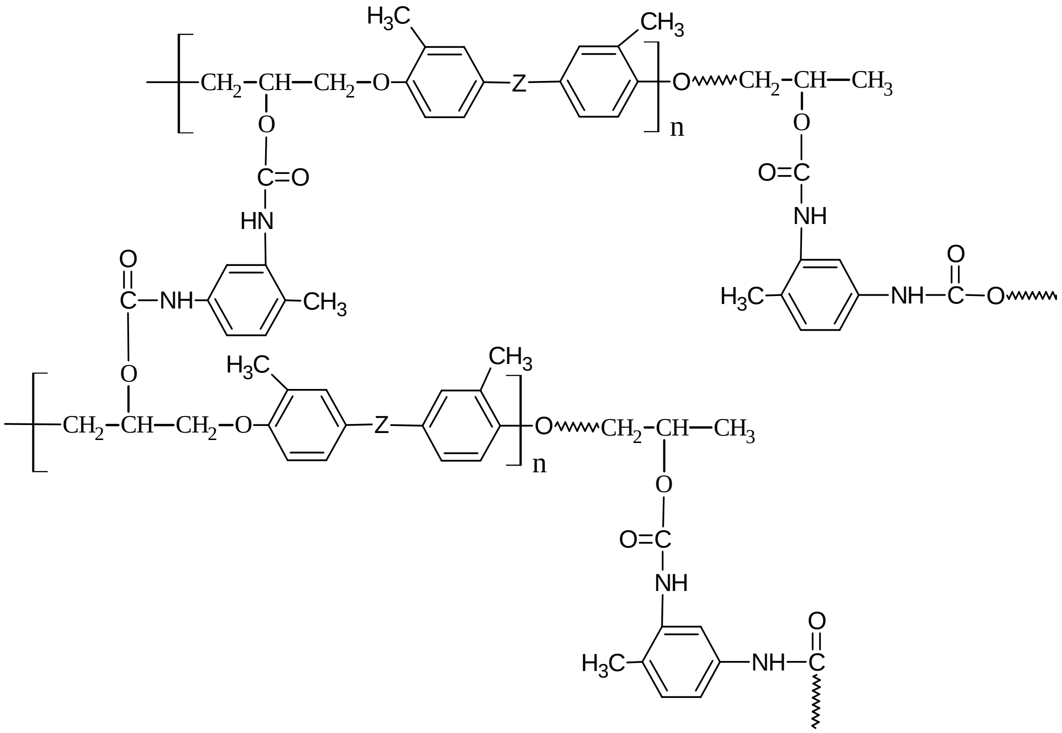


Section-5: Syntheses of polyurethanes

Copolyurethanes of polyester polyols are synthesized reacting corresponding polyester polyols and toluene diisocyante at room temperature using acetone or methyl ethyl ketone as a solvent. These copolyurethanes are used for coating study.



CHAPTER-3: Analyses of monomers and resins

This chapter describes spectral analysis of monomers, cured and uncured epoxy resins, epoxy acrylates, polyester polyols and copolyurethanes; and determination of molecular weights and molecular weight distribution, epoxy equivalents, hydroxyl and acid values. This chapter is further subdivided into three sections.

Section-1: Spectral analysis

This section describes the IR/NMR/Mass spectral characterization of monomers, cured and uncured resins, epoxy acrylates, polyester polyols and copolyurethanes.

Section-2: Molecular weights and molecular weight distribution

Number average and weight average molecular weights and molecular weight distribution of epoxy resins, epoxy acrylates and polyester polyols is described in this section

Section-3: Epoxy equivalent, hydroxyl and acid values

Epoxy equivalents of the epoxy resins are determined by pyridinium chloride method. Hydroxyl and acid values are determined according to standard methods.

CHAPTER-4: Thermal analysis

A complete thermal analysis system comprises different techniques. Each technique characterizes the sample in a particular way. The combination of all the results simplifies interpretation. TGA measures the weight curve, DSC the heat flow. All these measurement quantities change as a function of temperature or time. TGA is a technique that measures the change in weight of a sample as it is heated, cooled or held at constant temperature. Its main use is to characterize material with regard to their composition. Application areas include plastics, elastomers and thermosets, mineral compounds and ceramics as well as wide range of analyses in the chemical and the pharmaceutical testing. Differential scanning calorimetry (DSC) is the most frequently used thermal analysis technique.DSC measures enthalpy changes in samples due to changes in their physical and chemical properties as a function of temperature or time. Thermogravimetry provides quantitative information on the composition and thermal stability of many different types of materials. The method is fast and can even be used with very small samples. Thermogravimetry provides quantitative information on the composition and thermal stability of many different types of materials.

Monomers, cured and uncured resins, polyesters, polyester polyols and copolyurethanes are characterized by DSC and TGA at 10^{o}C/min heating rate in nitrogen atmosphere. Various thermal parameters are determined and discussed to support various reactions and pyrolysis mechanism.

CHAPTER-5: Fiber Reinforced composites

This chapter of the thesis is further subdivided into three sections.

Section-1: Fabrication of composites

Jute, glass and sandwich composites based on agricultural waste such as Pabadi, wheat husk and rice husks by hand layup compression molding technique by applying appropriate pressure and temperature.

Section-2: Mechanical and electrical properties of the composites

Fiber reinforced composites are useful in various fields such as building and construction, automobile, marine, electrical and electronic, transportation, aviation, packaging industries, etc because of their excellent physicochemical properties and economy as compared to conventional goods. Mechanical properties (tensile and flexural strengths) and electrical (electric strength and volume resistivity) properties of glass, jute and sandwich composites are determined according to standard test methods. The results are discussed in light of commercially available materials.

Section-3: Water uptake study

Water uptake behavior of the composites is studied in different environments namely H_2O, 10% NaCl and 10% HCl solutions at 35^oC and also in boiling water by change in mass method. The water uptake data are interpreted in light of effect of medium, nature of fibers and resins.

CHAPTER-6: Surface coating and chemical resistance

This chapter describes the use drying behavior of novel coating material on various substrates such as glass, tin, aluminum and mild steel. The chemical resistance of coated materials is tested against various chemical reagents and discussed.

CHAPTER -7 Comprehensive summery

Brief summary of the work carried out is described in this chapter.

(Dr. P. H. Parsania) **(Pooja P. Adroja)**

Professor and Head,

Department of Chemistry,

Saurashtra University,

Rajkot – 360 005

Date: 3-9-2010

CHAPTER-1

INTRODUCTION

1.1 General introduction

The mankind has passed through several eras such as the Stone Age, the Iron Age and the Bronze Age and we are living in polymer era. From the ancient civilizations of Egypt and Babylonia man was using a range of materials such as stones, woods, ceramics, glasses, skins and fibers. Polymeric materials have great 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. Polymers are substances containing a large number of structural units joined by the same type of linkage. Polymers in the natural world have been around since the beginning of time. Starch, cellulose and rubber all possess polymeric properties. Man-made polymers have been studied since 1832. Today, the polymer industry has grown to be larger than other industries like aluminium, copper and steeled. “The motivation behind all the research is necessity”.

For any living things protein is necessary, which is synthesized in nature by reacting simple chemical compounds like methane, ammonia and carbon dioxide. The protein is a natural polymer on which the life is supported. Polymers are also appeared in their other natural forms like wood, cotton, cellulose, starch, silk, etc.

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

Rubber and plastics are closely related classes of materials, 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 it is difficult to conceive how such everyday features of modern life such as the car, telephone, television set could ever been developed. Modern amenities such as home, tools, furniture and many more are made from varieties of these classes of materials. Thus potential uses of polymers are unlimited to mankind.

1.2 Literature survey on cardo bisphenols

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

Farbenind [1, 2] has reported the condensation of phenols and ketones in the presence of acetic acid, hydrochloric acid at 50^{o}C and also reported the

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1. I. G. Farbenind, Fr. Patent 647, 454 (1928); C.A. 23, 2540 (1929).
2. I. G. Farbenind, Ger. Patent 467, 728 (1927); C.A. 23, 1729 (1929).

melting points of 1,1'-bis(4-hydroxy phenyl)cyclohexane (186°C), 1,1'-bis(4-hydroxy phenyl)-4-methyl-cyclohexane (179°C). The products are useful as intermediates for dyes and drugs.

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

They have also proposed the following mechanism

(1) The addition of phenol to ketone

$$PhOH + R_2CO \rightarrow R_2C(OH)C_6H_4OH$$

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

Johnson and Musell et. al [4, 5] have reported synthesis of 1,1'-bis(4-hydroxy phenyl)cyclohexane (1) using 5 moles of phenol, 1 mole of a cyclohexanone, H_2S or BuSH below 40°C with 0.1-0.3 mole dry HCl gave (I) m.p. 186-87°C; 2Me-I, 236-40°C; 4-Me I 178°C; 1,1'- bis(4-hydroxy-3-methyl pheny)l

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3. M. E. McGreal, V. Niederl and J. B. Niederl, J. Am. Chem. Soc., 61, 345 (1939); C.A. 33, 2130 (1939).
4. J. E. Johnson and D. R. Musell, U.S. Patent 2,538,725 (1951); C.A. 45, 4412 (1951).
5. J. E. Johnson and D. R. Musell, U.S. Patent 2,535,014 (1950); C.A. 45, 2635 (1951).

cyclohexane m.p. 187^oC and 1,1’-bis(4-hydroxy-3-isopropyl-phenyl)cyclohexane, m.p. 109-111.5^oC. Mash containing small quantities of bisphenol (I) protect chickens from coccidiosis better than does a sulfaguanidine.

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

Bender et al [7] have reported the preparation of bisphenols by irradiating a mixture of ketone and phenol at 20-100^oC with β-rays or ultra violet in the presence of 37% aq. HCl or 70% aq. H_2SO_4 as condensing agent and stirring at 30-37^oC. 1,1’-Bis(4-hydroxy phenyl)cyclohexane (m.p. 186-9^oC) was obtained in 93% yield from 1 mole cyclohexanone and 4 moles phenol.

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

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6. H. L. Bender, L. B. Conte and F. N. Apel, U.S. Patent 2,858,342 (1958); C.A. 53, 6165 (1959).
7. H. L. Bender, F. N. Apel and L. B. Conte, U.S. Patent 2, 936,272 (1960); C.A. 54, 19,604 (1960).
8. Farbenfabriken, Ger. Patent 1,031,788 (1958); C.A. 54, 19,603 (1960).

Tumerman et al. [9] have reported condensation of o-cresol with aliphatic, aromatic and cyclicketones in the presence of HCl and BF_3 as catalysts.

The highest reaction rate was observed in the case of Me_2CO and cyclohexanone. The condensation of o-cresol with pinacolone yielded 10-12% after 450 h of condensation.

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

Bilik et al. [11] have reported the preparation of bis(3-chloro-4-hydroxy phenyl)alkanes by the reaction of bis(4-hydroxy phenyl)alkanes with $SOCl_2$ and a catalyst containing or generating a SH group in chloroform or carbon tetrachloride. A mixture of 1,1'-bis(4-hydroxy phenyl)cyclohexane(7.4 g), $SOCl_2$ 40 ml) and Na_2S (0.28 g) in CCl_4 (40 ml) was heated with stirring for 3 h at 55^oC, 1h at 70^oC yielded 63-75% 1,1'-bis(3-chloro-4-hydroxy phenyl)cyclohexane of m.p. 142.5^oC (CCl_4) 82-6% 2,2'-bis(3-chloro-4-hydroxy phenyl) propane of m.p.

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9. B. M. Tumerman, E. S. Gervits and I. V. Vesela, "Condensation of o-cresol with ketones in the presence of hydrogen chloride and boron fluoride compounds", Neffepererabotkai, Naftekhim, Nauchn-Tekhum, **8**, 46, (1965); C.A. 64, 4977, (1966).
10. Farbenfabriken, Ger. Patent 1,073,504, (1960); C.A. 55, 16,491, (1961).
11. M. Bilik, N. M. Bondarets, A. M. Serebryanyi, L. S. Rybkina and T. M. Cheryavskaya, "Bis(3-chloro-4-hydroxy phenyl) alkanes", Brit. Patent 1,047,058, (1966); C.A. 66, 10,737, (1967).

(30% aq. AcH) and 100% 3,3'-bis(3-chloro-4-hydroxyphenyl)pentane. The title compounds are used in the preparation of incombustible polycarbonate, nonflammable epoxy resins and herbicides.

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

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

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

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12. S. Maeda, J. Yurimoto, S. Samukawa and Y. Kojima, "Stabilized polyurethane", Japan 14, 752(66), (1963); C.A. 66, 86,263, (1967).
13. Y. Masai and M. Nakanishi, Japan 13, 248(67), (1964); C.A. 68, 3,557, (1968).
14. G. Farnham, F. N. Apel and H. L. Bender, "Bisphenols", Ger. Patent 1, 242, 237, (1967); C.A. 68, 59, 282, (1968).

Freudewald et al. [15] have reported the condensation of phenol (94 g) with cyclohexanone (98 g) in the presence of 2.0 g EtSH and anhydrous HCl (4.7 g) and heating at 70^{o}C in closed system for 3h to give 97% 1,1'-bis(4-hydroxyphenyl) cyclohexane.

Popova et al. [16] have reported the synthesis of monomers by condensing phenol and o-cresol with cyclohexanone to give 1,1'-bis(4-hydroxy phenyl) cyclohexane and 1,1'-bis(3-methyl-4-hydroxy phenyl)cyclohexane, respectively. These bisphenols are treated with HNO_3 in AcOH at 0^{o}C to give 1,1'-bis(3-nitro-4-hydroxy phenyl) cyclohexane and 1,1'-bis(5-nitro-3-methyl-4-hydroxy phenyl)cyclohexane, respectively. These monomers are useful for coordination polycondensation.

Kozlov et al. [17] have reported the condensation of o-cresol with cyclohexanone in the presence of polyphosphoric acid. The optimum conditions for this condensation were 40-45^{o}C, 70-100 wt % H_3PO_4 (72% P_2O_5), o-cresol to cyclohexanone molar ratio (3:1) for 3h; 94% 1,1'-bis (4-hydroxy-3-methylphenyl)cyclohexane was obtained with small quantities of other isomers.

Alexandru [18] has reported the preparation of bisphenols by reaction of a

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15. Freudewald, E. Joachim, Konrad and M. Frederic, “p-Phenylphenol”, Fr. Patent 1,537,574, (1968); C.A. 71, 21,868, (1969).
16. T. K. Popova and G. P. Nedonoskova, “New monomers for coordination polycondesation”, Zh. Khim, 5Zh338, (1970); C.A. 75, 6,391, (1971).
17. N. S. Kozlov, A. G. Klein and V. P. Sukhodolova, Vesti Akad Navuk B. SSR, Ser. Khim Navuk, 4, 109, (1976); C.A. 85, 176, 992, (1976).
18. B. S. Alexandru, U.S. Patent 4,766,255, (1988); C.A. 110, 38,737, (1989).

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.

Nagata et al. [19] have reported condensation of 4-hydroxy cyclohexanone with PhOH in 36% HCl at 60^oC for 4h to give 77% biphenyl cyclohexanol derivative. The decomposition and dehydrogenation of which in a mixture of NaOH, PhCMe: CH_2, H_2O and 5% Pd/C under N2 at 250^oC for 4h gave 83% 4, 4'-bisphenol.

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

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19. G. Subramaniam, R. Savithri and S. Thambipillai, "Synthesis and antifungal activity of bisphenolic derivatives", J. Ind. Chem. Soc., **66**, 797-799, (1989).
20. G. Subramaniam, R. Savithri and S. Thambipillai, "Synthesis and antifungal activity of bisphenolic derivatives", J. Ind. Chem. Soc., **66**, 797-799, (1989).

Islam et al. [21] have reported the synthesis of tetrahalogenated-4,4'-dihydroxydiphenylalkanes. The condensation of PhOH with MeCOMe, cyclohexanone, cyclopentanone and AcPh gave respective bisphenols in 66-80% yields. The condensation of o and m-cresol with ketones gave 70, 68 and 60% yields of respective bisphenols. They have also reported bromination of bisphenols by Br-AcOH in 61-70% yields. Chlorination of bisphenols by HCl in presence of H_2O_2 gave the respective tetrachlorobisphenol derivatives in 67-87% yields. The condensation of bisphenols with $ClCH_2COOH$ in aqueous NaOH gave dioxyacetic acid derivatives of bisphenols in 61-75% yields.

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

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

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21. M. Islam, E. A. Hassan, M. E. Rashad, and M. M. Wassel, "Tetrahalogenated 4,4'-dihydroxydiphenylalkanes, their synthesis and some of their reactions", Egypt. J. Chem., **20**(5), 483-490, (1980).
22. A. J. Dietzler, U.S. Patent, 3,029,291, (1962); C.A. 57, 9,744, (1962).
23. M. V. Rao, A. J. Rojivadiya, P. H. Parsania and H. H. Parekh, "A convenient method for the preparation of bisphenols", J. Ind Chem. Soc., **64**, 758-759, (1987).

cyclohexane and 1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane, respectively.

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

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24. H. H. Garchar and P. H. Parsania, "Optimization reaction conditions for synthesis of 1, 1'-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane", Asian J. Chem, **6**, 135-137, (1994).
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1.3 Literature survey on synthesis of epoxy resins, their modification, curing, and fabrication of fiber reinforced composites, characterization and applications of resins and composites

Epoxy resins are widely used as high-performance protective coatings [26, 27] structural adhesives, low-stress IC encapsulants and matrix resins for composites. When cured these resins are highly cross-linked and become amorphous thermosets. They are brittle and have poor resistance to crack growth. They are highly employed in ‘‘joining and fastening technology’’ in many industries. The epoxy resin network is formed during the cross-linking reaction using a wide variety of cross-linking agents or hardeners such as acids, anhydrides, and amines. The reaction leads to the formation of a three dimensional system, which is found to be insoluble in usual solvents. Toughening of epoxy resins with low-molecular weight liquid rubbers has been studied. Epoxy resins are extensively investigated and widely used in the electronic/electrical instruments because of their great versatility, good chemical and electrical and excellent adherence to many substrates [28,29].

Epoxy resins are widely used in coatings, adhesives and polymer composites, but the applications of cured epoxy resins are often restricted by

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26. M. Motawie, M.M. Badr, M.S. Amer, H.Y. Moustafa and I.M. Ali, “Some Coating Studies on Phenolic Epoxy/Poly (Vinyl Acetal)$_s$ Resins,” J. Appl. Sci. Res **4**(9), 1043-1051(2008).
27. Hemant Kumar, S.K Tripathi, S. Mistry and G. Bajpai, “Synthesis, Characteri - zation and Application of Coatings Based on Epoxy Novolac and Liquid Rubber Blend” E-J. Chem **6**(4), 1253-1259(2009).

by their poor toughness. Hyperbranched polyester [30] can be used as toughener to improve the toughness of epoxy resins due to its high-density functional terminal groups, and its low viscosity makes epoxy resins have good processability [31-36].

28.N. Kinjo, M. Ogata, K. Nishi, A. Kaneda, Adv. Polym. Sci, 1989, 88, 1-48.

29. X.H. Zhang, H. M. Wan, Yu Qin Min, Zuo Fang, Guo Rong Qi, "Synthesis and Thermal Properties of a Novel Nitrogen-containing Epoxy Resin," Chin Chem. Lett., **16**(4), 547-550, (2005).

30. X. X. Wang, Z. G. Jiang, Yi Feng Zhang,"Effect of Hyperbranched Polyester on Modification of Epoxy Resins Cured with Anhydride," Chin Chem. Lett.,**17**(1) 125-128 (2006).

31. R. Mezzenga, J. A. E. Manson, "Thermo-mechanical properties of hyperbranched polymer modified epoxies," J. Mat. Sci **36**(20), 4883-4891 (2001).

32. R. Mezzenga, C. J. G. Plummer, L. Boogh, "Morphology build-up in dendritic hyperbranched polymer modified epoxy resins: modeling and character ization," Polym., **42**(1), 305-317(2001).

33. D. Ratna, R. Varley, R. R. K. Singh, "Studies on blends of epoxy-functionalized hyperbranched polymer and epoxy resin," J. Mat. Sci., ***38*,** 147(2003).

34. L. Boogh, B. Pettersson, J. A. E. Manson, "Dendritic hyperbranched polymers as tougheners for epoxy resins" Polym., **40**(9), 2249-2261(1999).

35. A. Sidorenko, X. W. Zhai, F. Simon, "Hyperbranched molecules with epoxy-functionalized terminal branches: grafting to a solid surface," Macromol **35**(13), 5131-5139(2002).

Epoxy resins have been known to possess good mechanical properties and excellent adhesive properties, and thus have been widely used in industry, such as adhesive, coating, laminating, electronic encapsulating materials, and composite applications [37–43]. However, the conventional epoxy resins are inefficient to satisfy the required properties of advanced materials, such as, high

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36. J. H. OH, J. Jang, S. H. Lee, “Curing behavior of tetrafunctional epoxy resin/hyperbranched polymer system, ”Polym, **42**, 8339-8347(2001).
37. Gu J., S. C. Narang, E. M.Pearce, “Curing of epoxy resins with diphenyliodonium salts as thermal initiators,” J. Appl. Polym. Sci **30**, 2997–3007 (1985).
38. M.Kaji, K.Nakahara, T.Endo,”Synthesis of a bifunc-tional epoxy monomer containing biphenyl moiety and properties of its cured polymer with phenol novolac” J. Appl. Polym. Sci., **74**(3), 690–698 (1999).
39. R. J. Morgan, E. T.Mones, W. J.Steele, “Tensile deformation and failure processes of amine-cured epoxies,” Polym ., **23**(2), 295–305 (1982).
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42. Lee H., Neville K.: Handbook of epoxy resins. McGraw-Hill, New York (1967).
43. May C. A., Tanaka Y.: Epoxy resins chemistry and technology. Marcel Decker, New York (1973).

However, the conventional epoxy resins are inefficient to satisfy the required properties of advanced materials, such as, high thermal resistance [44-46]. It is known that several ways can be taken to enhance the thermal property of epoxy compound. Firstly, the aromatic ring was introduced into epoxy backbone during synthesis, for example, naphthalene ring and biphenyl group were often used to improve the heat resistance of epoxy resin [47-51]. Secondly, multifunctional epoxy resin is a way to enhance heat-resistant property because of higher curing density [52-55].

Recently, multifunctional epoxy resins attracted extensive interest of researchers and producers, and some multifunctional epoxy resins have been reported and even used in industrial application [56,57], for example [58-60], novolac epoxy resin, cycloalphatic epoxy resin, tetraglycidyl diamine diphenol methane (TGDDM), triglycidyl ether p-aminophenol (AGF-90) and resorcinol-formaldehyde type epoxy resin (F-76). Multifunctional epoxy resins are mainly employed as matrix for high performance fiber-reinforced composites in the aerospace industry and as encapsulant for electronic components.

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47. C. S. Wang, M. C. Lee , “Synthesis and modification of a naphthalene-containing trifunctional epoxy resin for electronic applications,” J. Appl. Polym. Sci., **70**(10), 1907–1921 (1998).
48. C-S. Wang, M-C. Lee, “Synthesis, characterization, and properties of multifunctional naphthalene-containing epoxy resins cured with cyanate ester,” J. Appl. Polym. Sci., **73**(9), 1611–1622 (1999).
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55. J. Cheng, J. Li, J. Y. Zhang, "Curing behavior and thermal properties of trifunctional epoxy resin cured by 4, 4'-diaminodiphenyl sulfone," E- Polym Lett **3**(8) 501–509 (2009).

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57 C. S. Wang, M. C. Lee, "Synthesis and properties of epoxy resins containing 2-(6-oxid-*6H*-dibenz(c,e) (1,2) oxaphosphorin-6-yl) 1,4-benzenediol (II)," Polym **41**(10), 3631–3638 (2000).

58 A. M. Atta, N. O. Shaker, N. E. Nasser, "Synthesis of bisphenol A novolac epoxy resins for coating applications," J. Appl. Polym. Sci , **107**, 347– 354 (2008).

59 Z. Qian, X. Chen, J. Xu, B. Guo, "Chain extension of PA1010 by reactive extrusion by diepoxide 711 and diepoxide TDE85 as chain extenders," J. Appl. Polym. Sci, **94**(6), 2347–2355 (2004).

60 S. J. Park, F. L. Jin, J. R. Lee, "Thermal and mechanical properties of tetrafunctional epoxy resin toughened with epoxidized soybean oil," Mater. Sci. Eng: A **374**(1-2), 109–114 (2004).

Epoxy resins contain two or more epoxy groups in a molecule. Their backbone may be aliphatic, cycloaliphatic, or aromatic. The epoxy groups react with curing agents to yield insoluble and infusible three dimensions networks. Curing agents have two or more reactive group in a molecule, which can react with epoxy groups. The epoxy prepolymer and the curing agent determine the properties of cured epoxy resins. Because of the versatility of their properties, epoxy resins are used in a variety of applications such as coatings, laminates, composites, bondings, and adhesives. To fulfill a demand for high-performance epoxy resins, novel curing agents are still being sought [61].

Parsania et.al[62-97] have reported a considerable work on epoxy resins containing cardo groups, their modification, curing by different hardeners, analysis of cured and uncured resins and also fabrication of synthetic as well as natural fibers (jute, bamboo, wheat straw, sugarcane, sisal, rice straw, etc) reinforced composites by hand layup technique. The composites have been analyzed for their mechanical (tensile and flexural strengths) electrical (electric strength and volume resistivity) properties and water absorption behavior against water, 10% aq. hydrochloric acid,10%, aq. sodium chloride and in boling water. Resins and composites possess good thermal, mechanical and electrical properties and stability against harsh environmental conditions.

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Composites and their applications

Composite is defined as “An anisotropic, heterogeneous medium, made by combining two or more materials with different properties. Properties of the composites are different do not merge completely into each other and can be physically identified along with the interface between them. The properties of the interface also contribute to the properties of the composite”. Composites are light weight, low density, high strength to weight ratio, stiffness property and corrosion resistance have come a long way in replacing the conventional materials such as steel, aluminum, timber, etc. Now a days composite [98-101] are being used for the manufacturing of prefabricated, portable and modular buildings as well as for exterior cladding panels, which can simulate masonry or stone.

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In interior applications composites are used in the manufacturing of the shower enclosures, trays, bath, sinks, troughs and spas. Cast composites products are widely used for the production of vanity units, bench tops and basins. Owing to their good combination of properties [102-107], recently composites are widely used in automotive and aircraft industries in the manufacturing of spaceships, sea vehicles, etc.

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102. Z. Yaakob, A. Min Min, M. N. Satheesh Kumar, S. S. K. Kamarudin, M. M. Hilmi and H. M. Khairul Zaman, "Oleic acid-based polyurethane and its biocomposites with oil palm trunk fiber dust", J. Thermoplas. Compo. Mater., **23**(4),447-458(2010).
103. E. I. Maafi, Lan Tighzert and Fouad Malek,"Elaboration and characterization of composites of castor oil-based polyurethane and fibers from alfa stems", J. Appl. Polym. Sci., **118**(2), 902-909(2010).
104. U. Ude, A. K. Ariffin, K. Sopian, A. Arifin and C. H. Azhari, "The impact damage response of plain woven natural silk/epoxy laminated composite plates", Intern. J. Engg., Sci. and Techn., **2**,128-140(2010).
105. Zhi-Hong Donga, Li Zhanga, Yu-Bao Lia, Gang Zhouab and Soo-Whon Leeb, "A guided bone regeneration membrane composed of hydroxyapatite and polyurethane", J. Ceramic Proc. Research **9**,478-481(2008).
106. F. O. Aramide, I. O. Oladele, and D. O. Folorunso, "Evaluation of the effect of fiber volume fraction on the mechanical properties of a polymer matrix composite" Leonardo Electro. J. Practices and Technol., **14**,134-141, (2009).

Composite consists of two major ingredients namely reinforcing fibers (dispersed phase) responsible for stress resistance and matrix materials (continuous phase) responsible for stress propagation. The base of the composite is fibers. It is often called reinforcing materials. A strength of composite is mainly depends upon the nature of reinforcing fibers [105,106]. The reinforcing fibers are classified according to their origin i.e. synthetic or natural fibers. They are available in different forms such as woven, non-woven or randomly oriented in more than one direction. The fibers like glass, aramid, kevlar, carbon, spectra (PE-fibers) etc are popular for load bearing applications. The glass fiber is most popular due to low price and suitable for engineering applications. Where cost is no factor, one can use strong fibers like kevlar, aramid, carbon and spectra fibers. The other cheap option for composite application is natural fibers in its raw form, originated directly from nature. Natural fibers have been used as reinforcement in composite materials since the beginning of our civilization, when grass, straw and animal hair were used to reinforce mud bricks also known as adobe. Recent years have seen a growing interest in the development of natural fiber reinforced composites in terms of both industrial applications and fundamental research. The natural fibers are incorporated into a matrix material such as thermosetting plastics, thermoplastics or rubber. The significant weight savings and the ease of low cost of the raw constituent materials make these composites an attractive alternative material to glass and carbon. The most commonly used natural fibers are shown in Table-1.1

Table-1.1: Properties of selected natural fibers

Properties	Jute	Banana	Sisal	Pineapple	Coir	Glass
Width or Diameter (mm)	-	80-250	50-200	20-80	100-450	7-8
Density (g/cc)	1.3	1.35	1.45	1.44	1.15	2.5
Volume Resistivity at 100 volts,cm x10^5	-	6.5-7	0.4-0.5	0.7-0.8	9-14	9-10
Micro-Fibrillar Angle (degree)	8.1	11	10-22	14-18	30-49	-
Cellulose/lignin content (%)	61/12	65/5	67/12	81/12	43/45	-
Elastic Modudlus GN/m^2	-	8-20	9-16	34-82	4-6	85.5
Tenacity (MN/m^2)	440-533	529-754	568-640	413-1627	131-175	4585
Elongation (%)	6-9	-	-	-	12	0.5

The advantages of natural fibers over the synthetic fibers are low cost, light weight, low density, easy availability, enhanced energy recovery and biodegradability, high strength to weight ratio, high specific strength, reduced tool wear and safer handling, reduced dermal and respiratory irritation ,easy surface modification, etc Various items such as school buildings, food grain silos, wood substitutes, low cost housing units, roofing, pipes [107], etc. have been fabricated from the jute fiber reinforced composites.

Hybrid composites are the materials made by combining two or more different types of fibers in a common matrix. They offer a range of properties that cannot be obtained with a single kind of reinforcement. By careful selection of reinforcing fibers, the material cost can be reduced substantially [108]. Low cost hybrid composites are produced by the use of biomass or agro waste in combination with jute. They are used for particle board, medium density board, pulp and composites [109]. The incentives of utilizing agro waste in the

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107. S. V. Joshi, L. T. Drzal, A. K. Mohanty and S. Arora, “Are natural fiber composites environmentally superior to glass fiber reinforced composites?”, Compos. Part-A, **35**(3), 371-376, (2004).
108. A. Khalil, H. Ismail, M. N. Ahmed, A. Ariffrin and K. Hassan, “The effect of various anhydride modifications on mechanical properties and water absorption of oil palm empty fruit bunches reinforced polyester composites,”Polym. Int. **50**,396-413, (2001).
109. J. P. L. Dwanisa, A. K. Mohanty, M. Misra, M. Kazemizadeh and L. T. Drzal, “Novel soy oil based polyurethane composites: Fabrication and dynamic mechanical properties evolution”, J. Mater. Sci, **39**(5), 1887-1890(2004).

the fabrication of composites are greater deformability, low density, less abrasiveness to equipments, low cost, etc.

The role of matrix (resin) is to hold reinforcement together. A loose bundle of fibers would not be of much use. In addition, though the fibers are strong, they can be brittle but matrix can absorb energy by deforming under stress. Thus, matrix adds toughness to the composites. Depending upon the properties required, different matrix materials are being used viz: epoxy, phenolic, unsaturated polyester, polyurethane, polyimide, etc. When going for cheaper application, phenolic and epoxy systems are used in combination with glass fibers with decent properties.

Unsaturated polyester resin is being used in combination with glass woven cloth for composite fabrication, but restricts their use due to high shrinkage when cured, more moisture absorption, lower impact strength and low chemical resistance. Another specialized matrix system is polyurethane, which possesses three dimensional network structures. The unique feature of polyurethane is that it can be tailor made to fit the application requires. Today, polyurethanes are finding a growing interest for the applications as composites virtually in all the sectors especially in the automotive market because of their flexibility, excellent adhesion, high cohesive strength, excellent hardness, impact resistance, high scratch and abrasion resistance and excellent chemical resistance. Another low cost system is vinyl ester resin derived from esterification of diepoxide with acrylic and methacrylic acids results in vinyl ester epoxy resin that is curable with vinyl monomers like styrene and divinyl benzene by free radical mechanism. Such a low cost system is advantageous over unsaturated polyester resin due to low shrinkage, low moisture absorption and good chemical resistance.

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

Effect of fiber pretreatment on physical properties

The pretreatment reactions directly influence the cellulosic fine structure of natural fiber. Chemically treated fibers show a considerable decrease in the tensile properties due to the substantial delignification and degradation of cellulosic chains during chemical treatment. Most of the chemical treatments have been found to decrease the fiber strength due to breakage of the bond structure, and disintegration of the noncellulosic materials but silane and acrylation treatment lead to formation of strong covalent bond and hence enhancement in fiber strength[110].

The reinforcing ability of the fibers depends upon various factors such as mechanical strength of the fibers, polarity of the fiber, surface characteristics and presence of reactive centers. All these factors control interfacial interaction between fiber and matrix. The improved stiffness of the fibers is attributed to the crystalline region (cellulosic) of the fiber. The fiber also shows very good elongation properties, with values increasing upon modifications. Lower elongation properties of the untreated fiber may be due to the three dimensionally cross-linked networks of cellulose and lignin.

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110. G.C. Yang, H.M. Zeng, J.J. Li, N.B. Jian, and W.B. Zhang, Acta. Scientiarum Naturalium. Universitatis. Sunyatseni. 35, 53 (1996).

Pretreatment breaks this network structure giving the fiber higher elongation and lower strength properties.Pretreatments of natural fibers result in the change of thermal stability [110-113,]. Lignin content and density of fibers get reduced with the chemical treatment and the N-isopropyl-acrylamide treatment causes a significant reduction in moisture absorption. The fiber becomes more thermally resistant upon alkali treatment [114-116]. Several workers have reported the influence of various types of chemical modifications on the properties of natural fiber-reinforced thermoplastic composites [117-119]. In addition to the fiber-matrix interfacial bond strength, the mechanical properties of a natural fiber-reinforced composite depend upon many parameters such as fiber strength, modulus, fiber length and orientation A strong fiber-matrix interface bond is significant for high mechanical properties and for effective stress transfer from the matrix to the fiber whereby maximum utilization of the fiber strength in the composite is achieved [120]. Moreover, factors like processing conditions/techniques have considerable effect on the mechanical properties of fiber-reinforced composites [121]. Chemically modified cellulosic fiber-reinforced thermoplastic composites offered better physical and mechanical properties under extreme conditions even after recycling. Different natural fibers (flax, ramie and curaua) and matrices (polyester and polypropylene) showed improved mechanical properties of natural fiber-reinforced composites by use of different coupling agents. Benzylation of wood particles was subsequently explored by comparing benzylated boards to particle boards containing phenol formaldehyde [122]. Although the benzylated boards had much greater internal bond strengths, the particle boards with phenol formaldehyde adhesive had greater modulus of elasticity (MOE) and modulus of rupture (MOR).

111. H.L. Bos, The Potential of Flax Fibres as Reinforcement for Composite Materials, Ph.D. Thesis, Thechnische Universiteit Eindhoven, University Press Facilities,Eindhoven,Netherlands(2004).

112. Van de Weyenberg, T. Chi Truong, B. Vangrimde, and I. Verpoest, Improving the properties of UD flax fibre reinforced composites by applying an alkaline fibre treatment Compos.A, **37**(9), 1368-1376(2006).

113. G. Gardea-Hernandez, R. Ibarra-Gomez, S.G. Flores-Gallardo, C.A. Hernandez-Escobar, P. Perez-Romo, and E.A. Zaragoza-Contreras, "Fast wood fiber esterification. I. Reaction with oxalic acid and cetyl alcohol,"Carbohyd.Polym., **71**(1),1-8(2008).

114. H.D. Thais Sydenstricker, S. Mochnaz, and S.C. Amico. "Pull-out and other evaluations in sisal-reinforced polyester biocomposites" Polym. Test., **22**(4), 375-380(2003).

115. D. Ray, B.K. Sarkar, R.K. Basak, and A.K. Rana, "Study of the thermal behavior of alkali-treated jute fibers" J. Appl. Polym. Sci., **85**(12), 2594-2599(2002).

116. J.J. Sunol, J. Saurina, F. Carrillo, and X. Colom, "Comparison of the thermal behavior of three cellulose fibers mercerized or submitted to solar degradation," J. Therm. Anal. Cal., **72**(2).753-758(2003).

117. O.Y. Mansour, A. Nagaty, A.D. Beshay, and M.H. Nosseir, "Graft polymerization of monomers onto cellulose and lignocelluloses by chemically induced initiator," J. Polym. Sci. Polym. Chem. Ed. **21**(3), 715-724(1983).

118. S. Manrich and J.A.M. Agnelli, "The effect of chemical treatment of wood and polymer characteristics on the properties of wood–polymer composites,"J. Appl. Polym. Sci., **37**(7), 1777-1790 (1989).

Treatment of jute fibers with alkali treatment and MPP emulsion has been found to be very efficient in improving the fiber-matrix adhesion and thus mechanical properties in jute fiber mat reinforced PP composites [123]. Banana fiber reinforced polyester composites were found to be dependent on the fiber content and the fiber surface modification. The mechanical properties of different alkali treated fiber composites showed improved fiber/matrix interactions [124].

119. D.L. Kenaga. V.T. Stannett, and J.P. Fennessey, "Radiation grafiting of vinyl monomers to wood," Forest. Prod. J., **16**, 161-168(1962).

120. R. Karnani. M. Krishnan, and R. Narayan, "Biofiber-Reinforced Polypropylene Composites," Polym. Eng. Sci., **37**(2). 476-487 (1997).

121. J. George, M.S. Sreekala, and S. Thomas, "A review on interface modification and characterization of natural fiber reinforced plastic composites," Polym. Eng. Sci., **41**(9), 1471–1485 (2001).

122. M. Kiguchi and K. Yamamoto, Mokuzai. Gakkaishi., "Chemical modification of wood surfaces by esterifacation III. Some properties of self-bonded benzylated particleboard," Mokuzai Gakkaishi, **38** (2), 150-158 (1992).

123. X.Y. Liu and G.C. Dai, "Surface modification and micromechanical properties of jute fiber mat reinforced polypropylene composites," E- Polym. Lett., **1**(5),299-307 (2007).

124. L.A. Pothan, C.N. George, M. Jacob, and S. Thomas, "Effect of Chemical Modification on the Mechanical and Electrical Properties of Banana Fiber Polyester Composites," J. Compos. Mater., **41**(19)2371-2386(2007).

Surface modification due to coupling agents caused noticeable improvements of the characteristics values of composites, depending on the fiber, matrix, and on the type of surface treatment used [125].

Pretreatment of fibers in natural fiber-reinforced composites often showed improvement in tensile properties owing to the increased fiber-matrix adhesion. Tensile properties can be explained on the basis of the changes in chemical interactions at the fiber-matrix interface. Sreekala et al. [126] studied the mechanical performance of treated oil palm fiber-reinforced composites. They investigated the tensile stress-strain behavior of composites having 40% (by weight) fiber loading. Silane, isocyanate, acrylated, latex coated and peroxide treated composites withstood tensile stress to higher strain level. Silane, benzoylation and peroxide treated flax fiber composites showed superior physical and mechanical properties due to better adhesion between fibers and matrix [127]. Morphological studies showed that the pretreatments improved the fiber-matrix adhesion and the dispersion of the fiber in the matrix [127].

