Koradiya, Suresh B., 2011, *“Studies on Polyster Polyols Based Composites and Coasting Materials”,* thesis PhD, Saurashtra University

STUDIES ON POLYESTER POLYOLS BASED COMPOSITES AND COATING MATERIALS

A

THESIS

SUBMITTED TO THE SAURASHTRA UNIVERSITY

FOR

THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

THE FACULTY OF SCIENCE (CHEMISTRY)

BY

SURESH B. KORADIYA

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

Date: -5-2011
Place: Rajkot.

(Mr. Suresh B. Koradiya)

This is to certify that the present work submitted for the Ph. D. Degree of Saurashtra University by Mr. Suresh B. Koradiya is his own work and leads to advancement in the knowledge of 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

DEDICATED
TO
MY
Family &
Guide

ACKNOWLEDGEMENTS

First and foremost, I would like to pay my homage to THE ALMIGHTY GOD for making me capable of completing my Ph.D. thesis; with his blessings only I have accomplished this huge task.

I express deep sense of gratitude to real mentor and philosopher Dr. P. H. Parsania - Professor and Head, Department of Chemistry, Saurashtra University, Rajkot. It is my immense pleasure and privilege to express my profound gratitudes to him for his never ending guidance and perseverance. His keen interest, patience and constant encouragement during my research work have enabled me to put my work in the form of the thesis. Association with him has been a life time achievement for me.

I am also thankful to all faculty members: Dr. A. K. Shah, Dr. V. H. Shah, Dr. H. S. Joshi, Dr. S. Baluja, Dr. M. K. Shah, Dr. Y. T. Naliapara, Dr. U. C. Bhoya, Dr. R. C. Khunt, Dr. F. D. Karia and administrative staff for their encouragement during my research work.

I would like to extend my sincere thanks to my seniors as well as juniors - Dr.Vrajesh, Dr.Viren, Dr.Bharat, Dr.Pankaj, Dr. Sandip, Urvishbhai, Punit, jignesh, Pooja, Lina, Ritesh, Rizwan for their help and cooperation.

I also thankful to my colleagues, Renish, Bhavesh, Govind, Piyush (motabhai), Dr, Ram Gaurang, Dr.Rahul, Dr.Ravi, Ashish, Dr, Mehul,

Deepak, Vaibhav, Dr.Rupesh, Ravi, Bhavin(Banti), Manisha, Harshad, Hardevsinh, Abhay, Ladva, Dilip, Ashish, Vishwa, Madhavi, Sabera, Amit, Vipul, Rakesh, Naimish, Minaxi, Savant, Piyush, Anil, vipul and Gami for continuous encoragement during my research work.

The never ending process of unsurpassable dedication on the name of friendship of the best friends: Jatin, Yogesh, Jayesh (gady), Chetan (Mastar).

I am also indebted to The Directors, ERDA–Vadodara for analysis. I am also thankful to UGC- New Delhi for major research project grant.

I express my deepest thanks to Mrs. Vijyaben, Jignesh and Maulik Parsania for the hospitality extended to me during prolonged research discussion at their home during this work.

The never ending process of unsurpassable devotion, love and affection, which was showered upon me by my father Batukbhai, my mother Hansaben, my sisters Kiranben, Meena, Sumi and my jiju Bharatkumar, jitukumar and Prakashkumar and my nephew Nil, Janak and Teju who have enlightened my path and always boosted me to go ahead to reach the goal.

Suresh B.Koradiya

CONTENTS

GENERAL INTRODUCTION

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

Polyurethanes constitute a class of polymers with great versatility such as excellent abrasion resistance, hardness, enhanced chemicals and solvent resistance, flexibility, high cohesive strength and amenable curing speed [3-5], which permit the manufacturing the products ranging from expanded materials to highly compact materials. Polyurethane can be tailor made according to their application as adhesive, additives, a catalyst or a coating material [6].

---

1. T. Jeevananda and Siddaramaiah, "Synthesis and characterization of polyaniline filled PU/PMMA interpenetrating polymer networks." Eur. Polym. J. 39(3), 569-578, 2003.
2. B.K. Kendagannaswamy and Siddaramaiah, "Chain extended polyurethane-synthesis and characterization." J Appl. Polym. Sci. 84(2), 359-369, 2002.
3. Y. Zhang and D. J. Hourston, "Rigid interpenetrating polymer network foams prepared from a rosin-based polyurethane and epoxy resin." J. Appl. Polym. Sci. 69(2), 271-281, 1998.

Epoxy resins are well known for their excellent physico-chemical properties and are chiefly used as adhesives, laminates, boards, molds for casting and composite materials in the aerospace and aircraft industries. In addition to these applications, they find their substantial applications in high performance surface coatings. Coatings from epoxies have been found to show marked resistance to chemicals and corrosive environments. However, these coatings fail to give satisfactory performance under strained conditions. Recently, vigorous interest has been shown in the modification of epoxies to overcome short comings such as low toughness, poor weathering resistance, low thermal stability, poor pigment holding ability, and yellowing.

Natural fibers based composites are emerging as realistic alternatives to glass reinforced composites in many applications especially as low cost, light weight and apparently environmentally superior alternatives to glass fibers in composites. Biomass is useful for particle board, medium density fiber board, medium density fiber board, pulp and composites.

---

4. Y. Zhang and D. J. Hourston, “Rigid interpenetrating polymer network foams prepared from a rosin-based polyurethane and epoxy resin.” J. Appl. Polym. Sci. 69(2), 271-281, 1998.

5. J. Stanley Stachelek, Ivan Alferiev, Masako Ueda, C. Edward Eckels, T Kevin Gleason, J. Robert Levy. ”Prevention of polyurethane oxidative degradation with phenolic antioxidants covalently attached to the hard segments.” J. Biomedi. Mater. Res.. Part A 94A (3), 751-759, 2010.

6. A. F. Yee and R. A. Pearson, “Toughening mechanisms in elastomer modified epoxies: Part-1 Mechanical studies” J. Mater. Sci. 21, 2462-2474, 1986.

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

CHAPTER 1: Literature survey

CHAPTER 2: Syntheses of monomers, epoxy resins and their polyester polyols, and polyurethanes

CHAPTER 3: Characterization of the resins

CHAPTER 4: Thermal analysis of the resins

CHAPTER- 5: Fabrication of fiber reinforced composites and their physico-chemical study

CHAPTER-6: Coating and chemical resistance study

CHAPTER-7: Summary

CHAPTER 1: LITERATURE SURVEY

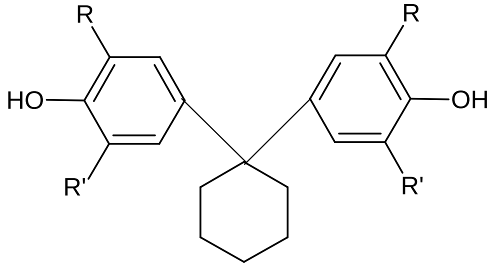
This chapter of the thesis describes up to date literature survey on syntheses, characterization of cardo bisphenols, epoxy resins, polyester polyols, polyurethanes fiber reinforced composites, coating and adhesives materials.

CHAPTER 2: SYNTHESES OF MONOMERS, EPOXY RESINS AND THEIR POLYESTER POLYOLS, AND POLYURETHANES

This chapter is further subdivided into five sections:

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

1, 1’-Bis (4-hydroxy phenyl) cyclohexane was synthesized by Friedel-Crafts condensation of cyclohexanone (0.5 mol) with phenol (1.0 mol) and mixture of HCl:CH_3COOH (2:1 v/v, 100:50 ml) at 55^{o}C for 4 h, and were crystallized repeatedly from methanol-water system. The yield and mp are 81%; and 186^{0}C, respectively.

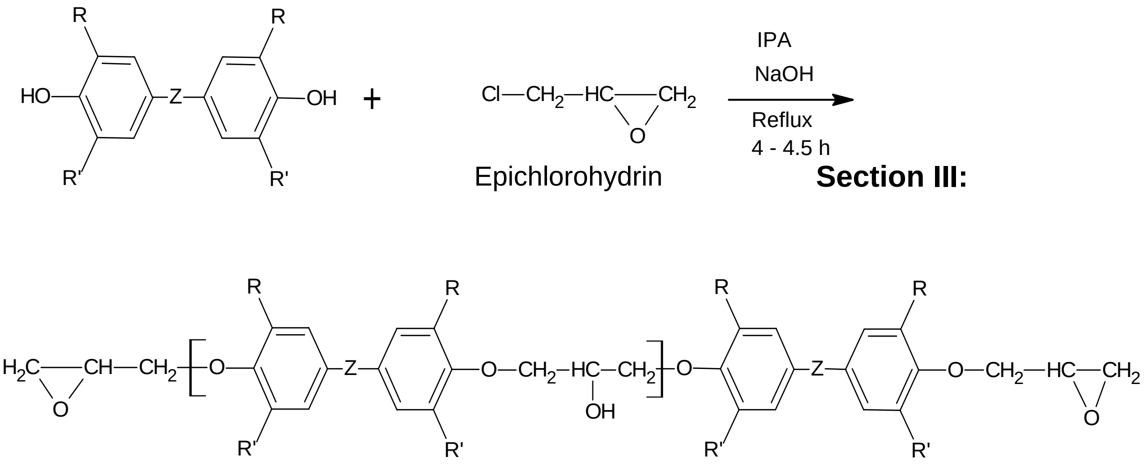


BC: R=R’=H and BrBC: R=R’=Br

BC was brominated by using bromine in glacial acetic acid at room temperature for 2h.

Section II: Syntheses of epoxy resins and their curing study

Epoxy resins were synthesized by condensing BC/BrBC (0.5mol) with epichlorohydrin (1.1 mol) using isopropanol (250 ml) as a solvent and sodium hydroxide (1.25 mol) in 50 ml water as a catalyst at reflux temperature for 4h. The resins are soluble in common solvents. Epoxy equivalents of the resins were determined by pyridine-pyridiniumchloride method. Epoxy resins are cured using varying amounts of phthalic anhydride and trimethyl amine at different temperatures.



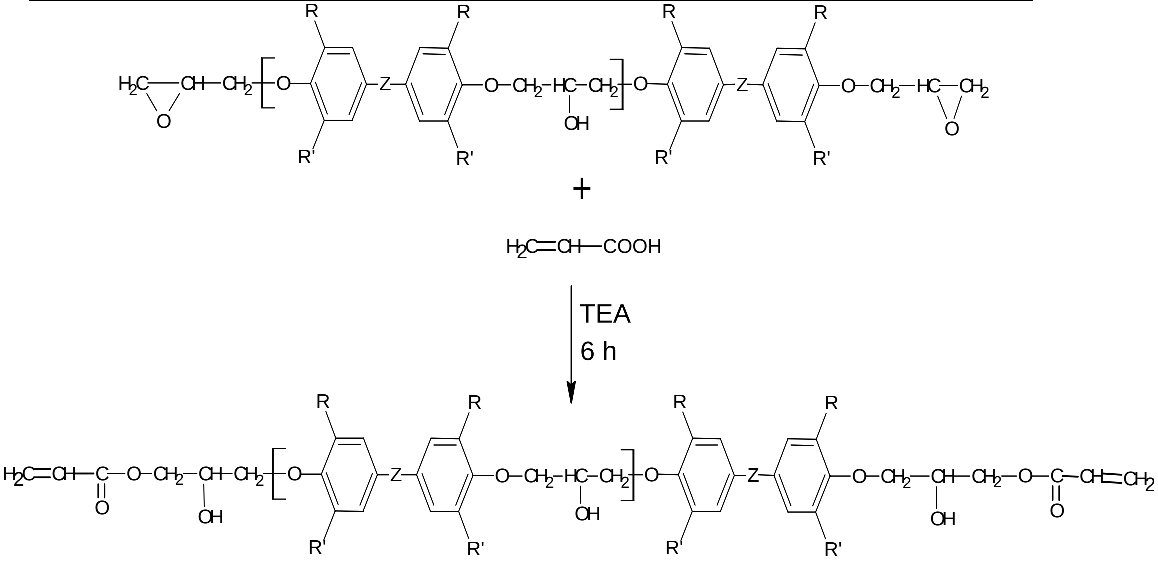
Section III:

EBC:R = R' = H and Z = Cyclohexyl

EBrBC: R = R' = Br and Z = Cyclohexyl

Syntheses of epoxy acrylates

Epoxy acrylates of EBC and EBrBC of required acid values (< 30) were synthesized by condensing EBC/ EBrBC with acrylic acid by using 1,4-dioxane as a solvent and triethyl amine as a catalyst at reflux temperature for 6h.

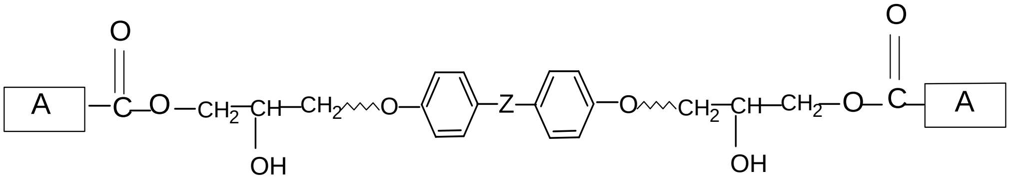


EBrBC: R = R' = Br and Z = Cyclohexyl

EBCA: R = R' = H and Z = Cyclohexyl

Section IV: Syntheses of epoxy based polyester polyols

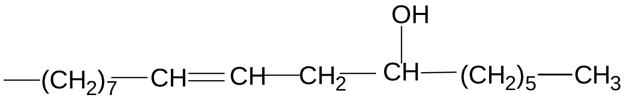
Epoxy based polyester polyols of required acid values (< 30) were synthesized by reacting EBC with ricinoleic acid/oleic acid/ lineloic acid by using 1, 4-dioxane as a solvent and triethyl amine as a catalyst at reflux temperature for 3-8h. The resins are soluble in common organic solvents. Hydroxyl values of polyester polyols were determined by acetic anhydride method and titrating with standard potassium hydroxide.



Polyester polyols

(1) Z=Cyclohexyl,

A=



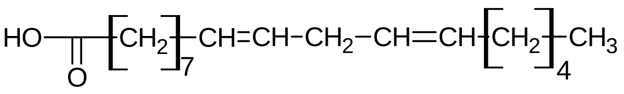
$-(CH_2)_7-CH=CH-CH_2-CH(OH)-(CH_2)_5-CH_3$

Ricinoleic acid (RA)

A = $H_3C—(CH_2)_7—CH{=}CH—(CH_2)_7—COOH$

Oleic acid (OA)

A =

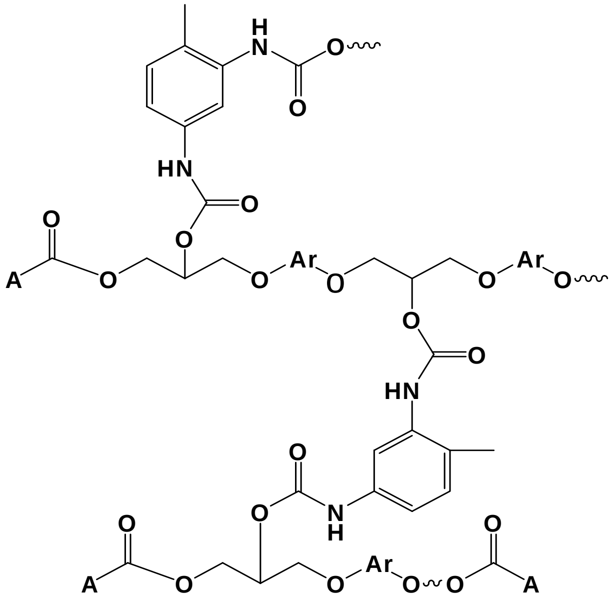


$$HO-\overset{\displaystyle\|}{\underset{O}{C}}-\left[CH_2\right]_7-CH{=}CH-CH_2-CH{=}CH-\left[CH_2\right]_4-CH_3$$

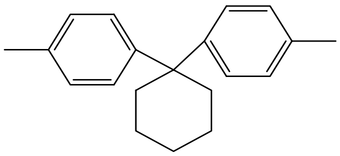
Linoleic acid (LA)

Section IV: Syntheses of polyurethanes

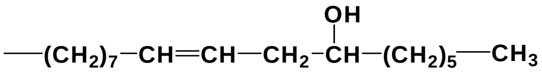
Polyurethane resins were synthesized by reacting polyester polyols with toluene diisocyanate by using MEK as a solvent at room temperature for 30 min.



Ar =



EBCRAT



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

EBCLAT A= $—(CH_2)_7—CH{=}CH—CH_2—CH{=}CH—(CH_2)_4—CH_3$

EBCOAT A= $—(CH_2)_7—CH{=}CH—(CH_2)_7—CH_3$

CHAPTER 3: CHARACTERIZATION OF THE MONOMERS AND RESINS

This chapter is subdivided into two sections:

Section I: IR spectral study

Formations of different linkages in the polymers are supported by IR spectral data.

Section II: Epoxy equivalent, acid and hydroxyl values of the resins

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 OF THE RESINS

Thermal analysis of polymers provides information on polymer molecular architecture as well as degradation mechanism under specified conditions. It also provides useful temperature range for various applications. DSC and TG analysis of cured and uncured epoxy resins, epoxy -polyester polyols and polyurethanes were carried out at 10^0C/min heating rate in nitrogen atmosphere. Various thermal parameters and kinetic parameters are determined and discussed.

CHAPTER- 5: FABRICATION OF FIBER REINFORCED COMPOSITES AND THEIR PHYSICO-CHEMICAL STUDY

This chapter is further subdivided into three sections.

Section I: Fabrication of fiber reinforced composites

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

Jute and Jute-biomass composites were fabricated by hand lay up technique using epoxy resins and polyester polyols. Required time, temperature, pressure, fibers and matrix conditions were used for composite fabrication.

Section II: Mechanical and electrical properties of the composites

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

Section III: Water absorption study of the composites

Water absorption study of composites was carried out at 35^0C as well as in boiling water. For this composites of 5cm X 5cm were fabricated. The Water uptake study was conducted periodically by change in mass method in water, acid and saline environments till equilibrium was established. The equilibrium water uptake, equilibrium time and diffusivity in different environments were determined and discussed in detail.

CHAPTER-6: COATING AND CHEMICAL RESISTANCE STUDY

This chapter is further subdivided into two sections.

Section I: Coating on various substrates

This chapter describes coating application of the polyurethane resins on different substrates such as mild steel, tin and glass. The drying behavior of the coated material is monitored with time and discussed.

Section II: Chemical resistance of coated materials

The hydrolytic stability of the coated resins in different environments was tested against water, acids and salts solutions by change in weight method till equilibrium was established. The effect in different environments on coating behavior is studied and discussed.

CHAPTER-7: Summary

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

(Dr. P. H. Parsania) (Suresh B. Koradiya)
Professor and Head,
Department of Chemistry
Date:

CHAPTER – 1

INTRODUCTION

CHAPTER-1

INTRODUCTION

1.1 General introduction

In recent years, there is a remarkable growth in the use of synthetic organic polymers in technology, both for high-tech and for consumers' product application. Polymers are able to replace the traditional engineering materials such as metal, due to their much desirable physical and chemical characterization like high strength to weight ratio, resistance to corrosion, low cost, etc. Because of the their versatile properties such as low density, ease of availability, ability to form intricate shapes, durability, proccessability, transparency electrical and thermal resistance, polymers has become ideal materials for many industrial applications. As scientific progress continued, polymers are introduced into every aspect of life, from medicine to food, packaging to computers. Since they have become a part of our day to day life, scientists and technologists have termed this era as the 'polymeric age'.

The polymers are mainly classified based on molecular structure, physical state , chemical structure and morphological behavior: Polymers can also be classified as fibers, plastics, resins and rubbers based on the nature and extent of secondary valence forces and mobility among the constitutional repeated units. They can be classified on the basis of properties: thermoplastic, thermosets and elastomers. The term thermoplastic is applied for most of the linear polymers, which can be soften and flow in response to the application of pressure and heat. Thus, most thermoplastic materials can be remolded many times, although chemical degradation may eventually limit the number of molding cycles.

Properties of polymers

The polymer properties are broadly divided into several categories based on the length-scale. At nano-micro scale, the properties that directly relate to the chain itself and represent polymer structure. At an intermediate macroscopic level, the properties describe the morphology of the polymer matrix. And at the macroscopic level, properties describe the bulk behavior of the polymer. For instance, few properties are given below to indicate how the polymer actually behaves on the macroscopic scale.

Electrical properties: Generally two types of polymers are available (i) insulating polymers and (ii) conducting polymers.

Crystallinity: A synthetic polymer can be termed as a crystalline if it contains the regions of the three-dimensional ordering on atomic (rather than macromolecules) length scales usually due to the intramolecular folding and/or stacking of adjacent chains. Synthetic polymer may consist of both crystalline and amorphous regions, the degree of crystalline materials.

Chemical properties: The attractive forces between polymer chain play major role in determining the polymers properties. Different side group in polymer structure can lead ionic bonding or hydrogen bonding between its own chains. These stronger forces typically result in higher tensile strength and melting point.

Mechanical properties: The tensile strength of materials quantifies how much stress the material will endure before failing. This is very important in applications; rely on the polymer's physical strength or durability.

Thermal properties: The term "melting point" when applied to polymers suggests not a solid-liquid phase transition but a transition from a crystalline or semi crystalline phase to a solid amorphous phase. Though abbreviated as simply" Tm", the property is more properly called "crystalline melting temperature". Among synthetic polymers, crystalline melting pertains only to thermoplastics, as thermosetting polymer will decompose at high temperature rather than melt. A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (Tg), which describes the temperature at which amorphous polymers undergo a second order phase transition from a rubbery, viscous amorphous solid to a brittle, glassy amorphous solid. The glass transition temperature can be altered by the degree of branching or cross-linking in the polymer or by adding plasticizer.