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125. J. Gassan and A.K. Bledzki, Die. Angew. "Einfluß von haftvermittlern auf das feuchteverhalten naturfaserverstärkter kunststoffe†," Makromaol. Chem., **236**(1), 129-138(1996).
126. M.S. Sreekala, M.G. Kumaran, S. Joseph, M. Jacob, and S. Thomas, "Oil palm fibre reinforced phenol formaldehyde composites: Influence of fibre surface modifications on the mechaical performance," Appl.Compos.Mater.,**7**(5-6),295-329(2000).
127. B. Wang, S. Panigrahi, L. Tabil, and W. Crerar, "Pre-treatment of Flax Fibers for use in Rotationally Molded Biocomposites," J. Reinf. Plast. Compos. , **26**(5), 447-463 (2007).

Silane treated, isocyanate treated, acrylated, acetylated and latex coated composites showed yielding and high extensibility. Mercerization and permanganate treatment showed slight enhancement in tensile modulus of the composites. The elongation at break of the composites with chemically modified fiber was attributed to the changes in the chemical structure and bonding ability of the fiber. Peroxide and permanganate treated fiber-reinforced sisal-LDPE composites showed an enhancement in tensile properties and dimensional stability. The influence of alkali treatment of jute on the performance of the biocomposites resulted in more than a 40% improvement in the tensile strength [128]. Biocomposites performance was also affected by jute fiber content and about 30% (by weight) of jute showed optimum properties of the biocomposites. Mishra et al. [129] reported that alkali treated (5%) sisal-polyester biocomposites showed about 22% increase in tensile strength. Ichazo et al. [130] found that addition of silane treated wood flour to PP produced a sustained increase in the tensile modulus and tensile strength of the composite.

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128. A.K. Mohanty, M. A. Khan and G. Hinrichsen, “Influence of chemical surface modification on properties of biodegradable jute fabrics – polyester amide composites”, Composites – Part A, **31**(2), 143-150 (2000).
129. S. Mishra, M. Misra, S.S. Tripathy, S.K. Nayak. and A.K. Mohanty, “The Influence of chemical surface modification on performance of Sisal-polyester Biocomposites,” Polym.Compos.,**23**(2),164-170(2002).
130. M. N. Ichazo, C. Albano, J. Gonzalez, R. Perera, and M. V. Candal, “Polypropylene/wood flour composites: treatments and properties,” Compos. Struct., **54**(2),207-214(2001).

Benzoyl peroxide treatment on short sisal fiber-reinforced polyethylene composites resulted in an enhancement in tensile properties due to peroxide induced grafting [131]. In oil palm fiber-reinforced phenol formaldehyde composites, fibers were coated with benzoyl peroxide in acetone solution after alkali pretreatments. High-temperature was favored for decomposition of the peroxide and it was observed that peroxide-treated fiber composites could withstand the tensile stress to higher strain level. Vazquez et al [132] studied the effect of mercerization, acrylation, isocyanate treatment and washing with alkaline solution of bagasse fiber on the tensile properties of bagasse-PP composites and it was found that chemical treatments enhance the tensile properties of composites. Tensile properties (modulus and tensile strength) of chemically treated short sisal fiber reinforced cellulose derivatives/starch composites with different fiber loading showed comparable results with calculated values obtained from theories of reinforcement [133]. Impact strength is defined as the ability of a material to resist the fracture under stress applied at

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131. J. Gassan and A.K. Bledzki, “Alkali Treatment of jute fibers: relationship between structure and mechanical properties,” J. Appl. Polym. Sci., **71**(4), 623-629 (1999).
132. A. Vazquez, V.A. Dominguez, and J.M. Kenny, Bagasse-Fiber-Poly-propylene based Composites, J. Thermoplast. Compos. Mater., **12** (6),477-497(1999).
133. V. A. Alvarez, R. A. Ruscekaite, and A. Vazquez, “Mechanical properties and water absorption behavior of composites made from a biodegradable matrix and alkaline-treated sisal fibers,” J. Compos. Mater, **37**(17), 1575-1588(2003).

high speed. Impact properties of the polymeric materials are directly related to the overall toughness of the material. Composite fracture toughness is affected by interlaminar and interfacial strength parameters. Natural fibers have a significant effect on the impact resistance through the principle of stress transfer. It has been reported that when an impact load is applied perpendicular to the reinforcing fibers, a good fiber-matrix adhesion is required for even moderate impact strength [188]. The impact properties of the polymeric materials are directly related to the overall toughness of the material [134]. Toughness means the ability of the polymer to absorb applied energy. Impact resistance is the ability of a material to resist breaking under a shock loading or the ability to resist fracture under stress applied at high speed. A lot of work has already been done on the impact resistance of short fiber reinforced composites [135-138] and it depends on fiber rigidity, interfacial stress resistance and fiber aspect ratio.

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134. V. Shah, Handbook of Plastics Testing Technology. 2nd ed., Wiley, New York (1998).
135. H. T. Kau, "A study of the impact behavior of chopped fiber reinforced composite," Polym. Compos, **11**(5), 253-264(1990).
136. B. Z. Jang. L. C. Chen. L. R. Hwang. J. E. Hawkes, and R. H. Zee, "The response of fibrous composites to impact loading," Polym. Compos., **11**(3),144-157(1990).
137. P. E. Reed and L. Bevan, "Impact damage in a composite material," Polym. Compos., **14**(4), 286-291(1993).
138. J. B. Zhong, J. Lv, and C. Wei. Express, "Mechanical properties of sisal fibre reinforced ureaformaldehyde resin composites," Polym. Lett., **1**(10), 681-687(2007).

The strength of the matrix, the weakest part of the material, should be related to the failure process. The involvement of fibers in the failure process is due to the separation of fibers, the matrix and loss of stress transferring capability. The total energy dissipated in the composite before final failure occurs is a measure of its impact resistance. The total energy absorbed by the composite is the sum of the energy consumed during plastic deformation and the energy needed for creating new surfaces.

1.4 Aim and objectives of the present work

The aim of the present work is to synthesize novel compounds and to use renewable resources for making value added biocomposites.

Following are the objectives of the present work:

1. To collect relevant literature on syntheses of monomers and resins, characterization and applications of the materials under investigation.
2. To synthesize bisphenols-C derivatives, epoxy resins and their polyester polyols.
3. To study curing behavior of epoxy resins.
4. To characterize synthesized compounds by suitable techniques.
5. To fabricate biofiber reinforced composites for value added applications.
6. To prepare coating materials and their testing against various environmental conditions.

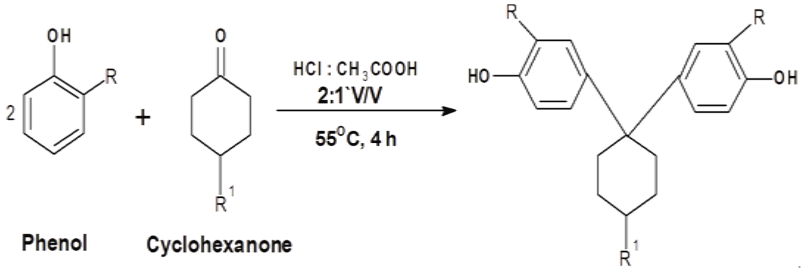
CHAPTER-2

SYNTHESIS OF BISPHENOL-C DERIVATIVES, EPOXY RESINS, POLYESTER POLYOLS AND POLYURETHANES

This chapter is further subdivided into five sections. Syntheses of bisphenol-C derivatives, epoxy resins, polyester polyols and polyurethanes are described in corresponding sections.

2.1 Synthesis of 1, 1’-bis(3-methyl-4-hydroxy phenyl)cyclohexane and 1,1’-bis(3-methyl-4- hydroxyphenyl)-4-methyl cyclohexane

1,1’-Bis(3-methyl-4-hydroxyphenyl)cyclohexane (MeBC) was synthesized according to reported methods [1, 2].



BC : R = H and R^1 = H
MeBC : R = CH_3 and R^1 = H
BMC : R =CH_3 and R^1 = CH_3

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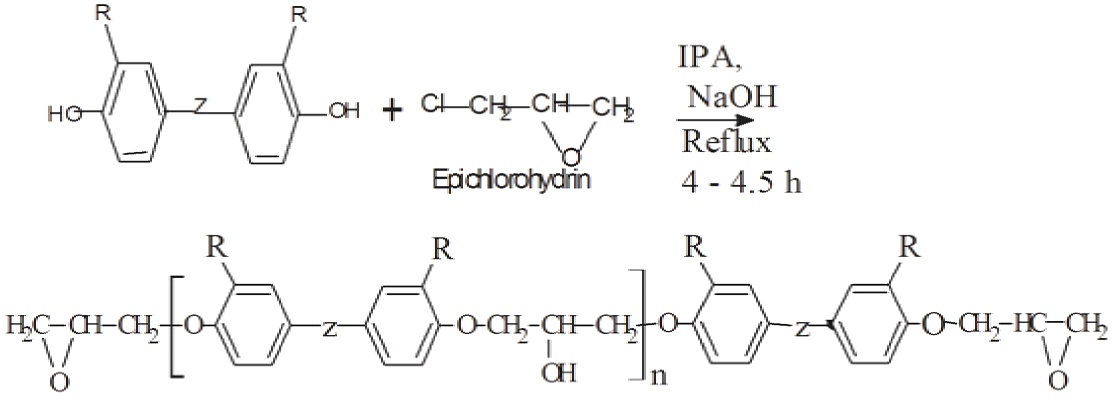
1. M. V. Rao, A. J. Rojivadia, P. H. Parsania and H. H. Parekh, "A convenient method for the preparation of bisphenols," J. Ind. Chem. Soc **64**, 758-759 (1987).
2. H. H. Garcher, H. N. Shukla and P. H. Parsania, "Kinetics of formation of 1,1’-bis(3-methyl-4-hydroxyphenyl)cyclohexane," Indian Acad.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

Thus, cyclohexanone /4-methyl cyclohexanone (0.5mol) was treated with o-cresol (1 mol.) in the presence of mixture of HCl: CH_3COOH (2:1 v/v, 100:50 ml) as a Friedel-Craft catalyst at 55^{o}Cfor 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution. The resinous material was removed by filteration through cotton plug. The yellowish solution so obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50^{o}C. MeBC and BMC were further crystallized repeatedly from benzene and methanol water systems. The process was repeated to get pure, white, shining crystals (MeBC 80~81% yield and m. p 186^{o}C and BMC 50-52% yield and mp 186^{o}C).

2.2 Synthesis of epoxy resins and curing study

Epoxy resin of MeBC here after designated as EMC was synthesized according to following method. Thus, MeBC (0.5 mol,) epichlorohydrin (1.1 mol) and isopropanol (250 ml) were placed into a 1 lit round bottomed flask equipped with a condenser. The mixture was brought to reflux with stirring and 1.25mol NaOH in 50 ml water was added slowly to the solution and refluxed for 4.5 h. The separated solid resin was filtered, washed well with warm water and dried at room temperature. White resin is soluble in $CHCl_3$, acetone, 1, 4-dioxane, DMF, 1, 2-dichloroethane and DMSO; and partially soluble in ethanol and isopropanol



EBMC : R = CH_3 and Z = 4-methyl cylohexyl
EMC : R = CH_3 and Z = cylohexyl

Curing of epoxy resin

In the present investigation curing study of EMC was carried by using varying amounts of triethylamine (TEA) as a hardener at 100 ^{o}C. Thus, into five different test tubes, 2 g EMC and varying amounts of TEA (5-25 Wt%) were dissolved in 5ml MEK and placed in water bath at 80^{o}C. The MEK was evaporated slowly with stirring and then the test tubes were placed in an oil bath at 100^{o}C and the time of curing was monitored (Table-2.1) and further post cured for 30 min. Here after cured samples are designated as EMCT-5 to EMCT-25.The cured samples are insoluble in most of the common solvents but they show swelling behavior in chloroform, 1, 2-dichloroethane, dichloromethane, 1, 4-dioxane, tetrahydrofuran, toluene, isopropyl alcohol, carbon tetrachloride, xylene, dimethly formamide, dimethylsulfoxide, etc.

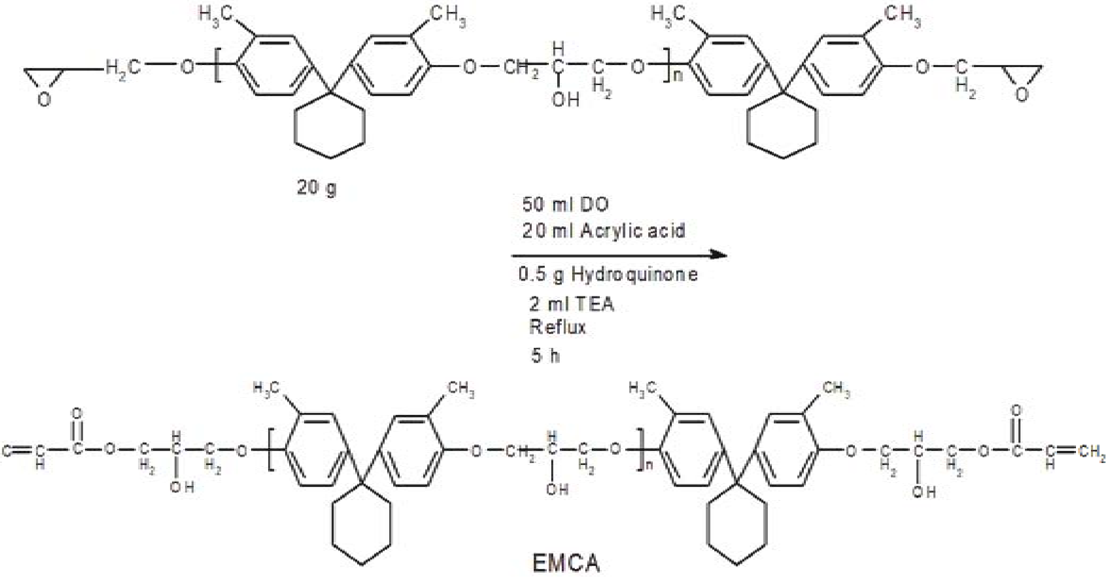
From Table 2.1, it is observed that curing time decreased with TEA concentration up to 15% and then remained practically constant. Thus, optimum hardener concentration and gel time are respectively 35 min and 15% TEA.

Table-2.1: TEA composition and gel time for EMC

TEA,%	Gel time, min.
5	185
10	70
15	35
20	40
25	35

2.3 Synthesis of epoxy acrylate

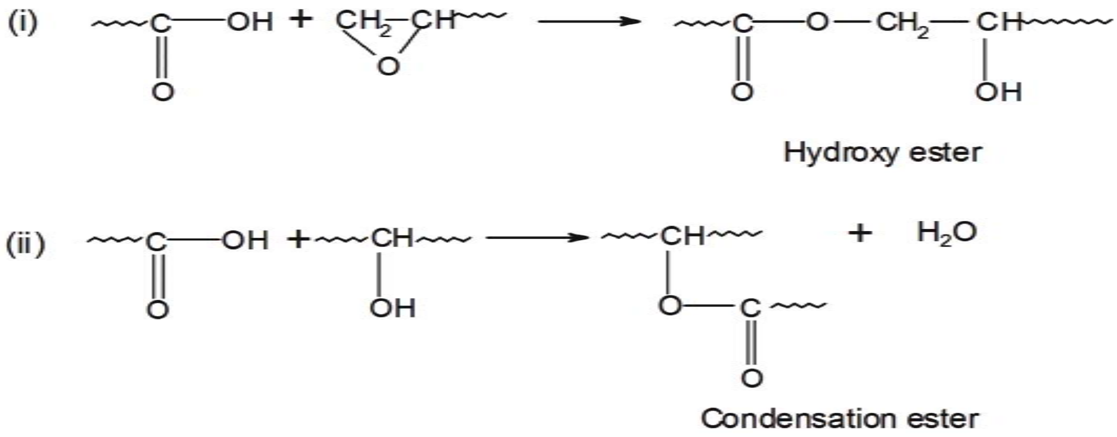
Into a 250 ml round bottomed flask containing 20 g EMC, 50 ml 1,4-dioxane, 50ml acrylic acid, 0.5 g hydroquinone and 2 ml triethylamine was placed in an oil bath. The reaction mass was refluxed for 5 h and cooled. Solid epoxy-acrylate was isolated from cold water, filtered washed well with distilled water till unreacted acrylic acid was removed completely and dried at 50^{o}C in an oven. The yield was 20 g. The resin is soluble in chloroform, 1,4-dioxane, THF, 1,2-dichloroethane, acetone, methylethylketone, etc. The resin was purified three times from chloroform-n-hexane system. Here after resin is designated as EMCA.



2.4 Synthesis of epoxy polyester polyols

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

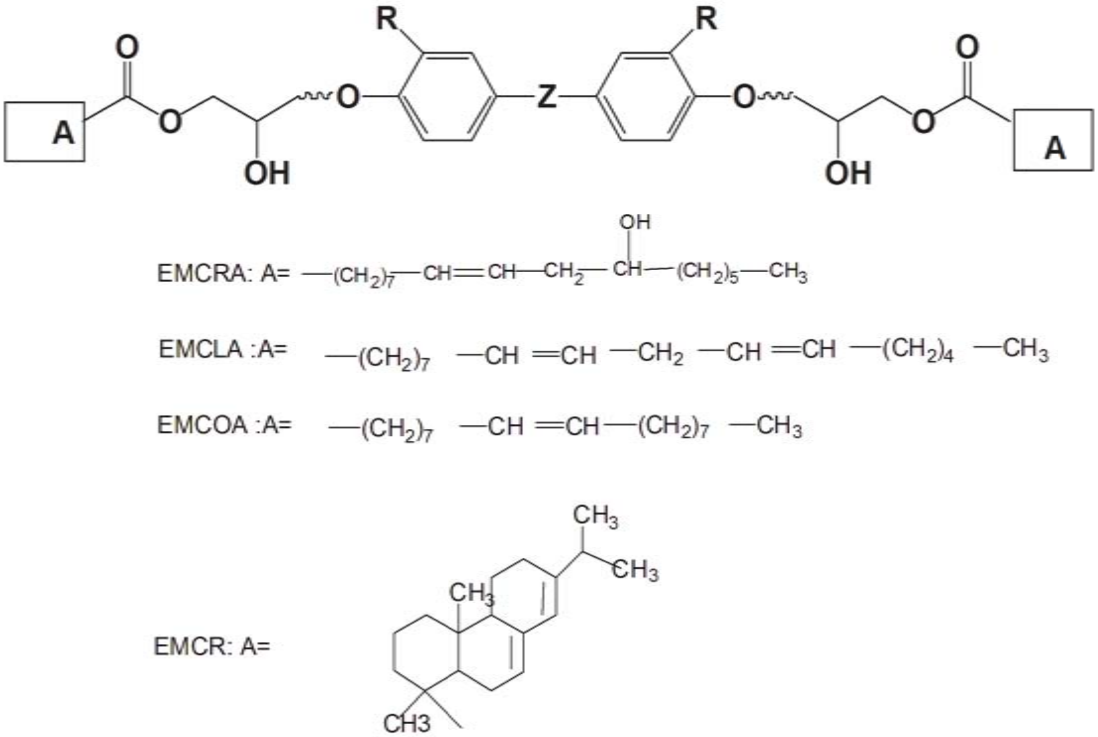
Esterification



Esterification reactions are favored by removing water of reaction. Generally xylene is used as a solvent to remove water azeotropically. The synthesis of epoxy esters (polyester polyols) based on ricinoleic acid/ linoleic acid/ oleic acid/rosin/terephthalic acid/isophthalic acid is described as under:

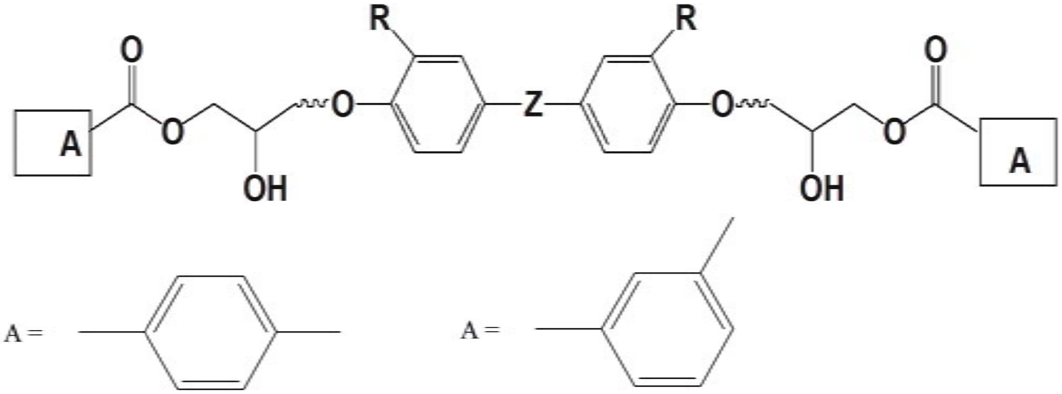
Into a 100 ml round bottomed flask equipped with a condenser and oil bath were placed, 0.05 mol EMC, 0.11 mol ricinoleic acid/linoleic acid/oleic acid/rosin, 20 ml 1,4-dioxane and 1.5 ml triethyl amine (TEA) as a catalyst and the resultant reaction mass was brought to reflux for varying time interval (2-6h) to get desired acid values (<30 mgKOH/g) of the resin. Solid polyester polyol was isolated from chilled water, filtered, washed well with saturated sodium bicarbonate and finally with distilled water and then extracted in chloroform.

Chloroform was distilled off using rotary evaporator. Polyester polyols are here after designated as EMCRA, EMCLA, EMCOA and EMCR. Polyester polyols are highly soluble in common solvents like acetone, chloroform, 1,4-dioxane, ethylacetate, toluene, methyl ethyl ketone, N,N-dimethylformamide, dimethylsulfoxide, tetrahydrofuran, 1,2-dichloroethane, dichloromethane, etc.



Syntheses of epoxy resin based polyisophthalate/terephthalate

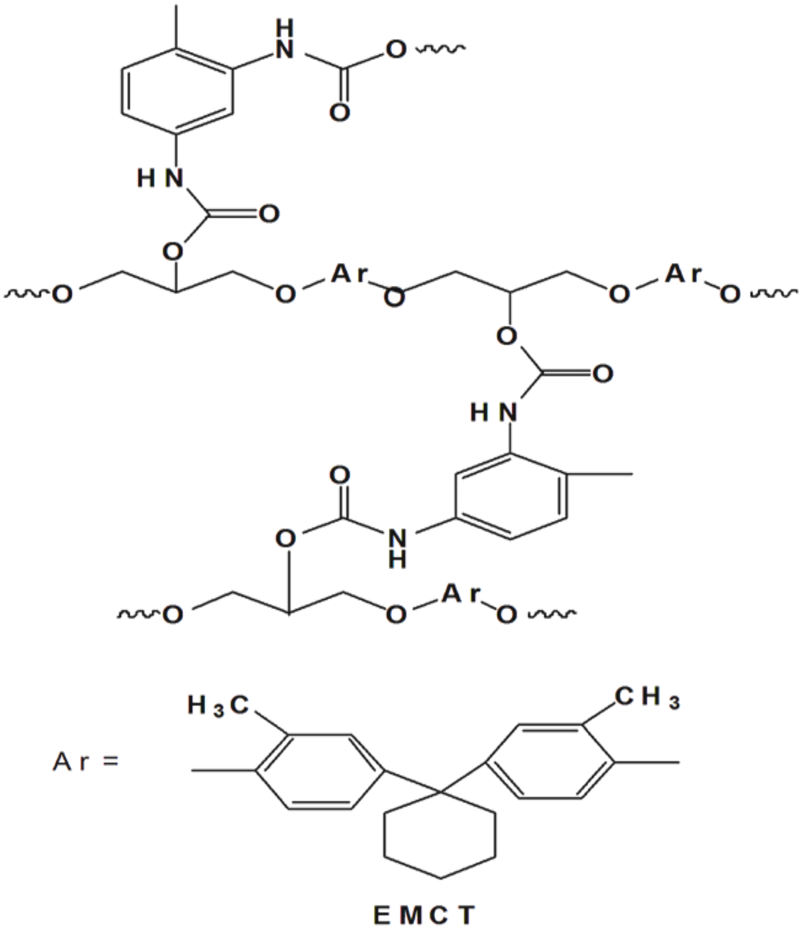
Epoxy resin of 1, 1’-bis (3-methy-4-hydroxy phenyl)cylcohexane (EMC) was synthesized as follows. Into a 250 ml round bottomed flask containing 1.54 g EMC, 10 ml DMF, and 0.166 g isophthalic/terephthalic acid was placed in an oil bath. The reaction mass was refluxed for 3h and cooled. Solid epoxy-polyester was isolated from cold water, filtered, washed well with distilled water and dried at 50^{o}C in an oven. The yield was 1.08 g. The epoxy-polyesters are soluble in chloroform, 1,4-dioxane, THF, 1,2-dichloroethane, acetone, methyl ethyl ketone, etc. The epoxy-polyesters were purified three times from chloroform-n-hexane system. Here after epoxy-isophthalate and epoxy-terephthalate are designated as EMCIP and EMCTP, respectively.



2.5 Synthesis of polyurethanes

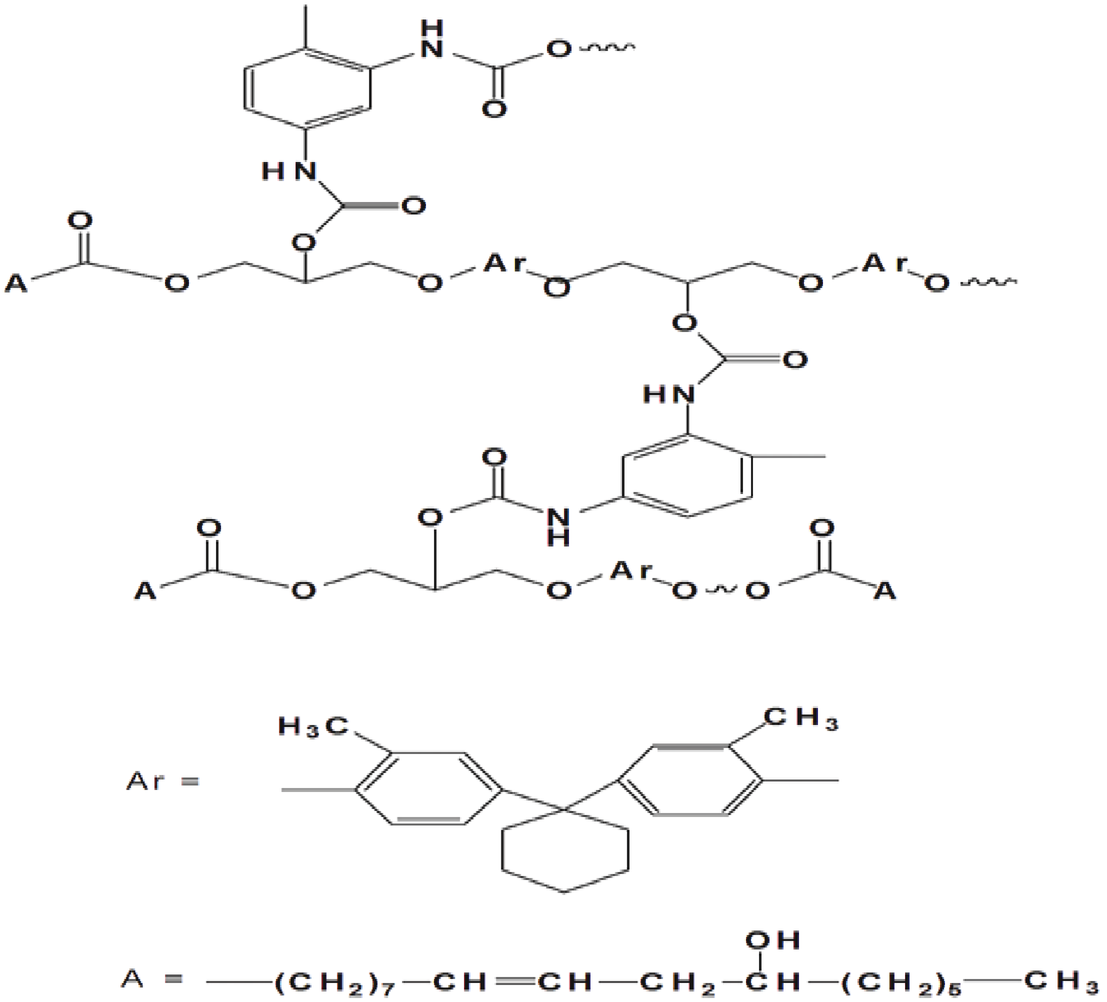
[A] Synthesis of polyurethane of EMC

Polyurethane resin of EMC was prepared by reacting 81.2g EMC in 250 ml MEK with 16.2 ml TDI in 30 ml MEK at room temperature. The reaction was stirred manually for about 25-30 min. The structure of polyurethane is as under:



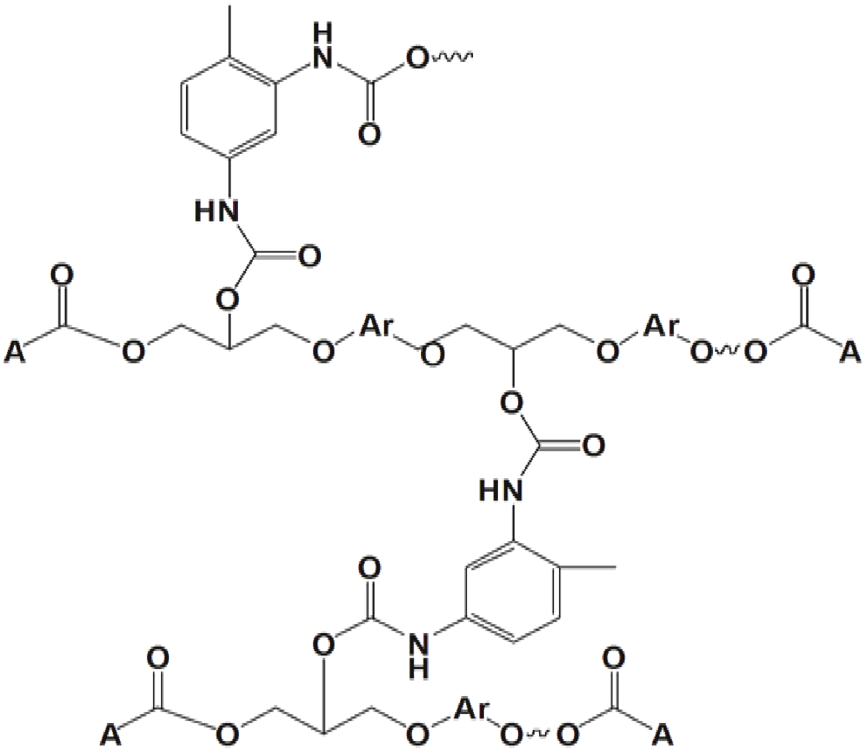
[B] Synthesis of polyurethanes of polyester polyols

Polyurethane resins of EMCRA, EMCLA, EMCOA, and EMCR were synthesized by reacting 0.5g EMCRA, EMCLA, EMCOA, EMCR in 5 ml methyl ethyl ketone (MEK) with 0.1ml TDI in 5 ml MEK at room temperature by manual stirring for about 15 min. The general structure of the polyurethane is as under



$$A = -(CH_2)_7-CH{=}CH-CH_2-\overset{OH}{\overset{|}{C}}H-(CH_2)_5-CH_3$$

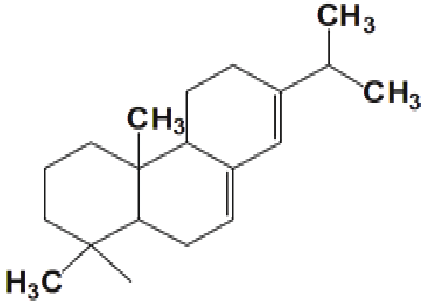
EMCRAT



EMCLAT A= $-(CH_2)_7-CH{=}CH-CH_2-CH{=}CH-(CH_2)_4-CH_3$

EMCOAT A= $-(CH_2)_7-CH{=}CH-(CH_2)_7-CH_3$

EMCRT A=



CHAPTER-3

ANALYSES OF MONOMERS AND RESINS

This chapter of the thesis describes characterization of monomers and resins. It is further subdivided into three sections.

3.1 Spectral analysis

This section describes IR, NMR and Mass spectral characterization of the monomers, cured and uncured resins, epoxy acrylate, polyester polyols and their polyurethanes.

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 for “below”).

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

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].

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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, Aromatic polysulphonates: Preparation and properties J. Polym. Sci. Part A-2, 1051-1056, (1964).

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

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

The IR spectra (KBr pellets) of all samples were scanned on a Shimadzu-8400 FT-IR spectrometer over the frequency range from 4000-400 cm^{-1}. The NMR spectra of all samples were scanned on a Bruker AVANCE II (400MHz) spectrometer by using $CDCl_3$ as a solvent and TMS as an internal standard.

1,1’-Bis(3-methyl-4-hydroxyphenyl)4-methylcyclohexane(BMC)

IR spectrum of BMC is presented in Fig.3.1. The characteristic IR absorption frequencies (cm^{-1}) for BMC are 3536.6-3416.1 (OH str.), 2947.3 (C-H v_{as}), 2865.4(v_s) 1506.5 (C=C str.), 1450.5 (C=C str. and C-H def.), 1248 (C-O str.) besides other normal modes of vibrations.

^{1}HNMR (CDCl$_3$) spectrum of BMC is presented in Fig.3.2 .The observed chemical shifts (ppm) and types of protons are assigned as follows: 0.830-0.814 [d, 3He], 1.169 - 1.102 and 1.902 - 1.827 [m, β-CH$_2$-], 2.178 - 2.169 and 2.222 [d, α-CH$_2$-], 6.613 - 6.592 [d,1 Ar H], 6.724 - 6.701 [t, 1 Ar H], 6.864 - 6.836 [q,1 Ar H], 6.94 - 6.935 [d,1 Ar H], 7.066 - 7.047 [q, 2 Ar H]. Residual chloroform appeared at 7.257 ppm.

Mass spectrum of BMC is presented in Fig.3.3. Important mass fragments (m/e) are 310(M$^+$), 311(M^{+1}), 254 (M-C$_3$H$_6$), 253, 240, 227, 145, 121, 91 and 77. Possible structure of the fragments are shown in Scheme-I

Thus, IR, ^{1}HNMR and MS data confirmed the structure of BMC

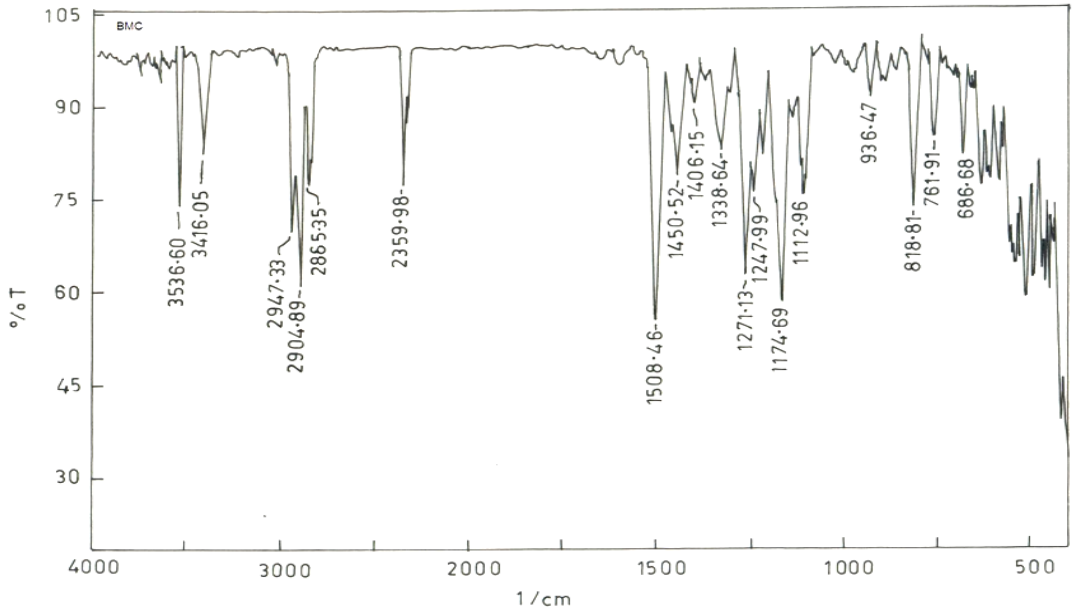
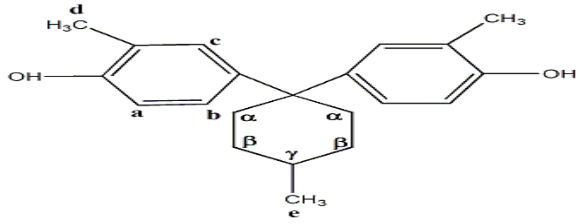


Fig. 3.1: IR KBr (spectrum)of BMC



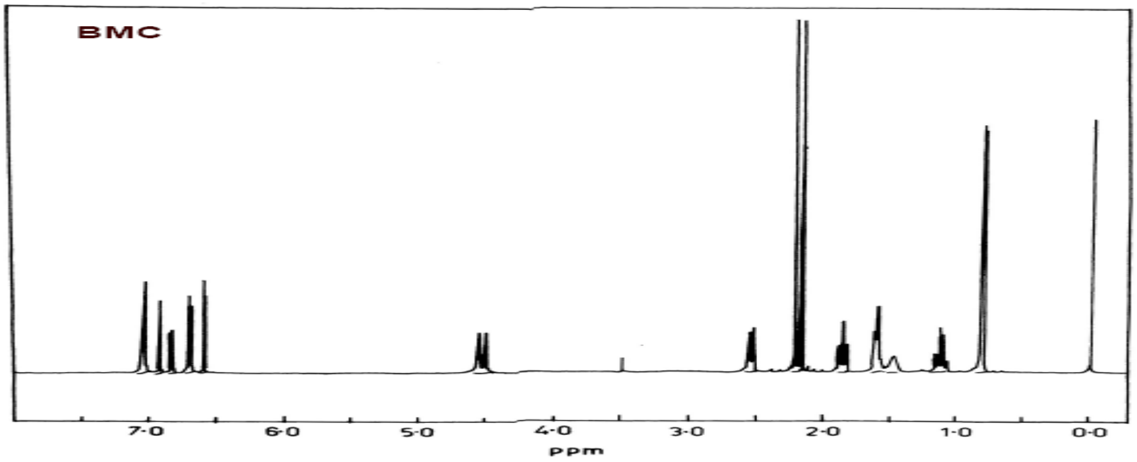


Fig.3.2: ^{1}HNMR (400 MHz) spectrum (CdCl3) of BMC

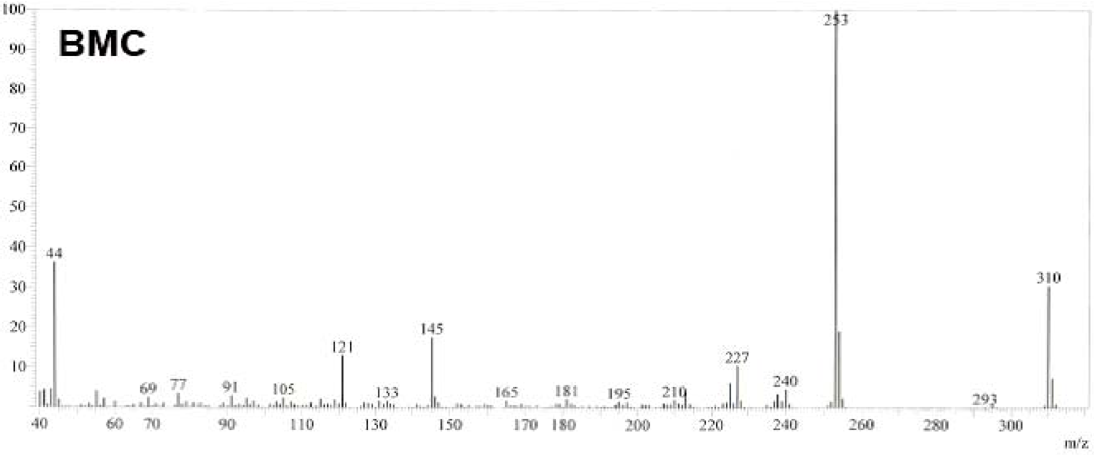
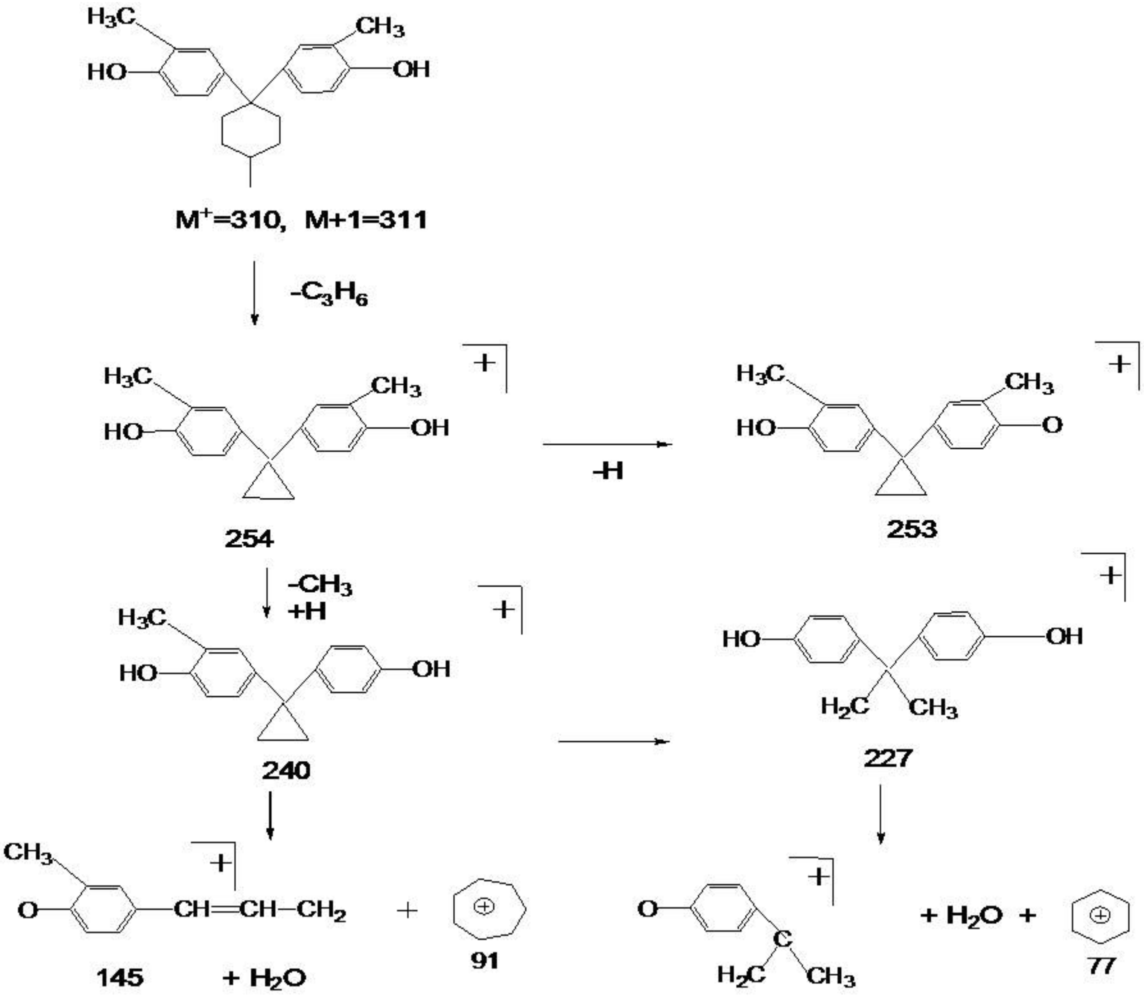


Fig.3.3: Mass spectrum of BMC



Scheme 1: MASS Fragments of BMC

Epoxy resin of 1,1'-bis(3-methyl-4-hydroxyphenyl)4-methyl cyclohexane

IR spectrum of EBMC is presented in Fig.3.4 The characteristic IR absorption frequencies (cm^{-1}) for EBMC are 3599-3563 (OH str.), 2928(C-H V_{as}), 2860.5(C-H V_s),3034(=C-H str.),1604.8 (C=C str.),1456.3 (C-H def.),1248 (aryl C-O-C str.),1132.9(C-O str),1035.8(alkyl C-O str.)