Polymer composites

Various metals, ceramics and polymers are considered suitable for the use in biomedical and industrial applications. However, some drawbacks of these materials make alternatives desirable. Disadvantages of metals include corrosion, high density, much higher stiffness, release of metal ions which may cause allergic reaction and low biocompatibility. Problem with ceramics include brittleness, low fracture strength, lack of resilience and low mechanical reliability. Polymers are too flexible and too weak to be used in certain applications and their properties can adversely be affected by sterilization processes. They may also absorb liquids and swell, or leach undesirable product. One of the goals of materials research is to create new materials with physical properties tailored to a particular application and to understand the mechanisms controlling these properties.

Composites materials can be developed by mixing two or more basic constituents with improved physical properties are new field of materials science with dramatically increasing interest. In composites polymers, the second component with very different properties is added to the polymer so that both components contribute to the properties of the product. The second component often increases the strength or stiffness of the product and said to reinforce it. Although composites are very important class of polymeric materials and they form a separate subject of study, it is necessary to consider the properties of both polymer matrix and reinforcing material.

In composites materials, insulating materials with embedded metal particles are under focus because of their special structure properties and the extraordinary optical and electrical properties.

Application of polymers/polymer composites

Generally plastics, fibers, rubber, adhesives, paints and coating are familiar as consumer products. All of these products are based on polymers and usually the same polymer can also be used for more than one application. New or expanded applications are the main reasons for the consistent growth of plastics in the last two decades. The use of PVC for pipe, conduit and sliding in construction become common. The water and soft drink bottles made of PET, which now dominates grocery shelves, have almost completely displaced glass bottles. Similarly, polypropylene used in the casing for almost all automobile batteries has the same basic formula as the polymer used for indoor-outdoor carpeting overwrap films, lawn, furniture, and polyolefin intimate apparel.

Polymer composites materials overcome many of the shortcomings of these homogeneous materials. They are currently being used in various medical procedures and many additional applications have been proposed. Polymer composites have also been developed as candidates for different types of sensing application. The conductive and absorptive properties of the insulating polymers doped with conducting materials and the absorptive properties of insulating polymers with nonconducting fillers are sensitive to exposure to gas vapors. Therefore, they can be used to monitor the existence and concentration of gases in the environment. Composites and plastics are used in a wide variety of products from advanced spacecraft to sporting goods to joint implants.

1.2 Literature survey on bisphenols

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

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

Mc Greal et al [3] have reported the condensation of ketones (0.5 mole) and phenols (1.0 mole) in acetic acid. The solutions were saturated with dry HCl for 3-4h and kept the reaction mixture for varying periods up to 4 weeks until the crystallized. The yields with aliphatic and aromatic, ketones were 10-25% and with cyclicketones 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 [4,5] have reported synthesis of 1,1'-bis(4-hydroxyphenyl) cyclohexane 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 phenyl)cyclohexane m.p. 187°C and 1,1'-bis(4-hydroxy-3-isopropylphenyl) cyclohexane, m.p. 109-111.5°C. Mash containing small quantities of bisphenol (I) protect chickens from coccidiosis better than does a sulfaguanidine.

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

Dietzler [7] has reported bromination of bisphenol in methanol-water system. Thus, bisphenol was treated with bromine at 42°C with stirring (4h). The mixture was kept for 2h at 40°C yielded 94.4% 4, 4'-isopropylidene-bis (2, 6-dibromophenol) (181-182°C), 4, 4'-cyclohexylidene bis(2,6-dibromo-phenol) (m.p. 190°C).

---

1. I. G. Farbenind, Ger. Patent 467, 728 (1927); C.A. 23, 1729 (1929).
2. I. G. Farbenind, Fr. Patent 647, 454 (1928); C.A. 23, 2540 (1929).
3. M. E. McGreal, V. Niederl and J. B. Niederl, "Condensations of ketones with phenols". J. Am. Chem. Soc. 61, 345 (1939); C.A. 33, 2130 (1939).
4. J. E. Johnson and D. R. Musell,' Diphenolcompound compositions for coccidiosis control". U.S. Patent 2,535,014 (1950); C.A. 45, 2635 (1951).
5. J. E. Johnson and D. R. Musell, "Cyclohexylidenediphenol composition for suppression coccidiosis". U.S. Patent 2,538,725 (1951); C.A. 45, 4412 (1951).H. L. Bender, L. B. Conte and F. N. Apel," Preparation of Bis-phenol". U.S. Patent 2,858,342 (1958); C.A. 53, 6165 (1959).
6. H. L. Bender, L. B. Conte and F. N. Apel," Preparation of Bis-phenol". U.S. Patent 2,858,342 (1958); C.A. 53, 6165 (1959).
7. A. J. Dietzler," Method for making alkylidene bis (dibromophenol)". U.S. Patent, 3,029,291, (1962); C.A. 57, 9,744, (1962).

Maeda et al. [8] have reported that polyurethane can be stabilized by 4,4’-thiobis(6-tert-butyl-3-methylphenyl) with 1,1’-bis(4-hydroxyphenyl) cyclohexane thermally and against UV light by adding a mixture of 4, 4’-thio bis(6-tert-butyl-3- methyl phenyl) with 1, 1’-bis (4-hydroxy phenyl)cyclohexane or 1, 1’-bis (3-methyl-4-hydroxy phenyl)cyclohexane.

Freudewald et al. [9] 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-hydroxy phenyl) cyclohexane.

Alexandru [10] has reported the preparation of bisphenols by reaction of a ketone (cyclohexanone) with phenol, BuSH, $ClCH_2CH_2Cl$ and Me_3SiCl. The mixture was stirred and heated to 50-55^{o}C and finally at 65^{o}C to give bisphenol-Z.

Subramaniam et al. [11] 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.

---

8. S. Maeda, J. Yurimoto, S. Samukawa and Y. Kojima, “Stabilized polyurethane”. Japan 14, 752(66), (1963); C.A. 66, 86,263, (1967).
9. S.Freudewald, E. Joachim, Konrad and M. Frederic, “p-Phenylphenol”.Fr. Patent 1,537,574, (1968); C.A. 71, 21,868, (1969).
10. B. S. Alexandru, U.S. Patent” Processes for bisphenols”. 4,766,255, (1988); C.A. 110, 38,737, (1989).
11. G. Subramaniam, R. Savithri and S. Thambipillai, “Synthesis and antifungal activity of bisphenolic derivatives”. J. Indian Chem. Soc. 66, 797-799, (1989).

Garchar et al. [12, 13] have studied optimization reaction conditions for the synthesis of 1,1'-bis (R,R'-4-hydroxyphenyl)cyclohexane by condensing cyclohexanone (0.05 mole) and phenol, o-cresol and 2, 6-dimethylphenol (0.1 mole) in the presence of varying mixture of hydrochloric acid and acetic acid (2:1 v/v) at four different temperatures 40°, 50°, 60° and 70°C. They have reported optimum catalyst concentration (10-15 ml), time (30-90 min) and temperature (55-70°C) for obtaining yields greater than 80%. They have also synthesized chloro, bromo and nitro derivatives and screened for their potential antimicrobial and antifungal activities against microbes. Some of these compounds are significantly found active against B. subtilis, S. pyogens and A. niger. The nitro compounds are found to be the most active as antifungal agents.

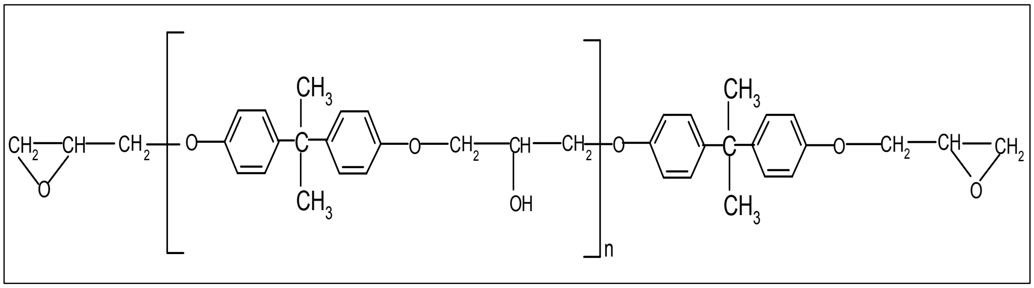
1.3 Literature survey on epoxy, epoxy ester (poly ester polyols) and their hybrid composites

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

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

---

12. H. H. Garchar, S. H. Kalola and P. H. Parsania, "Synthesis and evaluation of bisphenol-C and its derivatives as potential antimicrobial and antifungal agents". Asian J. Chemistry. 5, 340-347, (1993).
13. H. H. Garchar and P. H. Parsania, "Optimization reaction conditions for synthesis of 1,1'-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane". Asian J. Chemistry. 6, 135-137, (1994).



(I)

Various types of epoxy resins have been produced: glycidyl ethers, glycidylamines, linear aliphatics and cycloaliphatics. However, epoxy resin, which is a reaction product of epichlorohydrin and bisphenol-A, is most commonly used epoxy resin today, known as diglycidyl ether of bisphenol-A (DGEBA)(I). The resin can be obtained with different degrees of polymerization ranging from low viscosity liquids to high melting solids [14] as shown in Table 1.1.

In order to prepare high molecular weight resin and to avoid contamination the epoxy resin can be prepared by two-stage process. This Involves first the preparation of lower molecular weight polymers with a degree of polymerization of about three and then reacted with bisphenols-A in the presence of a suitable polymerization catalyst such that the reaction takes place without evolution of by product.

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

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

---

14. H. Lee and K. Neville, “Epoxy resins in their application and technology”. Mc Graw-Hill New York, (1957).

Table – 1.1: Effect of reactant ratios on molecular weight

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

Chemie Produkte [15] has reported the sealing composition for pipe joints and building materials. A typical composition consists of a mixture of an epoxy resin, a hardener and tar, which polymerized rapidly.

Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes [16], acrylates, etc. This modification of epoxy resin is feasible due to highly reactive epoxy ring, which can also undergo ring opening reaction in the presence of acids [17] to yield polyester polyol containing a free hydroxyl group that can be utilized to produce polyurethanes. To make an economic production of polyurethanes, efforts have been made to prepare polyester polyols from the low cost natural oils and their derivatives.

---

15. Chemie Produkte, “Epoxy resins containing sealing compositions”. Ger. 1,020,140, (1957); C.A. 54, 179704, (1957).
16. A. V. Cunliffe, M. B. Huglin, P. J. Pearce and D. H. Richards, “An anionically prepared flexible adhesive”. Polymer. 16, 654-658, (1975).