^{1}HNMR ($CDCl_3$) spectrum of EBMC is presented in Fig.3.5. The observed chemical shifts (ppm) and types of protons are assigned as follows: 0.893-0.81 [q, He], 1.157-1.068 & 1.90-1.837 [m, β-CH_2-], 1.621 – 1.263[m, γ-CH-], 1.621-1.588 [d, Hd], 2.213-2.094[m, α-CH_2-], 2.896 – 2.544 [m, CH-OH], 4.203-3.879 [m, - OCH_2-], 4.452-4.4238 [s, CH-OH], 6.788 – 6.616[m, Ar Ha],6.970-6.887 [m, Ar Hb], 7.138-7.099 [m, Ar Hc]. Residual chloroform appeared at 7.246 ppm.

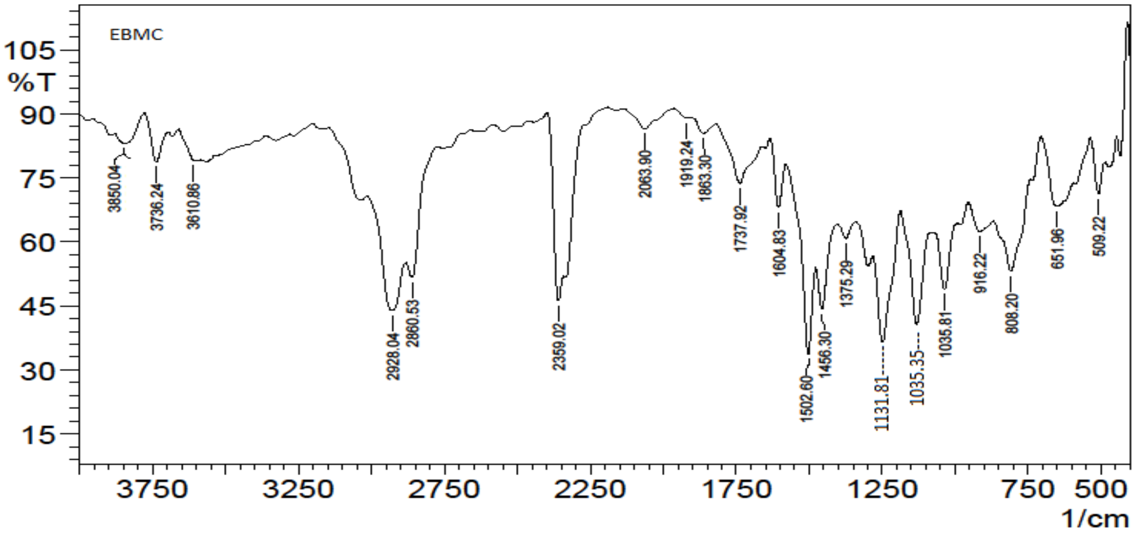
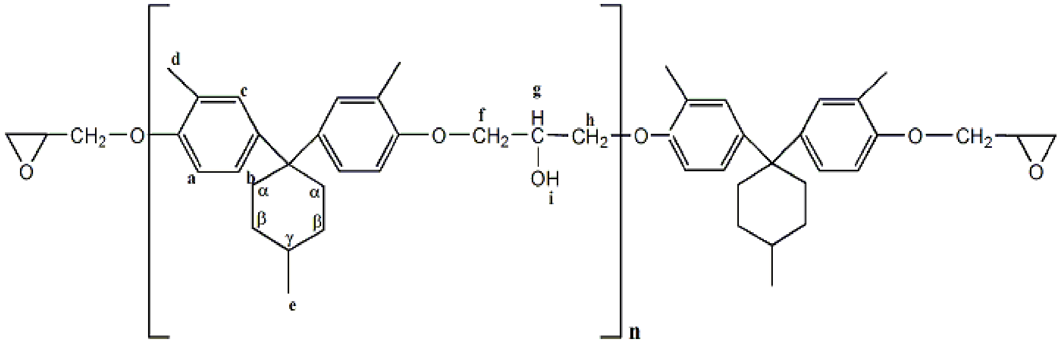


Fig.3.4 IR (KBR) spectrum of EBMC



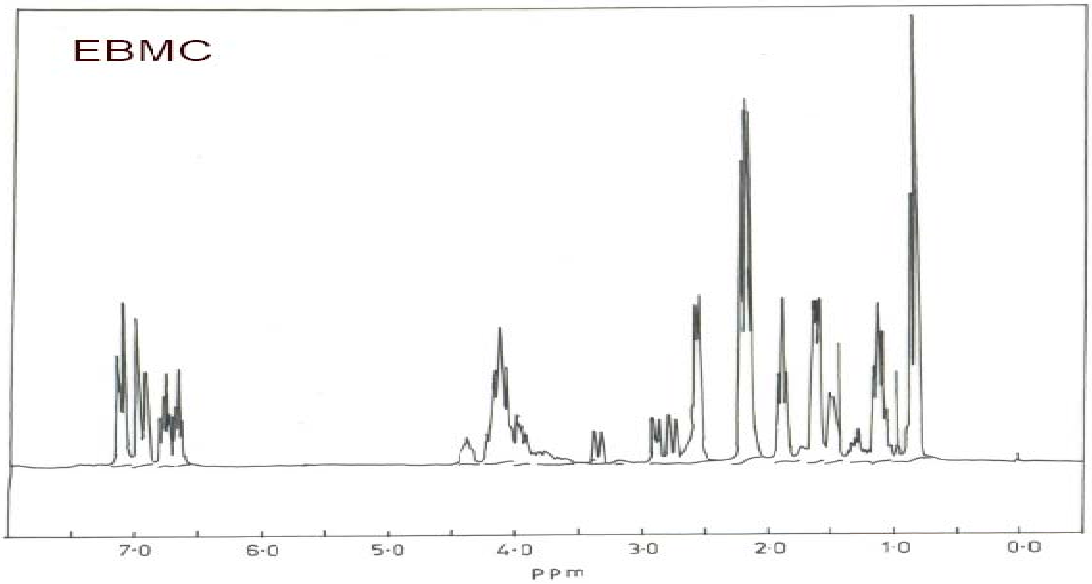


Fig.3.5 NMR spectrum of EBMC

Epoxyacrylate

IR spectrum of EMCA is presented in Fig. 3.6. The characteristic IR frequencies (cm^{-1}) for EMCA are 3489.3 OH str., 1722.5 C=O str. (ester), 1404.2 C-H ipd (-CH=$\underline{CH_2}$), 1290.4 C-H ipd (-$\underline{CH}$=CH_2), 991.4 C-H oopd(-CH=$\underline{CH_2}$), 943.2 C-H oopd (-$\underline{CH}$=CH_2), 1249.9 aryl C-O-C str. and 1045.5 alkyl C-O str. Thus, IR spectral data confirmed the formation of EMCA

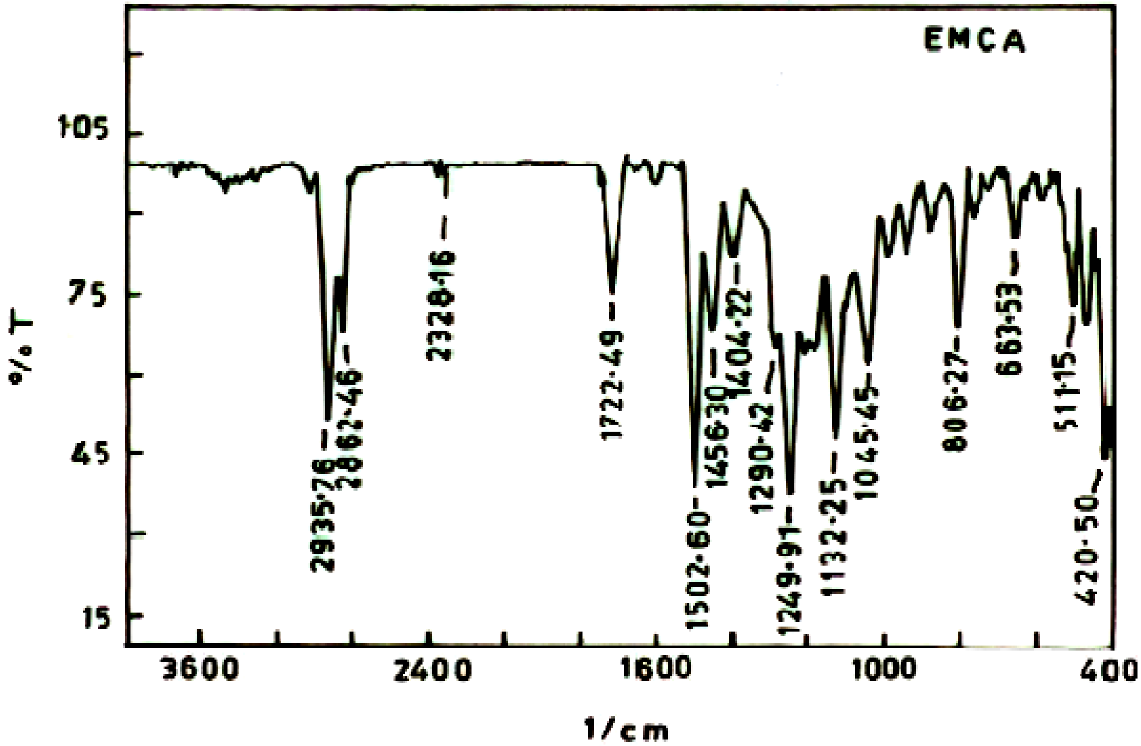


Fig.3.6 IR (KBr) spectrum of EMCA

Triethyl amine cured epoxy resins

IR spectra of EMCT-5 and EMCT-20 are presented in Figs.3.7 and 3.8. The characteristic IR frequencies (cm^{-1}) for EMCT-5 and EMCT-20 are 3254-3474 OH str., 1244-1245 aryl C-O-C str. 1040-1049 C-O-C alkyl str. and 1134-1136 C-O str. and OH def. besides normal modes of aliphatic, alicyclic and aromatic groups. Thus, IR spectral data confirmed the formation of EMCT-5 and EMCT-20.

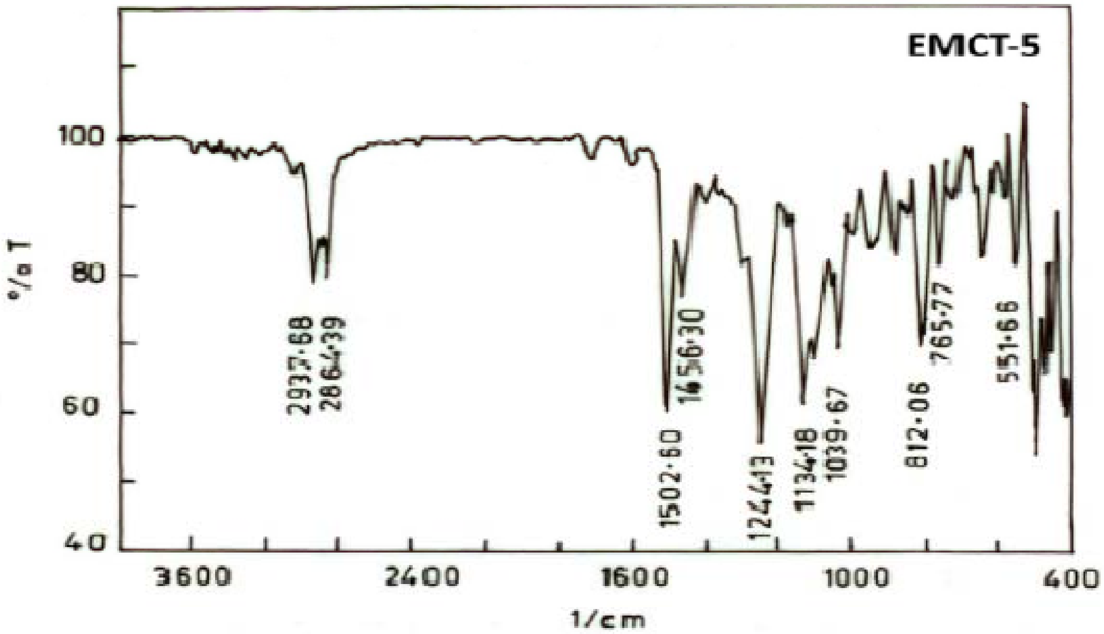


Fig.3.7 IR (KBR) spectrum of EMCT-5

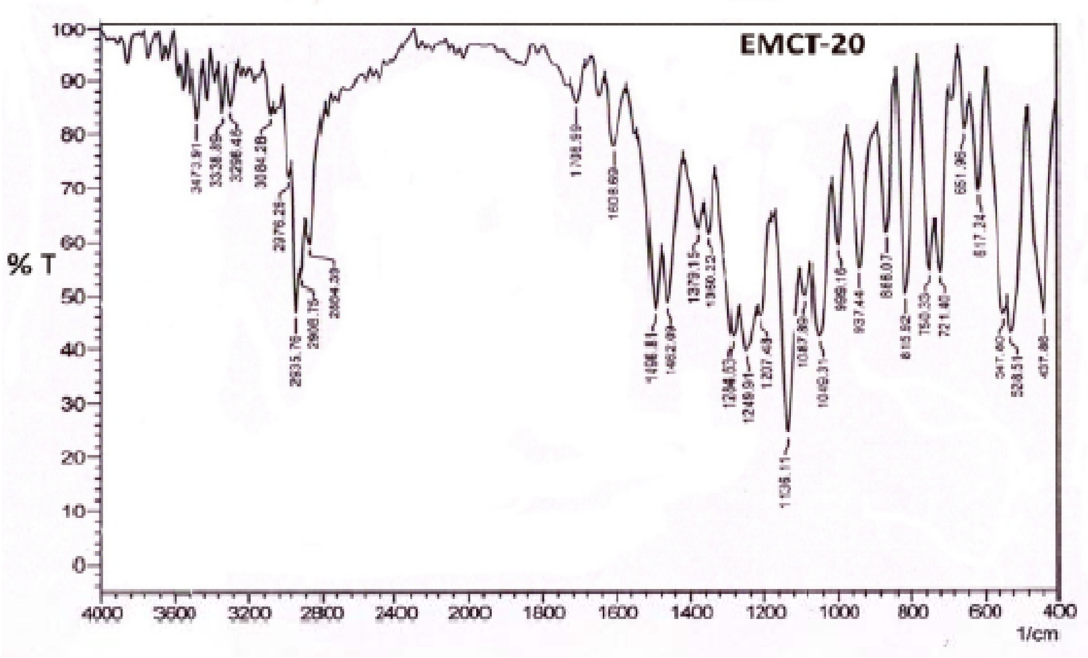


Fig.3.8 IR (KBR) spectrum of EMCT-20

Epoxy polyester polyols

IR spectra of EMCRA, EMCLA, EMCOA and EMCR are presented in Figs.3.9-3.12, respectively. The characteristic IR absorption frequencies (cm^{-1}) are 3379-3239 OH str., 1740-1726 C=O str. (ester), 1248-1244 aryl C-O-C str. and 1045-1040 C-OH def. besides normal modes of aliphatic, alicyclic and aromatic groups. Thus, IR spectral data confirmed formation of epoxy polyester polyols

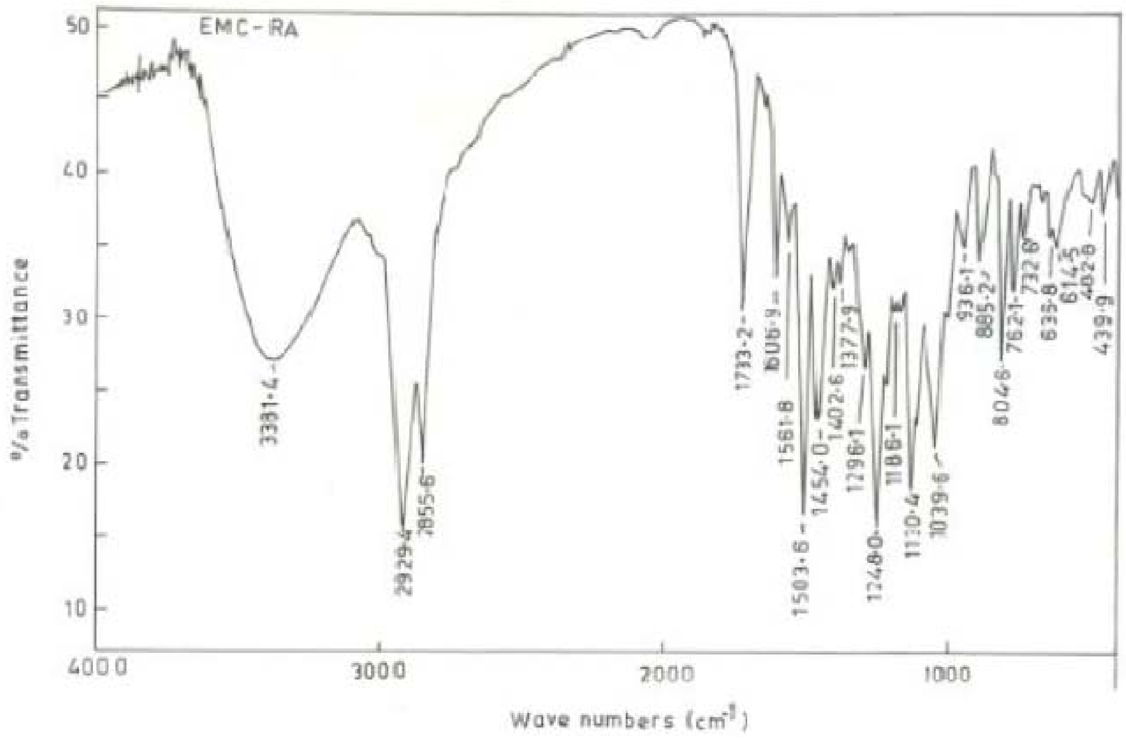


Fig.3.9 IR (KBR) spectrum of EMCRA

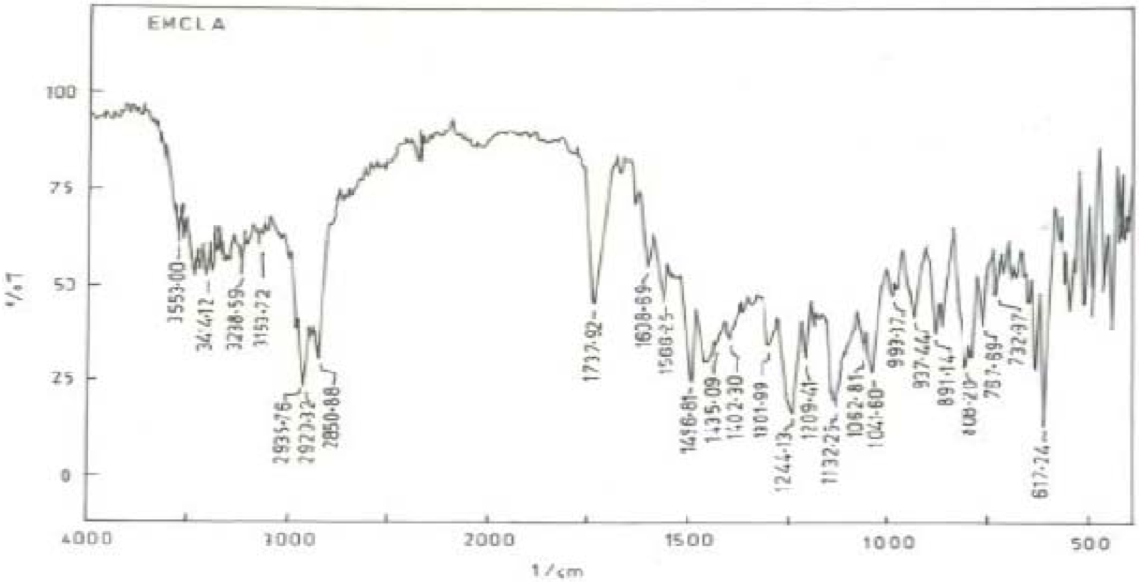


Fig.3.10 IR (KBR) spectrum of EMCLA

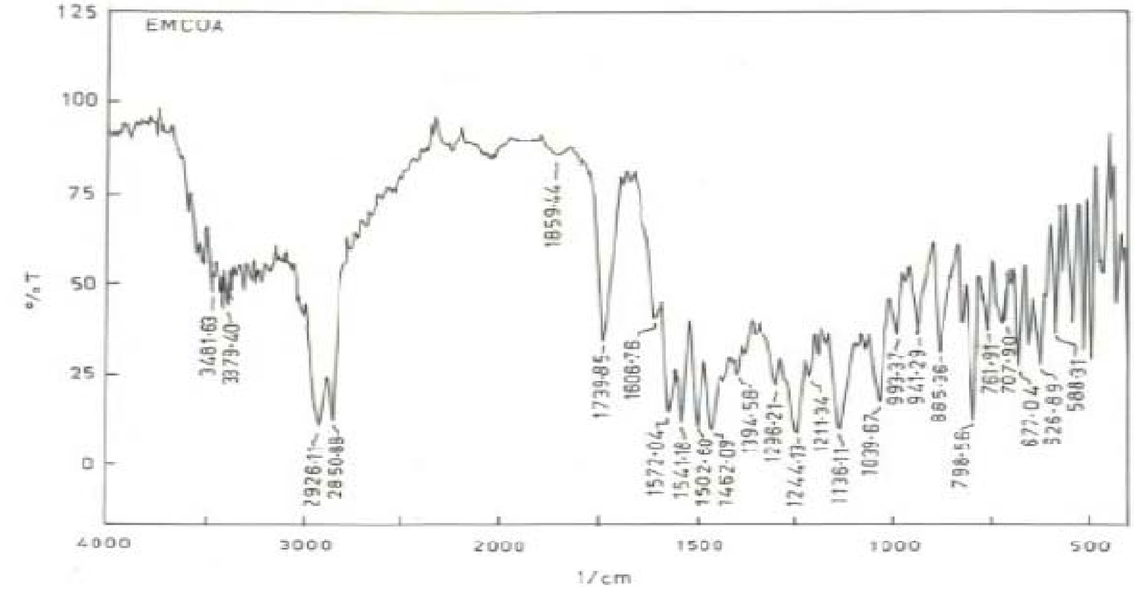


Fig.3.11 IR (KBR) spectrum of EMCOA

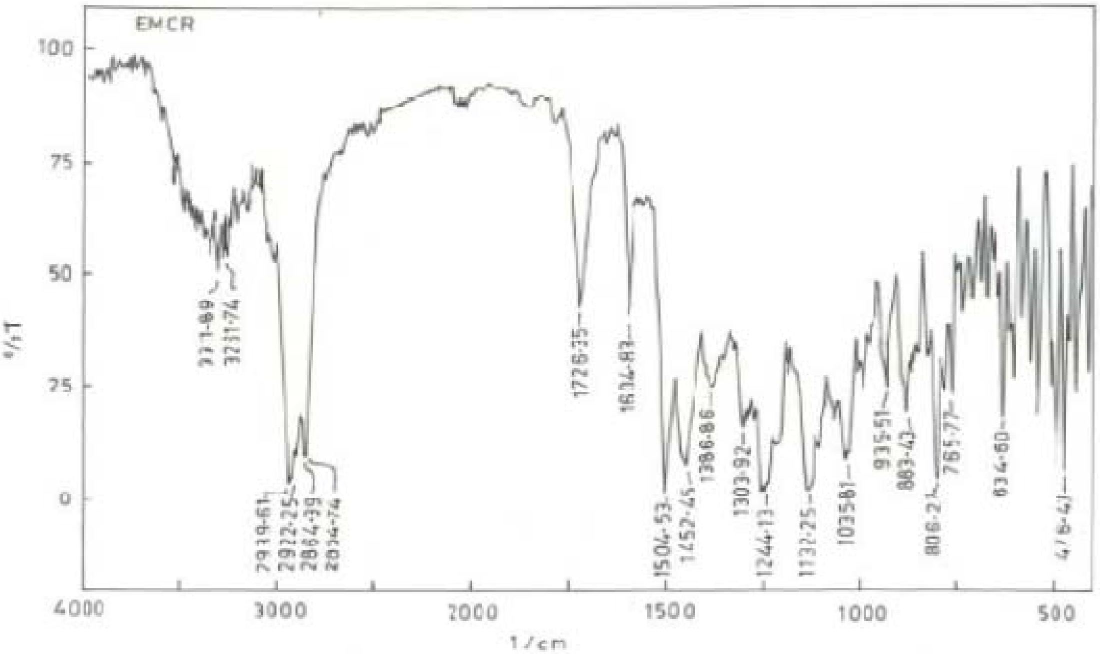


Fig.3.12 IR (KBR) spectrum of EMCR

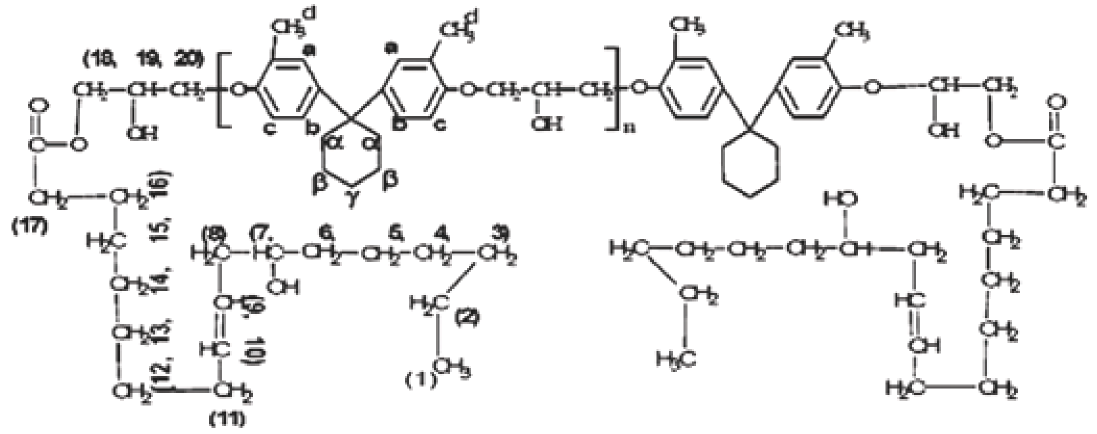
^{1}HNMR ($CDCl_3$) spectra of EMCRA, EMCLA, EMCOA and EMCR are presented in Figs.3.13 - 3.16, respectively. The observed chemical shifts (ppm) and types of protons are assigned as follows:

For EMCRA: 0.856-0.844[t, H(1)], 1.620-1.295[m, H(2-6,12-16, β + γ-CH_2)], 2.344-2.001[m, H(8, 11, 17, d, α-CH_2)], 3.1 and 2.8(s.-OH), 3.597-3.530[m, H(7)], 4.174-3.724[m, H(19-23)], 4.358-4.346[d, H(18)], 6.3-5.3[m, H(9, 10)], 6.727-6.706[d, ArH(c), J=8.4] and 7.021-6.996[d, ArH(a,b), J= 10].

For EMCLA: 0.886-0.873[t, H(1)], 1.611-1.150[m, H(2-4, 12-16, β + γ-CH_2)], 2.336-2.015[m, H(5, 8, 11, 17, d, α-CH_2)], 2.768(s.-OH), 4.096-3.463[m, H(19-23)], 4.359[s, H(18)], 5.336-5.324[m, H(6, 7, 9, 10)], 6.724-6.705[d, ArH(c), J= 7.6] and 7.016-7.002[d, ArH(a, b), J= 5.6].

For EMCOA: 0.890-0.857[t, H(1)], 1.329-1.133[m, H(2-7, 12-16], 1.502[s, β + γ-CH_2)], 2.150-1.988[m, H(8, 11, 17, d, α-CH_2)], 2.582-2.574(t.-OH), 4.105-3.241[m, H(19-23)], 4.261-4.249[d, H(18)], 5.320- 5.297[t, H(9,10)], 6.741-6.721[d, ArH(c), J=8] and 7.005-6.981[d, ArH(a,b), J= 9.6].

For EMCR: 1.273-1.155[m, H(1, 6, 10)], 1.514-1.466[d, H(4, 7, 8, β + γ-CH_2)], 1.764 [s, H(9)], 2.172-2.092[d, H(2, 3 5, 7, 8, d, α-CH_2], 4.095-3.967[d, H(16-20)], 4.358[s, H(15)], 6.704[s, ArH(c)] and 7.017[s, ArH(a,b)]. Thus, IR and ^{1}HNMR spectral data supported the structure of the polyester polyols.



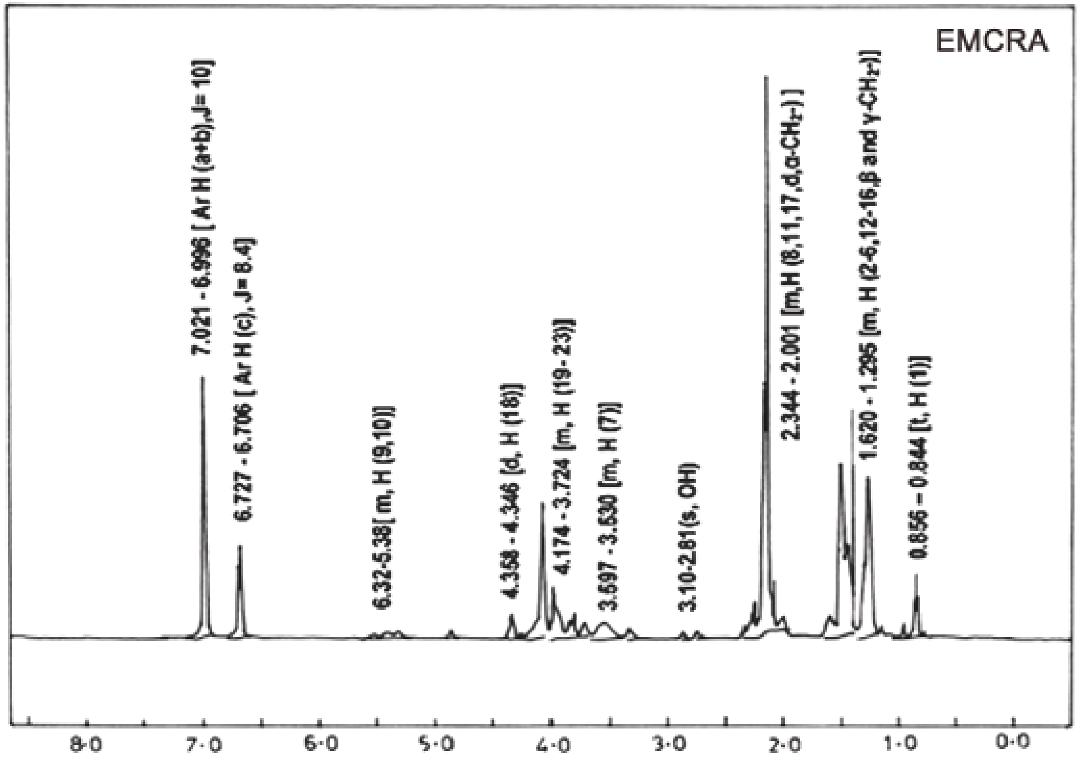
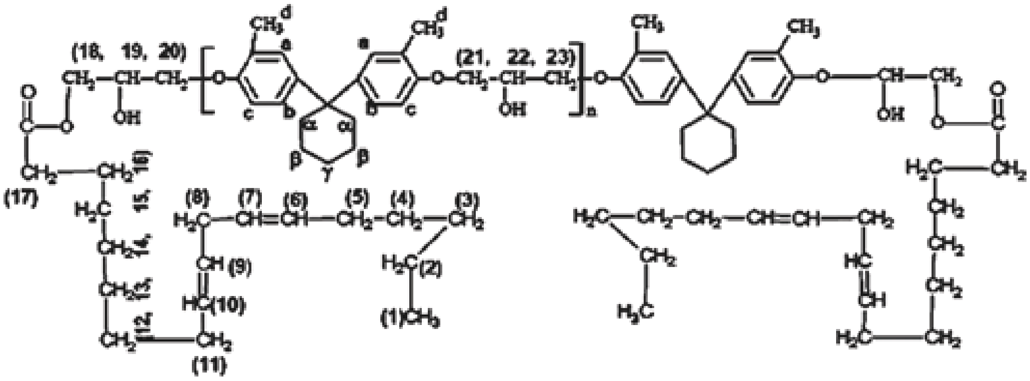


Fig. 3.13 NMR spectrum of EMCRA



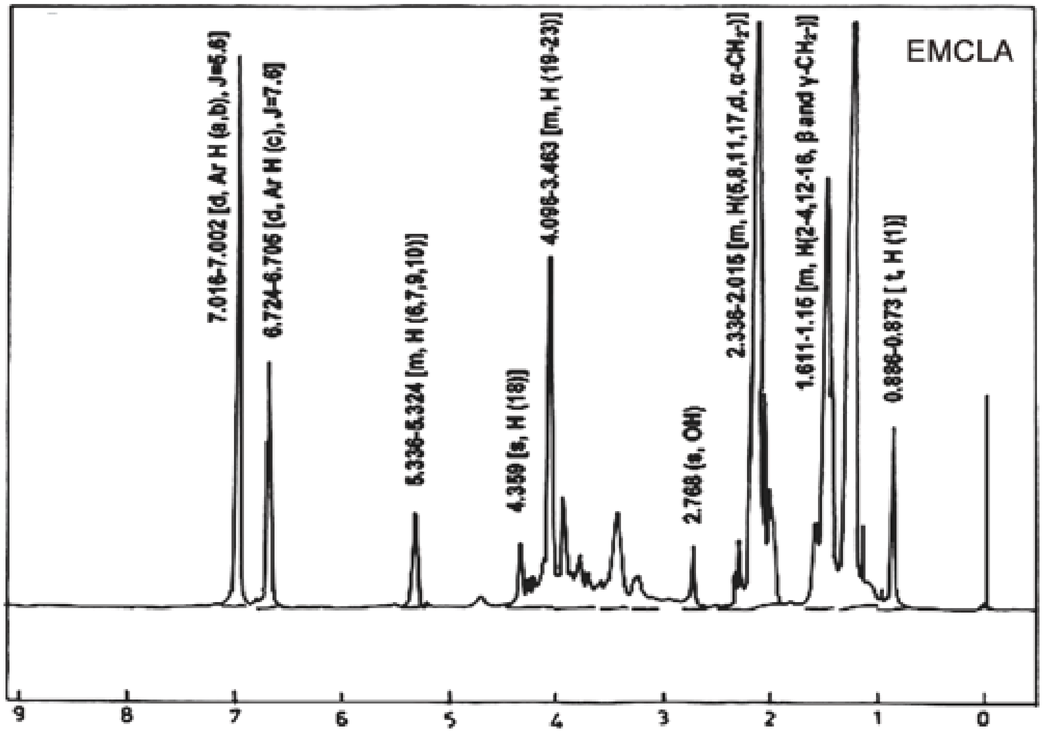
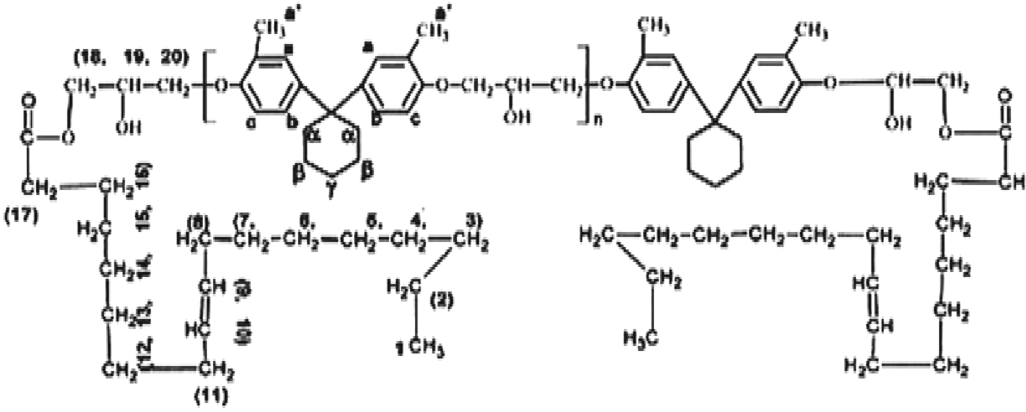
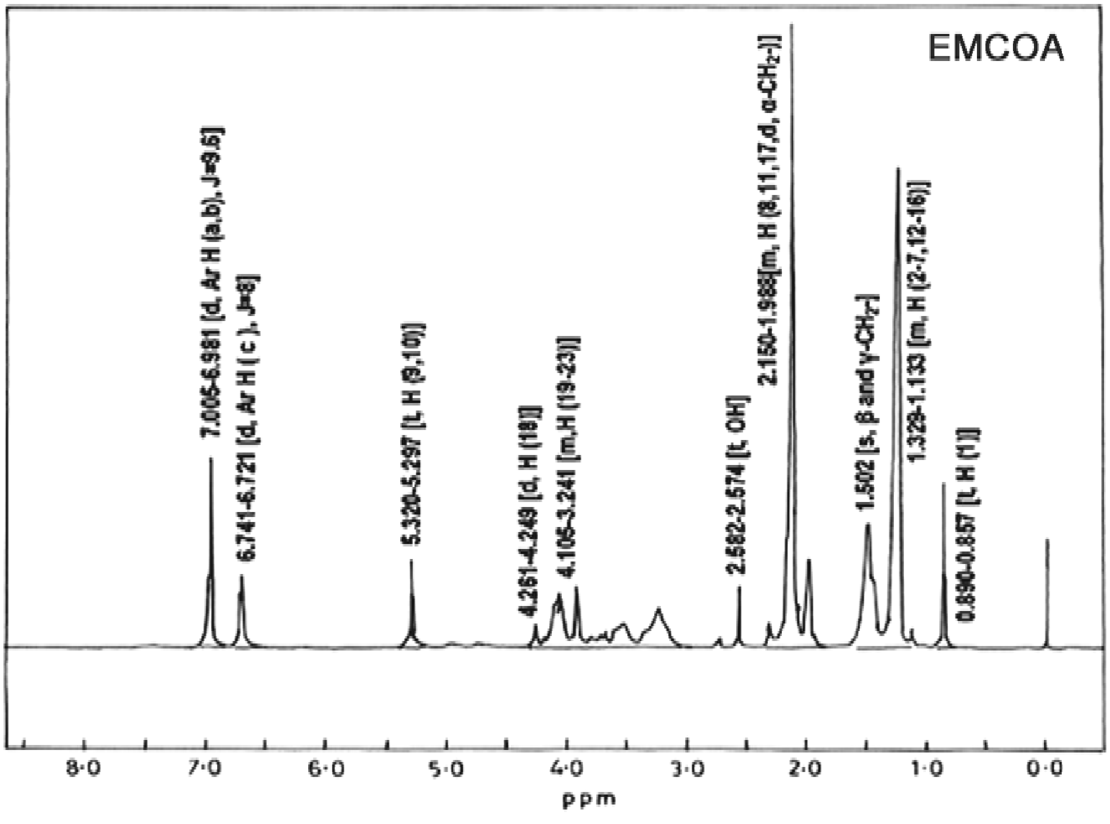


Fig. 3.14 NMR spectrum of EMCLA





Flig. 3.15 NMR sprctrum of EMCOA

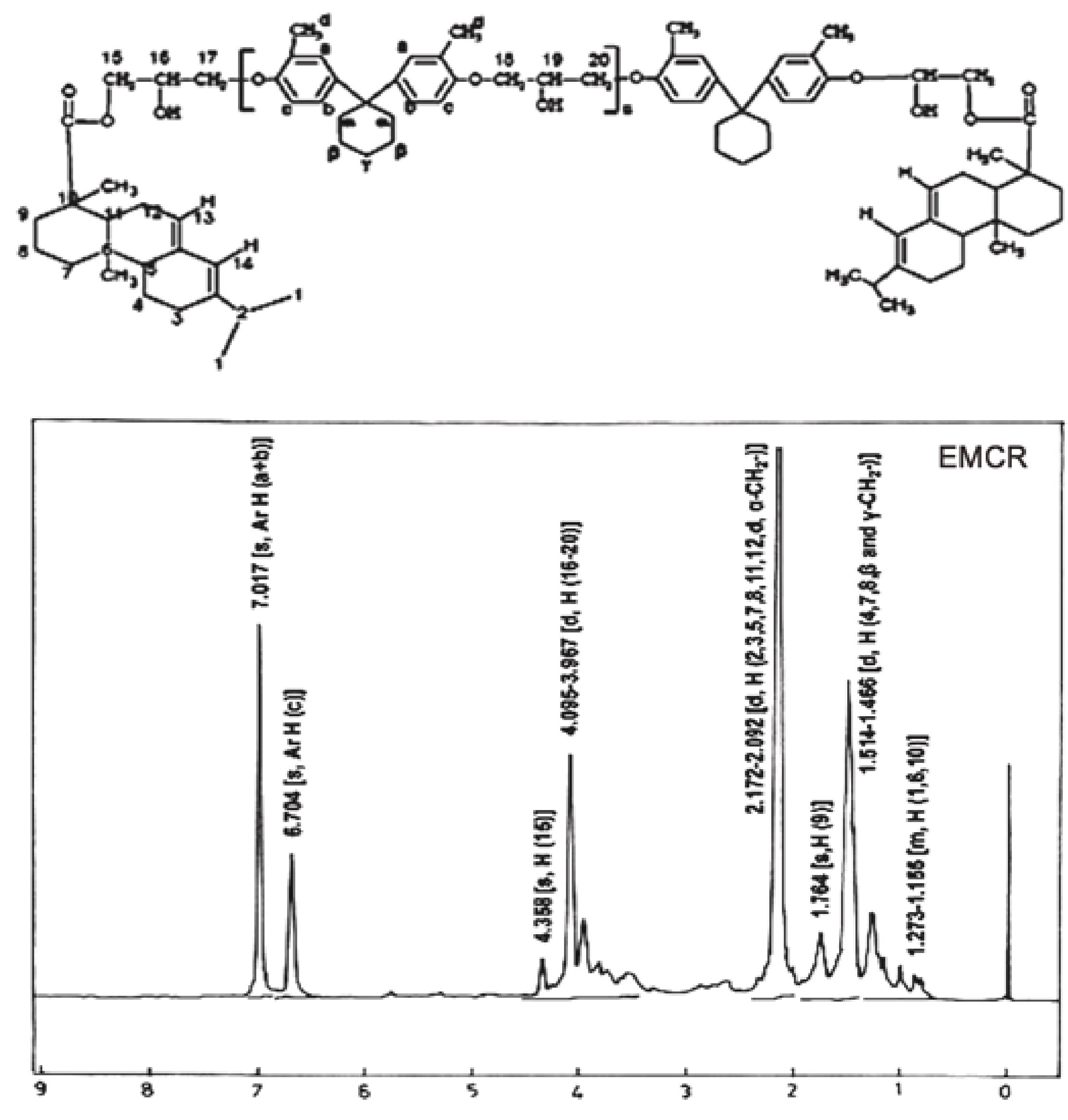


Fig. 3.16 NMR sprectrum of EMCR

Epoxy-Isophalate/terephalate

IR spectra of EMCIP and EMCTP are presented in Figs.3.17and 3.18, respectively. The characteristic IR absorption frequencies (cm^{-1}) are 3439-3354 OH str., 1726-1715 C=O str. (ester), 1250-1244 aryl C-O-C str. and 1040-1036 alkyl C-O str. and 1130-1128 C-O str. and OH def. besides normal modes of aliphatic, alicyclic and aromatic groups. Thus, IR spectral data confirmed polyester formation.

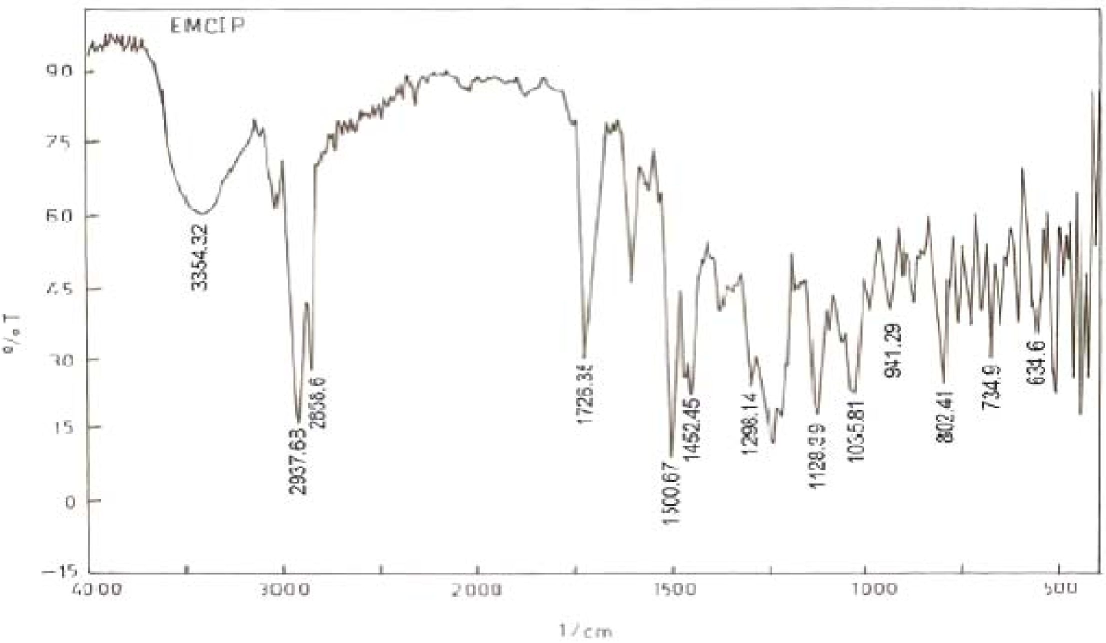


Fig.3.17IR (KBR) spectrum of EMCIP

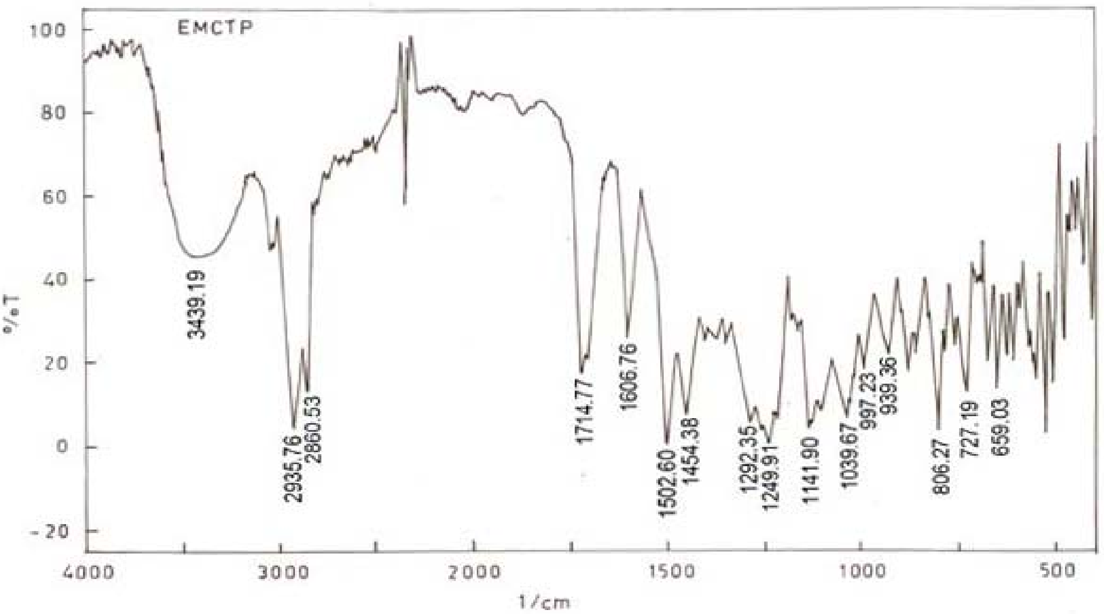
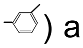


Fig.3.18 IR (KBR) spectrum of EMCTP

^{1}HNMR($CDCl_3$) spectra of EMCIP and EMCTP are presented in Figs.3.19 and 3.20, respectively. The observed chemical shifts (ppm) and types of protons are assigned as follows: For EMCIP: 1.508-1.426 (d, β+γ-CH_2-), 2.174-2.158 (d, α -CH_2- +-CH_3), 2.955-2.821(m, $\underline{\text{CH}}$-OH), 4.090-3.854(m, -OCH_2-), 4.349-4.090(d, -CH-$\underline{\text{OH}}$), 6.700 [s, ArH(a)], 7.013[s, ArH(b+c)], 8.211-8.053(m, ) and 8.737-8.632(d, ). For EMCTP: 1.508-1.426 (d, β+γ-CH_2-), 2.173-2.158 (d, α -CH_2- +-CH_3), 2.955-2.800(m, $\underline{\text{CH}}$-OH), 4.089-3.763(m, -OCH_2-), 4.534-4.353(d,-CH-$\underline{\text{OH}}$), 6.701 [s, ArH(a)], 7.258[s, ArH(b+c)], 8.054-8.006(m, ). Residual chloroform is observed at about 7.258ppm. Thus, IR and NMR spectral data support the formation of EMCIP and EMCTP.

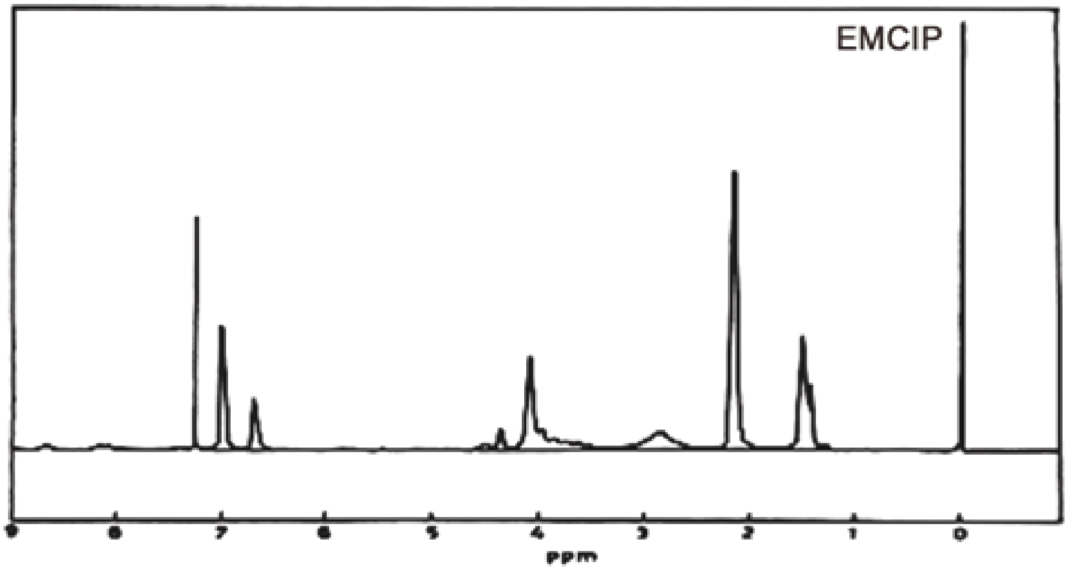


Fig. 3.19 NMR spectrum of EMCIP

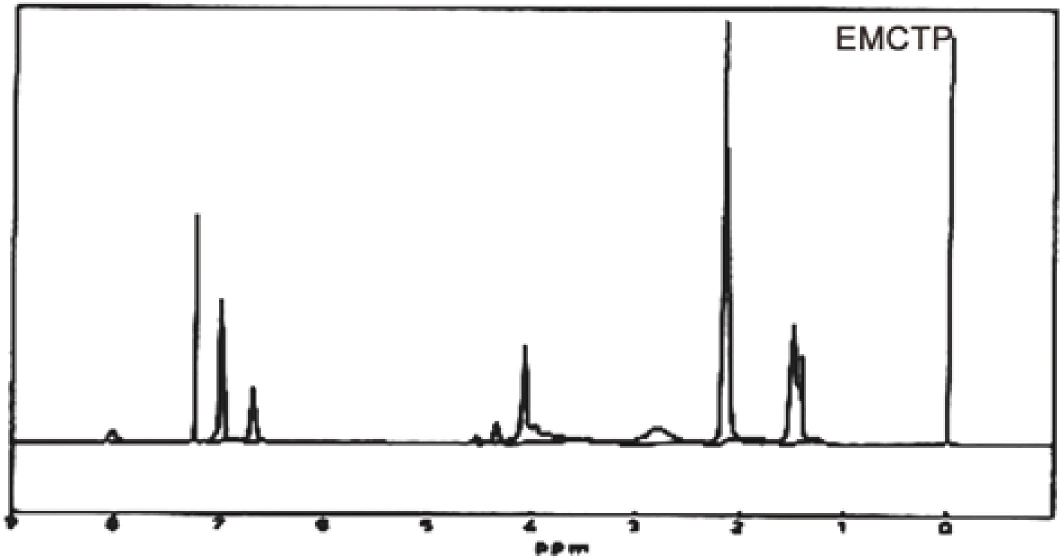


Fig. 3.20 NMR spectrum of EMCTP

3.2 Molecular weight and molecular weight distribution

Gel permeation chromatography is a separation technique, which is based on size exclusion principle, which separates analytes on the basis of their sizes and is also applied to polymers in particular. Size exclusion chromatography was first developed in 1955 by Lathe and Ruthven [6]. The gel permeation chromatography (GPC) was invented in 1964 by J. C. Moore (Dow Chemical Company)[7].

When characterizing polymers, it is important to consider the polydispersity index (PDI) as well the molecular weights. Polymers can be characterized by a variety of definitions for molecular weight including the number average molecular weight ($\overline{M}_n$), the weight average molecular weight ($\overline{M}_W$), the size average molecular weight ($\overline{M}_Z$), or the viscosity molecular weight ($\overline{M}_V$). GPC allows the determination of PDI as well as all types of molecular weights.

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6. G. H. Lathe and C. R. J. Ruthven, “The separation of substance and estimation of their relative molecular sizes by the use of columns of starch in water, Biochem. J., **62**, 665–674, (1956).
7. J. C. Moore, Gel permeation chromatography. I. A new method for molecular weight distribution of high polymers. J. Polym. Sci., ***2***, 835-843, (1964).

Gels are used as stationary phase for GPC. The pore size of a gel must be carefully controlled in order to be able to apply the gel to a given separation. Commercial gels like Sephadex, Bio-Gel (cross-linked polyacrylamide), agarose gel and Styragel are often used based on different separation requirements [8].

The most common eluents that dissolve polymers at room temperature are tetrahydrofuran (THF), o-dichlorobenzene and trichlorobenzene at 130–150 °C for crystalline polymers, m-cresol and o-chlorophenol at 90 °C for crystalline condensation polymers such as polyamides and polyesters. There are two types of pumps available for uniform delivery of relatively small liquid volumes for GPC: piston or peristaltic pumps. There are many detector types available and they can be divided into two main categories. The first is concentration sensitive detectors, which include UV absorption, differential refractometer (DRI) or refractive index (RI) detectors, infrared (IR) absorption and density detectors. Molecular weight sensitive detectors include low angle light scattering detectors and multi angle light scattering [9].

Advantages of GPC

As a separation technique, GPC has many advantages. First of all, it has a well-defined separation time due to the fact that there is a final elution volume for all unretained analytes. Additionally, GPC can provide narrow bands, although this aspect of GPC is more difficult for polymer samples that have broad ranges of molecular weights present. Finally, since the analytes do not interact chemically or physically with the column, there is a lower chance for analyte loss to occur. GPC provides a more convenient method of determining the molecular weights of polymers. In fact most samples can be thoroughly analyzed in an hour or less.[10].

Experimental

Molecular weights and molecular weight distribution of copolymers were determined by gel permeation chromatograph using Perkin Elmer GPC (series 200) using THF as a solvent and standard polystyrene mixed bed at 30^0C. Gel permeation chromatograms of epoxy and epoxy polyester polyols are presented in Figs.3.21 - 3.27. Molecular weights and molecular weight distribution data of the said compounds are summarized in Table-3.1 from which it is clear that chain extension resulted upon polyesterification of EMC with, ricinoleic, linoleic, oleic, rosin, isophtalic and terephthalic acids.

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8. D. Helmut, Gel Chromatography, Gel Filtration, Gel Permeation, Molecular Sieves: A Laboratory Handbook; Springer-Verlag, (1969).
9. J. M. G. Cowie, V. Arrighi, "*Polymers: Chemistry and Physics of Modern Materials*", 3rd ed. CRC Press, (2008).
10. Odian, "*Principles of Polymerization*", 3rd ed.; Wiley Interscience Publication, (1991)

Table-3.1: Molecular weight and molecular weight distribution data of EMC, EMCRA, EMCLA, EMCOA, EMCR, EMCIP, EMCTP

Sample Code	GPC data		
	$\overline{M_W}$	$\overline{M_n}$	$\overline{M_W}/\overline{M_n}$
EMC	3992	1929	2.1
EMCRA	2584	1121	2.304
EMCLA	2655	1878	1.413
EMCOA	1915	800	2.392
EMCR	4525	1780	2.542
EMCIP	4111	1997	2.095
EMCTP	4003	1960	2.043

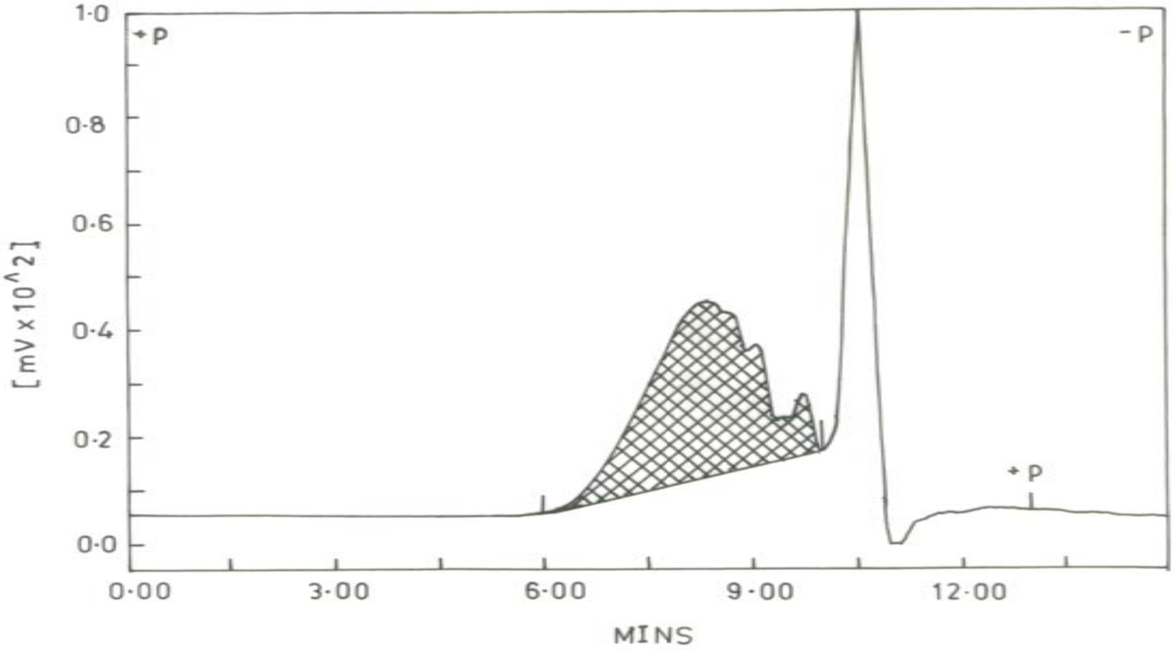


Fig. 3.21 Gel permeation chromatograph of EMC

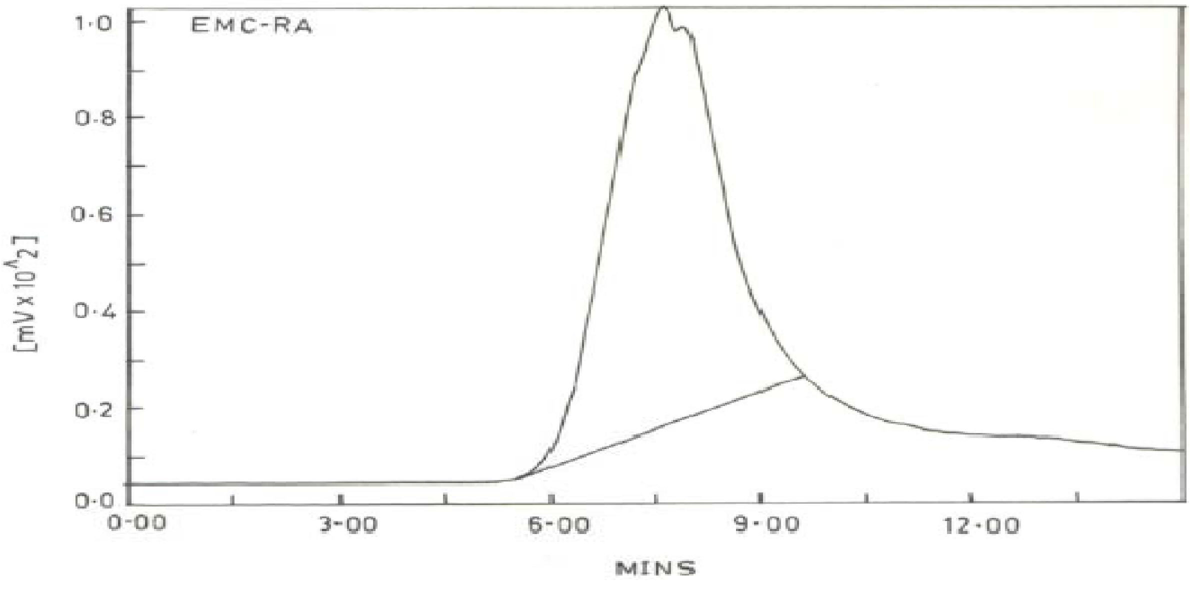


Fig. 3.22 Gel permeation chromatograph of EMCRA

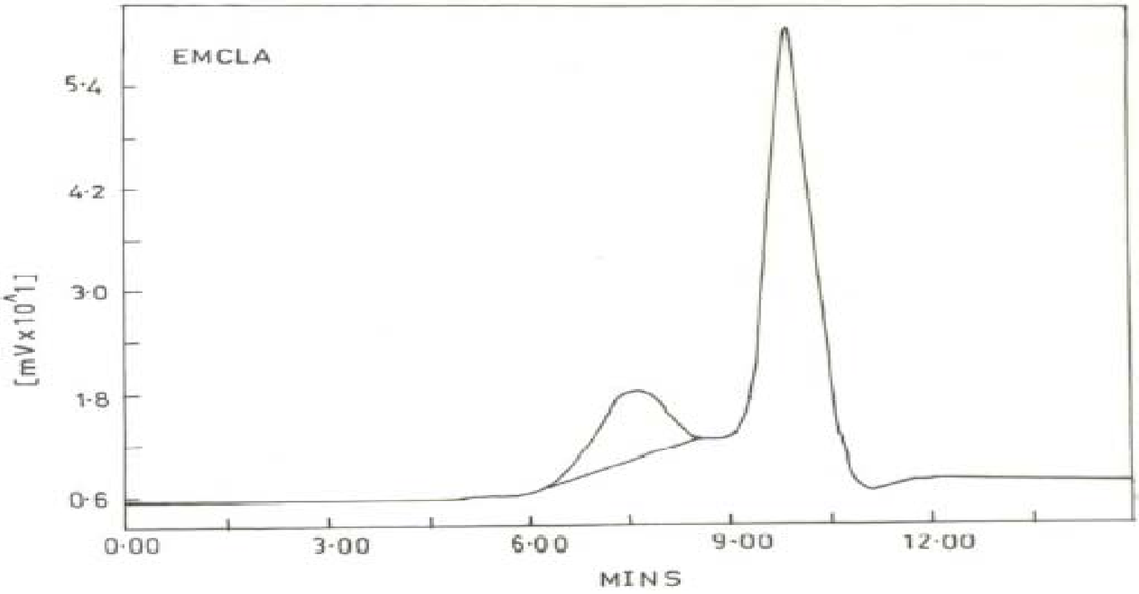


Fig. 3.23 Gel permeation chromatograph of EMCLA

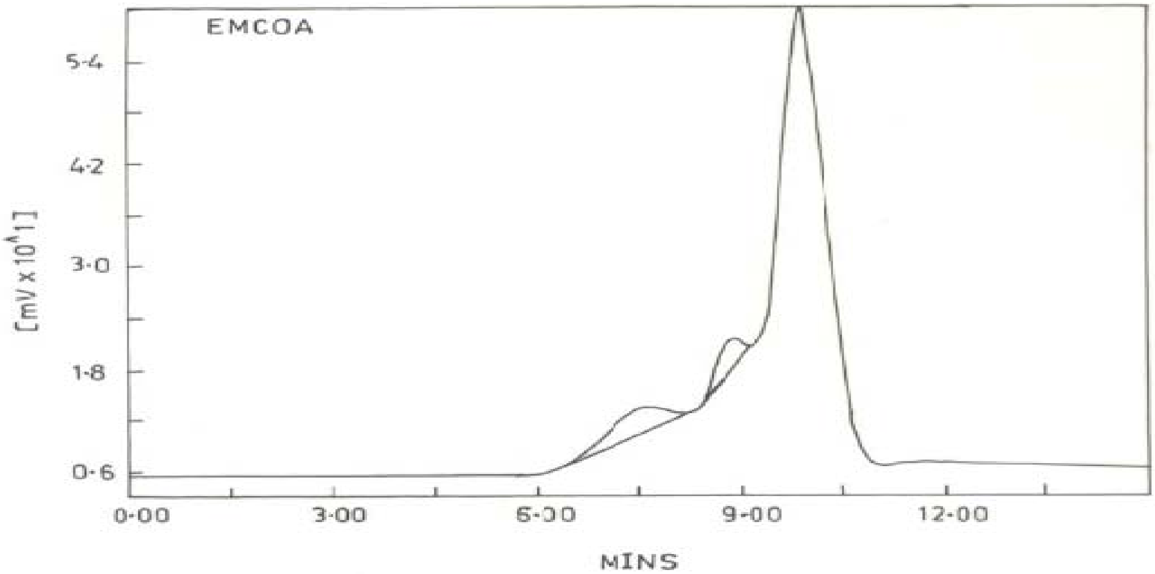


Fig. 3.24 Gel permeation chromatograph of EMCOA

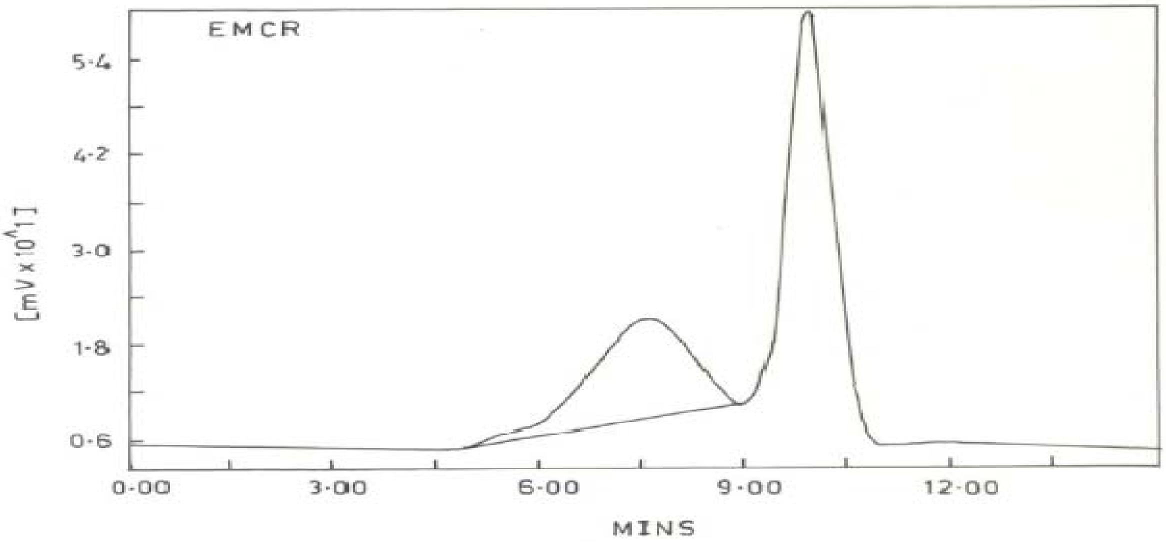


Fig. 3.25 Gel permeation chromatograph of EMCR

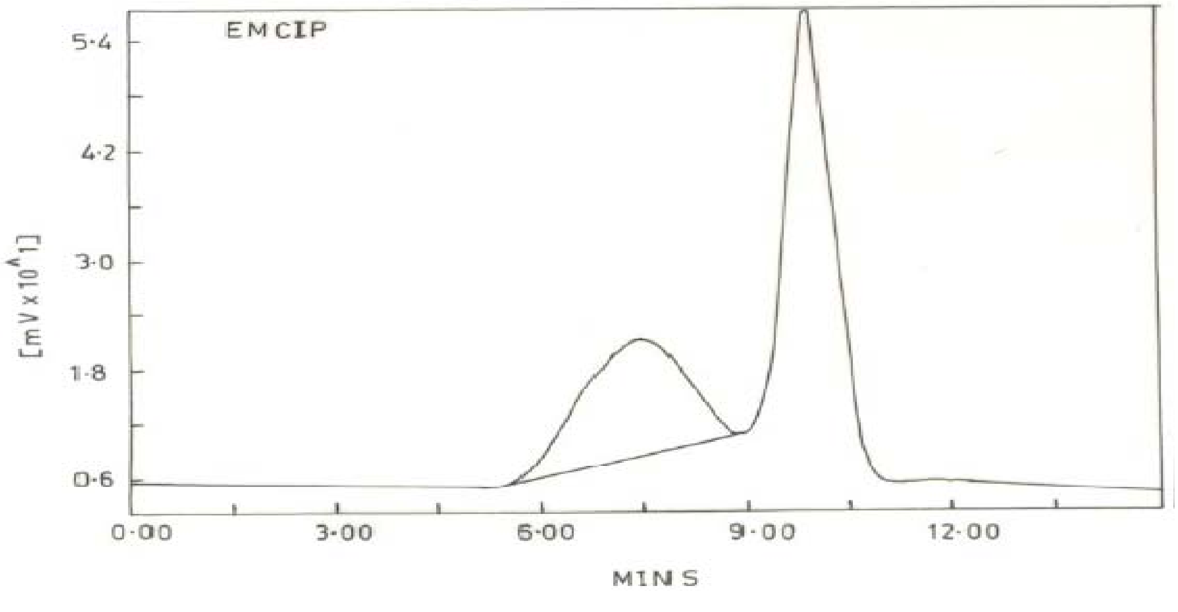


Fig. 3.26 Gel permeation chromatograph of EMCIP

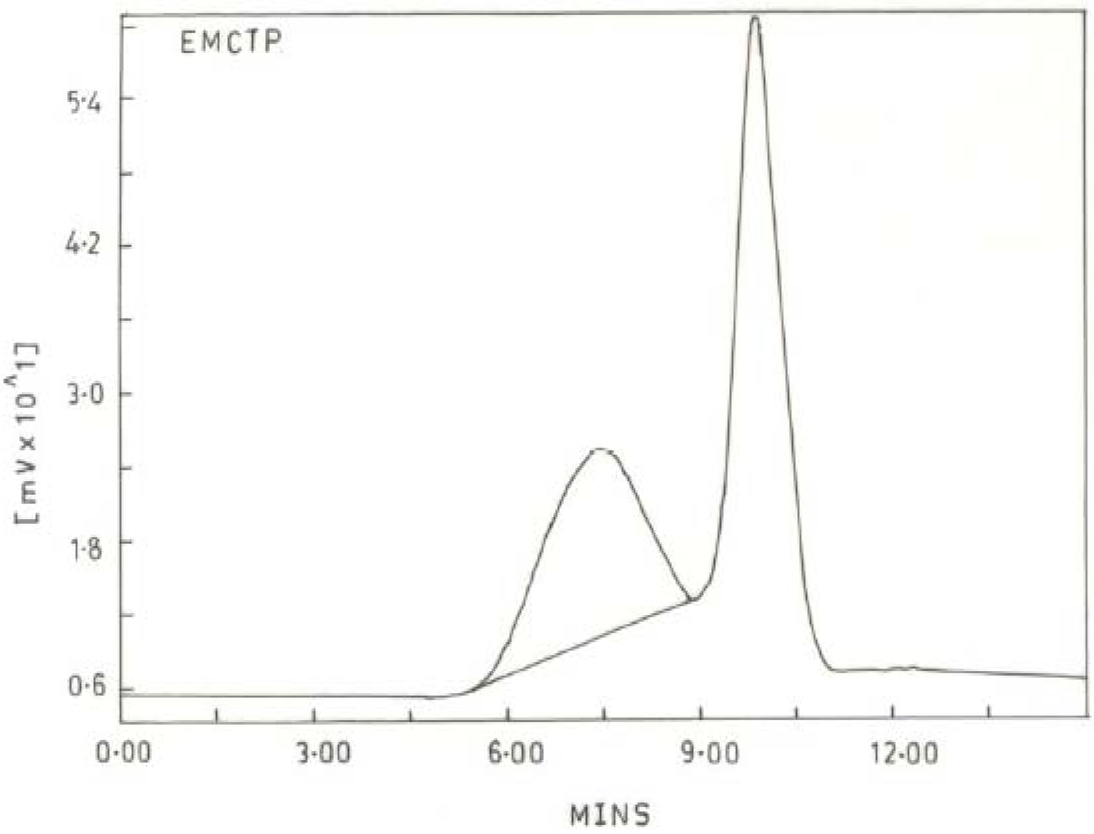


Fig. 3.27 Gel permeation chromatograph of EMCTP

3.3 Epoxy equivalent, hydroxyl and acid values

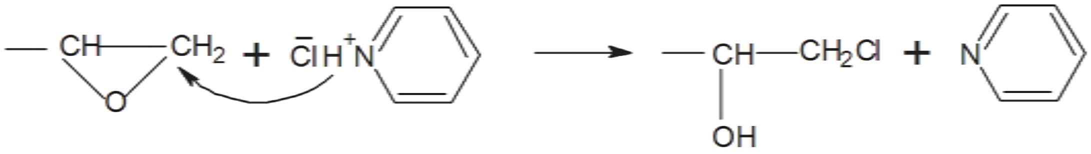
[A] Epoxy equivalent of epoxy resins

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

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

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

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



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

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 min., 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:

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

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

The number 0.016 is the miliequivalent weight of oxygen in grams. The epoxide equivalent of the resins under study was determined according to above mentioned method and mean of three measurements for EMC is 2000, 1538, 835, 2500 and for E-BMC 699

[B] Determination of acid values of the polyester polyols

Acid value is a measure of the free fatty acids content of oil and is expressed as the number of milligrams of potassium hydroxide required to neutralize the free acid in 1 gram of the sample. Acid value quantifies the reaction, which is in the beginning of the reaction, the acid value is high but as Acid values of polyester polyols were determined according to standard reported method [15].

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11. J. Bomstein; 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).

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.