Epoxy resins are widely used for land, marine and space transportation, automobile and electrical components, rehabilitations products and pollution control equipments. Despite of excellent properties their brittle behavior with low elongation restricts their use for high performance applications [18-20]. Epoxy resins are widely used as a matrix in composites in different applications, where chemical, mechanical, thermal, and dielectric properties are necessary. In addition, epoxy resins are versatile cross linked thermosetting polymers with an excellent chemical resistance and good adhesion properties to different substrates. Due to these properties, they are used as adhesives and coatings. Epoxy is best for laminates in combination with glass fiber to achieve excellent electrical insulators. Excellent chemical and corrosion resistance, thermal and dimensional stability, superior mechanical and electrical properties, together with the ease of handling and processability, have made epoxy resins highly useful as surface coatings, and structural adhesive [21-25].

---

17. C. A. May, "Epoxy resins- chemistry and technology". Marcel Dekker, New York, (1988).
18. A. F. Yee, and R. A. Pearson, "Toughening mechanisms in elastomer modified epoxies: Part-1 mechanical studies". J. Mater. Sci. 21, 2462-2474, (1986).
19. S. Singh, A. K. Mohanty, T. Sugie, Y. Takai, H. Hamada." Renewable resource based biocomposites from natural fiber and polyhydroxybutyrate-co-valerate(PHBV) bioplastic". Composites Part A; 39,875–886, (2008).
20. Z. Florjanczyk, M. Debowski, E. Chwojnowska, K. Lokaj, J. Ostrowska,"Synthetical and natural polymers in modern polymeric materials". Part I: Polymers from renewable resources and polymer nanocomposites. Polymer. 10, 689–774, (2010).
21. I. Hackman, and L. Hollaway, "Epoxy-layered silicate nanocomposites in civil engineering". Composites Part A, 37, 1161-1170, (2006).
22. L. A. Marcad, A. M. Galia and J. A. Rina, "Silicon-containing flame retardant epoxy resins synthesis, characterization and properties". Polym. Degr. and Stab. 91, 2588–2594, (2006).

Ester

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

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

Greenlee [26] has prepared the rapid drying composition from diphenols and epichlorohydrin and esterified this product with Tall–oil.

---

23. R. Hua, J. Zhong Sun, A. Binjie, Q. Zhou., “Synthesis and properties of a phosphorus-containing flame retardant epoxy resin based on bis-phenoxy(3-hydroxy)phenyl phosphine oxide”. Polym. Degr. and Stab. 6, 956–961, (2007).
24. P. Guoyuan, D. Zhongjie, C. Zhanga, L. Congju ,Y. Xiaopin and L. Hang Quan. “Synthesis and characterization, and properties of novel novolac epoxy resin containing naphthalene moiety”. Polymer. 13, 3686–3693, (2007).
25. Y. Gue, B. Shao-Yun and J. Yang, “Preparation and mechanical properties of modified epoxy resins with flexible amines”. Polymer. 1, 302–310, (2007).
26. S. O. Greenlee, “Tall-oil esters”, U.S. 2,493,486 (1949) C.A. 44, 2770, (1950).

Table-1.2 Fatty acids and properties of epoxy esters

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

Lederman [27] has reported varnish based on bisphenols. A wrinkle varnish or base comprising a blend of tung-oil varnish and fish-oil varnish is described. It gives a fine texture wrinkle finish, good toughness and flexibility.

Petri et al. [28] have prepared epoxy resin foams from aqueous dispersions. Epoxy resin based on bisphenol-A, benzsulfohydrazide, dipropylene triamine were dispersed in water by 2,3-dibromopropyl phosphate as a dispersing medium. Rigid foam was obtained by this composition, which is suitable for architectural uses.

CIBA Ltd. [29] has reported coating composition for floors, roofs and walls based on bisphenol–A epoxy resin. The composition was room temperature hardenable having quartz sand, epoxy resin, dibutyl phthalate together with triethylene tetramine. This composition has consistency of mortar and a pot life of 2.0 – 2.5h. It is spread on a concrete floor to a depth of 4mm.Hardening required 24-48h. The composition shows excellent adhesion in non-cracking and is highly resistance to chemical.

---

27. B. E. Lederman (Midland Chemical Co.) ”Bisphenol-modified wrinkle varnish”. C.A. 53, 1779, (1959).
28. R. Petri, H. Reinhard and L. Keller, “Epoxy resin foams from aqueous dispersions”. Ger. 1,080,774 (1960); C.A. 55, 14,982, (1961).

Castan and Gandillon [30] have reported esterified epoxy resin of phenol formaldehyde with long chain fatty acids, which may be unsaturated, and dehydration is affected with acid catalyst to produce rapid drying films. Co. or Pb naphthenate were also used. The resulting films are relatively resistant to alkali. The use of saturated acids in the esterification step gives resins, which can be hardened in the kiln.

Union Carbide Co. [31] has reported curing of polyepoxides with liquid glycol diamines. The cured compounds have excellent impact strength and flexibility and are stable as protective coatings. Thus, 100 g of diglycidyl ether of 2,2'-bis(p-hydroxyphenyl) propane was mixed with 29.4 g stoichiometric amount of glycol diamine for 5 min. The mixture was applied on cold-rolled steel and was cured by storing 7 days at room temperature.

Minnesta Mining and Manufacturing Co. [32] have reported synthesis of flexible adhesive film having honeycomb structure. Thus, an epoxy resin mixture (I) was prepared by heating 100 parts of glycidyl ether of bisphenol – A at 121°C, adding 2-parts fine SiO_2 and stirring at 149°C for 10-20 min. A mixture of 145 parts isophthaloyl dihydrazide, 10 parts MgO and 1 part dimethyl diocta decyl ammonium bentonite was added to epoxy mixture at 104°C and the resulting mixture was milled at 77°C to complete dispersion.

Bremmer [33] has synthesized flame-retardant epoxy resin. In a typical composition tetrabromobisphenol-A was added to bisphenol-A-diglycidyl ether (epoxide equivalent 186) at 70°C under an N_2 atmosphere with stirring. The composition was cured by triethyl amine.

---

29. CIBA Ltd., "Epoxy resin containing coatings". Brit. 883,521, 1961 C.A. 56, 11746, (1962).
30. P. Castan and C. Gandillon (to Stella S.A.) "Process for the manufacture of synthetic resins obtained by condensation and esterification". U.S. 3,028, 348 (1958); C.A., 57, 11,338, (1962).
31. Union Carbide Co. (by Norman H. Reinking.), "Liquid glycol diamine curing agent for polyepoxides". Brit. 904,403 (1962) C.A. 58, 1643, (1963).
32. Minnesta Mining and Manufacturing Co. "Flexible adhesive film", Ger. 1,100,213 (1961); C.A. 58, 11551, (1963).

Karl [34] has reported phenol-HCHO resins for building materials. A typical material composed of phenol-HCHO resin precondensate, acid hardener, an ethylene glycol, BuOH or terpineol ester, mineral fillers such as CaO, $Ca(OH)_2$, $CaSO_4$ and an additive such as sand were suitable for use as building material.

Shimizu et al. [35] have esterified epoxy resins with higher fatty acids like dehydrated linseed oil fatty acid in the presence of alkali metal salt catalyst and xylene for 8 h at 230 – 240ºC under nitrogen atmosphere to give polyester with Q Gardner viscosity (as a 50 % xylene solution).

Sanariya et al. [36] have reported a convenient method for the preparation of epoxy resins based on bisphenol-C. The epoxy resins of bisphenol-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mol in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was 75-80 %.

Li et al. [37] have studied properties of sisal fiber and its composites.

---

33. B. J. Bremmer (Dow Chemicals Co.), “Flame retardant epoxy resin”. U.S.3, 294,742 (1966); C.A. (66) 38487, (1967).
34. A. Karl, “Phenol-HCHO resins for building materials”. Ger. 1,544,609 (1965); C.A. 73, 4516-4520, (1970).
35. Shimizu, S. Tachibana, A. Akihiro, M. Michio, T. Suzuki, (Toko Chemical Industry Co., Ltd) Japan Kokai. 4, 90, 14,600, (1974); C.A. 81, 1, 53,510, (1974).
36. M. R. Sanariya, D. R. Godhani, S. Baluja and P. H. Parsania, “Synthesis and characterization of epoxy resins based on 1,1’-bis(4-hydroxyphenyl)cyclohexane and 1,1’-bis(3-methyl-4-hydroxyphenyl) cyclohexane”. J. Polym. Mater. 15, 45-49, (1998).
37. Y. Li, Y. W. Mai and L. Ye, “Sisal fiber and its composite”. A review of recent developments”. Compos. Sci. and Technol. 60, 2037-2055, (2000).

They have modified the surface morphology of fibers by coupling agents such as N-substituted methacrylic acid, gamma-methacryloxy propyl trimethoxy silane, neopentyl (diallyl) oxytri (dioctyl) pyrophosphate titanate and neopentyl (dially) oxytriacryl zirconate. Composites were fabricated using modified fibers with polyester, epoxy, polyethylene, etc. both mechanical and moisture absorption resistance properties can be improved. They have also studied dynamic mechanical, electrical and ageing properties. They concluded that the modified sisal fiber reinforced composites are result of their good mechanical, environmental and economical properties.

Singh et al. [38] have fabricated jute fiber reinforced phenolic composites for the study of durability and degradation due to outdoor exposure. The physical and mechanical properties of jute composites have been studied under various conditions. The ageing induced deterioration effect of their conditions on the dimensional stability, surface topology and mechanical properties of the composite was observed.

Joffe et al. [39] have studied the composites based on flex as a reinforcing fiber. They have fabricated natural fiber composites (NFC) and compared their mechanical properties with glass mat thermoplastics (GMT). The investigation showed that NFC have mechanical properties such as matrix/fiber compatibility, stiffness, strength and fracture toughness are as high as GMT or even higher in some cases. They have concluded that such a good mechanical properties in combination with lightweight makes use of NFC very attractive for automotive industries.

Kagathara et al. [40] have reported a convenient method for the preparation of epoxy resins based on halogenated bisphenol-C. The epoxy

---

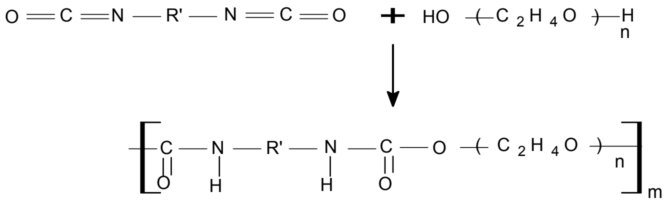
38. B. Singh, M. Gupta and A. Verma, “The durability of jute fiber reinforced phenolic composites”. Compos. Sci. and Technol. 60, 581-589, (2000).
39. R. Joffe, L. Wallstrom and L. A. Berflund, “Natural fiber composites based on flax matrix effects”. Proceedings of International Scientific Colloquium. Modeling for Saving Resources. Riga. May 17, (2001).
40. V. M. Kagathara, M. R. Sanariya and P. H. Parsania, “Selected topics in polymer science”. S.K. Dolui Edi., Prof. Sukumar Maiti, Polymer Award Foundation. Kolkata. PP 1-8, (2001).

resins of bisphenol-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mole in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was 75-80 %.