Into a 250 ml stoppered flask, 1g EMCRA /EMCLA /EMCOA/EMCR was dissolved in 50 ml MEK and heated gently for some time. The solution was cooled and 10-15 drops of phenolphthalein was added as an indicator and titrated with standard 0.1 N alcoholic potassium hydroxide solution.

The procedure was repeated for blank titration under similar condition. The acid value of a given sample was determined according to following relationship.

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

Where N = Normality of KOH
A = Sample burette reading
B = Blank burette reading
W = Weight of sample in grams

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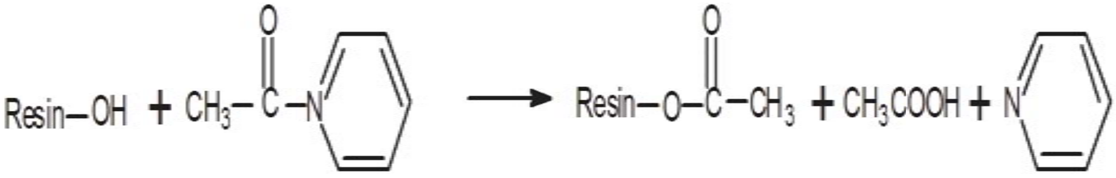
13. J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss “Organic analysis (J. Mitchell Jr., ed.)”, 1, 127, Interscience, New York, (1953).
14. R. E. Burge, Jr. and B. P. Geyer “Analytical chemistry of polymers” (G. M. Hline, ed.) Vol. XII/1, Interscience New York, (1959).

The average of three measurements of each of polyester polyols is reported in Table 3.2

[C] Determination of hydroxyl values of polyester polyols

Hydroxyl value is a measure of free hydroxyl groups present in the polyester polyols (epoxy esters) and it is expressed as number of milligrams of potassium hydroxide equivalent to the quantity of acetic acid that binds with 1 g of hydroxyl containing substances. The hydroxyl value gives information about the number of free hydroxyl group present in a material. The determination is carried out by acetylation with acetic anhydride in pyridine. Aldehyde and primary and secondary amines interfere with the determination and if present then phthalic anhydride is used in place of acetic anhydride.



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

Hydroxyl values of polyester polyols and epoxy esters were determined according to standard reported method. Into a 250 ml round bottomed flask equipped with a condenser and oil bath, was dissolved 1g EMCRA/EMCLA/EMCOA/EMCR in 25 ml of acetylating mixture of acetic anhydride and pydrine(1:7 v/v). The reaction mass was brought to reflux for 40-45 min, cooled to room temperature and 10 ml cold water was added slowly down to condenser and titrated with standard 1N alcoholic potassium hydroxide using 10-15 phenolphthalein as an indicator. Hydroxyl values were determined according to following relationship [15]:

$$\text{Hydroxyl value} = \frac{56.1 \times (B-A) \times N}{\text{Wt. of sample}} \quad \text{... 3.3}$$

Where N= Normality of alcoholic KOH,
B= Blank Reading
A= Sample burette reading
W= Wt of sample

The average of three measurements of each of polyester polyols is reported in Table3.2. From Table3.2 it is clear that 2h reaction time is sufficient to achieve desired acid values (0- 6.7 mg KOH/g of resins). Low acid values and high hydroxyl values of the resins confirmed almost conversion of epoxide groups into corresponding esters.

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15. ASTM-D-1639-Rev.90, “Standard Test Method for Acid Value of Organic Coating Material.

TABLE 3.2: Acid and hydroxyl values of epoxy polyester polyols

Time, H	Acid value, mg KOH/g				Hydroxyl Value,mg KOH/g			
	EMCRA	EMCLA	EMCOA	EMCR	EMCRA	EMCLA	EMCOA	EMCR
2	0	6.7	6.4	1.8	117	134	244	152
3	0	5.8	5.7	1.6	132	258	268	242
4	0	5.3	4.5	1.1	195	268	322	270
5	0	4.8	3.4	1.0	332	298	361	303
6	0	3.1	1.5	0.5	356	356	444	318

3.4 Spectral analyses of polyurethanes

IR spectra of EMCRAT, EMCLAT, EMCOAT and EMCRT are presented in Figs.3.28-3.31, respectively. The characteristic IR absorption frequencies (cm^{-1}) are. 1726.35-1735.99 (urethane str.), 1508.38-1510.31 C=C str. and 1219.05-1240.27 C-O-C str. besides normal modes of aliphatic, alicyclic and aromatic groups. Thus, IR spectral data confirmed formation of polyurethanes.

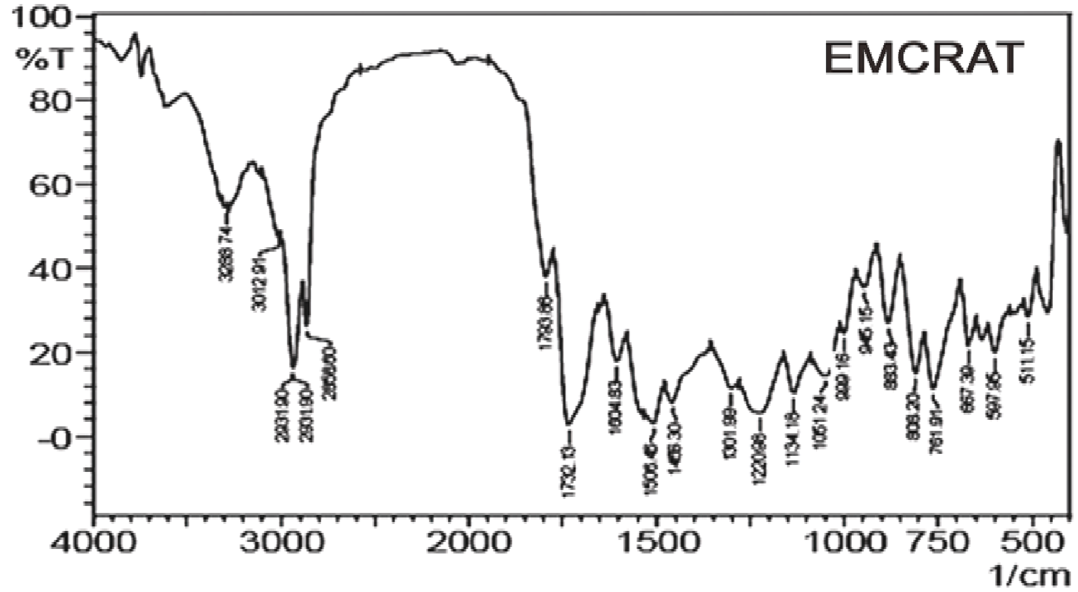

Fig.3.28 IR (KBr) spectrum of EMCRAT

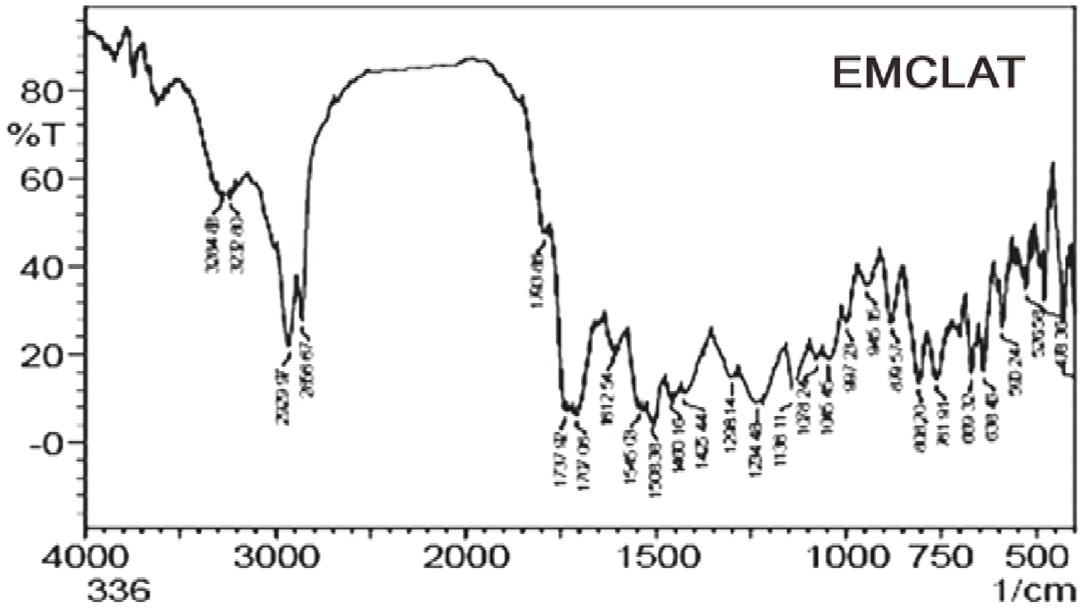

Fig.3.29 IR (KBr) spectrum of EMCLAT

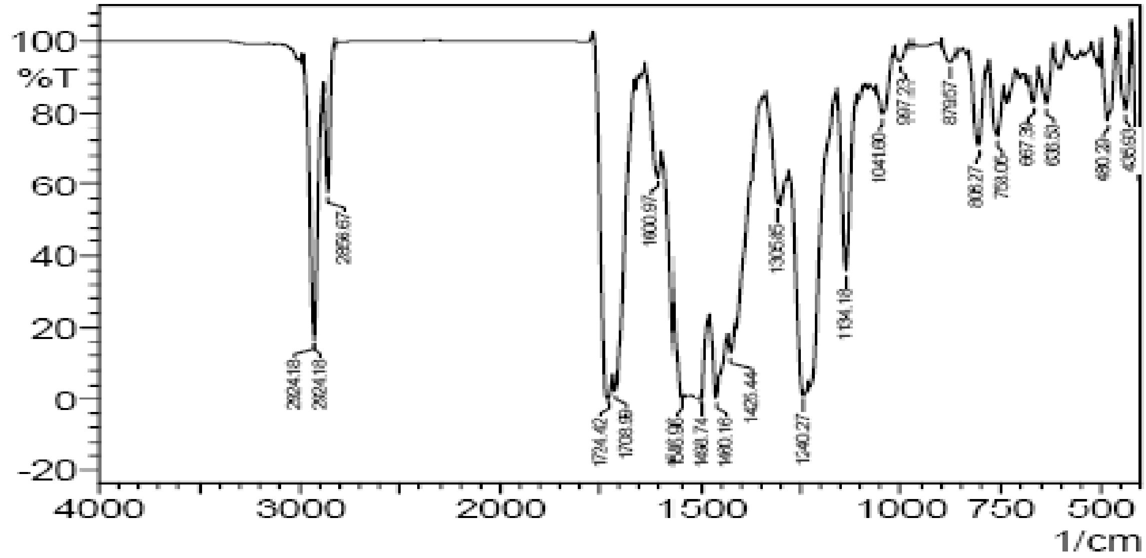

Fig.3.30 R (KBR) spectrum of EMCOAT

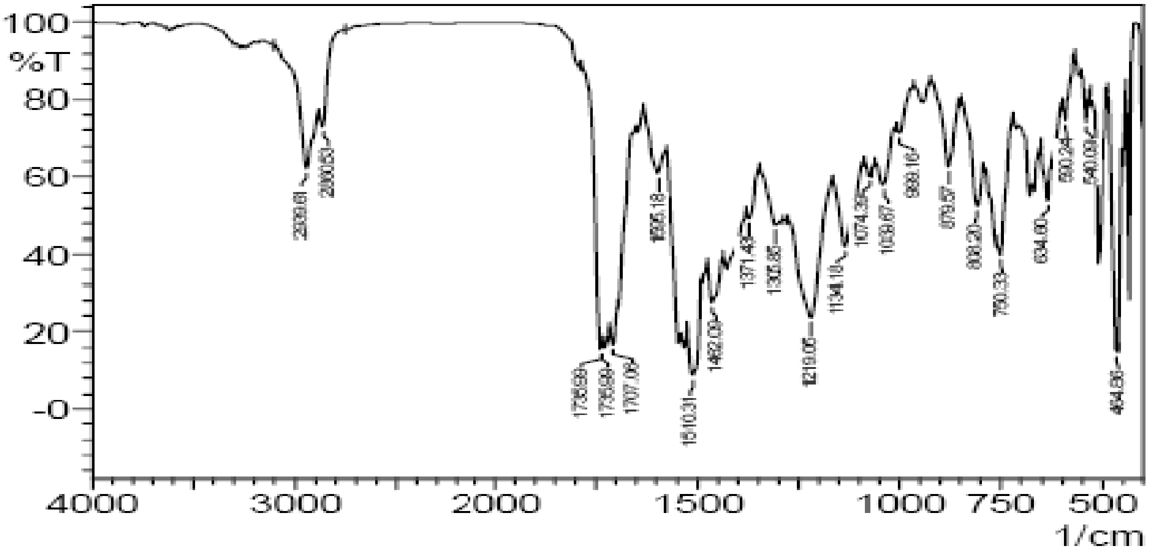

Fig.3.31 IR (KBR) spectrum of EMCRT

Extent of reaction

The extent of reaction(P) can be determined according to following relationship:

$$P = 1 - \frac{M}{M0} \qquad \ldots 3.4$$

Where M_0 = initial acid value and M = acid value at time ‘ T ’

Degree of polymerization can be determined according to following relationship

$$\overline{Xn} = \frac{1}{1-P} \qquad \ldots 3.5$$

The extent of polymerization and degree of polymerization epoxy poyester polyos are reported in Tables-3.3 and 3.4, respectively.

Table-3.3: The extent of polymerization for EMCRA, EMCLA, EMCOA and EMCR

Time, h	EMCRA	EMCLA	EMCOA	EMCR
2	1	0.958	0.971	0.960
3	1	0.964	0.974	0.964
4	1	0.967	0.979	0.977
5	1	0.970	0.985	0.977
6	1	0.981	0.993	0.990

Table-3.4: Degree of polymerization for EMCRA, EMCLA, EMCOA and EMCR

Time hr	EMCRA	EMCLA	EMCOA	EMCR
2	0	23.9	34.2	25.3
3	0	27.6	38.5	28
4	0	30.2	48.8	43.3
5	0	33.4	64.5	43.7
6	0	51.5	147.1	101

CHAPTER-4

THERMAL ANALYSIS

4.1 General introduction

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 [1] 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.

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1. R. T. Conley., “Thermal Stability of Polymers," Marcell Dekker,New York (1973).

Thermal analysis of materials furnishes good account of their thermal stability, which is necessary in determining their end uses [2,3]. Many high polymers when heated above 300°C in an inert atmosphere tend to degrade and much of their non-carbon content is lost as gases leaving behind different forms of carbon [4]. Thermal performance of materials is crucial in many industries, ranging from pharmacy, battery and aerospace and electronics and construction industries. For optimum thermal stability, heat dissipation, bonding and homogeneity are key parameters of thermal characterization; thermal conductivity, thermogravimetric analysis and differential thermal analysis are of paramount importance [5].

Thermogravimetry provides quantitative information on the composition and thermal stability of many different types of materials. The method is fast and can even be used with very small samples. The TGA/DSC is an exceptionally versatile tool for the characterization of materials under precisely controlled atmospheric conditions.

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2. S. Singha and Vijay Kumar Thakur, " Grewia optiva fiber reinforced novel, low cost polymer composites," E-Journal of Chemistry **6** (1), 71-76 (2009).
3. T. Behjat, R. A. Rahman, L. C. Abdulah, N. A. Ibrahim, Y. A. Yusof, "Thermal properties of low density polyethylene - filled kenaf cellulose composites," Europ. J. Sci. Res **32** (2), 223-230 (2009).
4. V. Jha, A. K. Banthia, and A. Paul, "Thermal analysis of phenolic resin based pyropolymers," J. Thermal Ana **35** (4), 1229-1235 (1989).
5. S. C. Mojumdar, L. Raki , N. Mathis, K. Schimdt and S. Lang, "Thermal, spectral and AFM studies of calcium silicate hydrate-polymer nanocomposite material," J. Thermal Ana. and Calorim **85** (1), 119-124 (2006)

It yields valuable information for research, development and quality control in numerous fields such as plastic, building material, minerals, pharmaceuticals and foodstuffs.

Kinetic study of thermal decomposition of epoxy resins containing flame retardant components has studied by Wang and Shi [6]. 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. [7] 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.

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6. Q. Wang and W. Shi, "Kinetics study of thermal decomposition of epoxy resins containing flame retardant components," Polym. Degrad. Stab **91** (8), 1747-1754 (2006).
7. 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** (12), 1548-1555 (2005).

Thermal degradation and decomposition products of electronic boards containing BFRs have been studied by the Barontini et al. [8]. They have investigated the thermal degradation behavior of electronic boards manufactured using tetrabromobisphenol-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. [9] 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

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8. 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** (12), 4186-4199 (2005).
9. M. Wang, L. Wei, and T.Zhao, "Cure study of addition-cure-type and condensation-addition-type phenolic resins," Eur. Polym. J **41** (5), 903-912 (2005).

the parent novolac, on the processing and cure behavior was studied in details. Processing parameters and curing kinetic parameters were obtained. Both resins exhibit excellent processing properties. Thermal cure of PN resins possessed one cure mechanism and that of MPN resins possessed two cure mechanisms according to DSC analysis. The dual-cure-type mechanism made MPN resins superior to PN resins in terms of a mild and controllable cure process. Compared with thermal cure, catalytic cure of PN resins showed lower initiation temperature and cure temperature by about 60 °C. These novel resins have a bright prospect of application as matrix for thermal-structural composite materials.

Nair et al. [10] 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 cross linked 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

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10. C. P. Reghunadhan Nair, R. L. Bindu, and K. N. Ninan, "Thermal characteristics of addition-cure phenolic resins," Polym. Deg. and Stab **73** (2), 251-257 (2001).

degradation in at least two steps, except in the case of ethynyl phenyl azo resin, which showed apparent single step degradation.

Physical transformation such as glass transition, cold crystallization and crystallization from melts, crystallization disorientation, and melting can be studied by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). 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. DSC is a method where by the energy necessary to establish a zero transition occurs, the energy input to the sample is compensated by an increased energy input to the sample in order to maintain a zero temperature difference. The 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 multi step reactions in polymers [11, 12].

DTA is more versatile and gives data of more fundamental nature than TGA. This technique involves recording of difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment

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11. Bo Lin, H. Zhang and Y. Yang, "Synthesis and thermal analysis of linear triblock copolymers based on methacrylate ester," J. Thermal Ana. and Calorim, DOI : 10.1007/ S10973-010-1095-Z, **102** (2010).
12. Yi Cheng Yanchun Li, Yinghua Ye and Ruiqi Shen, "Supplement on applicability of the Kissinger equation in thermal analysis," Journal of Thermal Analysis and Calorim **102** (2), 605-608 (2010).

heated or cooled at a programmed heating rate. Any transition, which the polymer sample undergoes, will result in absorption or liberation of energy by the sample with a corresponding deviation of its temperature from that of the reference. In DTA, as soon as the sample reaches the temperature of the change of its state (chemical or physical), the differential signal appears as a peak. The number, position, shape and nature (exothermic or endothermic) of the DTA peaks give information about glass transition temperature, crystalline rearrangement, melting, curing, polymerization, crystallization, decomposition of polymer, etc.

Different polymers decompose over different range of temperatures yielding different proportion of volatile and residues. Thermogravimetry is a useful analytical technique for recording weight loss of a test sample as a function of the temperature or time, which may be useful for understanding the chemical nature of the polymer. Thus, the weight of a substance in an environment heated or cooled at a controlled rate is recorded as a function of time or temperature. There are three types of thermogravimetry namely

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

Most of the studies of polymers are generally carried out with dynamic thermogravimetry. Normally sample starts losing weight at a very slow rate up to a particular temperature and thereafter, the rate of loss becomes large over narrow range of temperature. After this temperature the loss in weight levels off. TGA curves are characteristic for given polymers because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at the rates that are function of the polymer structures. The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evaluation of volatile products in the formation of heavier reaction products. Pyrolysis of many polymers yields TG curves, which follow relatively simple sigmoidal curves. In such a case weight of sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction gets completed. The shape of the curve depends on the kinetic parameters: reaction order (n), frequency factor (A) and activation energy (Ea). The values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation [13, 14].

Reich and Levi [15] have described several temperature characteristics for qualitative assessment for relative thermal stability of polymers:

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

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13. L. Reich, "Kinetic parameters in polypropylene degradation from DTA traces," J. Appl. Polym. Sci **10** (3), 465-472 (1966).
14. C. Bouster, P. Vermande, and J. Veron, "Study of the pyrolysis of polystyrenes: I. Kinetics of thermal decomposition," J. Ana. and Appl. Pyrolysis **1** (4), 297-313 (1980).
15. L. Reich and D. W. Levi., Macromol. Rev.Eds. Peterlin Goodman Willey

Interscience, New York, 173 (1968).

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

4.2 Thermal analysis of EMCA, EMCT-5 and EMCT-20

DSC and TG measurements were done on a Perkin Elmer DSC-TGA (Model Pyris-I) at 10°C/min heating rate in nitrogen atmosphere. DSC thermograms of EMCA, EMCT-5 and EMCT-20 are shown in Figs.4.1- 4.3. Observed DSC transitions are presented in Table.-4.1. Endothermic transition of EMCA at 65°C (ΔH 0.988 Jg^{-1}) is due to melting transition. The endothermic transitions for EMCT- 5 at 72.6°C (ΔH 4.81 Jg^{-1}) and EMCT-20 at 71.1 (ΔH 6.632 Jg^{-1}) are due to melting transition of uncrossed linked cured EMC. A broad endothermic transition for EMCA at 222.4 (ΔH 4.214 Jg^{-1}) is probably due to some physical change, which is further confirmed by no weight loss over that temperature in TG thermogram. Similarly broad endothermic transition for EMCT-5 (195 °C) and EMCT-20 (212.6 °C) is also due to some physical change. For EMCT-20 an endothermic transition at 124°C is ascribed probably due to traces of moisture release, which is further confirmed by small weight loss over 100-150°C in its TG thermogram.

TG thermograms of EMCA, EMCT-5 and EMCT-20 are presented in Figs.4.4- 4.6 from which it is observed that all the three samples followed apparently single step decomposition reaction. EMCA, EMCT-5 and EMCT-20 are thermally stable up to about 285-308°C. The initial decomposition temperature (IDT), temperature of maximum decomposition, final decomposition temperature (FDT), decomposition range, percentage weight loss involved in decomposition reaction and percentage residue remained above 450°C are recorded in Table- 4.1. From Table-4.1, it is clear that thermal stability increased slightly with TEA concentration confirming increase in degree of cross-linking.

EMCA and EMCT-20 have practically almost same thermal stability (300-308°C). T_{max} of EMCA (398°C) is also somewhat greater than those of EMCT-5(382.6°C) and EMCT-20(389.1°C). The % weight loss involved in the decomposition reaction for EMCA (85.7%) EMCT-5 (86.3%) is almost same but it is somewhat low for EMCT-20 (79.5%).

The associated kinetic parameters namely energy of activation (E), frequency factor (A), order of the reaction (n) and entropy change (ΔS*) were derived according to Freeman-Anderson method [16]:

$$\Delta \ln dW/dt = n \, \Delta \ln W - (E/R) \, \Delta (1/T) \qquad ...1$$

$$A = (E\beta / RT^{2}) \, e^{E/RT} \qquad ...2$$

$$\Delta S^* = R \ln (Ah/kT) \qquad ...3$$

where β is rate of heating, h is Planck's constant and k is Boltzmann constant, R is gas constant and T is temperature. The least square derived values of E, A, n and ΔS* along with regression coefficients (R^2) are reported in Table-4.2. The values of ΔS* are derived at respective Tmax of the sample. From Table-4.2, it is observed that decomposition reactions followed fractional order (0.63-1.44) kinetics. It is also observed that derived kinetic parameters have increased with TEA concentration. EMCA and EMCT-20 possess almost same magnitudes of E, A and ΔS*, but degradation order is almost double for EMCT-20.

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16. E. S. Freeman and D. A. Anderson, "The kinetics of the thermal degradation of polystyrene and polyethylene," J. Polym. Sci **54** (159), 253-260 (1961).

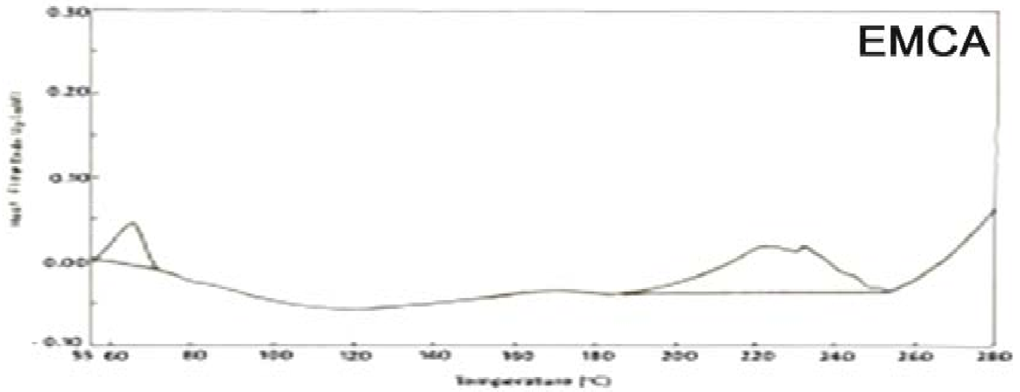

Fig. 4. 1: DSC thermogram of EMCA at 10° C min^{-1} in nitrogen atmosphere

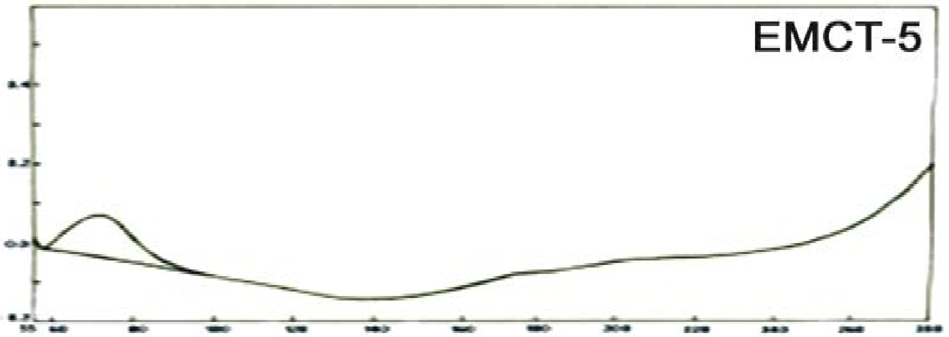

Fig. 4. 2: DSC thermogram of EMCT-5 at 10° C min^{-1} in nitrogen atmosphere

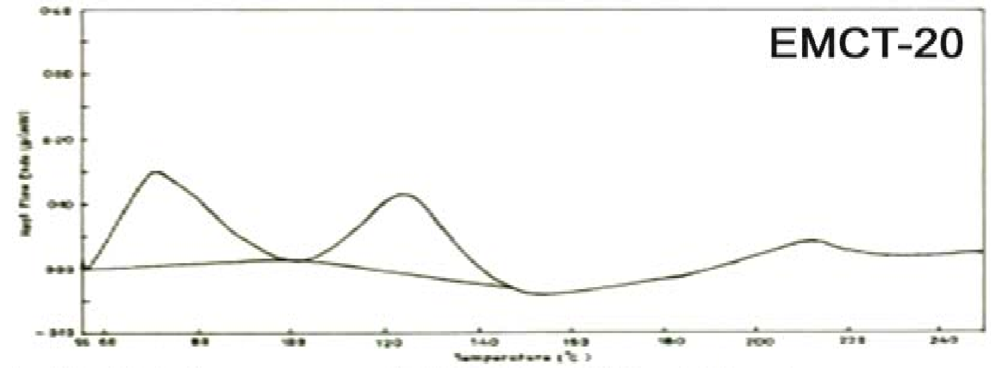

Fig.4.3: DSC thermogram of EMCT-20 at 10° C min^{-1} in nitrogen atmosphere

Table-4.1: DSC transition and TGA data of EMCA, EMCT-5, EMCT-20

Sample	**DSC transition °C**	**IDT, °C**	**FDT, °C**	**Tmax, °C**	**Decompn. range, °C**	**% wt loss**	**% Residue at 450 °C**
EMCA	65 (endo) 222.4 (endo)	308	435	398	308-435	85.7	7.3
EMCT-5	72.6 (endo) 195 (endo)	285	423	382.6	285-423	86.3	7.4
EMCT-20	71.1 (endo) 124.1 (endo) 212.6 (endo)	300	450	389.1	300-450	79.5	10.3

Table- 4.2: Kinetic parameters of EMCA, EMCT-5 and EMCT-20

Sample	E, kJ	A, S^{-1}	n	ΔS^* JK^{-1} mol^{1}	R^{2}
EMCA	204.52	7.54 x 10^{13}	0.88	14.01	0.946
EMCT-5	49.88	21.88	0.63	-225.8	0.981
EMCT-20	202.86	9.29 x 10^{13}	1.44	15.85	0.988

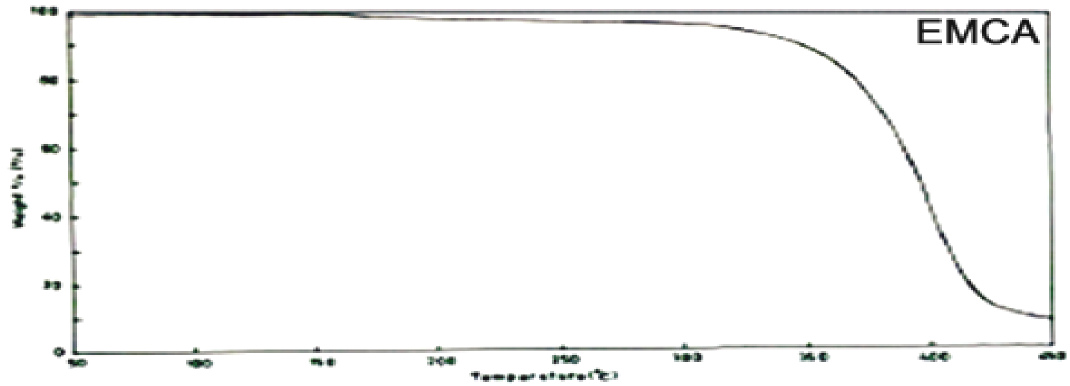

Fig. 4. 4: TG thermogram of EMCA at 100 °C min⁻¹ in nitrogen atmosphere

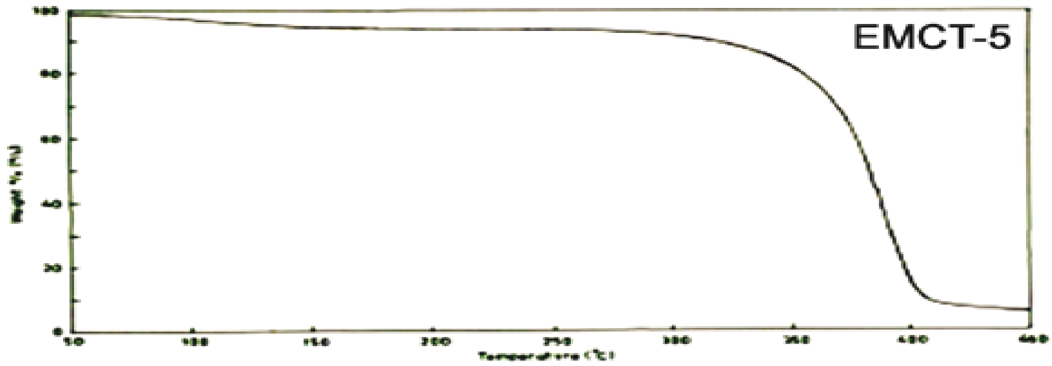

Fig. 4. 1: TG thermogram of EMCT-5 at 100° C min⁻¹ in nitrogen atmosphere

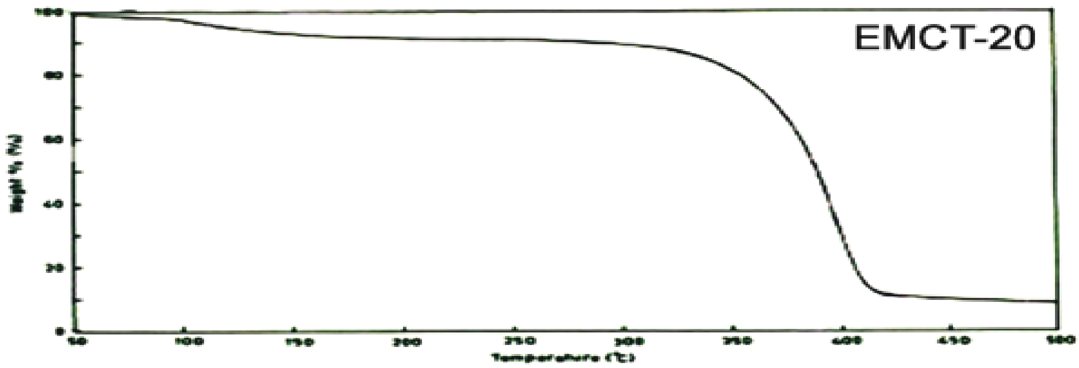

Fig. 4. 6: TG thermogram of EMCT-20 at 100°C min⁻¹ in nitrogen atmosphere

Positive magnitude of ΔS* suggested that transition state could be less ordered than that of individual molecules [17]. For EMCT-5 a large and negative magnitude of ΔS* suggested that transition state is more ordered than that of individual molecules [17]. Polymer degradation is a complex reaction and involves varieties of reactions such as cross-linking branching, rearrangement and decomposition of segments. It is supposed that ether and acrylate (EMCA) and amine (EMCT-5 and EMCT-20) linkages are weak points in the samples, which degrade selectively forming radicals. The radicals that formed could recombine and form new compounds, which would subsequently degrade at elevated temperatures. The decomposition of acrylate linkage would lead to evolution of carbon dioxide. A small residue (7-10%) above 450°C indicates that it would be due to a highly thermally stable cross linked product of the degradation.

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17. V. M. Kagathara and P. H. Parsania, "Thermal analysis of cured chloro epoxy resins and epoxy-acrylate-styrene copolymers," Polym. Test **21** (6), 659-663 (2002).

4.3 Thermal analysis of *e*poxy-isophthalate/terephthalate polyesters

DSC and TG measurements were done on a Shimadzu DSC60 and Perkin Elmer TGA (Model Pyris-I) at 10^{o}C/min heating rate in nitrogen atmosphere. DSC thermograms of EMCIP and EMCTP are presented in Figs.4.7 and 4.8, respectively. Observed DSC transitions are presented in Table-4.3. Endothermic transition of EMCIP at 103.5^{o}Cand that of EMCTP at 103.8 ^{o}C is due to melting transition. Both the samples started degrading above 300 ^{o}C, which is further confirmed by weight loss in corresponding TG (Figs. 4.9 and 4.10).

TG thermograms of EMCIP and EMCTP are presented in Figs.4.9 and 4.10 from which it is observed that both the samples followed apparently single step decomposition reaction. They are thermally stable up to about 300-310^{o}C. The initial decomposition temperature (IDT), temperature of maximum decomposition T_{max}, decomposition range, percentage weight loss involved in decomposition reaction and percentage residue remained above 450^{o}C are recorded in Table-4.3. From Table-4.3, it is clear that thermal stability of EMCTP (310^{O}C) is somewhat greater than that of EMCIP (300^{O}C) which is due to symmetry effect. T_{max} (396-397 ^{O}C), the % weight loss (86-87%) involved in the decomposition reaction and the % residue (9-10%) remained at 450 ^{o}C are practically same in both the cases.

The associated kinetic parameters namely energy of activation (E), frequency factor (A), order of the reaction (n) and entropy change (ΔS^*) were derived according to Freeman-Anderson method [16]. The calculation scheme for EMCTP and EMCIP are presented in Tables-4.4 and 4.5, respectively and Freeman-Anderson plots are presented in Figs.4.11 and 4.12, respectively. The least square derived values of E, A, n and ΔS^* along with regression coefficients

(R^2) are reported in Table-4.3. The values of ΔS^* are derived at respective T_{max} of the sample. From Table-4.3, it is observed that decomposition reactions followed apparently first order (1.05- 1.26) kinetics. Other derived kinetic parameters for EMCIP are considerably greater than that of EMCTP confirming more rigid nature of EMCIP. Positive magnitude of ΔS^* suggested that transition state could be less ordered than that of individual molecules [17].

Polymer degradation is a complex reaction and involves varieties of reactions such as cross-linking, branching, rearrangement and decomposition of segments. Ether and ester linkage and pendant groups are weak points in the samples, which degrade selectively forming radicals. These radicals further recombine and form new compounds, which would subsequently degrade at elevated temperatures. The decomposition of ether and ester linkages would lead to evolution of carbon dioxide and hydrocarbons. A small residue (9-10%) above 450 ^{o}C would be due to formation of highly thermally stable cross linked product of the degradation.

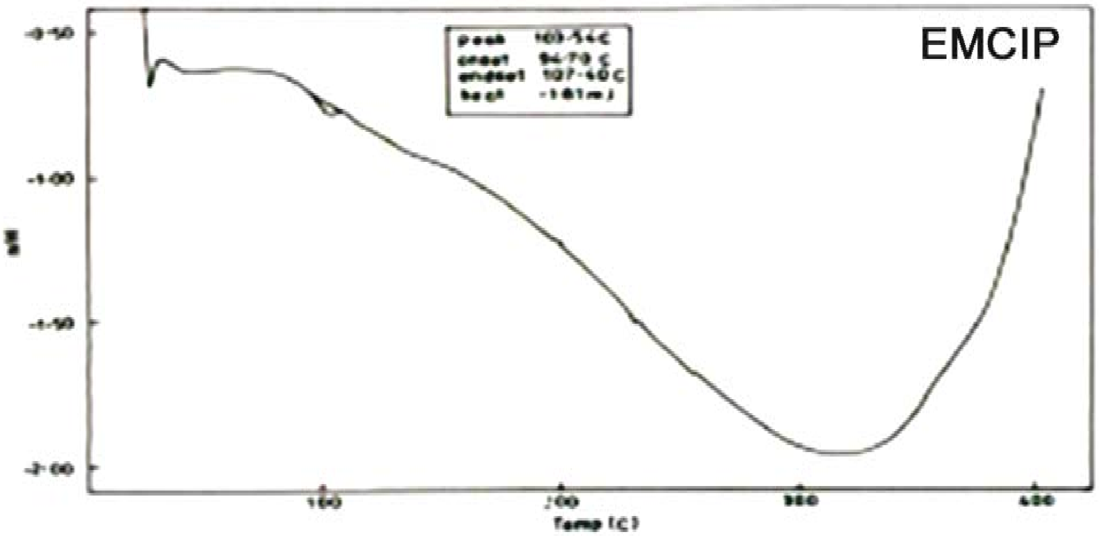


Fig. 4. 7: DSC thermogram of EMCIP at the heating rate of 10°C/min in nitrogen atmosphere

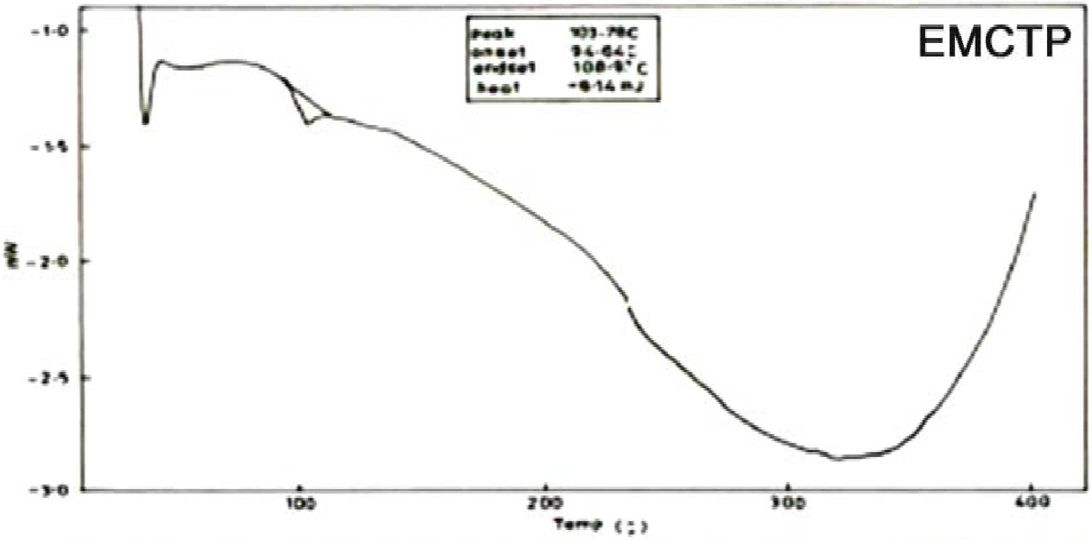


Fig. 4. 8: DSC thermogram of EMCTP at the heating rate of 10°C/min in nitrogen atmosphere

Table -4.3: Thermal and kinetic parameters of EMCTP and EMCIP

Parameter	**Epoxy polyester**	
	EMCTP	**EMCIP**
DSC endothermic transition, °C	103.8	103.5
IDT,°C	310	300
Decomposition range, ^{0}C	310-440	300-440
T_{max}, ^{0}C	396.2	397.1
% Wt.loss	86.4	86.9
% Residue at 450^{0}C	9.3	10.0
E, kJ mol^{-1}	200.4	230.1
N	1.26	1.05
A,s^{-1}	3.88×10^{13}	9.12×10^{15}
ΔS^* JK^{-1} mol^{-1}	8.5	53.9
R^2	0.975	0.963

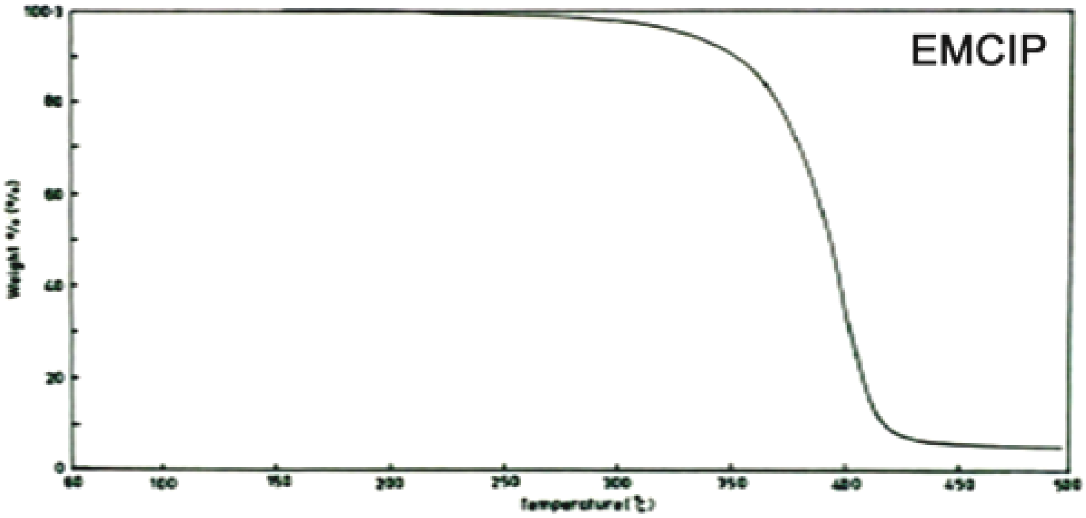


Fig.4.9: TG thermogram of EMCIP at the heating rate of 10°C/min in nitrogen atmosphere

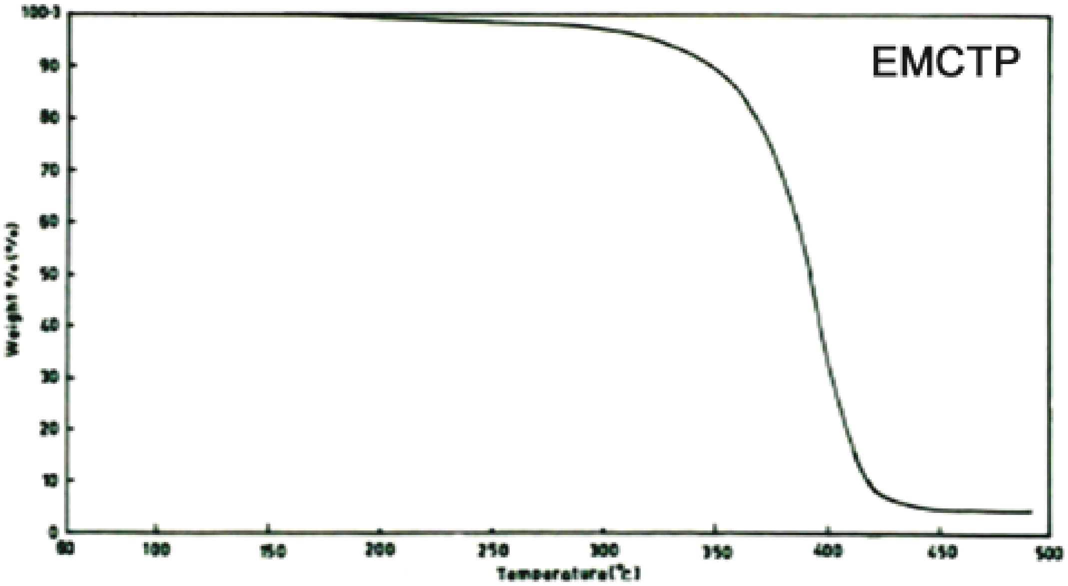


Fig.4.10: TG thermogram of EMCTP at the heating rate of 10°C/min in nitrogen atmosphere

Table-4.4: Calculation scheme for EMCTP

1000/T	% Wt loss	%W	dW/dt	ln W	lndW/dt	∆lnw	∆lndw/dt
1.57	14.75	75.95	6.636	4.3301	1.8925	0.04	-0.20
1.56	17.47	73.23	8.073	4.2936	2.0885	0.05	-0.21
1.55	20.95	69.75	9.932	4.2449	2.2958	0.06	-0.17
1.54	25.18	65.52	11.817	4.1824	2.4695	0.08	-0.14
1.53	30.15	60.55	13.592	4.1035	2.6095	0.10	-0.11
1.52	35.8	54.9	15.117	4.0055	2.7158	0.12	-0.07
1.51	42.02	48.68	16.259	3.8853	2.7886	0.15	-0.04
1.5	48.68	42.02	16.897	3.7381	2.8271	0.18	0.00
1.49	55.62	35.08	16.93	3.5576	2.8291	0.22	0.04
1.48	62.62	28.08	16.289	3.3351	2.7905	0.28	0.09

Table-4.5: Calculation scheme for EMCIP

1000/T	% Wt loss	dw/dt	W	ln W	lndw/dt	∆lnw	∆lndw/dt
1.56	16.31	6.45	70.59	4.26	1.86	0.05	-0.25
1.55	19.95	8.25	66.95	4.20	2.11	0.07	-0.22
1.54	24.41	10.33	62.49	4.14	2.34	0.09	-0.19
1.53	29.64	12.49	57.26	4.05	2.52	0.11	-0.15
1.51	42.05	15.15	44.85	3.80	2.72	0.17	-0.13
1.5	48.95	17.21	37.95	3.64	2.85	0.21	-0.02
1.49	56.1	17.48	30.8	3.43	2.86	0.26	0.04
1.48	63.27	16.83	23.63	3.16	2.82	0.35	0.10
1.47	70.21	15.16	16.69	2.81	2.72	0.49	0.19

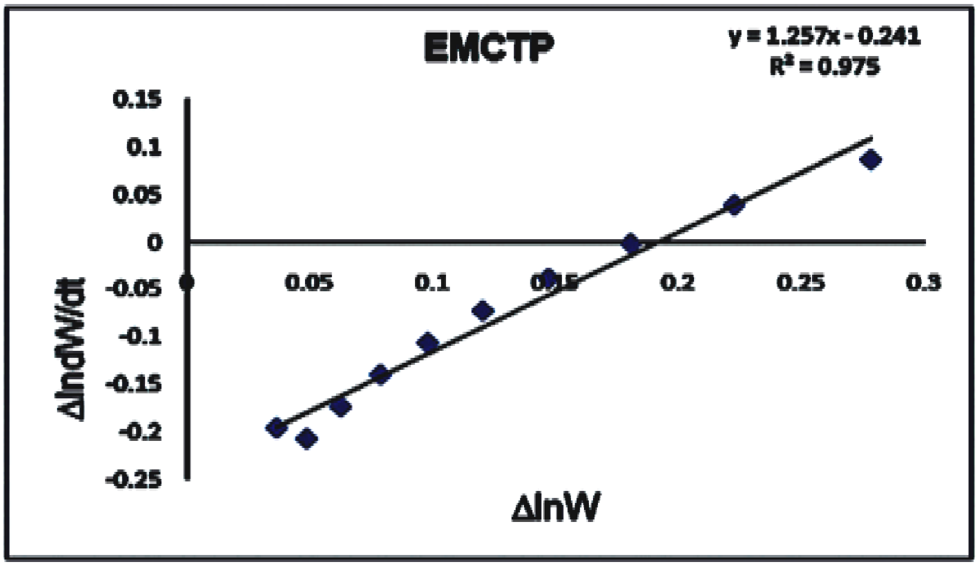


Fig.4.11. The Freeman- Anderson plot for EMCTP

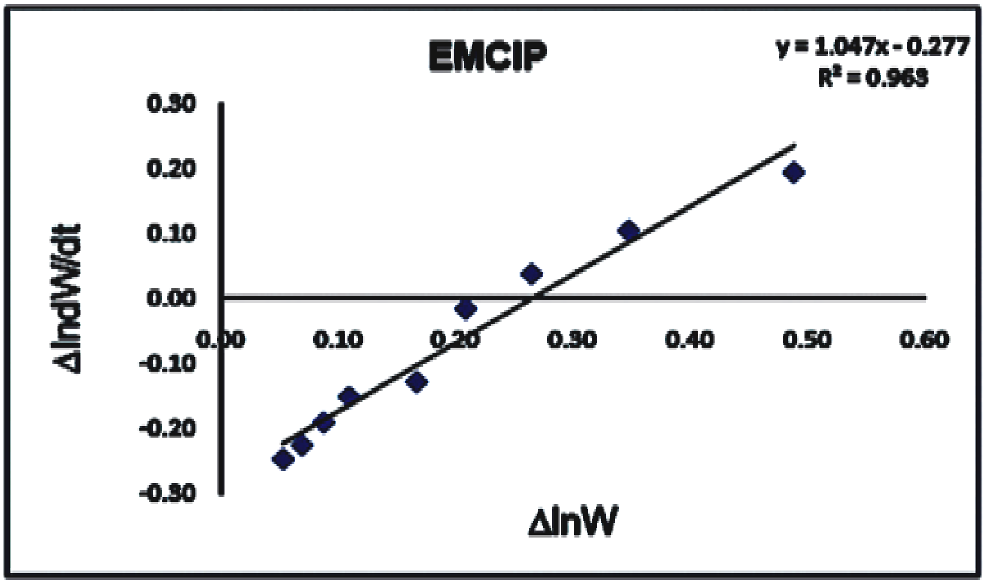


Fig.4.12. The Freeman- Anderson plot for EMCIP

4.4 Thermal analysis of epoxy polyester polyols

DSC and TG measurements were done on a Shimadzu DSC60 and Perkin Elmer TGA (Model Pyris-I) at 10°C/min heating rate in nitrogen atmosphere. DSC thermograms of epoxy polyester polyols at the heating rate of 10°C in an N_2 atmosphere are presented in Fig. 4.13. Observed DSC transitions are presented in Table-4.6. Endothermic transition (°C) at 103.1(EMCRA), 91.6(EMCLA) and 95.5(EMCR) is due to melting transition. Other transitions at 124.4 (endo) and 238.9(exo) for EMCRA; 132.2 and 145.8 (endo) and 247.6(exo) for EMCLA; 232.9(endo) for EMCOA and 197.5(endo) for EMCR is/ are due to some physical changes and further confirmed by no weight loss over those temperatures in corresponding TG thermogram(Fig.4.14). Exothermic transition(s) at 356.3 and 389 foe EMCRA; 382.4 for EMCLA; 338.3 and 345.4 for EMCOA and 332.3 and 348.6 for EMCR is / are due to decomposition of polyester polyols and confirmed by weight loss in corresponding TG thermogram (Fig. 4.14).

From Fig.4.14, it is observed that EMCRA followed apparently three steps decomposition reaction, while EMCOA followed two steps; and EMCLA and EMCR followed single step decomposition. They are thermally stable up to about 267-295 °C. The initial decomposition temperature (To), temperature of maximum weight loss T_{max}, decomposition range, percentage weight loss involved in decomposition reaction and percentage residue remained at 450°C are recorded in Table-4.6. Observed thermal stability order is EMCLA > EMCRA > EMCOA= EMCR. T_{max} is different for these polyols. EMCRA decomposed completely, while EMCLA, EMCOA and EMCR left 7, 19 and 16 % residue at 450 °C.

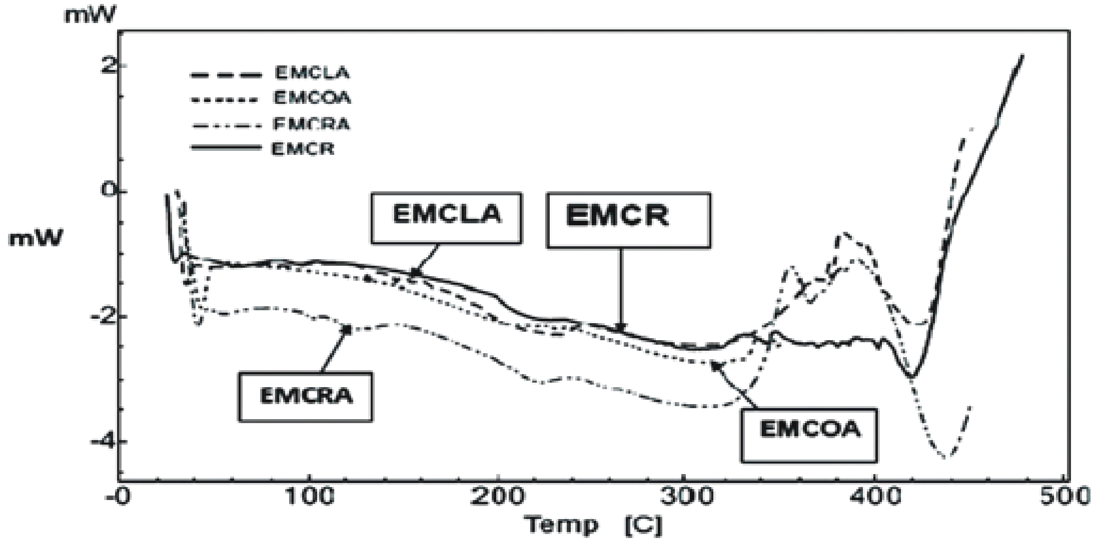


Fig. 4.13. DSC thermograms of EMCRA, EMCLA, EMCOA and EMCR at the heating rate of 10^{0}C/min in an N_2 atmosphere.

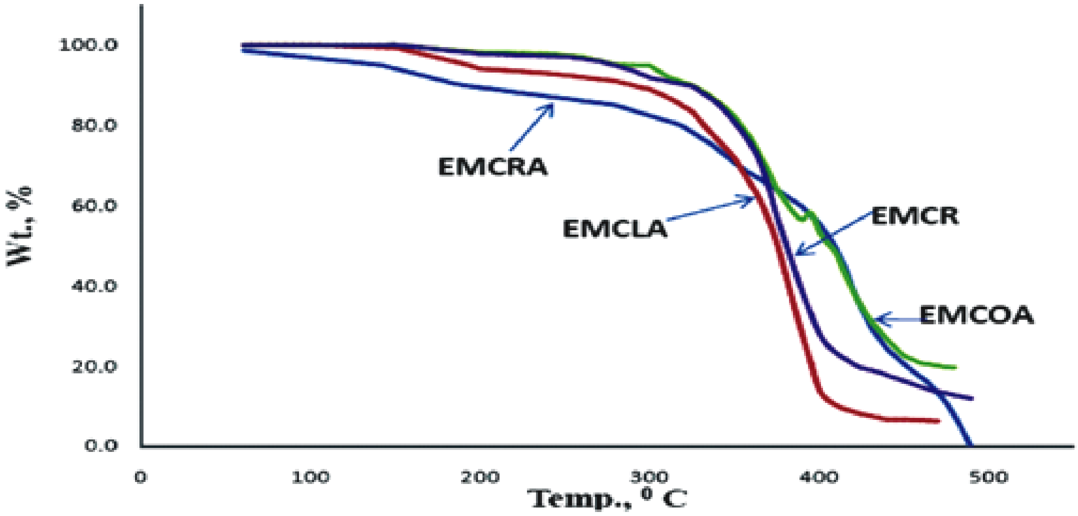


Fig. 4.14. TG thermograms of EMCRA, EMCLA, EMCOA and EMCR at the heating rate of 10^{0}C/min in an N_2 atmosphere.

Table-4.6: Thermal and kinetic parameters of epoxy polyester polyols

Parameter	Epoxy Polyester			
	EMCRA	**EMCLA**	**EMCOA**	**EMCR**
DSC transition, °C	103.1 (endo)	91.6 (endo)	220.3 (endo)	95.5 (endo)
	124.4(endo)	132.2 (endo)	232.9 (endo)	197.5 (endo)
	238.9 (exo)	145.8 (endo)	338.3 (exo)	332.3 (exo)
	256.3 (exo)	247.6 (exo)	345.4 (exo)	348.6 (exo)
	389 (exo)	382.4 (exo)		
T_0, °C	280			
	390	295	268	267
	455		400	
Decomposition range, °C	280-360		268-380	
	390-445	295-428	400-465	267-440
	455-465			
Tmax, °C	345			
	420	384.7	372.8	380
	485		416.5	
% Wt. loss	32			
	37.2	84.5	36.3	79.3
	18.8		32.6	
% Residue at 450 °C	-	7	19	16
E, KJ mol^{-1}	163			
	364.2	176.3	176.3	219.5
	264.4		56.2	

n	1			
	1.75	0.85	0.66	1.53
	0.34		1.39	
A, s^{-1}	5.1 X 10^{11}			
	4.26 X 10^{25}	8.06 X 10^{11}	1.51 X 10^{12}	3.68 x 10^{15}
	1.53 X 10^{16}		42.77	
ΔS^* JK^{-1} mol^{-1}	-26.9			
	238.7	-23.6	-18.2	46.6
	57.2		-220.7	
R^2	0.982			
	0.97	0.985	0.978	0.983
	0.99		0.98	

The associated kinetic parameters namely energy of activation (E), frequency factor (A), order of the reaction (n) and entropy change (ΔS^*) were derived according to Freeman-Anderson method [16]. The calculation scheme for EMCRA, EMCLA, EMCOA and EMCR are presented in Tables- 4.7–4.10 and Freeman-Anderson plots are presented in Figs.4.15- 4.18, respectively. The least square derived values of E, A, n and ΔS^* along with regression coefficients (R^2) are reported in Table-4.6. The values of ΔS^* are derived at respective T_{max} of the sample. From Table-4.6, it is observed that decomposition reactions followed either integral or fractional order kinetics. Observed order of E is EMCR > EMCLA = EMCOA > EMCRA. The magnitude of A depends both on E and T. Positive magnitude of ΔS^* suggested that transition state could be less ordered than that of individual molecules and vice versa [17]. Polymer degradation is a complex reaction and involves varieties of reactions such as cross-linking, branching, rearrangement and decomposition of segments. Ether and ester linkages and pendant groups are weak points in the polyester polyols, Selective degradation starts from such weak points resulting in formation of radicals. These radicals further recombine and form new compounds, which would subsequently degrade at elevated temperatures. The decomposition of ether and ester linkages would lead to evolution of carbon dioxide and hydrocarbons. A small residue (7-19 %) above 450 ^oC would be due to formation of highly thermally stable cross linked products of the degradation.

Table- 4.7: Calculation scheme for EMCRA (Step- I)

1000/T	%Wtloss	W	lnW	dW/dt	lndW/dt	ΔlnW	ΔlndW/dt
1.64	25.00	7.12	1.962	3.073	1.123	0.075	-0.025
1.645	24.45	7.67	2.037	2.996	1.097	0.068	-0.030
1.65	23.91	8.21	2.105	2.906	1.067	0.062	-0.035
1.655	23.39	8.73	2.167	2.805	1.032	0.056	-0.040
1.66	22.89	9.23	2.223	2.695	0.991	0.051	-0.045
1.665	22.40	9.72	2.274	2.577	0.947	0.046	-0.050
1.67	21.94	10.18	2.320	2.452	0.897	0.042	-0.054
1.675	21.50	10.62	2.362	2.322	0.842	0.039	-0.059
1.68	21.09	11.03	2.401	2.188	0.783	0.035	-0.064
1.685	20.69	11.43	2.436	2.052	0.719	0.032	-0.069

Step-II

1000/T	%Wtloss	W	lnW	dW/dt	lndW/dt	ΔlnW	ΔlndW/dt
1.435	64.1217	13.478	2.601	9.437	2.245	0.160	0.046
1.44	61.787	15.813	2.761	9.885	2.291	0.137	0.021
1.445	59.4617	18.138	2.898	10.100	2.313	0.118	-0.003
1.45	57.1825	20.418	3.016	10.068	2.309	0.102	-0.028
1.455	54.9816	22.618	3.119	9.788	2.281	0.089	-0.054
1.46	52.8861	24.714	3.207	9.276	2.227	0.077	-0.080
1.465	50.9186	26.681	3.284	8.560	2.147	0.066	-0.108
1.47	49.0967	28.503	3.350	7.683	2.039	0.057	-0.137

Step-III

1000/T	%Wtloss	W	lnW	dW/dt	ln dW/dt	ΔlnW	ΔlndW/dt
1.325	93.6257	6.374	1.852	7.25611	1.982	0.268	-0.069
1.33	91.6683	8.332	2.120	6.7716	1.913	0.191	-0.090
1.335	89.915	10.085	2.311	6.18869	1.823	0.145	-0.108
1.34	88.346	11.654	2.456	5.55579	1.715	0.114	-0.122
1.345	86.9412	13.059	2.569	4.91986	1.593	0.092	-0.129

Table- 4.8: Calculation scheme for EMCLA

1000/T	%Wtloss	%W	dW/dt	ln W	ln dW/dt	∆lnw	∆lndw/dt
1.59	31.23	61.4	6.255	4.117	1.833	0.044	-0.210
1.58	33.9	58.73	7.717	4.073	2.043	0.059	-0.194
1.57	37.26	55.37	9.369	4.014	2.237	0.077	-0.165
1.56	41.36	51.27	11.052	3.937	2.403	0.099	-0.130
1.55	46.21	46.42	12.59	3.838	2.533	0.126	-0.092
1.54	51.72	40.91	13.806	3.711	2.625	0.160	-0.052
1.53	57.78	34.85	14.54	3.551	2.677	0.203	-0.008
1.52	64.18	28.45	14.658	3.348	2.685	0.259	0.041
1.51	70.67	21.96	14.067	3.089	2.644	0.336	0.100
1.5	76.94	15.69	12.732	2.753	2.544	0.446	0.175
1.49	82.59	10.04	10.687	2.307	2.369	0.611	0.283
1.48	87.18	5.45	8.05	1.696	2.086	0.808	0.469

Table- 4.9: Calculation scheme for EMCOA (Step-I)

1000/T	%Wtloss	%W	dW/dt	ln W	ln dW/dt	∆lnw	∆lndw/dt
1.64	12.7	27.3	2.716	3.3069	0.9992	0.0411	-0.1917
1.63	13.8	26.2	3.29	3.2658	1.1909	0.0541	-0.1826
1.62	15.18	24.82	3.949	3.2116	1.3735	0.0710	-0.1671
1.61	16.88	23.12	4.667	3.1407	1.5405	0.0910	-0.1483
1.6	18.89	21.11	5.413	3.0497	1.6888	0.1170	-0.1273
1.59	21.22	18.78	6.148	2.9328	1.8161	0.1496	-0.1046
1.58	23.83	16.17	6.826	2.7832	1.9207	0.1939	-0.0807
1.57	26.68	13.32	7.4	2.5893	2.0015	0.2571	-0.0535

Step-II

1000/T	% Wt. loss	% W	dW/dt	ln W	ln dW/dt	Dlnw	Dlndw/dt
1.47	51.01	28.99	7	3.367	1.9459	0.139	-0.1123
1.46	54.78	25.22	7.832	3.228	2.0582	0.163	-0.0442
1.45	58.57	21.43	8.186	3.065	2.1024	0.189	-0.0108
1.44	62.26	17.74	8.098	2.876	2.0916	0.218	-0.0606
1.43	65.73	14.27	7.622	2.658	2.031	0.252	-0.1107
1.42	68.91	11.09	6.823	2.406	1.9203	0.292	-0.165
1.41	71.72	8.28	5.785	2.114	1.7553	0.342	-0.2281
1.4	74.12	5.88	4.605	1.772	1.5271	0.408	-0.3042
1.39	76.09	3.91	3.397	1.364	1.2229	0.492	-0.3957

Table- 4.10: Calculation scheme for EMCR

1000/T	% Wt. loss	% W	dW/dt	ln W	ln dW/dt	∆lnw	∆lndw/dt
1.62	15.8	3.438	67.2	4.208	1.235	0.026	-0.222
1.61	17.5	4.291	65.5	4.182	1.457	0.034	-0.251
1.6	19.68	5.518	63.32	4.148	1.708	0.043	-0.236
1.59	22.37	6.987	60.63	4.105	1.944	0.055	-0.202
1.58	25.6	8.554	57.4	4.05	2.146	0.068	-0.164
1.57	29.37	10.077	53.63	3.982	2.31	0.083	-0.126
1.56	33.64	11.429	49.36	3.899	2.436	0.101	-0.086
1.55	38.37	12.459	44.63	3.798	2.522	0.121	-0.049
1.54	43.45	13.089	39.55	3.678	2.572	0.145	-0.011
1.53	48.8	13.233	34.2	3.532	2.583	0.174	0.03
1.52	54.26	12.846	28.74	3.358	2.553	0.209	0.074
1.51	59.69	11.927	23.31	3.149	2.479	0.252	0.126
1.5	64.88	10.52	18.12	2.897	2.353	0.305	0.187
1.49	69.64	8.725	13.36	2.592	2.166	0.363	0.263
1.48	73.71	6.705	9.29	2.229	1.903	0.411	0.357

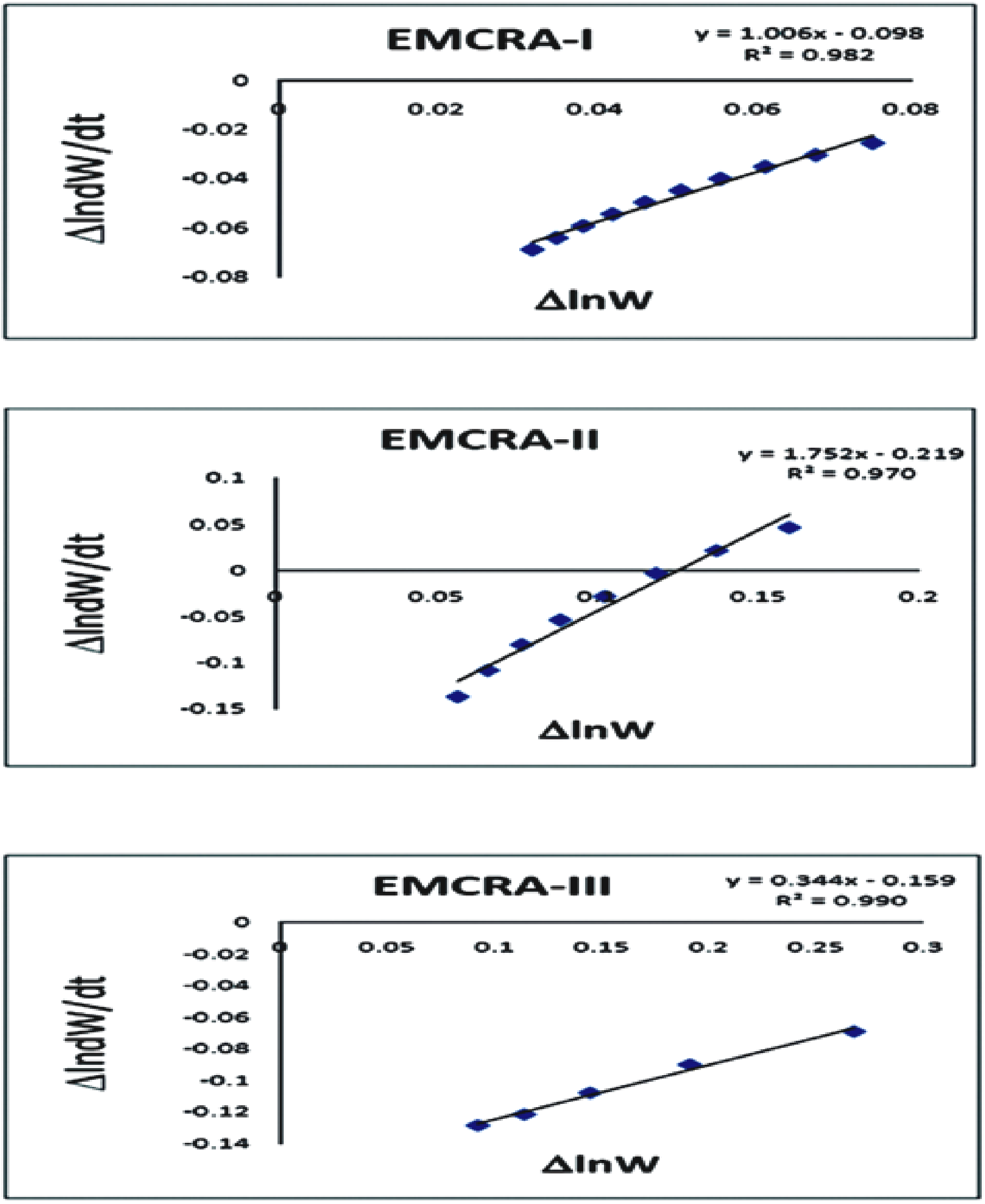


Fig.4.15. The Freeman-Anderson plots for EMCRA

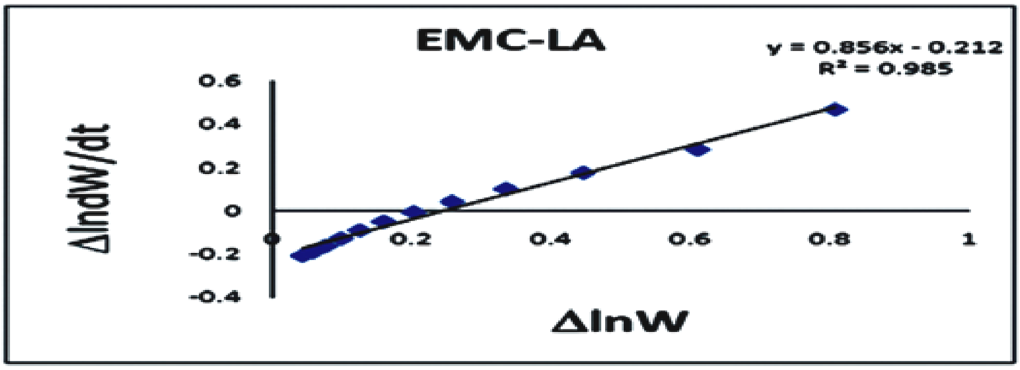


Fig. 4.16. The Freeman-Anderson plot for EMCLA

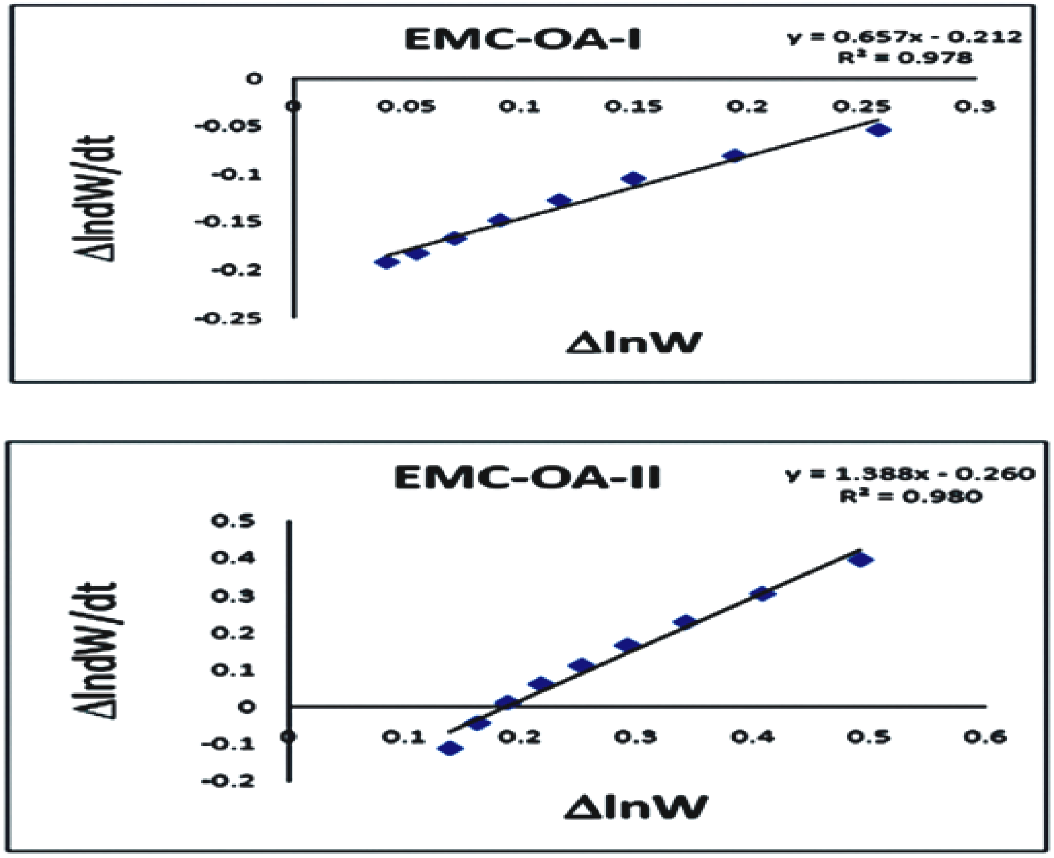


Fig. 4.17. The Freeman-Anderson plot for EMCOA

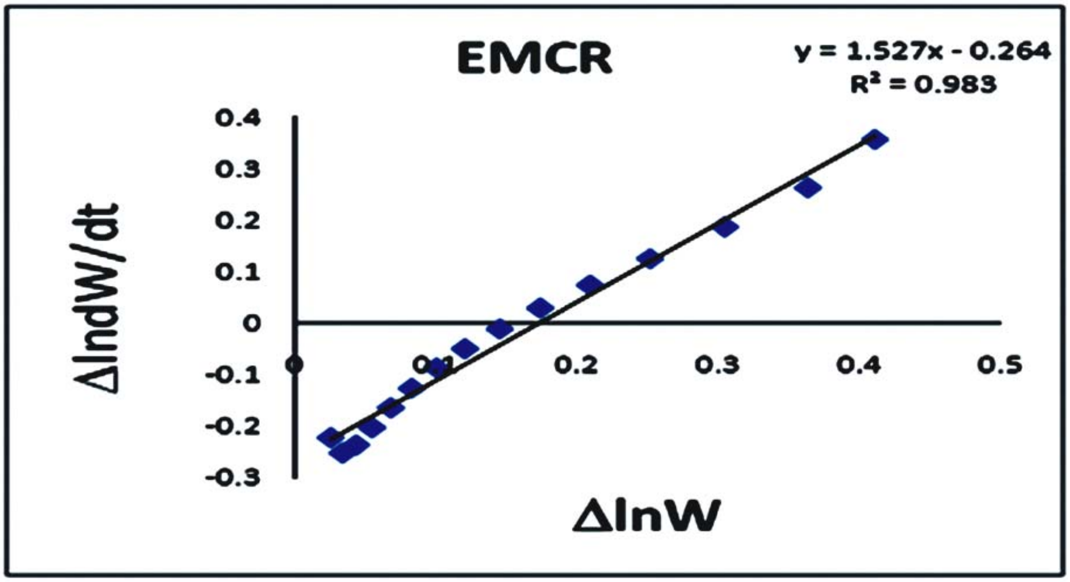


Fig. 4.18. The Freeman-Anderson plot for EMCR

4.5 Thermal analysis of EMCT-20-JWA and EMCT-20-JCN

DSC thermograms of EMCT-20-JWA and EMCT-20-JCN are presented in Fig.4.19. Observed DSC transitions are presented in Table-4.11. Endothermic transition at 74.1°C for EMCT-20-JWA and at 84.9°C are probably due to mixed melting of uncured EMC, partial crystallinity in wild almond and coconut fibers, which are further confirmed by endothermic transition at 78.6°C for wild almond, 61.5°C for coconut fibers and 71.1°C for EMCT-20. Other endothermic transitions at 265.3 and 364.5°C for EMCT-20-JCN are due to decomposition reactions, which are further confirmed by weight loss in its TG thermogram(Fig.4.20).

EMCT-20-JWA and EMCT-20-JCN are thermally stable up to 290°C and 230°C; and followed three and four steps decomposition reactions, respectively. Thermal stability of EMCT-20(300°C) is considerably greater than both the fibers (220-240°C). Initial decomposition temperature (T_o), temperature of maximum decomposition (T_{max}), decomposition range, the % weight loss involved in each decomposition reaction and the % residue remained at 550°C are recorded in Table-4.11. EMCT-20-JWA is 1.3 times more thermally stable than that of EMCT-20-JCN. T_{max} is somewhat higher and the % weight loss involved in the first step decomposition reaction is almost one half for EMCT-20-JWA as compared to EMCT-20-JCN. The % residue remained at 550°C is 23 % and 2%, respectively for EMCT-20-JWA and EMCT-20-JCN. Considerable residue at 550°C for EMCT-20-JWA is due to formation of highly thermally stable cross linked product. EMCT-20-JCN is practically converted into low molecular mass hydrocarbon products.