1.4 Literature survey on polyurethane resins and their composites

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

A urethane is essentially an ester of carbamic acid or substituted carbamic acid. The main advantage of polyurethane is that it can be tailor made to meet the diversified demands of modern technologies such as coatings, adhesives, foams, rubbers, reaction molding plastics, thermoplastic elastomers and composites. The pioneering work on polyurethane polymers was conducted by Otto Bayer and his coworkers in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany [41]. They recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities,



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

Especially when compared to already existing plastics that were made by polymerizing olefins, or by polycondensation. The new monomer combination also circumvented existing patents obtained by Wallace Carothers on polyesters [42].

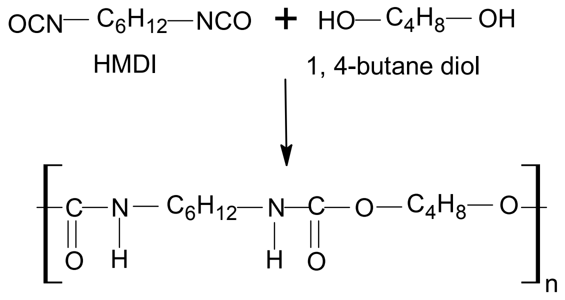
Initially, work focused on the production of fibers and flexible foams. With development constrained by World War II (when PUs were applied on a limited scale as aircraft coating), it was not until 1952 that polyisocyanates became commercially available. Commercial production of flexible polyurethane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

In 1969, Bayer AG exhibited a plastic car in Dusseldorf, Germany. Parts of this car were manufactured using a new process called RIM, Reaction Injection Molding. RIM technology uses high-pressure impingement of liquid components followed by the rapid flow of the reaction mixture into a mold cavity. Large parts, such as automotive fascia and body panels, can be molded in this manner. Polyurethane RIM evolved into a number of different products and processes. The history of polyurethane can be traced back to the 1930s in the World War II, when Germany was looking for the synthetic material for tyre. Bayer made aromatic diisocyanate in 1930 and he produced the first polyurethane in 1937 by reacting hexamethylene diisocyanate (HMDI) with 1, 4–butane diol (BDO).

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

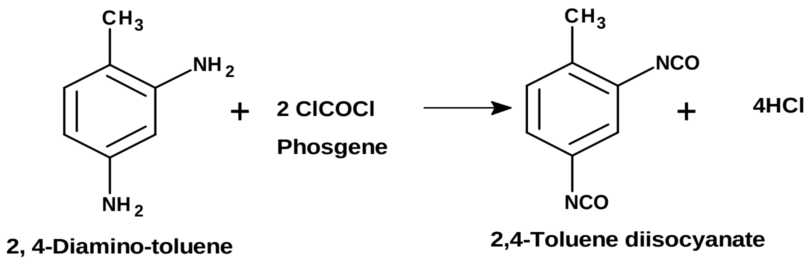
---

41. I. G. Farben, German Patent. 728,981, (1937).
42. B. Raymond, Seymour George, B. Kauffman, “Polyurethanes: A class of modern versatile materials”. J. Chem. Ed. 69, 909-914 (1992).



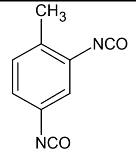
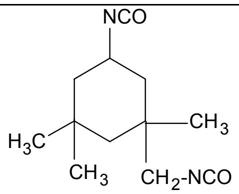
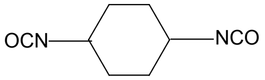
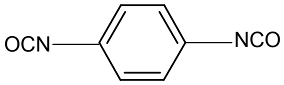
Full scale commercial isocyanate manufacture began in the United State during 1954-55. The primary use for toluene diisocyanate was in flexible foam based on polyesters; the flexible foam obtained from these products, however had two major drawbacks, high cost and poor hydrolysis resistance, which limited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

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



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

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

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

1.5 Polyester and acrylic resins

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

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

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

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

1.6 Other products with reactive hydroxyl groups

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

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

Polyurethane resins are characterized by a segmented structure, consisting of flexible segment, the polyol chains, and hard segments, crystallizability of segment, segmental length, intra and inter segment interactions such as H-bonding, overall compositions and molecular weight.

Polyurethanes possess a unique combination of performance and application properties with excellent abrasion resistance, flexibility, hardness, chemical resistance, UV light resistance and anti-microbial characteristics [43]. A great number of factors, which affect or influence the properties of polyurethane resins, are nature of polyol and diisocyanate, crosslinking density, NCO/OH ratio, curing conditions, etc [44]. Various uses of polyurethanes (US data 2000) are summarized in Table 1.4. Over the last few decades polyurethanes are widely used as adhesive materials and have developed a reputation for reliability and high performance in many applications including footwear industry, packaging applications, plastic bonding, furniture assembly and the automotive industry. Polyurethanes are rapidly developing products of coating and paint industry because of unique combinations of performance and application properties such as excellent elasticity, high hardness, high scratch and abrasion resistance, excellent impact resistance, high water, solvents, acids and alkali resistance and resistance to degradation from light and weathering.

---

43. M. X. Xu, W. G. Liu, Y. L. Guan, Z. P. Bi and K. D. Yao, "Study on phase behavior-impact strength relationship of unsaturated polyester/PU hybrid polymer network". Polym. Inter. 38, 205-209, (1995).
44. J. M. Buist, "Development in polyurethane-1". Applied Science Publishers Ltd. London, (1978).

Table-1. 4 Applications of polyurethane in various fields

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

Castor oil is a triglyceride of fatty acids, whose main constituent is ricinoleic acid, extracted from Ricinus Communis [45, 46]. Commercial castor oil consists of triglycerides that contain 90% of ricinoleic acid and 10% of non-functional acid and it has an effective functionality of 2.7. Thus, castor oil acts as a polyol, which reacts with polyfunctional isocyanates to form polyurethanes, whose properties range from rigid polymers to elastomers. Because of unique structure of castor oil, it provides better water resistance and lower viscosity as compared to the polyols. Castor oil exhibits exceptional ability in pigment wetting and penetration due to the presence of ricinoleate. The castor oil based polyurethane systems have been widely used in the telecommunication/ electrical industries, coatings, adhesives and sealants.

---

45. K. Othmer, “Encyclopedia of Chemical Technology” 4th Edition, John Wiley and Sons. Inc. New York. 5, (1979).
46. R. W. Johnson and E. Iritz, “Fatty acids in industries process properties derivatives and applications”. Marcel Dekker. New York.13, (1989).

Opera [47] has synthesized epoxy urethane acrylate from epoxy resins, acrylic acid and 4,4'-diphenylmethane diisocyanate using two stage polymerization. The oligomer obtained was studied by IR and ^{1}H NMR spectroscopy. The oligomer was cured using thermal treatment. All of these materials formed transparent films used for testing. The low molecular weight oligomers can be used as solvent less coating.

Kendagannaswamy et al. [48] have synthesized polyurethane elastomers using castor oil, 4, 4'-methylene bis (phenyl isocyanate) (MDI) and toluene 2,4-diisocyanate (TDI) and studied the effect of different aromatic diamines on the physico-mechanical and optical properties of polyurethane. The study showed that tensile strength and percent elongation were in the range of 13-24MPa and 76-32%, respectively. Higher tensile strength was observed for 4,4'-diamino diphenyl sulphone (DDS) than the 4,4'-diaminodiphenyl methane (DDM) chain extender. The properties imparted by the chain extenders were explained on the basis of the groups present in the diamines and changes have been interpreted by wide angle X-ray scattering data.

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

---

47. S. Opera, “Epoxy-urethane acrylate”. Eur. Polym. J. 36, 373-378, (2000).
48. B. K. Kendagannaswamy, V. Annadurai, V. Siddaramaiah and R. Somashekar, “Physico-mechanical, optical and waxes studies on chain extended PU”. J. Macromol. Sci. 37, 1617-1625, (2000).

tensile strength of composite is four to six times greater than that, of steel or aluminium, Improved torsional stiffness and impact properties, Composites have greater fatigue endurance limit (up to 60% of the ultimate tensile strength), Composite materials are 30-45% lighter than aluminium structures designed to the same functional requirement, lower embedded energy as compared to other structural materials like steel, aluminium, Composites have lower vibration transmission than metal, long life offers excellent fatigue, impact, environmental resistance and reduced maintenance; Composites enjoy reduced life cycle cost as compared to metals, improved appearance with smooth surface and wood like finis.

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

Polyurethanes are very appealing class of polymers for use in the biomedical field. This is because of their relatively good biocompatibility, their physical properties and the ease with which their properties can be tailored to end use. They are widely used in the development of medical devices, for tissue and blood contact such as mammary prosthesis, vascular catheters, artificial skins, vascular grafts, artificial heart diaphrams and valves. They can be biodegradable depending upon their chemical structures [49].

Swada [50] has synthesized epoxy modified polyurethane resin for a coating comprising curing agent (B) and an epoxy modified PU resin (A), which is the byproduct of reacting a carboxyl group containing polyurethane polyol containing repeat units derived from reacting an isocyanate compound

---

49. R. Jayakumar, M. Rajkumar, R. Nagendran and S. Nanjundan, "Synthesis and characterization of metal-containing polyurethanes with antibacterial activity", J. Appl. Polym. Sci. 85, 194-206, (2002).
50. H. Swada, "Epoxy-modified PU resin for a coating material". GB 2,369,123A, (2002).

(a) and a polyol (b) with a hydroxyl carboxylic acid (c) with an epoxy compound (d) in such a proportion that the epoxy group falls in a range of 0.1 to 1 equivalent per equivalent of the carboxyl group.

Desai et al. [51] have synthesized polyester polyols using vegetable oil fatty acids having different characteristics (mainly in terms of hydroxyl functionality) and epoxy resin, using triethyl amine as a catalyst. Polyols were characterized by FTIR spectroscopy. PU adhesives were synthesized from it and used in bonding the rubber. Treatment of sulphuric acid on the non-polar styrene-butadiene rubber (SBR) surface was studied for the bond strength improvement via an increase in wettability of the rubber surface. Wettability was found by measuring the contact angle using Goniometer. Bond strength was evaluated by 1800 T-peel strength test. The surface modification and mode of bond failure were studied by scanning electron microscopy (SEM).

Mehdizadeh and Yeganeh [52] have synthesized polyurethane elastomers based on difunctional castor oil and poly (propylene glycol), 2,4-diisocyanate and 1,4-butane diol and cured using toluene diisocyanate dimmer as cross linking agent. The elastomers were characterized by conventional methods. Physical, mechanical and thermal properties of the elastomers were studied. Investigation of these properties showed that the elastomers could be tailor made in order to fulfill industrial needs.