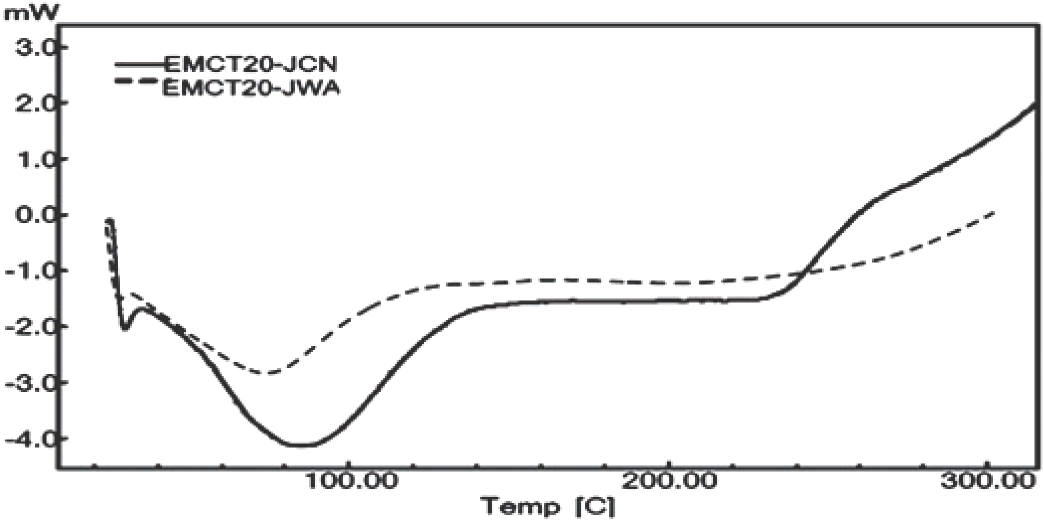


Fig.4.19: DSC thermograms of EMCT-20-JWA and EMCT-20-JCN at the heating rate of 10°C/min in an N_2 atmosphere

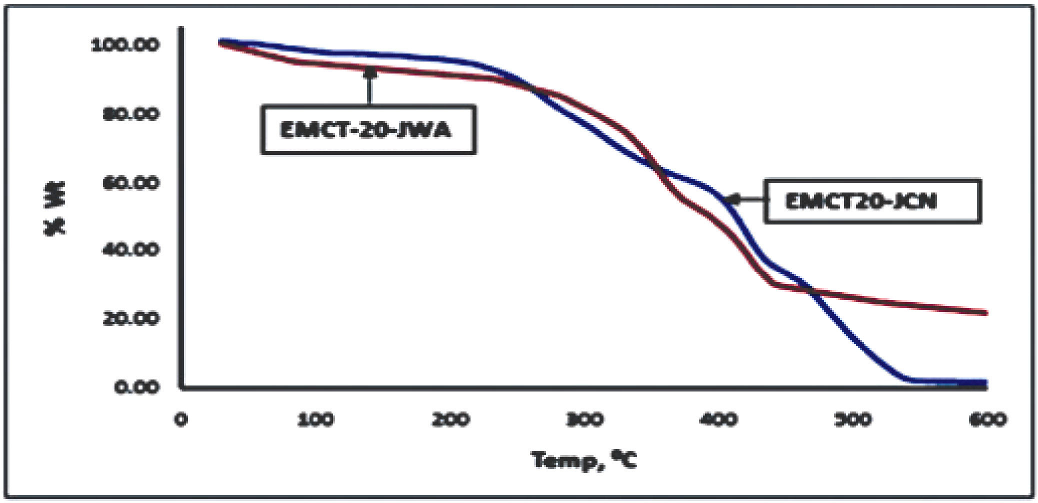


Fig.4.20: TG thermograms of EMCT-20-JWA and EMCT-20-、 JCN at the heating rate of 10°C/min in an N_2 atmosphere

Table-4.11: Comparative thermal characteristics of EMCT-20-JWA and EMCT-20-JCN

Parameter	EMCT-20-JWN	EMCT-20-JCN
DSC, transition, °C	74.1	84.9
		265.3
		364.5
		230
T_0, °C	290	230
Decomposition range, °C	290-320	230-290
	320-360	290-385
	380-445	385-470
		470-550
Tmax, °C	313	269
	352.6	313.5
	422.2	419
		476
% Wt. loss	6.4	13.6
	19.2	19.9
	23.2	31.7
		25.2
% Residue at 550, °C	23	2

The associated kinetic parameters namely energy of activation (E), frequency factor (A), order of the reaction (n) and entropy change (ΔS*) were derived according to Freeman-Anderson method [16]. The calculation scheme for EMCT-20-JCN and EMCT-20-JWA are presented in Tables 4.12 and 4.13. Freeman-Anderson plots are presented in Figs.4.21 and 4.22, respectively. The least square derived values of E, A, n and ΔS* along with regression coefficients (R^2) are reported in Table-4.14. The values of ΔS* are derived at respective T_{max} of the sample. From Table-4.14, it is observed that decomposition reactions followed apparently different decomposition mechanisms. Derived kinetic parameters are also different for both the composites. Large magnitudes of E and A of EMCT-20-JWA as compared to EMCT-20-JCN confirmed more rigid nature of EMCT-20-JWA. Positive magnitudes of ΔS* suggested that transition states could be less ordered than that of individual molecules and vice versa [17]. Polymer degradation is a complex reaction and involves varieties of reactions such as cross-linking, branching, rearrangement and decomposition of segments. Ether and ester linkage and pendant groups are weak points in the resin, which degrade selectively forming radicals. These radicals further recombine and form new compounds, which would subsequently degrade at elevated temperatures.

Table- 4.12: Calculation scheme for EMCT-20-JCN

Step-I

1000/T	%Wtloss	dw/dt	W	ln W	lndw/dt	∆ ln W	∆lndw/dt
1.850	14.688	2.773	6.01	1.794	1.020	0.068	-0.004
1.855	14.265	2.762	6.44	1.862	1.016	0.063	-0.007
1.860	13.848	2.745	6.85	1.925	1.010	0.058	-0.009
1.865	13.439	2.719	7.26	1.983	1.000	0.054	-0.012
1.870	13.039	2.685	7.66	2.036	0.988	0.050	-0.016
1.875	12.649	2.644	8.05	2.086	0.972	0.046	-0.019
1.880	12.270	2.595	8.43	2.132	0.954	0.043	-0.022
1.885	11.903	2.539	8.80	2.174	0.932	0.040	-0.025
1.890	11.548	2.476	9.15	2.214	0.907	0.037	-0.028
1.895	11.205	2.407	9.49	2.251	0.878	0.034	-0.032
1.900	10.876	2.332	9.82	2.285	0.847	0.032	-0.035
1.905	10.560	2.253	10.14	2.316	0.812	0.029	-0.038
1.910	10.258	2.169	10.44	2.346	0.774	-2.346	-0.774

Step-II

1000/T	%Wt loss	dw/dt	W	ln W	ln dw/dt	Δ ln W	Δlndw/dt
1.67	29.923	2.540	10.677	2.368	0.932	0.042	0.020
1.675	29.462	2.591	11.138	2.410	0.952	0.041	0.018
1.68	28.994	2.637	11.606	2.451	0.970	0.040	0.015
1.685	28.522	2.678	12.078	2.491	0.985	0.039	0.013
1.69	28.046	2.713	12.554	2.530	0.998	0.037	0.010
1.695	27.567	2.740	13.033	2.567	1.008	0.036	0.007
1.7	27.088	2.758	13.512	2.604	1.014	0.035	0.003
1.705	26.610	2.767	13.990	2.638	1.018	0.033	-0.001
1.71	26.134	2.765	14.466	2.672	1.017	0.032	-0.005
1.715	25.664	2.751	14.936	2.704	1.012	0.031	-0.010
1.72	25.202	2.723	15.398	2.734	1.002	0.029	-0.015
1.725	24.749	2.682	15.851	2.763	0.986	-2.763	-0.986

Step-III

1000/T	%Wt loss	dw/dt	W	ln W	ln dw/dt	Δ ln W	Δ ln dw/dt
1.420	60.917	4.971	11.383	2.432	1.604	0.113	0.079
1.425	59.552	5.381	12.748	2.545	1.683	0.107	0.060
1.430	58.111	5.714	14.189	2.652	1.743	0.099	0.042
1.435	56.627	5.958	15.674	2.752	1.785	0.091	0.025
1.440	55.129	6.106	17.172	2.843	1.809	0.083	0.008
1.445	53.643	6.156	18.657	2.926	1.817	0.075	-0.008
1.450	52.193	6.105	20.107	3.001	1.809	0.067	-0.025
1.455	50.797	5.956	21.503	3.068	1.784	0.060	-0.041
1.460	49.473	5.716	22.827	3.128	1.743	0.053	-0.058
1.465	48.233	5.392	24.067	3.181	1.685	0.047	-0.076
1.470	47.086	4.997	25.214	3.227	1.609	0.041	-0.095
1.475	46.039	4.545	26.261	3.268	1.514	0.035	-0.114
1.480	45.094	4.054	27.206	3.303	1.400	0.030	-0.134
1.485	44.252	3.547	28.048	3.334	1.266	-3.334	-1.266

Step-IV

1000/T	%Wt loss	dw/dt	W	ln W	ln dw/dt	Δ ln W	Δ ln dw/dt
1.285	87.186	3.740	10.714	2.372	1.319	0.103	0.030
1.29	86.025	3.855	11.875	2.474	1.349	0.095	0.028
1.295	84.844	3.963	13.056	2.569	1.377	0.088	0.025
1.3	83.649	4.064	14.251	2.657	1.402	0.081	0.023
1.305	82.441	4.157	15.459	2.738	1.425	0.076	0.020
1.31	81.224	4.240	16.676	2.814	1.445	0.071	0.017
1.315	80.001	4.311	17.899	2.885	1.461	0.066	0.013
1.32	78.773	4.368	19.127	2.951	1.474	0.062	0.010

Table- 4.13: Calculation scheme for EMCT-20-JWA

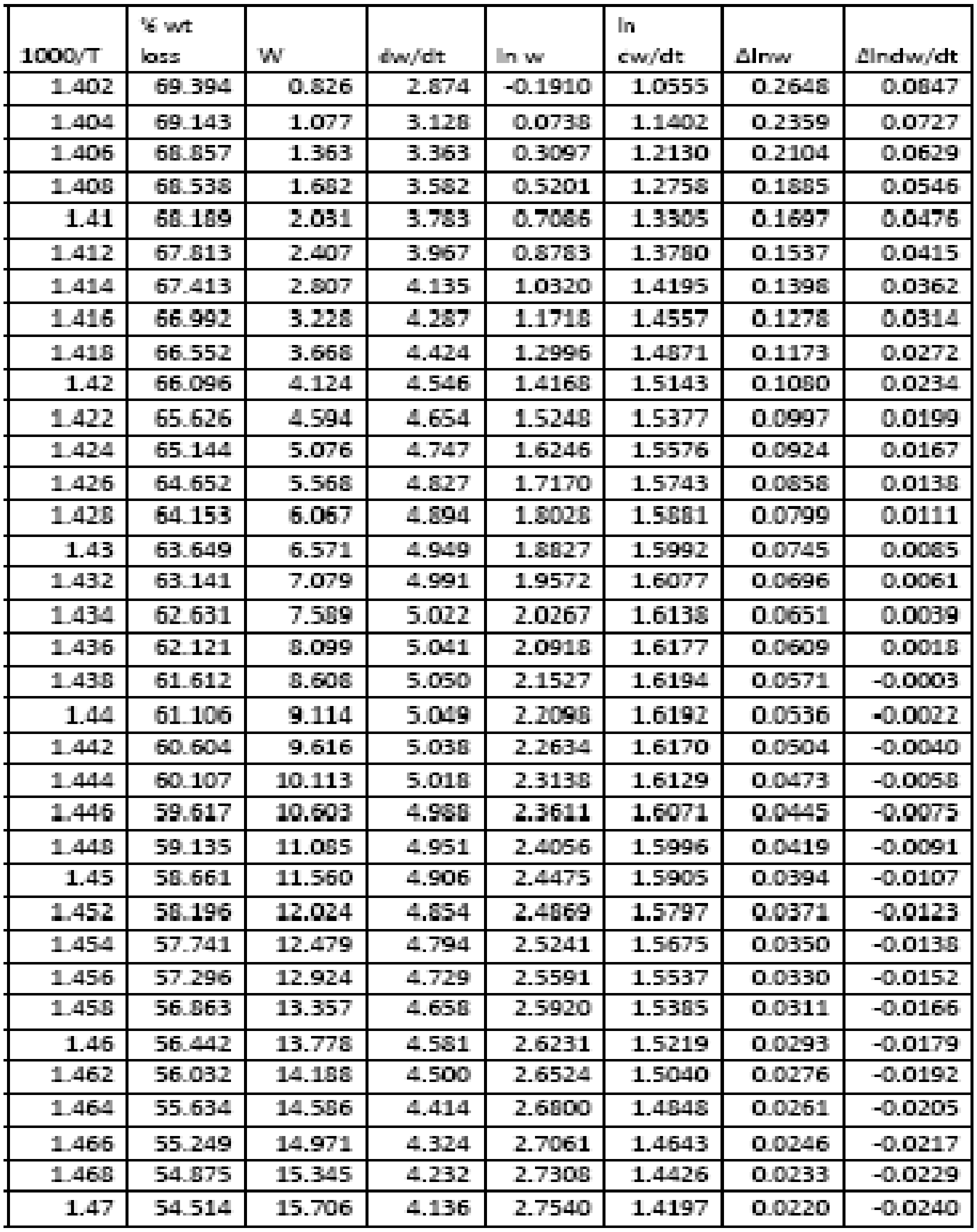
Step-I

1000/T	% wt loss	W	dw/dt	ln w	ln dw/dt	Δlnw	Δlndw/dt
1.706	21.2787	1.6213	2.43216	0.483	0.889	0.098	0.000
1.708	21.1124	1.7876	2.43107	0.581	0.888	0.088	-0.004
1.71	20.9477	1.9523	2.42167	0.669	0.884	0.080	-0.007
1.712	20.785	2.115	2.4045	0.749	0.877	0.073	-0.010
1.714	20.6247	2.2753	2.3801	0.822	0.867	0.067	-0.013
1.716	20.4672	2.4328	2.34899	0.889	0.854	0.061	-0.016
1.718	20.313	2.587	2.31169	0.950	0.838	0.057	-0.019
1.72	20.1625	2.7375	2.26873	1.007	0.819	0.052	-0.021
1.722	20.0162	2.8838	2.22063	1.059	0.798	0.048	-0.024
1.724	19.8744	3.0256	2.16791	1.107	0.774	1.107	-0.774

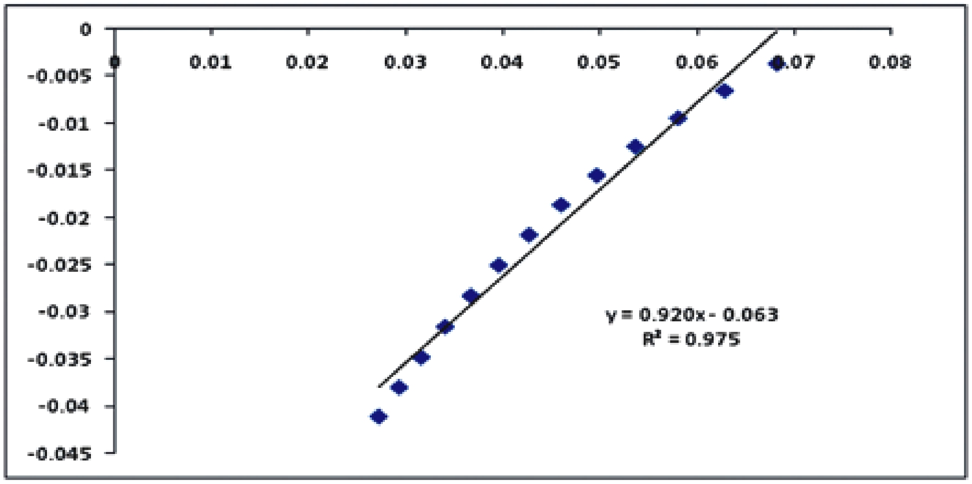
Step-II

1000/T	% wt loss	W	dw/dt	ln w	ln dw/dt	Δlnw	Δlndw/dt
1.592	40.69	1.37	9.579	0.3139	2.2596	0.4281	0.1236
1.594	39.96	2.10	10.840	0.7420	2.3833	0.3501	0.0664
1.596	39.08	2.98	11.585	1.0921	2.4497	0.2863	0.0250
1.598	38.09	3.97	11.878	1.3784	2.4747	0.2356	-0.0080
1.6	37.04	5.02	11.783	1.6140	2.4667	0.1946	-0.0360
1.602	35.96	6.10	11.367	1.8086	2.4307	0.1605	-0.0612
1.604	34.90	7.16	10.692	1.9692	2.3695	0.1312	-0.0845
1.606	33.89	8.17	9.826	2.1004	2.2850	0.1051	-0.1067
1.608	32.99	9.07	8.831	2.2054	2.1783	0.0808	-0.1274
1.61	32.22	9.84	7.775	2.2863	2.0509	0.0573	-0.1456
1.612	31.64	10.42	6.721	2.3436	1.9053	2.3436	-1.9053

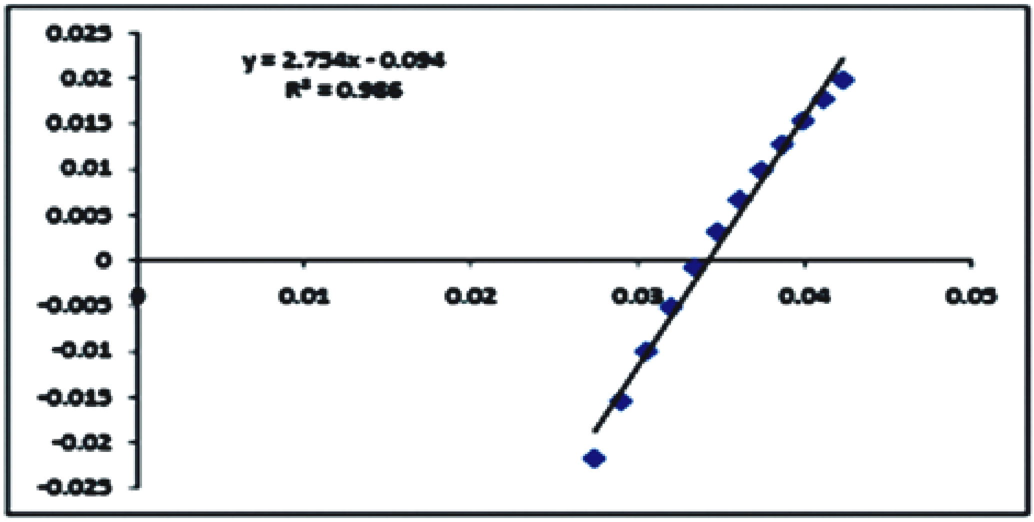
Step-III



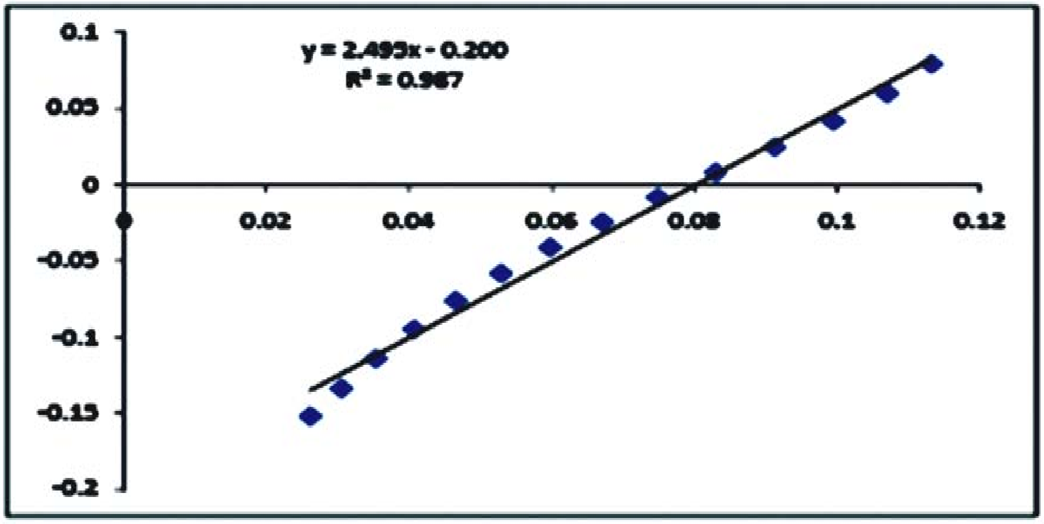
1000/T	% wt loss	W	dw/dt	ln w	ln dw/dt	Δlnw	Δlndw/dt
1.402	69.394	0.826	2.874	-0.1910	1.0555	0.2648	0.0847
1.404	69.143	1.077	3.128	0.0738	1.1402	0.2359	0.0727
1.406	68.857	1.363	3.363	0.3097	1.2130	0.2104	0.0629
1.408	68.538	1.682	3.582	0.5201	1.2758	0.1885	0.0546
1.41	68.189	2.031	3.783	0.7086	1.3305	0.1697	0.0476
1.412	67.813	2.407	3.967	0.8783	1.3780	0.1537	0.0415
1.414	67.413	2.807	4.135	1.0320	1.4195	0.1398	0.0362
1.416	66.992	3.228	4.287	1.1718	1.4557	0.1278	0.0314
1.418	66.552	3.668	4.424	1.2996	1.4871	0.1173	0.0272
1.42	66.096	4.124	4.546	1.4168	1.5143	0.1080	0.0234
1.422	65.626	4.594	4.654	1.5248	1.5377	0.0997	0.0199
1.424	65.144	5.076	4.747	1.6246	1.5576	0.0924	0.0167
1.426	64.652	5.568	4.827	1.7170	1.5743	0.0858	0.0138
1.428	64.153	6.067	4.894	1.8028	1.5881	0.0799	0.0111
1.43	63.649	6.571	4.949	1.8827	1.5992	0.0745	0.0085
1.432	63.141	7.079	4.991	1.9572	1.6077	0.0696	0.0061
1.434	62.631	7.589	5.022	2.0267	1.6138	0.0651	0.0039
1.436	62.121	8.099	5.041	2.0918	1.6177	0.0609	0.0018
1.438	61.612	8.608	5.050	2.1527	1.6194	0.0571	-0.0003
1.44	61.106	9.114	5.049	2.2098	1.6192	0.0536	-0.0022
1.442	60.604	9.616	5.038	2.2634	1.6170	0.0504	-0.0040
1.444	60.107	10.113	5.018	2.3138	1.6129	0.0473	-0.0058
1.446	59.617	10.603	4.988	2.3611	1.6071	0.0445	-0.0075
1.448	59.135	11.085	4.951	2.4056	1.5996	0.0419	-0.0091
1.45	58.661	11.560	4.906	2.4475	1.5905	0.0394	-0.0107
1.452	58.196	12.024	4.854	2.4869	1.5797	0.0371	-0.0123
1.454	57.741	12.479	4.794	2.5241	1.5675	0.0350	-0.0138
1.456	57.296	12.924	4.729	2.5591	1.5537	0.0330	-0.0152
1.458	56.863	13.357	4.658	2.5920	1.5385	0.0311	-0.0166
1.46	56.442	13.778	4.581	2.6231	1.5219	0.0293	-0.0179
1.462	56.032	14.188	4.500	2.6524	1.5040	0.0276	-0.0192
1.464	55.634	14.586	4.414	2.6800	1.4848	0.0261	-0.0205
1.466	55.249	14.971	4.324	2.7061	1.4643	0.0246	-0.0217
1.468	54.875	15.345	4.232	2.7308	1.4426	0.0233	-0.0229
1.47	54.514	15.706	4.136	2.7540	1.4197	0.0220	-0.0240



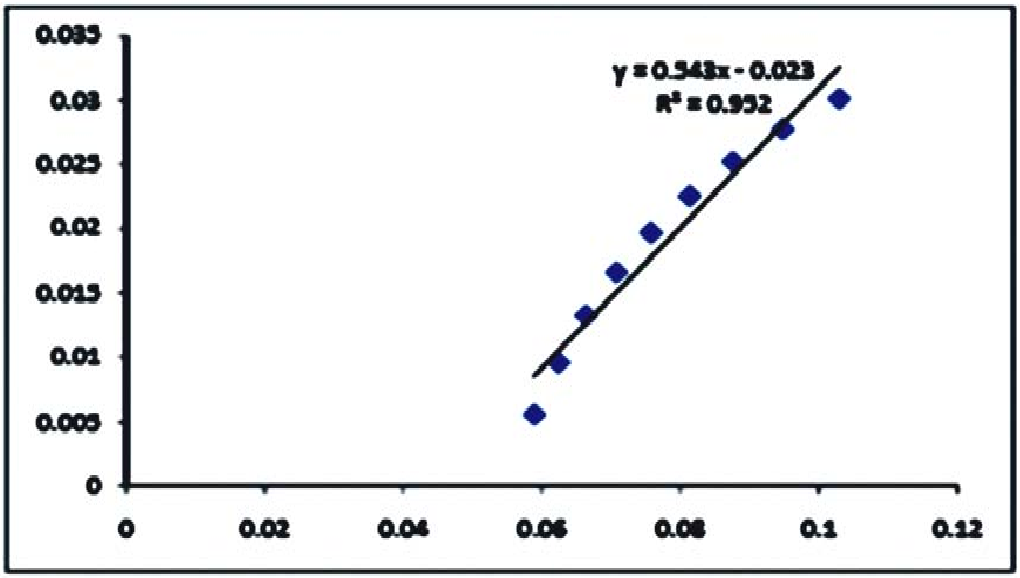
Step-1 JCN



Step 2 JCN

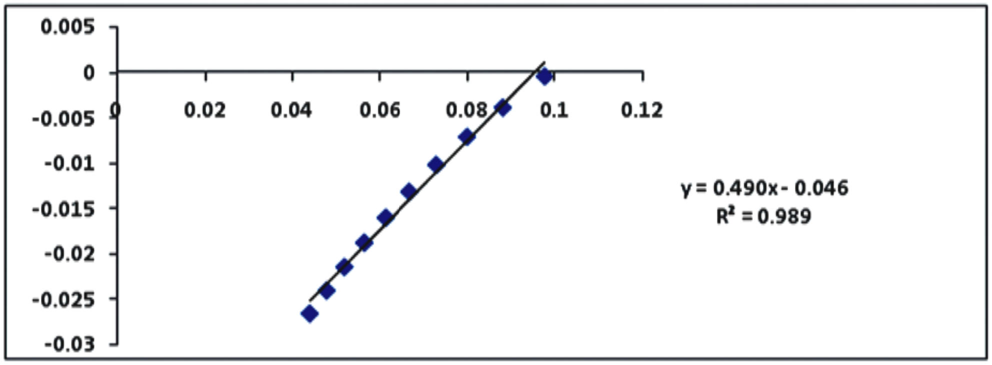


Step3 JCN

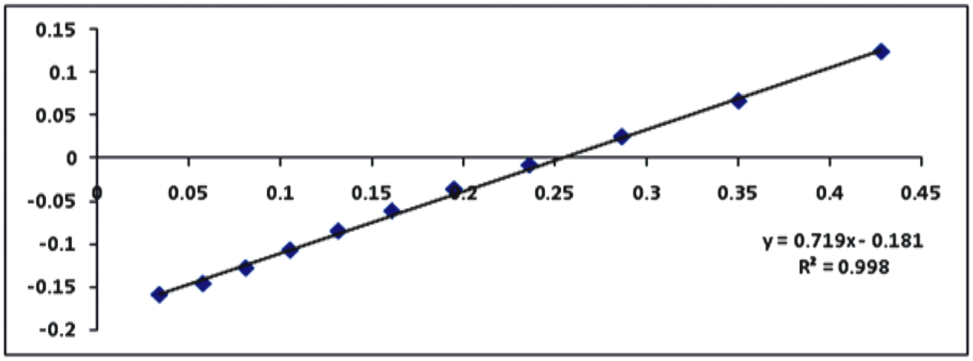


Step 4 JCN

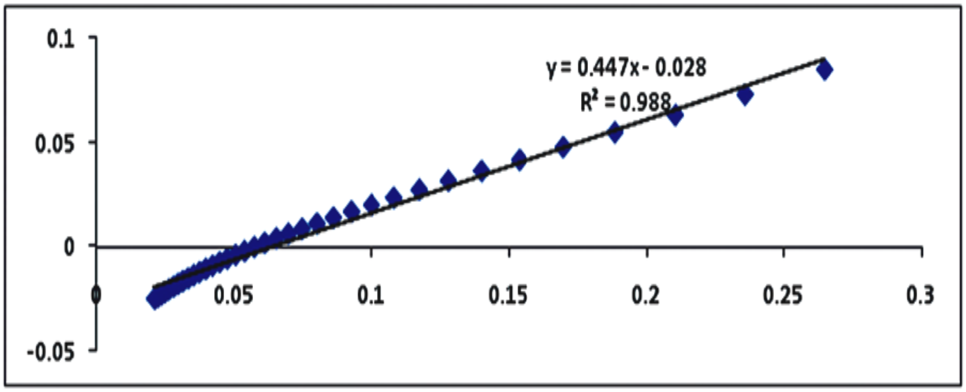
Fig.4.21 : Freeman Anderson plots for EMCT-20-JCN



Step-I JWA



Step- II JWA



Step- III JWA

Fig.4.22 : Freeman Anderson plots for EMCT-20-JWA

Table- 4-14: Comparative kinetic parameters of EMCT-20-JWA and EMCT-20-JCN

Parameter	EMCT-20-JWA	EMCT-20-JCN
E, kJ mol^{-1}	191.2	104.8
	752.4	156.3
	116.4	332.6
		38.2
A, s^{-1}	1.22×10^{15}	8.91×10^{7}
	2.46×10^{61}	7.59×10^{11}
	2.67×10^{6}	1.76×10^{23}
		0.64
n	0.49	0.92
	0.72	2.75
	0.45	2.5
		0.54
ΔS^* JK^{-1}mol^{-1}	+38.3	-97.7
	+924.2	-23.1
	-128.9	+193.1
		-256.
R^2	0.989	0.975
	0.998	0.986
	0.988	0.987
		0.952

4.6 Thermal analysis of epoxy resin of 1,1’-bis(3-methyl-4-hydroxyphenyl)-4-methylcyclohexane

TG measurements were done on a Perkin Elmer TGA (Model Pyris-I) at 10°C/min heating rate in nitrogen atmosphere. TG thermogram of EBMC is presented in Fig.4.23. EBMC is thermally stable up to about 275°C and followed two steps degradation. First step (275-350°C) involved 22.6% weight loss, while second step (350-440°C) involved 46.2% weight loss. The maximum temperature of weight loss is 387°C. The % residue left at 450 °C is 24.7%. The associated kinetic parameters were determined according to Freeman-Anderson method [16]. The calculation scheme is presented in Table-4.15 and Freeman-Anderson plot is shown in Fig.4-24. The least square values of E, n, A, ΔS^* and R^2 for second step are 405.7 $kjmol^{-1}$, 0.67, $2.38x10^{30}$ s^{-1}, $330JK^{-1}mol^{-1}$ and 0.991, respectively. High amount of residue left at 450°C indicating formation highly thermally stable cross linked product, which may further degrade at elevated temperature.

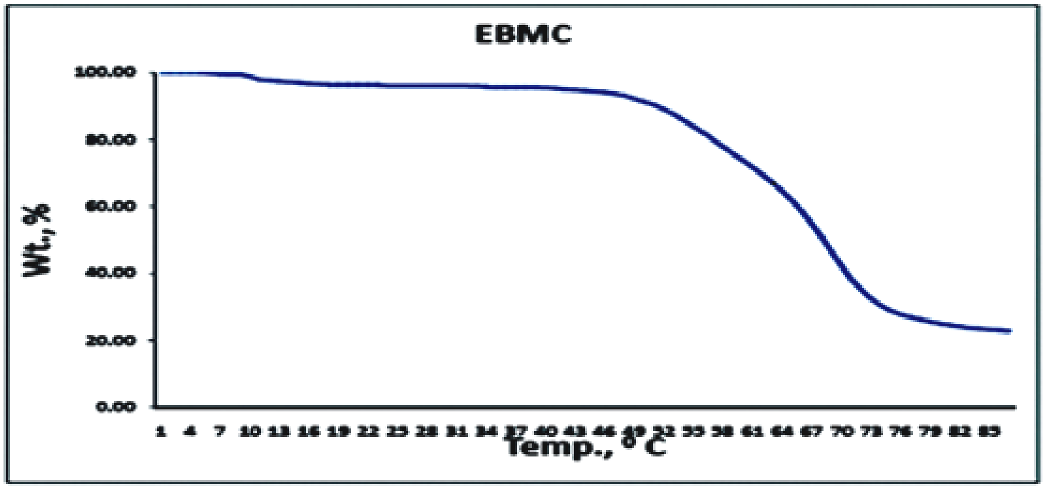


Fig:4.23: TG thermogram of EBMC at the heating rate of 10°C/min in an N_2 atmosphere

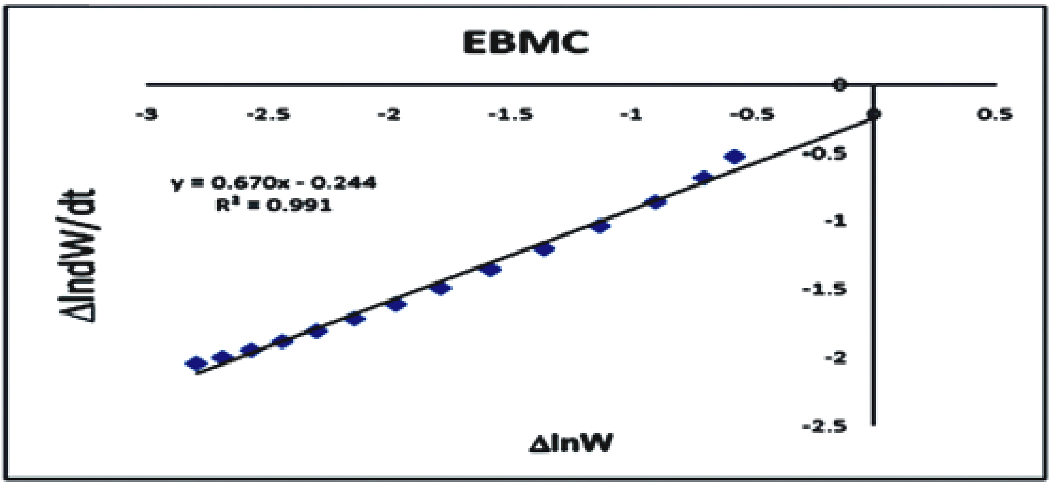


Fig.4.24. The Freeman- Anderson plot for EBMC

Table- 4.15: Calculation scheme for EBMC

1000/T	dW/dt	%wt loss	W	Lnw	lndw/dt	Lnw	∆lndw/dt
1.425	1.52776	72.6426	1.76	0.5638	0.4238	-0.564	-0.424
1.43	1.69306	72.624	1.78	0.5744	0.5265	-0.574	-0.527
1.435	1.97816	72.3821	2.02	0.7021	0.6822	-0.702	-0.682
1.44	2.35959	71.9345	2.47	0.9024	0.8585	-0.902	-0.858
1.445	2.81542	71.2985	3.10	1.1319	1.0351	-1.132	-1.035
1.45	3.32522	70.4908	3.91	1.3633	1.2015	-1.363	-1.202
1.455	3.87007	69.5278	4.87	1.5835	1.3533	-1.584	-1.353
1.46	4.43257	68.4251	5.97	1.7876	1.4890	-1.788	-1.489
1.465	4.99684	67.198	7.20	1.9744	1.6088	-1.974	-1.609
1.47	5.54851	65.8613	8.54	2.1446	1.7135	-2.145	-1.714
1.475	6.07471	64.4292	9.97	2.2997	1.8041	-2.300	-1.804
1.48	6.5641	62.9155	11.48	2.4410	1.8816	-2.441	-1.882
1.485	7.00686	61.3333	13.07	2.5701	1.9469	-2.570	-1.947
1.49	7.39467	59.6955	14.70	2.6882	2.0008	-2.688	-2.001
1.495	7.72072	58.0144	16.39	2.7964	2.0439	-2.796	-2.044

CHAPTER-5

FIBER REINFORCED COMPOSITES

5.1 Opportunities and potential applications of composites

The potential and future benefits of polymers to mankind are unlimited. Polymer composites are lightweight materials with specific physico-chemical properties and are found very important in space, defense, transportation, electronics, communications, engineering, furniture industry, etc. Fiber reinforced polymeric composites offer many potential advantages over traditional materials such as steel and aluminium. Some benefits are low density, low thermal conductivity, excellent corrosion and chemical resistance high strength to weight ratio, better design flexibility, cost effective production of complex 3D structures, excellent fatigue and impact properties, improved acoustic performance, radar/sonar transparency, low maintenance, etc.

In India, natural fibers such as jute, coir, sisal, pineapple, ramie, bamboo, banana, etc are available in abundant. Natural fibers based composites are well suited as wood substitutes for housing and construction applications. They prevent depletion of forest resources and ensure good returns to the cultivators. During natural calamities like earthquakes, floods, cyclones, etc light weight building materials are very important in saving the life and house hold commodities. Wood flour and other fibers are primarily used as fillers in thermoplastic decking, building materials, furniture and automotive components. Long agricultural fibers such as flax, kenaf, hemp and jute are used as structural reinforcements in thermoplastic/thermoset composites as a replacement of glass fiber. Advantages of natural fiber composites for automotive components includes weight reduction of 10-30%, excellent acoustical absorption properties, good impact properties with convenience of forming complex shaped parts in a single moldings process. Products such as car underbody coverings, interior door panels, dash and back panels, package trays, truck liners, door trims are being fabricated by natural fiber composites. Natural fiber is a very potential candidate in making of composites, especially for partial replacement of high-cost glass fibers for low load bearing applications. The glass provides strength and stiffness, while natural fiber reduces the overall weight.

The strong and light material has always fascinated mankind for typical applications. The idea of combining two or more different materials resulting in a new material with improved properties exists from ages. Composites bestowed with unique advantages like light-weight, high strength-to-weight ratio, drew attention from the developed world towards novel applications. Composites have proved to be worthy alternatives to other traditional materials even in the high-pressure and aggressive environmental conditions of chemical processing. Besides superior corrosion resistance, composite materials exhibit excellent fatigue performance, good resistance to temperature extremes and wear, especially in industrial sectors. The tailor ability of composites for specific applications has been one of its greater advantages such as imparting low thermal conductivity and low coefficient of thermal expansion, high axial strength and stiffness, etc.

In infrastructure they are used in pipes for potable and sewage applications, in building applications, automotive and mass transport and electrical applications. Corrosion resistance is one of the best characteristic features of composite. India having a large coastline offers plenty of opportunities for composites due to their excellent life cycle and low cost. In agricultural sector food storage silos, cold storage, body of agricultural vehicles, farm equipments and many other products suiting Indian conditions and requirements can be developed. There are plenty of opportunities in defense and aerospace. In marine sector major structural elements such deckhouses, hatch covers, kings posts and bow modules appears to be very well suited for composite construction. In automobiles they are used in cars and trucks.

In chemical industry uses of composites have become popular due to their excellent chemical resistance, lightweight, mouldability and fire resistance properties. Besides superior corrosion resistance, composite materials exhibit excellent fatigue performance, good resistance to temperature extremes and wear especially in industrial sectors. Composites are extensively used in industrial gratings, structural supports, storage tanks, scrubbers, ducting, piping, exhaust stacks, pumps and blowers, columns, reactors, etc. for acidic and alkaline environments. Some of the potential applications are composite vessels for liquid natural gas for alternative fuel vehicle, racked bottles for fire service, double-wall FRP vessels with an early warning system for leakage detection, casings for electrostatic precipitator, drive shafts, fan blades(for both axial and centrifugal fans), ducts and stacks, aerial man-lift device, etc.

Composites equipped with good electric insulation, antimagnetic and spark-free, good adhesion to glue and paint, self-extinguishing qualities are used for the construction of distribution pillars, link boxes, profiles for the separation of current-carrying phases to prevent short circuits, etc. The other potential applications of composites in this sector are for underground railway, structural for overhead transmission lines for railway, power line insulators, lightning poles, power pole cross arms, fiber optic tensile members, switchgear frames, aerial lift-truck booms etc.

Composite materials find their extensive uses in construction in place of conventional materials being used like doors and windows, paneling, furniture, non-structural gratings, long span roof structures, tanks, bridge components and complete bridge systems and other interiors. With the advantages like corrosion resistance, longer life, low maintenance, ease in workability, fire retardancy, etc. Use of composites for damage repairing, seismic retrofitting and upgrading of concrete bridges finds increased adoption as a way to extend the service life of existing structures, they are also being considered as an economic solution for new bridge structures. They are extensively used in the oil and gas sector, especially in offshore platforms. The composite pipes could be effectively used in oil refineries, offshore platforms, desalination, chemical/pharmaceutical industry, sewerage etc. They are also used in wind mill blade and turbine. There are a lot of potential applications of composites in the consumer and sports goods including canoes and kayaks, vaulting pole, golf and polo rods, archery equipment, javelin, hand gliders, wind surfer boards, protective sportswear, etc.