Prabu and Alagar [53] have prepared two different inter crosslinked networks (ICN) of siliconized polyurethane-epoxy / unsaturated polyester (UP) coatings. Epoxy and unsaturated polyester resins were modified with poly

---

51. S. D. Desai, A. L. Emanuel and V. K. Sinha, “Polyester-polyol based PU-adhesives; effect of treatment on rubber surface”. J. Polym. Research. 10, 141-149, (2003).
52. M. R. Mehdizadeh and H. Yeganeh, “Synthesis and properties of isocyanate curable millable polyurethane elastomers based on castor oil as a renewable resource polyol”. Eur. Polym. J., 40, 1233-1238, (2004).
53. A. A. Prabu and M. Alagar, “Mechanical and thermal studies of inter-crosslinked networks based on siliconized polyurethane-epoxy/unsaturated polyester coatings”. Prog. Org. Coatings. 49, 236-243, (2004).

urethane prepolymer and hydroxyl terminated polydimethylsiloxane (HTPDMS) using γ-amino propyl triethoxysilane and vinyl triethoxysilane as silane crosslinker and dibutyltindilaurate as a catalyst. The coating materials were obtained in the form of tough films and characterized for their mechanical properties such as tensile strength and impact strength as per ASTM methods, while thermal stability of the ICN coatings was studied using differential thermal analysis and thermogravimetric analysis and compared with unmodified epoxy/PU systems. The results revealed that the mechanical properties was increased by the incorporation of the PU (10 wt %) and silicone (10 wt %), while the thermal stability was decreased. Whereas, the incorporation of 10% silicone into the PU modified epoxy/PU system, the thermal stability was increased due to the partial ionic nature, high energy and thermal stability of Si-O-Si linkages.

Joshi and Athawale [54] have synthesized polyurethane resins from chemoenzymatically modified castor oil and different isocyanates and studied the difference in hardness, flexibility, impact strength and chemical resistance, when the different isocyanate precursors were used. The interesterification of castor oil and linseed oil was carried out near ambient temperature using lipase as a catalyst. The resultant interesterification product (IP) was reacted with isocyanate to form polyurethane resins. Polyurethane synthesized by this method is light in color and compared to conventional ones obtained from chemically catalyzed interesterification reactions at high temperature.

Somani et al. [55] have developed high solids polyurethane coating formulation by reacting different castor oil based polyester polyols with aromatic as well as aliphatic isocyanate adducts in different NCO/OH ratios. The structure of polyurethane resins was confirmed by FTIR spectroscopy,

---

54. K. R. Joshi and V. D. Athawale, “Structure-property relationship in polyurethane coatings synthesized from chemoenzymatically modified castor oil”. J. Polym.Mater. 21, 165-174, (2004).
55. K. Somani, S. Kansara, R. Parmar and N. Patel”. High solids polyurethane coatings from castor-oil-based polyester polyols”. Int. J. Polym. Mater. 53, 283-293, (2004).

while molecular weight between the crosslinks and solubility parameter of the samples were determined by swelling method. The polyurethane resins were coated on test panels and tested for flexibility, scratch hardness, cross-hatch adhesion, impact, pencil hardness and solvent resistance as per standards. The effect of catalyst, structure of isocyanate and flexibility of polyols on the final properties was also studied. Thermal stability of these polymers was determined by thermo gravimetric analysis (TGA).

Pechar et al. [56] have synthesized the polyurethane networks (PUNs) using polyols derived from soybean oil, petroleum, or a blend of the two in the conjunction with diisocyanate. The soybean-based polyols (SBPs) were prepared using air oxidation, or by hydroxylating epoxidized soybean oil. Some of the networks were subjected to several solvents to determine their respective swelling behavior and solubility parameters. Sol-fractions were also determined, and DMA experiments were utilized to monitor the changes in storage modulus and tan δ with temperature for networks with sol and with the sol extracted. A linear relationship was noted between the hydroxyl number of a SBP and the glass transition temperature of its corresponding unextracted PU network within the range of hydroxyl numbers (i.e., 55-237 mg KOH/g) and glass transition temperatures (i.e., -21 to +83°C) encountered in this work. This same linear relationship was realized between the weighted hydroxyl number of soy and petroleum-based polyol blends and the glass transition temperature of the resulting unextracted and extracted network PUs within the ranges utilized in this study (i.e., 44-57 mg KOH/g, -54-19°C).

Eren et al. [57] have synthesized simultaneous interpenetrating polymer networks (SINs) based on bromoacrylated castor oil polyurethane. In the first step, simultaneous addition of bromine and acrylate to the double bonds of castor oil was achieved. In the second step, bromoacrylated castor oil (BACO) was reacted with toluene diisocyanate (TDI), to form a

---

56. T. W. Pechar, S. Sohn , S. Ghosh , C. E. Frazier , A. Fornof , T. E. Long and G. L. Wilkes, “Characterization and comparison of polyurethane networks prepared using soybean-based polyols with varying hydroxyl

content and their blends with petroleum-based polyols**”.** J. Appl. Polym. Sci. 101, 1432-1443, (2006).

prepolyurethane (BACOP). The prepolyurethanes were reacted with styrene (STY), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and 3-(acryloxy)-2-hydroxy propyl methacrylate (AHPMA) free radically, uses the acrylate functional group to prepare the simultaneous interpenetrating polymer networks (SINs). 2,2′-Azobis (isobutyronitrile) (AIBN) was used as the initiator and diethylene glycol dimethacrylate (DEGDMA) was used as the crosslinker. BACO and BACOP were characterized by IR ^{1}H-NMR, and ^{13}C-NMR techniques. Synthesized polymers were characterized by their resistance to chemical reagents, thermogravimetric analysis, and dynamic mechanical and thermal analyzer (DMTA). All the polymers decomposed with 6-10% weight loss in a temperature range of 25-240°C. MMA-type SIN showed the highest Tg (126°C), while STY-type SINs showed the highest storage modulus (8.6 × 10^{9} Pa) at room temperature, with respect to other synthesized SINs.

Kumar et al. [58] have prepared polyethylene glycol-400 (PEG) based polyurethane (PU) and polyacrylonitrile (PAN) semi-interpenetrating polymer networks (SIPNs) (PU/PAN; 90/10, 70/30, 60/40 and 50/50) by sequential polymerization method. The prepared SIPNs have been characterized by physico mechanical properties. The microcrystalline parameters such as crystal size (⟨N⟩, lattice disorder (g), surface (Ds) and volume (Dv) weighted crystal size of SIPNs were estimated using wide angle X-ray scattering studies, and quantification of the polymer network has been carried out on the basis of these parameters. The microstructural parameters were established using exponential, lognormal, and reinhold asymmetric column length distribution functions and the results are compiled.

---

57. T. Eren, S. Çolak and S. H. Kusefoglu , “Simultaneous interpenetrating polymer networks based on bromoacrylated castor oil polyurethane”. J. Appl. Polym. Sci.100, 2947-2955, (2006).
58. H. Kumar, R. Somashekar, S. S. Mahesh, S. Abhishek, T. N. Guru Row, G. S. Kini and Siddaramaiah, “Structure-property relationship of

polyethylene glycol-based PU/PAN semi-interpenetrating polymer networks". J. Appl. Polym. Sci. 99, 177-187, (2006).

Rath et al. [59] have synthesized novel two component polyurethane sealant from hydroxy-terminated polybutadiene (HTPB) end capped with toluene diisocyanate(TDI) and polyoxypropylene triol. The 4,4′-diamino-3,3′-dichlorodiphenylmethane(DADCDPM)and4,4′-diamino-3,3′-dichloro triphenyl methane (DADCTPM) were used as chain extenders and fillers.Evaluation of mechanical properties and ageing studies indicated that the sealant possessed excellent mechanical properties and stability in different environments.

Parsania et al. [60-70] have carried out considerable work on natural fiber/ glass fiber reinforced composites based on polyurethanes composites. They reported encouraging results on the use of biofibers in making value added composites.

Ansell et al. [69] have synthesized the polyurethane networks (PUNs) using polyols. Little attention has been paid to joining unidirectionally-reinforced high strength natural fiber composites in the manufacture of engineered structures. Therefore the main objective of the paper is to investigate the effect of joint geometry on the strength of natural fiber composite joints. Epoxy-bonded single lap shear joints (SLJs) between henequen and sisal fiber composite elements were manufactured and tested in tension to assess the shear strength of the structural bonds. The performance of co-cured joints, termed ‘‘intermingled fiber joints" (IFJs) and ‘‘laminated fiber joints" (LFJs) was also evaluated.

---

59. S. K. Rath, U. G. Suryavansi and M. Patri, "A novel polyurethane sealant based on hydroxy-terminated polybutadiene". J. Appl. Polym. Sci. 99, 884-890, (2006).
60. S. I. Mavani, N. M. Mehta and P.H. Parsania, "Synthesis and physicochemical study of bisphenol-C-formaldehyde-toluene diisocyanate polyurethane–jute and jute–rice husk/wheat husk composites". 101, 2363-2370, (2006).

61. P. J. Vasoya, V. A. Patel, B. D. Bhuva and P. H. Parsania, “Synthesis and physico-chemical study of high performance cardo copoly(ether-sulfone-sulfonates)”. Polym. Plast. Techno. Eng. 47, 826-835, (2008).
62. V. A. Patel, P. J. Vasoya, B. D. Bhuva and P. H. Parsania, “Preparation and physico-chemical study of hybrid glass-jute (treated and untreated) bisphenol-C based mixed epoxy-phenolic resins composites”. Polym. Plast. Techno. Eng., 47, 842-846, (2008).
63. V. A.Patel, B. D. Bhuva, and P. H. Parsania,”Performance evaluation of treated–untreated jute–carbon and glass–carbon hybrid composites of bisphenol-C based mixed epoxy–phenolic resins”. J. Reinf. Plast. and Compos. 28, 2549-2556, (2009).
64. V. A. Patel, B. D. Bhuva, and P. H. Parsania,”Preparation and physico-chemical study of jute–carbon hybrid composites of bisphenol-C based mixed epoxy–phenolic resins”. J. Reinf. Plast. and Compos.28, (16), 2025-2033, (2009).
65. B. D. Bhuva and P. H. Parsania,”Studies on jute/glass/hybrid composites of polyurethane based on epoxy resin of 9,9’-bis(4-hydroxy phenyl) anthrone-10(EBAN) and PEG-200”. J. Appl. Polym. Sci. 118, 1469-1475, (2010).
66. J. P. Patel, N. M. Mehta and P. H. arsania,”Preparation and physico-chemical study of sandwich glass-jute-bisphenol-C-formaldehyde resin”. Polym. Plast. Technol. and Engg. 49,(8), 822-826, (2010).
67. Pooja P. Adroja, J. P. Patel, N. M. Mehta and P. H. Parsania, ”Physico-chemical study of CPOL-701–glass/jute composites”. Polym. Plast. Techno. Engg. 49(5), 449-453,(2010).
68. V. A. Patel and P. H. Parsania, ”Preparation and physico-chemical study of glass–sisal (treated– untreated) hybrid composites of bisphenol-C based mixed epoxy–phenolic resins”, J. Reinf. Plas. Compos., 29(1), 52-59, (2010).
69. C. Gonjalej-Murillo and M. P. Ansell “Co-cured in-line joints for natural fiber composites”. Compo. Sci. and Techno. 70, 442-449, (2010).

Jaszkiewicz et al [70] have synthesized novel resins the effects of reinforcing polylactic acid (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) biopolymers on the mechanical performance were studied. Both PLA and PHBV were compounded with man-made cellulose, jute and abaca fibers. The test bar specimens were processed via injection molding. Various testing methods, including tensile and impact tests, were used to investigate the composites' mechanical performance. Scanning electron microscopy was carried out to study the fiber–matrix interfacial adhesion. To determine the fiber-size distribution, optical microscopy was used. Finally, the obtained results were compared to composites on PP basis with the same reinforcing fibers. The reinforcing with fibers increased the tensile stiffness and strength significantly; however, depending on the fiber type, different improvements of the mechanical parameters were achieved.

Carsten Mai et al. [71] have synthesized novel resins. Poor fiber–matrix interfacial adhesion may, however, negatively affect the physical and mechanical properties of the resulting composites due to the surface incompatibility between hydrophilic natural fibers and non-polar polymers (thermoplastics and thermosets). A variety of silanes (mostly trialkoxysilanes) have been applied as coupling agents in the NFPCs to promote interfacial adhesion and improve the properties of composites.

---

70. A. Bledzki, A. Jaszkiewicz, "Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibers– A comparative study to PP". Compo. Sci. Techno. 70, 1687–1696, (2010).
71. Yanjun Xie, Callum A.S. Hill, Zefang Xiao, Holger Militz, Carsten Mai, "Silane coupling agents used for natural fiber/polymer composites. Composites: Part A, 41, 806–819, (2010).

1.7 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

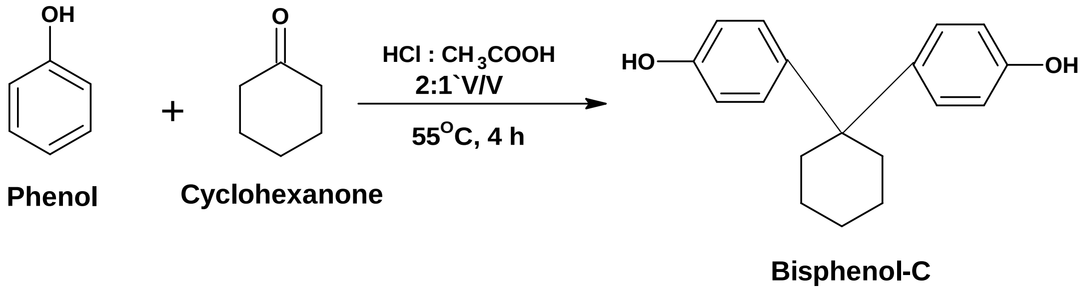
CHAPTER-2

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

This chapter is further subdivided into five sections.

2.1: Bisphenol-C derivatives

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



(I)

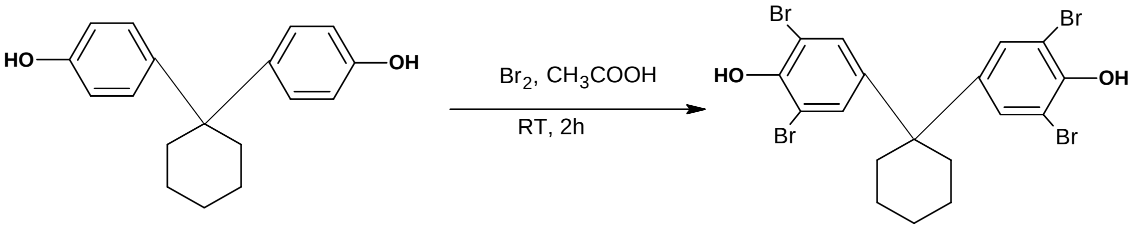
1, 1'- Bis (4-hydroxy phenyl) cyclohexane here after designated as BC was synthesized according to reported methods [1-2]. Thus, cyclohexanone (0.5 mol, 49 g) was treated with phenol (1.0 mol, 94 g) in the presence of mixture of HCl :CH_3COOH (2:1 v/v, 100:50 ml) as a Friedel-Craft catalyst at 55^0C for 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution. The resinous material was removed by filteration through cotton plug. The yellowish solution so obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50^oC. BC was further crystallized repeatedly from benzene and methanol-water systems. The process was repeated to get pure, white, shining crystals of ~81% yield and m. p. of BC was 186^oC.

---

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).

Synthesis of 1-1’-bis (3, 5-dibromo-4-hydroxy phenyl) cyclohexane

To a 250 ml three necked flask equipped with a mechanical stirrer, thermometer and thermostat was placed 0.01 mol BC in 20ml acetic acid at room temperature and 5ml bromine in 10ml acetic acid was added dropwise through a separating funnel over a period of 15min with stirring [3]. The reaction mixture was stirred at room temperature for 2h and then neutralized with a dilute sodium hydroxide solution. Separated creamish product was filtered, washed well with sodiumbisuphite solution till unreacted bromine was removed completely and finally with distilled water and dried at 50^{0}C. The product was charcoalized twice in methanol and crystallized three times from methanol-water to get shining crystals. Hereafter product is designated as BrBC. The purity of BrBC was checked by TLC and the structure is supported by spectroscopic techniques



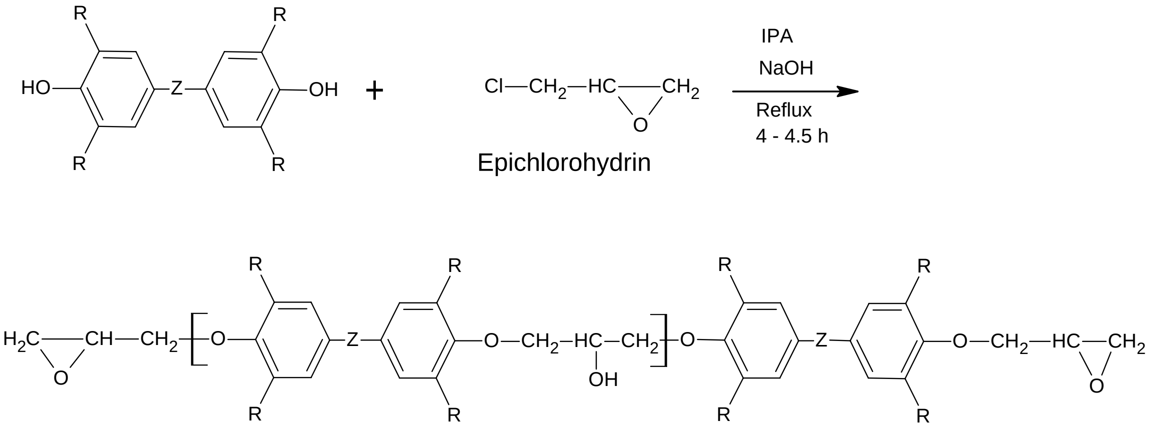
(II)

---

2. H. H. Garchar, H. N. Shukla and P. H. Parsania, “Kinetics of formation of 1,1’-bis(3-methyl-4-hydroxyphenyl)cyclohexane”. Indian. Acad. Sci. (Chem. Sci.). 103, 149-153, (1991).
3. P. H. Parsania, **“**Physico-chemical studies on some industrially important bisphenols”. Asian J. Chem.2, 211-213, (1990).

2.2: Syntheses of epoxy resins and their curing study

Epoxy resins were synthesized [4] by condensing BC/BrBC (0.5mol) with epichlorohydrin (1.1mol) and using isopropanol (250mol) as a solvent and 1.25 mol sodium hydroxide in 50 ml water as a catalyst at reflux temperature for 4h. 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 are soluble in $CHCl_3$, acetone, 1,4-dioxane, DMF, 1,2-dichloroethane, dichloromethane, and DMSO and partially soluble in ethanol and isopropanol.



(III)

EBC:R = H and Z = Cyclohexyl

EBrBC: R = Br and Z = Cyclohexyl

---

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

Curing of epoxy resin

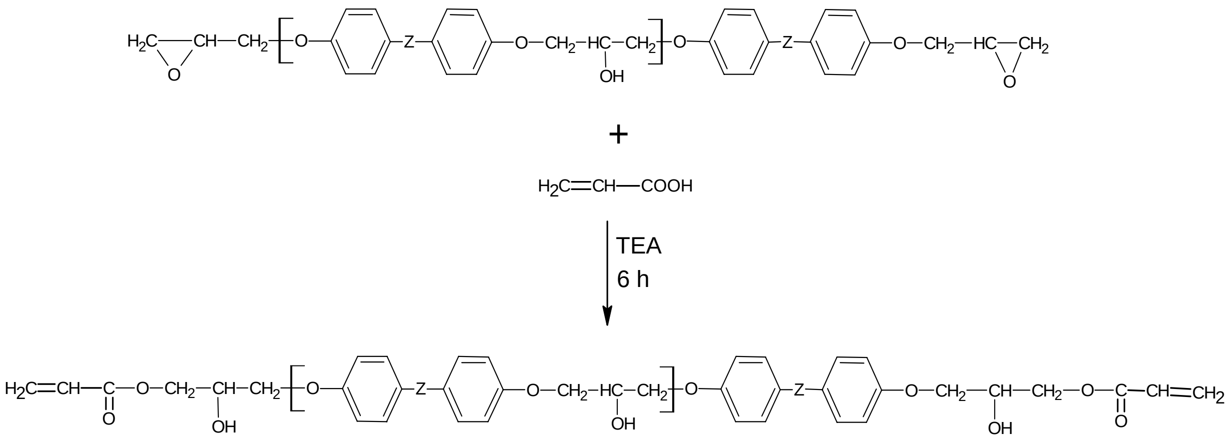
Curing study of EBC was carried by using varying amounts of triethylamine (TEA) and phthalic anhydride (PA) as hardeners at 100 °C. Thus, into five different test tubes, 2 g EBC and varying amounts of TEA and PA (5-25 Wt%) were dissolved in 5ml MEK and placed in water bath at 80°C. The MEK was evaporated slowly with stirring and then the test tubes were placed in an oil bath at 100°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 EBCT-5 to EBCT-25 and EBCP-5 to EBCP-20. The cured samples are insoluble in most of the common solvents but they show swelling behavior in chloroform, 1-2 dichloroethane, dichloromethane, 1,4-dioxance, tetrahydrofuran, toluene, isopropyl alcohol, carbon tetrachloride, xylene, dimethly formamide, dimethylsulfoxide, etc. From Table-2.1, it is observed that gel time decreased with hardener concentration.

Table-2.1: Gel time for TEA and PA cured for EBC at 100°C

% Hardener	Gel time, min For TEA	Gel time, min For PA
5	190	220
10	170	205
15	140	195
20	125	180
25	95	175

2.3: Syntheses of epoxy acrylate

Into a 250 ml round bottomed flask containing 20 g EBC, 50 ml 1,4-dioxane, 50ml acrylic acid and 2 ml triethylamine was placed in an oil bath. The reaction mass was refluxed for 5 h and cooled. Liquid 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 EBCA.