During last few years the fiber reinforce plastics (FRP) Industry in India has achieved growth rate ranging from 20 to 25% over the last few years. The per capita consumption of composites in India is 0.23 kg as compared to 10kg in the United States of America. This indicates that there is an enormous opportunity for the growth in consumption of these materials in the near future. Indian market needs to identify and explore products that have proven potential applications in India as well as abroad.

5.2 Experimental

Solvents and chemicals used were of laboratory grade and purified prior to their use [1]. Woven jute fabric (Brown jute, Corchorus capsularis) was collected from local market. Silane treated E-glass fabric (7 mil) (Unnati Chemicals, India) was used for composite purpose. The toluene diisocyanate (2,4-TDI: 2,6-TDI, 80:20) was supplied by Narmada Chematur Petrochemicals Ltd., Bharuch, India was used as received. Coconut fruit, wild almond (Sterculia foetida) fruit, ground nut, wheat straw, banana and sugarcane fibers were collected from local farms and were used after appropriate treatments. Vinyl ester resin (CPOL-701) was obtained from Crest Composites and Plastics Pvt. Ltd, Ahmadabad.

5.3 Measurements

The tensile strength (ISO/R 527-1996 Type-I) and flexural strength (ASTM-D-790-2003), electric strength (IEC-60243-(Pt-1)-1998) and volume resistivity (ASTM- D-257-2007) measurements were made on a Shimadzu Autograph Universal Tensile Testing Machine, Model No. AG-X Series at a speed of 10mm/min, Universal Tensile Testing Machine Model No. 1165, a high voltage tester (Automatic Electric Mumbai) in air at 27°C by using 25/75mm brass electrodes and a Hewlett Packard high resistance meter in air at 25°C and 500 V DC applied voltage after charging for 60 sec, respectively. Dielectric constant (ASTM-D-150-98) measurements were made on a Schering Bridge Tettex Switzerland. Measurements were carried out in four to five times and the mean values were considered.

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1. A. I. Vogel, A. R. Tatchell, B. S. Funis, A. J. Hannaford and P. W. G. Smith "Vogel's Textbook of Practical Organic Chemistry, 5th Ed., Addison Wesley Longman Ltd., U. K. ," 395 (1998).

5.4 Surface modification of jute fibers

Woven jute fabrics (100cm x 100cm) were soaked in a 4 % NaOH solution at room temperature (35 ± 2^0C) for 12 h. The fabrics were washed several times with distilled water to remove residual NaOH from the fiber surface. The fabrics were sun dried for 6h and cut into required sizes.

5.5 Fabrication of jute and glass fiber composites of EMC

For the preparation of glass/jute composites, 70% EMC(EE 2000) of reinforcing fibers and 20% triethylamine/20%phthalic anhydride as a hardener were used (Table-5.1). Thus, required quantity of EMC and TEA/PA were dissolved into a 500 ml beaker containing 100-125 ml MEK at room temperature. The resultant solution was heated at 80^0C with stirring for 40 min. The solution was allowed to cool to room temperature and was applied to glass/ jute fabrics (20cmx20cm) with a smooth brush and prepregs were dried in sun light for about 20 min. Eight such prepregs were staked one over the other between two preheated stainless steel plates and Teflon sheets and pressed under 27.58 MPa pressure at 150 ^{0}C for 4h and 12h at room temperature. Here after composites are designated as G-EMCT-20 and J-EMCT-20. The numerical figures indicate TEA composition.

Fiber-matrix interfacial bonding in natural fiber reinforced polymer composites is of paramount importance for potential applications in various fields. Tensile strength, flexural strength and elastic modulus of the G-EMCT-20, J-EMCT-20, J-EMC-PA and G-EMC-PA are presented in Table-5.2 from which it is clear that both types of the composites possess fairly good to good tensile and flexural properties. TEA hardener resulted into better curing property and hence good mechanical properties due to very good interfacial bonding. G-

EMCT-20 showed good electric strength and volume resistivity as compared to J-EMCT-20, J-EMC-PA due to silane treatment. The properties of the composites also depend upon amount, type and arrangement of fibers within the composites as well as on the interactions between matrix and reinforcing agent, humidity, interfacial bonding, additives like fillers, compatibilizers and impact modifiers and mode of testing, degree of cross linking, humidity, etc. Fairly good electrical properties of G-EMCT-20 and J-EMCT-20 composites may find their usefulness in electrical and electronic appliances.

5.6 Fabrication of jute-biofiber reinforced epoxy resin sandwich composites

For preparation of jute-biofiber sandwich composites (Table-5.3) required quantity of EMC and TEA were dissolved into a 500 ml beaker containing 160-175 ml MEK at room temperature. The resultant solution was heated at 80^{0}C with stirring for 40 min. The solution was allowed to cool to room temperature and was applied to two jute fabrics (20cmx20cm) with a smooth brush and remaining solution was mixed with chopped wild almond (WA)/coconut (CN)/banana (BN)/ groundnut (GN)/sugarcane (SC)/wheat straw (W) fibers (1-2mm) and dried at about 70^{o}Cfor about 8-10 min. Impregnated fibers were sandwiched uniformly between two jute prepregs and kept between two Teflon sheets. These Teflon sheets were arranged between two preheated stainless steel plates and pressed under 27.58 MPa pressure at 150 ^{0}C for 4h and 12h at room temperature. Tensile strength, flexural strength, electric strength and volume resistivity data of JWA-EMCT-20, JCN-EMCT-20, JGN-EMCT-20, JW-EMCT-20, JBN-EMCT-20 and JSC-EMCT-20 are reported in Table-5.4.

Table-5.1: Experimental details for fabrication of jute and glass composites of EMC

Composite	Fiber	Wt. of fiber, g	Wt. of EMC, g	TEA, ml	PA, g
G-EMCT-20	Glass	60.91	42.64	12	-
J-EMCT-20	Jute	115.1	80.56	22.2	-
J-EMC-PA	Jute	101.1	70.8	-	14.1
G-EMC-PA	Glass	46.7	32.7	-	6.5

Table-5.2: Mechanical and electrical properties of epoxy (EMC) jute, glass composites

Composite	Tensile strength, MPa	Flexural strength, MPa	Electric strength, kV/mm	Volume resistivity, ohm-cm
J-EMC-PA	19	27	1.2	1.2×10^{10}
G-EMC-PA	59	73	-	-
J-EMCT-20	96.5	84	7.1	1.1×10^{11}
G-EMCT-20	275	351	24.6	1.4×10^{13}

Table-5.3: Compositions for jute-biofiber reinforced epoxy (EMC) resin sandwich composites

Composite	Wt. of fibers, g		EMC, G	TEA, ml
	Jute	Biofiber		
JWA-EMCT-20	*30.3*	40	49	10
JCN-EMCT-20	31.7	40	71.7	19
JGN-EMCT-20	30.15	80	110.15	30.38
JW-EMCT-20	30.4	40	70.36	19.4
JBN-EMCT-20	31	40	71	19.6
JSC-EMCT-20	30.3	40	70.3	19.4

Table-5.4: Mechanical and electrical properties of jute-biofiber reinforced epoxy resin (EMC) sandwich composites

Composite	Tensile strength, MPa	Flexural strength, MPa	Electric strength, kV/mm	Volume Resistivity, Ω cm
JWA-EMCT-20	26.2	26	1.87	1.4×10^{9}
JCN-EMCT-20	7.9	23.6	1.4	2.7×10^{10}
JGN-EMCT-20	10.6	7.3	1.2	7×10^{14}
JW-EMCT-20	18	2.8	2.48	5×10^{14}
JBN-EMCT-20	6	52.7	0.81	2.7×10^{15}
JSC-EMCT-20	9.7	5.3	1.8	2.5×10^{14}

J: Jute; **W**: Wheat fibers; **CN**: Coconut fibers, **GN**: Groundnut fibers and **BN**: Banana fibers **WA**: Wild almond, **SC**: Sugar cane fibers

Observed tensile strength and flexural strength orders are JWA-EMCT-20 > JW-EMCT-20 > JGN-EMCT-20 > JSC-EMCT-20 > JCN-EMCT-20 > JBN-EMCT-20 and JBN-EMCT-20 > JWA-EMCT-20 > JCN-EMCT-20 > JGN-EMCT-20 > JSC-EMCT-20 > JW-EMCT-20. Tensile strength and flexural strength of JWA-EMCT-20 are almost same. Flexural property of JCN-EMCT-20 and JBN-EMCT-20 is improved approximately 4 and 9 times respectively, while it is decreased 1.5, 1.8 and 6.4 times respectively for JGN-EMCT-20, JSC-EMCT-20 and JW-EMCT-20. Comparatively wild almond, coconut and banana fibers are stiffer than those of ground nut, wheat and sugar cane fibers. Amongst biofibers used wild almond and wheat fibers based sandwich composites showed better tensile property. Wild almond, coconut and banana fibers based sand composites showed better flexural property due to their better stiffness property as compared to other biofibers.

Observed electric strength and volume resistivity trends for sandwich composites are JW-EMCT-20 > JWA-EMCT-20 ≈ JSC-EMCT-20 > JCN-EMCT-20 > JGN-EMCT-20 > JBN-EMCT-20 and JBN-EMCT-20 > JGN-EMCT-20 > JW-EMCT-20 > JSC-EMCT-20 > JCN-EMCT-20 > JWA-EMCT-20. Comparatively banana, wild almond and sugar cane based sandwich composites showed good electric strength, while JBN-EMCT-20 showed poor electric strength, but it showed excellent insulating property. JWA-EMCT-20 and JCN-EMCT-20 showed poor insulating property as compared to rest of sandwich composites indicating their polar nature.

Mechanical and electrical properties of the composites depend on various factors as mentioned previously. Low tensile property of the composites is mainly due to random orientation of biofibers, poor interfacial adhesion and brittle nature of EMCT-20. Fairly good tensile and flexural properties and fairly good to excellent insulating property of the composites signify their usefulness for low load bearing applications especially for housing units and in electrical and electronic appliances. Thus, judicious uses of biofibers in combination with appropriate matrix materials will bring environmental Green Revolution.

5.7 Fabrication of jute -polyurethane of epoxy resin reinforced composites

For the preparation of jute- epoxy- polyurethane composites, 70% EMC (EE 835) of jute fibers and 20% toluene diisocyenate of EMC were used (Table-5.5). Thus, required quantity of EMC was dissolved into a 500ml beaker containing 250-275 ml MEK at room temperature. To this solution required quantity of toluene diisocyanate in 30 ml MEK was added dropwise through a dropping funnel over a period of 10 min with stirring. The reaction mixture was stirred manually for about 15 min at room temperature. The resultant polyurethane solution was applied to jute fabrics (20cmx20cm) with a smooth brush and prepregs were dried in sun light for about 20 min. Eight such prepregs were staked one over the other between two preheated stainless steel plates and Teflon sheets and pressed under 27.58 MPa pressure at 150 ^{o}C for 4h and 12h at room temperature. Here after composites are designated as J-EMCT and TJ-EMCT.

Mechanical and electrical data of Jute-EMCT and Jute-TJ-EMC are presented in Table-5.6. Treated and untreated Jute-EMCT composites showed much lower mechanical properties as compared to J-EMCT-20 composite indicating brittle nature of EMCT, low cross- linking density and poor interfacial bonding in the composites. Tensile strength of TJ-EMCT decreased to some extent as compared to J-EMCT but flexural strength and elastic modulus are improved 2.4 and 1.3 times upon alkali treatment confirming increase in stiffness of the composite. The decrease in tensile strength of TJ-EMCT is probably due to fiber degradation. Alkali treatment can remove natural and artificial impurities and produce a rough surface topography. In addition, alkali treatment leads to breakdown of fiber bundles into smaller fibers. This increases the effective surface area available for wetting by the matrix resin. The most important aspect in natural fiber reinforced composites is the fiber-matrix adhesion because load is transferred to stiff fibers through shear stresses at the interface and it requires a good bond between the polymeric matrix and the fibers. Due to the presence of hydrophilic hydroxyl and other polar groups in the natural fibers result in poor wettability and high moisture absorption tendency of the fibers giving rise to poor interfacial bonding with the hydrophobic polymer matrix materials. Low mechanical properties of the Jute-EMCT composites is mainly due to brittle nature of EMCT, lower cross linking and poor interfacial bonding between fiber and matrix. Good to excellent mechanical properties of the composites signify their usefulness in building and construction industries.

Electric strength and volume resistivity of J-EMCT and TJ-EMCT are much lower than J-EMCT-20 due to presence of hydroxyl, urethane and other polar groups, which resulted in poor wettability and hence weak interfacial fiber-matrix bonding. EMCT is much more polar than EMCT-20, which resulted in lowering of electrical properties.

Table-5.5: Experimental details for fabrication of jute -EMCT and jute-TJ-EMC

Composite	Fiber	Fiber, g	EMC, g	TDI, ml
J-EMCT	Jute	116	81.2	16.2
TJ-EMCT	Treated Jute	120	84	18.5

Table-5.6: Mechanical and electrical data of jute -EMCT and jute-TJ-EMC

Composite	Tensile strength, MPa	Flexural strength, MPa	Elastic modulus, MPa	Electric strength, kV/mm	Volume resistivity, ohm cm
J-EMCT	37.3	10	1277	1.9	$7.7\text{x}10^{10}$
TJ-EMCT	31.5	24	1619	1.6	$3.6\text{x}10^{10}$

5.8 Fabrication of glass/jute- vinyl ester resin (CPOL-701) composites

Vinyl ester resin (CPOL-701) used for composite fabrication was 50% of glass/jute fabric (20cmX20cm). Required CPOL-701 was dissolved in 115 ml $CHCl_3$ for jute and 25 ml for glass and was added 2.5 ml MEKP and 2.5 ml cobalt naphthenate and the solution was stirred at room temperature for 5-10 min. Resultant solution was applied to jute/glass fabric with a smooth brush and dried in sunlight for 10-15 min. Eight such prepregs were stacked one over other and pressed between two preheated stainless steel plates under 27.6 MPa pressure at 50 ^{o}C for 3-4 h. Silicone spray was used as a mold releasing agent. Here after composites are designated as CPOL- 701–J and CPOL-701- G.

Water absorption study of the cured CPOL-701 films against water and 10% each of aq. HCl and NaCl was carried out by a change in weight method at 35^{o}C according to our previous work [2].

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2. N. M. Mehta, S. I. Mavani and P. H. Parsania N. M. Mehta, S. I. Mavani and P. H. Parsania , "Preparation, mechanical and electrical properties and moisture absorption study of novel bisphenol-C-formaldehdye treated and untreated jute composites," J. Polym. Mater **22**, 205-212 (2005).

Mechanical and electrical properties

Thermal, mechanical and electrical properties of the composites are very important for specific applications. Tensile strength, flexural strength, dielectric strength, volume resistivity and dielectric constant of CPOL-701-G and CPOL-701-G are reported in Table-5.7 from which, it is clear that both the composites possess excellent tensile strength and flexural strengths. CPOL-701-G possesses > 44 times volume resistivity. Both the composites possess comparable dielectric constant as those of most dielectric materials. CPOL-701-G possesses excellent dielectric strength as compared to CPOL- 701-J. In case of CPOL-701-G no puncture was observed. Flashover occurred at and above 11kV confirming excellent dielectric strength.

Mechanical and electrical properties of composites are dependent upon many factors like fiber content, fiber nature, fiber orientation, fillers, compatibilizers, impact modifier, mode of testing, etc. [3]. Excellent mechanical properties and good electrical properties of both the composites signify their usefulness for high load bearing applications as well as in electronic and electrical industries.

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3. 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 fibers," Compo. Sci. Technol **62**, 911-917 (2002).

Water absorption

The percentage weight gain/loss with the passage of time ($t^{1/2}$) is shown in Figs.5.1 and 5.2 for water, 10% aq. HCl, and 10% aq. NaCl, respectively. It is observed from Figs.5.1 and 5.2 that percent water absorption increased with time except CPOL-701-G in HCl system in which it is decreased and remained practically constant after equilibrium was established. Decrease of % water absorption with time in HCl for CPOL-701-G is due to leaching of small molecules [4]. Equilibrium water content and equilibrium time for both the composites are shown in Table-5.2. Practically no change in water absorption is observed for CPOL-701-G in NaCl system, while for CPOL-701-G in water system it has increased continuously probably due to formation of microcacks For CPOL-701-G equilibrium time in HCl is longer, while it is 42-60h for CPOL-701-J. Water absorption tendency of CPOL-701-J in HCl and water systems is > 2 times than that in NaCl system. The presence of strong electrolytes in water affects water structure and hence diffusivity. High equilibrium content for CPOL-701-J in water and HCl systems is due to solvolysis of the composite. Absorbed water plays a significant role in influencing mechanical behavior and long term durability of the polymers and polymer matrix composites. Water absorption in polymeric composites is shown to be Fickian as well as non-Fickian in character. Viscoelastic nature of polymers and cracks are responsible for non-Fickian diffusion. Water absorption continues till the cell

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4. L. R. Bao and A. F. Yee , "Effect of temperature on moisture absorption in a bismalimide resin and its carbon fiber composites," Polymer **43**, 3987-3997 (2002)

walls are saturated with water. Beyond saturation point, water exists as free water in the void structure leading to delamination or void formation [5]. Absorbed water leading to weakening of interface and accelerates delamination and decreases the strength of the composites [6]. Absorbed water causes hydrolytic degradation of both matrix and interface during service [7]. Formation of voids and blistering result in high water absorption [4,8]. Water absorption in fibrous composites depends on temperature, fiber loading, fiber orientation, permeability of fibers, surface protection, area of the exposed surface, diffusivity, void content, hydrophilicity of the individual components, etc.

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5. J. Gassan A. K. Bledzki., "The Influence of fiber-surface treatment on mechanical properties of jute-polypropylene composites," Composites **28A**, 1001-1005 (1997)
6. T. A. Collings and F. R. Jones, "Hand Book of Polymer Fiber Composites, U.K," 366 (1994).
7. J. Crank and G. S. Park, "Diffusion in Polymers," Academic Press, New York (1968)
8. C. S. Tyberg, K. M. Bergeron, Sankarpandian , P. Shih, A. C., Loos, D. A., Dollard, J. E. Mcgrath, J. S. Riffle, and U. Sorathia, "Structure-property relationships of void-free phenolic-epoxy matrix materials," Polymer **41**, 5053-5062 (2000)

DIFFUSIVITY

Assuming unidirectional diffusion, water absorption in semi infinite plate exposed on both sides to the same environment was calculated according to following relation [4]:

$$\%M = \frac{W_m - W_d}{W_d} \times 100 \qquad \dots 1$$

Where, M = % water content at time t,

W_m = Weight of moist material and

W_d = Weight of dry material

Diffusivity is related with moisture uptake with the passage of time as under,

$$M = \frac{4M_m}{h}\sqrt{\frac{t}{\pi}}\sqrt{D_x} \qquad \dots 2$$

Where, M_m = Equilibrium water content in the sample,

D_x = Diffusivity and

t = time

Diffusivity in a given environment can be determined from initial slope of the plot of M against square root of time:

$$D_x = \pi\left(\frac{h}{4M_m}\right)^2 (slope)^2 \qquad \dots 3$$

Diffusivity in different environments was determined according to Eqns. 2 and 3 and is reported in Table -5.7. Observed diffusivity order CPOL-701-J is NaCl > H_2O > HCl.

High diffusivity in saline environment indicates structure breaking tendency of NaCl, while low diffusivity in acidic environment indicates structure forming tendency of HCl, i.e. high solvating tendency. Increase in size of solvated molecules restricts the diffusion. Moreover, hydrated ions also undergo surface solvolysis due to presence of polar groups in the composites resulting in high water uptake [9]. Thus, smaller is the size of the hydrated ions, greater is the diffusivity.

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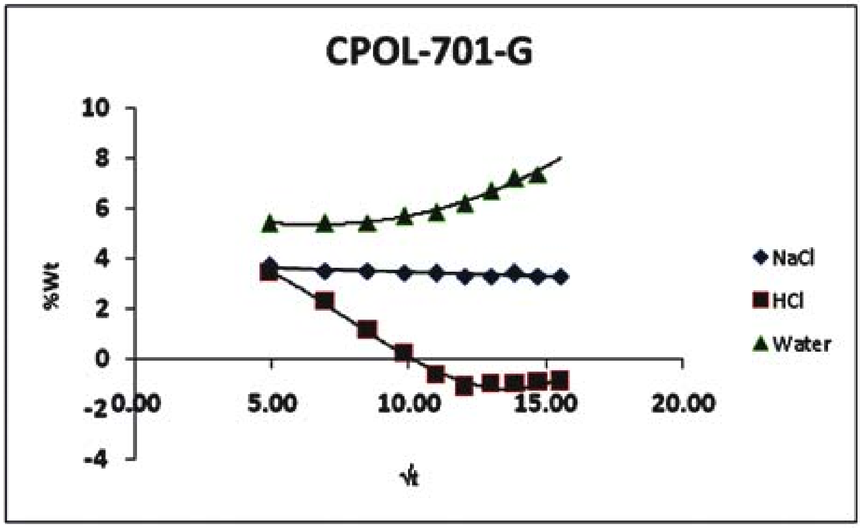

Fig.5.1. The plots of % Wt. change against $t^{1/2}$ for CPOL-701-G at 35°C

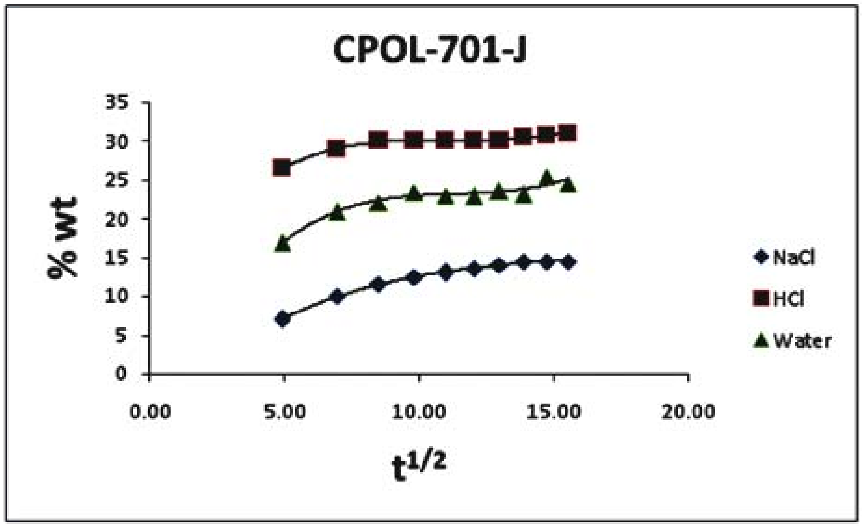

Fig.5.2. The plots of % Wt. change against $t^{1/2}$ for CPOL-701-J at 35°C

Table-5.7: Equilibrium water content, equilibrium time and diffusivity data for CPOL-701-J and CPOL-701-G

Parameter	**CPOL-701-J**			**CPOL-701-G**		
	H_2O	**10% HCl**	**10% NaCl**	**H_2O**	**10% HCl**	**10% NaCl**
Equilibrium time,h	60	42	48	-	140	-
Equilibrium water content, %	26	29	12	-	-1	-
Diffusivity, 10^{-12}, m^2s^{-1}	3.2	1.8	14.3	-	-	-

CHAPTER-6

SURFACE COATING ANDCHEMICAL RESISTANCE

6.1 Introduction

The growing concerns for environmental protection and energy conservation have driven coatings technologists to substitute sustainable resources for petro-based feed stocks [1]. Oils obtained from vegetable seeds may be categorized as an excellent example of a readily available sustainable resource [2]. Vegetable seed oils have been actively utilized to develop various valuable resins [3-10]. Such resins have found extensive applications as varnishes and surface-coating materials as well as their other applications. Among vegetable oils, castor oil represents a promising raw material based on its low-cost, low toxicity, and its availability as a renewable agricultural resource. Castor oil (CO) is used commercially in large amounts, and its major constitution, ricinoleic acid (12-hydroxy-cis-9-octadecenoic acid), is a hydroxyl fatty acid [11]. There have been many studies on the synthesis and characterization of a wide variety of polymers, especially polyurethanes, based on CO and its derivatives such as Interpenetrating Polymer Networks [12-14], cast elastomers [15-19], and insulating coatings [20].

Polyurethanes have found a wide range of applications as insulating materials in the electrical industry. The coating of magnet wire with polyurethane varnishes is one of the most important uses of polyurethane insulating materials. The property, which has led to the popularity of polyurethane enamel magnet wire, is solderability at 360–425°C, without the necessity of fluxing or stripping. Another feature of polyurethane insulated wire is its superior *Q* factor (reciprocal of dissipation factor). The desired levels of electrical insulation, environmental stability and chemical resistance are all a function of the raw material building blocks chosen to formulate the polyurethane. Although the choice of isocyanate to be used will have various effects on the final performance of the polyurethane, by far the most significant contribution comes from the polyols. The polyol backbone can be completely hydrocarbon, polyether, polyester or silicon in nature. Each has their favorable attributes, but rarely can they completely fulfill all of the specific application requirements. Ricinoleate-based polyol, however, combines many of attributes of the individual polyols into the polyurethane compound. In comparison with hydrocarbon and silicon-based polyurethanes the ricinoleates offer a better balance of chemical resistance and physical performance. They also outperform polyether-based compounds as an electrical insulator, have a better balance of chemical resistance and have a better level of reactivity. The ricinoleate can also enhance the performance of the other polyols, when blended for specific properties. A high level of compatibility with these compounds can improve electrical insulation, environmental stability, chemical resistance and physical properties.

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The purpose of coating may be decorative, functional, or both. Textile coating is a process to cover a substrate on one or both sides with a finish or a layer of protective or enclosing material. The distinct features of the substrate and coating materials are thus combined to produce a new structure with properties that are (hopefully) the best from each component [21-26]. The major coating materials used with textile substrates at the present time is vinyl, urethane, and acrylic copolymers. Films of acrylic emulsions are colorless and odorless, while exhibiting good adhesion to a variety of commonly used textile substrates, both natural and synthetic. These products have outstanding resistance to the degrading effects of ultra-violet (UV) light, heat, and ozone. Unlike conventional lattices, acrylic copolymer emulsions will not yellow with use or stiffen with age or heat; instead, acrylics maintain clarity and flexibility with time and use. This factor is of prime importance for the preparation of quality coated textile materials [22].

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Electric cables are extensively used in all major industries. These are mostly run through underground cable tunnels, trenches, overhead cable trays and ducts. Any fire incidence in the vicinity of the cables may result in initiation of fire at their surface and its spread along the cables laid in trays as modern production facilities demand long runs of power and control cables all over the plant area. Other ignitions may be due to a short circuit or overheating of the cable itself. In a majority of cases, any fire incidence to the cables causes extensive damage to the occupancy, when it spreads along the electric cables and through these to other combustible materials. In order to prevent vertical or lateral spread of fire through cables, all apertures or openings, which are part of vertical or horizontal partition elements, through which cable or cable trays pass, should therefore be segregated. It is essential that these are sub-divided into smaller zones. This may be done by providing fire barriers at different intervals by sealing all the openings with the use of materials which may result in providing adequate fire resistance. Such barriers may not be applicable for existing electric cable systems. Rapid and unrestrained propagation of fire can also be checked by applying an effective fire retardant coating on electric cables. Application of a coating is also possible in existing cable systems. Various fire retardant coatings have been studied by different researchers to find their efficacy in retarding the burning characteristics of cellulosic materials such as wood and wood-based products [27-33].

PUs are also extensively used as resins for lacquers, varnishes and coatings, composites in synthetic leather, adhesives, and spandex fibers, and they can be cast, injection molded, or extruded as elastomers [34,35]. Recently, PU-based coatings have established place in the coatings industry. In some applications, they dominate the market because of their high level of quality.

First, they combine outstanding resistance to solvents and chemicals with good weather stability. Secondly, the films have excellent mechanical properties and provide the idea balance of hardness and flexibility, even at low temperatures [36].

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Polyurethane has been broadly applied to waterproof-breathable fabric, synthetic leather, antishrink wool, adhesives and fine chemicals [37-39]. The green chemical revolution has provided an alternate mode for the chemists and industries to develop polymers by the eco-friendly route, to minimize using toxic chemicals, particularly organic solvents, which are hazardous to health and the environment. Therefore, developing volatile organic carbons (VOCs)-free waterborne PU (WBPU) resin has attracted great attention. WBPU can be divided into three ionic types: cationic, nonionic and anionic. Cationic aqueous PU (CAPU) is often applied to adhesives, coagulants, and used in membranes and synthetic leathers with micropores [40–43]. The physical properties of CAPU are greatly affected by the hard segment, soft segment, chain extender, and dispersing center [44], whereas the hard segment gives CAPU casting film superior tensile strength and hardness [45–47]; and the soft segment offers fine elasticity, abrasion resistance, flexibility and weatherability. Owing to the incompatibility with other textile finishing agents, it is applied to only a limited number of industries. According to the relevant works on anionic WBPU [48-51], Kim and Lee [48] changed the kinds of soft segments (polyethylene glycol (PEG), polypropylene glycol (PPG) and polytetramethylene glycol (PTMG)) on PU backbone, dimethylol propionic acid (DMPA) as the dispersing center to synthesize anionic WBPU. They pointed out the PU with PTMG presented an excellent tensile strength. Kim et al. [49] also used isophorone diisocyanate and polytetramethylene adipate glycol with different chain lengths to synthesize the anionic WBPU. They found the tensile strength decreased on increasing the Mn of the soft segment, while the strain showed the opposite trend.

Polyurethanes have very interesting surface properties, high water repellency and low surface energy, in particular [52, 53]. Polyurethanes (PU) have been developed into many types and classes of products with a large variety of properties [54, 55]. Due to the large variety of isocyanates and polyols, which can react together, polyurethane products possess a broad range of properties and have many applications, including foams, elastomers, adhesives and coating [55]. Like the vast majority of organic materials, polyurethanes are combustible. Consequently, their use can be restricted in buildings or in mass transport applications.

Fire-retardant intumescent coatings have found widespread use as passive fire protection for structural steel used in public buildings, petroleum refineries, and other facilities. The coatings are designed to expand and degrade, when subjected to a flame so as to provide an insulating, foamed char surface over the underlying substrate. Ideally, the char is of low reactivity and provides an impermeable barrier of high thermal resistance.

Fire-retardant coatings can safely be grouped under two categories, the non-intumescent and the intumescent coatings. While the fire-retardant non-intumescent coatings comprise additives such as borax, boric acid, antimony trioxide, zinc oxide and chlorinated compounds that do not support combustion [56,31], the fire-retardant intumescent coatings are those that swell up on heating, due to the evolved gases. The resulting expanded residual carbonaceous matter forms a toughened insulating layer over the substrate, which protects it [31]. Several researchers have studied various fire-retardant coatings to find their efficacy for retardation of the burning of cellulosic materials such as wood and wood-based products [57, 58]. However, sufficient attention has not been paid toward the use of suitable coatings to impart fire protection to PVC-sheathed electric cables.

There are two types of coatings which retard the spread of fire. One type of coating, called fire retardant non-intumescent coatings, uses additives such as borax, boric acid, antimony trioxide, zinc oxide and chlorinated compounds, which do not support combustion [27, 33]. The other type is called fire retardant intumescent coatings, which, on heating, produce residues, which are puffed up or are swelled by escaping gases. A combustion residue can be efficiently puffed up in order to produce a tough insulating foam over the surfaces to protect the materials [27, 28-32, 59, 60]. These coatings perform better than simple fire retardant coatings. This paper deals with the development and evaluation of fire retardant intumescent coatings for electric cables.

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Like the vast majority of synthetics, PU-based coatings are combustible, which consequently limits their use in buildings or in transport applications. The most practical approach to enhance fire safety performances is the incorporation of flame-retardant (FR) additives in the PU polymeric matrix. The use of intumescent additives allows both fire properties and mechanical behavior of the materials to be optimized [61, 62]. During the heating process, intumescent flame-retardant (IFR) agent generates a cellular charred layer on the surface of the material, which protects the underlying material from the action of the heat flux or flame and limits the diffusion of combustible volatile products toward the flame and of oxygen toward the polymer. The proposed mechanism is based on the charred layer acting as a physical barrier, which slows down heat and mass transfer between the gas and condensed phases [63].

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One way to flame retard polymers is to use intumescent systems [5–6]. Intumescent materials bubble and foam on heating to form a cellular charred layer on their surface, which protects the underlying material from the action of heat flux or flame. The accepted mechanism is based on the charred layer acting as a physical barrier, which slows down heat and mass transfer between the gas and the condensed phases [64].

6.2 Preparation of polyurethanes and surface coating

Polyurethanes of epoxy polyester polyols were prepared for surface coating on different substrates such as glass, tin and aluminium.The detail experimental procedure is as follows: Into a 50 ml beaker 0.5 g EMCRA / EMCLA / EMCOA / EMCR was dissolved in 5 ml chloroform and cooled to about 22-250C. Into a 50 ml conical flask, 0.1ml TDI was dissolved in 5ml chloroform and cooled to about 22-250C. This solution was added drop wise with manual stirring to polyol solution over a period of 3 min. The resultant solution was stirred with a glass rod for 5 min and then applied to 10cm x 3cm glass/aluminium /tin plates with a smooth on both the sides and solvent was allowed to evaporate at room temperature. The coated plates were dried at room temperature for a week. Multiple plates were prepared for environmental effect study.

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6.3 Chemical resistance study

Chemical resistance of coated substrates was tested against distilled water, 10% aq. HCl, 10% aq. HNO3, 10% aq. NaOH and 10% NaCl solutions at 350C. Into three different 100ml stoppered wide mouth bottles containing test solutions thermostated at 350C, each of the coated plates were dipped in the solution and their physico-chemical change were noticed with the passage of time up to 20 days.

Coating remained intake in water and saline environments without any physical and chemical change. The coating was removed within 24 h in alkaline environment in case of tin substrate and 120 h in aluminum substrate. In case of acidic environments (HCl and HNO3) coating was found to be removed within 24-48 h. In nitric acid environment coated materials became dark and both the metals got corrode. Thus, developed coating materials possess excellent hydrolytic stability against water and saline solution indicating their coating application in humid and saline environments but they failed in acidic environments due to chemical degradation.

CHAPTER-7

COMPREHENSIVE SUMMARY

This part of the thesis describes comprehensive summary of the work incorporated in the thesis.

CHAPTER-1: This chapter describes up to date relevant literature survey on cardo bisphenols, syntheses of epoxy resins, their modification, curing, and fabrication of fiber reinforced composites, characterization and applications of resins and composites and effect of fiber pretreatment on physical properties.

CHAPTER-2: This chapter describes syntheses of 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane,1,1'-bis(3-methyl-4-hydroxyphenyl)-4-methylcyclohexane, epoxy resins, epoxy acrylate, epoxy polyester polyols: EMCRA, EMCLA, EMCOA and EMCR, polyisophthalate/terephthalate, polyurethanes of EMC and epoxy polyester polyols. Polyester polyols are highly soluble in common solvents. Epoxy resins were cured using 20% phthalic anhydride and 5-25% triethyamine at 100^{o}C. It is observed that curing time decreased with TEA concentration up to 15% and then remained practically constant. Thus, optimum hardener concentration and gel time are respectively 35 min and 15% TEA.

CHAPTER-3: This chapter of the thesis describes characterization of monomers and resins mentioned in Chapter-2 by IR, NMR and Mass spectroscopic techniques. Molecular and molecular weight distribution of EMC, EMCRA, EMCLA, EMCOA and EMCR are determined by GPC. Epoxy equivalent of epoxy resins was determined by pyridinium chloride method, acid and hydroxyl values of polyester polyols. Low acid values and high hydroxyl values of the resins confirmed almost conversion of epoxide groups into corresponding esters.

CHAPTER-4: DSC and TG analyses of EMCA, EMCT-5 and EMCT-20 epoxy-isophthalate/terephthalate, epoxy polyester polyols of EMCT-20-JWA and

EMCT-20-JCN and, EBMC at the heating rate of 10^{o}C in nitrogen atmosphere. The associated kinetic parameters namely energy of activation (E), frequency factor (A), order of the reaction (n) and entropy change (ΔS^*) were derived according to Freeman-Anderson method and discussed in light of nature and structure of the resins synthesized. All the compounds are found to possess good thermal stability and followed either single/multistep degradation with fractional/integral order of degradation kinetics.

CHAPTER-5: This chapter describes opportunities and potential applications of composites, surface modification of jute fibers, fabrication of jute and glass fiber composites of EMC, jute-biofiber reinforced epoxy resin sandwich composites, jute -polyurethane of epoxy resin reinforced composites and glass/jute- vinyl ester resin (CPOL-701) composites. Tensile strength, flexural strength, electric strength and volume resistivity of all the composites have determined according to standard test methods and discussed in light of nature of fibers, matrix materials, compositions ,orientation, etc. Water absorption behavior of CPOL-701-J/G composites was studied in different environments. Good thermal behavior, mechanical and electrical properties of the composites signify their importance as low load bearing load bearing applications for housing units, in electronic and electrical appliances and for marine applications also.

CHAPTER-6: This chapter deals with literature back ground on coating materials, preparation of polyurethanes and surface coating chemical resistance study. Chemical resistance of coated substrates was tested against distilled water, 10% aq. HCl, 10% aq. HNO_3, 10% aq. NaOH and 10% NaCl solutions at 35^{0}C. Coating remained intake in water and saline environments without any physical and chemical change. The coating was removed within 24 h in alkaline environment in case of tin substrate and 120 h in aluminum substrate. In case of acidic environments (HCl and HNO_3) coating was found to be removed within 24-48 h. In nitric acid environment coated materials became dark and both the metals got corrode.

LIST OF PAPERS PUBLISHED/ACCEPTED/COMMUNICATED

1. Ultrasonic velocity and related acoustical parameters of 2-(2-4-dinitrophenoxy)-1-[2-(2,4-dinitrophenoxy)naphthalene-1-yl]naphthalene solutions at 35^oC, **Pooja P. Adroja**, S. P. Gami, J. P. Patel and P. H. Parsania. J. Indian Chem. Soc., 87(6), 679-683(2010)
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Papers Presented at Conferences/Workshops/Seminars/Symposia

1. National Seminar on Emerging Trends in Polymer Science and Technology(Poly-2011)- Jan. 2,3, 2011 at Jadavpur University, Kolkata, (**First Prize**).
2. Third conference on Recent advances in Polymer Techonology (RAPT-2011)-Jan.15, 2011 at North Maharashtra University, Jalgaon.
3. International Conference on Bridging Gaps in Discovery and Development: Chemical & Biological Sciences for Affordable Health, Wellness and Sustainability, jointly organized by Indian Society of Chemist and Biologist-Feb.4-7, 2011 at Saurashtra University, Rajkot.
4. National Conference on Recent Advances in Chemistry and Technology of Carbohydrates,(CARBO-XXV)- Nov.11-13, 2010 at Himachal Pradesh University, Shimala.
5. International Conference on Recent Trends in Materials and Characterization (RETMAC-2010)-Feb.14,15, 2010 at National Institute of Technology Karnataka, Surathkal.
6. National Seminar on Emerging Trends in Polymer Science and Technology(Poly-2009)-Oct.8-10, 2009 at Saurashtra University, Rajkot (**First Prize**).

Conferences/Workshops/Seminars/Symposia attended

1. 3rd International Workshop on Databases, Search Engines and Software (An Update for the Synthetic and Medical Chemists)- Feb. 3,4, 2011 at Saurashtra University, Rajkot.
2. Two Days National Workshop on Patents & IPR Related Updates-Sept.19, 20, 2009 at Saurashtra University, Rajkot.
3. International Seminar on Recent Developments in Structure and Ligand Based Drug Design-Dec.23, 2009 at Saurashtra University, Rajkot
4. National Conference on Spectroscopy & stereochemistry- March 18-20, 2009 at Saurashtra University, Rajkot
5. National Workshop on Updates in Process & Medicinial Chemistry-March 3,4, 2009 at Saurashtra University, Rajkot
6. National workshop on " Management & Use of Chemistry Databases & Patent Literature,"held on 27-29th February,2008 at Department of Chemistry, Saurashtra University, Rajkot