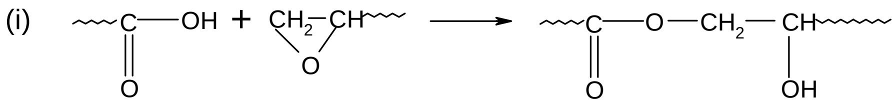
where EBCA : Z = Cyclohexyl

IV

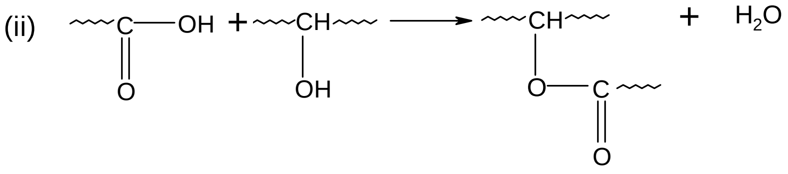
2.4: Syntheses of epoxy polyester polyols and their polyurethanes

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



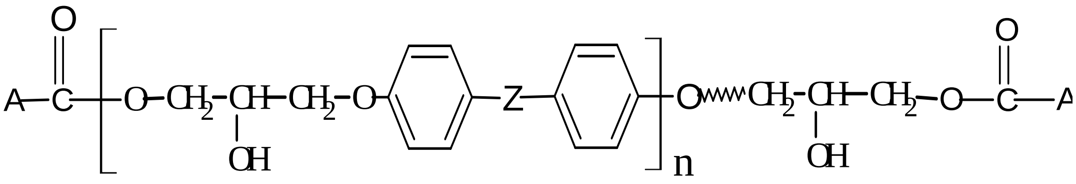
Hydroxy ester



Condensation ester

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 are described as under:

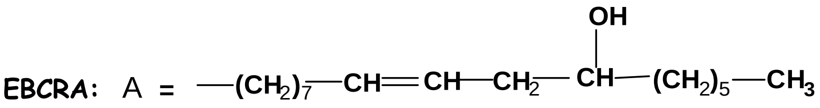
Into a 100 ml round bottomed flask equipped with a condenser and oil bath were placed, 6.0 g EBC, 12.0 g ricinoleic acid/linoleic acid/oleic acid, 20 ml 1,4-dioxane and 1.5 ml triethyl amine (TEA) as a catalyst and the resultant reaction mass was brought to reflux for varying time interval (3-8h) to get desired acid values (<30 mgKOH/g) of the resin. Liquid 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 hereafter designated as EBCRA, EBCLA, and EBCOA. Polyester polyols are highly soluble in common solvents like acetone, chloroform, 1,4-dioxane, ethylacetate, toluene, methylethylketone, N,N-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, 1,2-dichloroethane, dichloromethane, etc.



Polyester polyols

(V)

Where Z=Cyclohexyl,



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

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

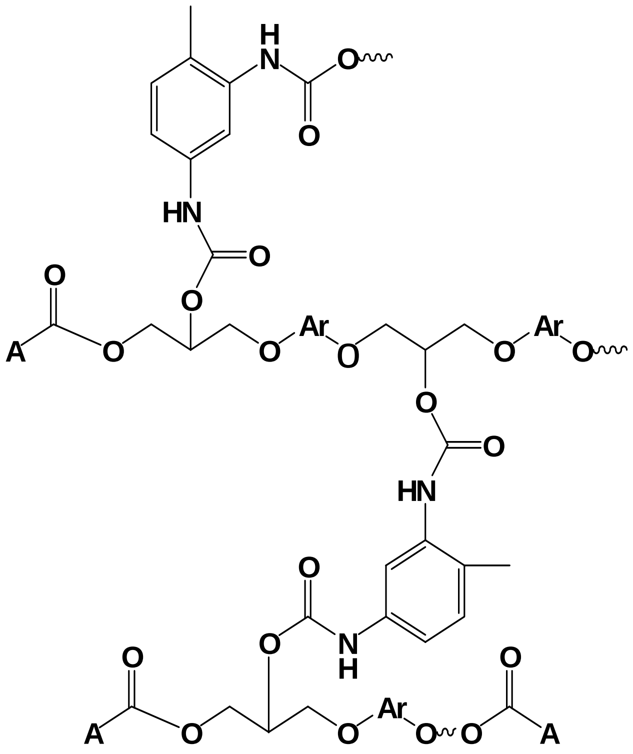
EBCLA: $A = -(CH_2)_7-CH{=}CH-CH_2-CH{=}CH-(CH_2)_4-CH_3$

Curing study of epoxy polyester polyols

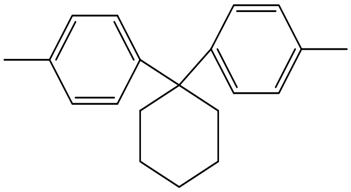
Curing study of EBCRA, EBCLA and EBCOA were carried by using varying amounts of toluene diisocynates as a hardener at 140^{o}C. Thus, into five different test tubes, 2 g EBCRA/EBCLA/EBCOA and varying amounts of TDI (5-25 Wt%) were dissolved in 5ml MEK and placed in water bath at 80^{o}C. MEK was evaporated slowly with stirring and then the test tubes were placed in an oil bath at 140^{o}C and the time of curing was monitored (Table-2.2) and further post cured for 30 min. Here after cured samples are designated as EBCRAT-5 to EBCRAT-25 EBCLAT-5 to EBCLAT-25 and EBCOAT-5 to EBCOAT-25. General structures of polyurethanes are shown in Scheme VI. The cured samples are insoluble in most of the common solvents but they showed swelling behavior in chloroform, 1,2 dichloroethane, dichloromethane, 1,4-dioxance, tetrahydrofuran, toluene, isopropylalcohol, carbontetrachloride, xylene, dimethlyformamide, dimethyl sulfoxide, etc. From Table-2.2, it is observed that gel time decreased with TDI concentration.

Table-2.2: Gel time for epoxy polyester polyols cured using TDI at 140^{o}C

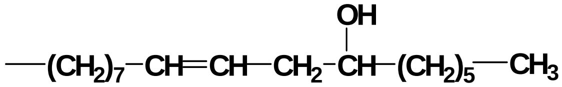
% TDI	Gel time, min		
	EBCRA	EBCLAT	EBCOAT
5	185	145	180
10	175	140	165
15	170	135	155
20	160	130	145
25	155	125	140



Ar =



EBCRAT A =



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

EBCLAT A= $-(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$

EBCOAT A= $-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$

VI

CHAPTER – 3

CHARACTERIZATION OF THE RESINS

CHAPTER-3

CHARACTERIZATION

This chapter of the thesis is subdivided into two subsections.

3.1: IR spectral study

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

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

The IR spectra of resins and polymers were scanned on a Shimadzu-8400 FTIR spectrometer over the frequency range from 4000-400 cm^{-1}.

1,1'-Bis(4-hydroxyphenyl)cyclohexane and 1-1'-bis(3,5-dibromo-4-hydroxy phenyl)cyclohexane

IR spectrum of BrBC and EBrBC are presented in Figs. 3.1 and 3.2, respectively. The characteristic IR absorption frequencies (cm^{-1}) for BrBC and EBrBC are 505-606(C-Br str.), 2929-2934 (C-H v_{as}), 2865(v_s) 1595-1501 (C=C str.), 1491-1445 (C=C str. and C-H def.), 1228 (C-O str.), 945(epoxy group) besides other normal modes of vibrations.

Epoxyacrylate

IR spectrum of EBCA is presented in Fig. 3.3. The characteristic IR frequencies (cm^{-1}) for EBCA are 3423 OH str., 1733 C=O str. (ester), 1456 C-H ipd ($-CH=\underline{CH_2}$), 1248 C-H ipd ($-\underline{CH}=CH_2$), and 1041 alkyl C-O str. Thus, IR spectral data confirmed the formation of EBCA

Triethyl amine and phthalic anhydride cured epoxy resins

IR spectra of EBCT-5 and EBCP-5 are presented in Figs.3.4 and 3.5 respectively. The characteristic IR frequencies (cm^{-1}) for EBCT-5 and EBCP-5 are 3356-3592 OH str., 12321254 aryl C-O-C str., 1044 alkyl str. and 1136 C-O str. and OH def. besides normal modes of aliphatic, alicyclic and aromatic groups. Thus, IR spectral data confirmed the formation of EBCT-5 and EBCP-5.

Epoxy polyester polyols

IR spectra of EBCRA, EBCLA and EBCOA are presented in Figs.3.6-3.8, respectively. The characteristic IR absorption frequencies (cm^{-1}) are 3408-3420 OH str., 1736-1733 C=O str. (ester), 1248-1249 aryl C-O-C str. and 1041-1040 C-OH def. besides normal modes of aliphatic, alicyclic and aromatic groups. Thus, IR spectral data confirmed formation of epoxy polyester polyols

Polyurethanes

IR spectra of EBCRAT, EBCLAT and EBCOAT are presented in Figs.3.9-3.11, respectively.The characteristic IR absorption frequencies (cm^{-1}) are. 1734-1717 (urethane str.), 1536-1503 C=C str. and 1247-1226 C-O-C str. besides normal modes of aliphatic, alicyclic and aromatic groups. Thus, IR spectral data confirmed formation of polyurethanes.

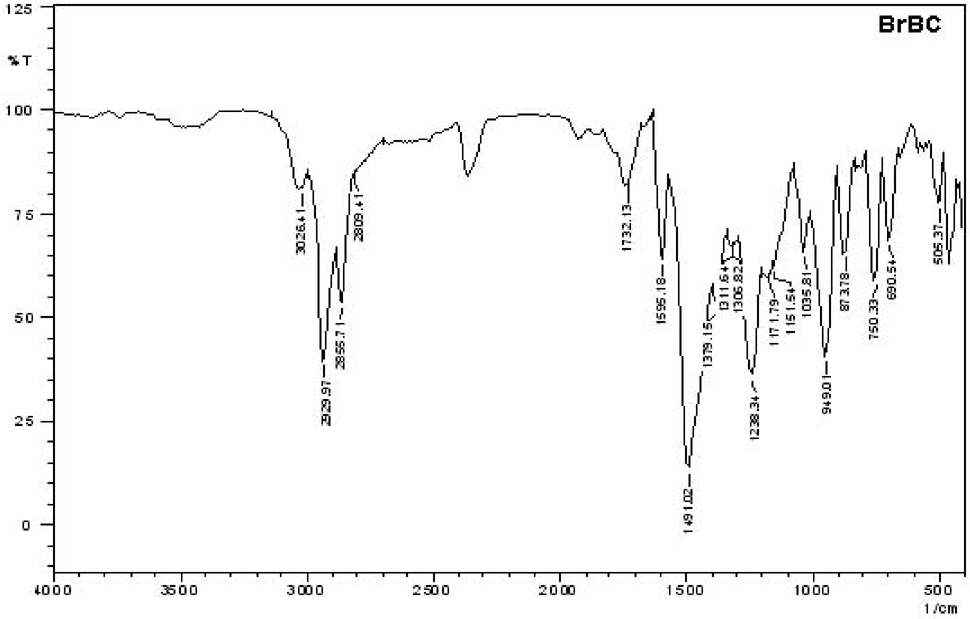


Fig.3.1: IR spectrum (KBr pellet) of BrBC

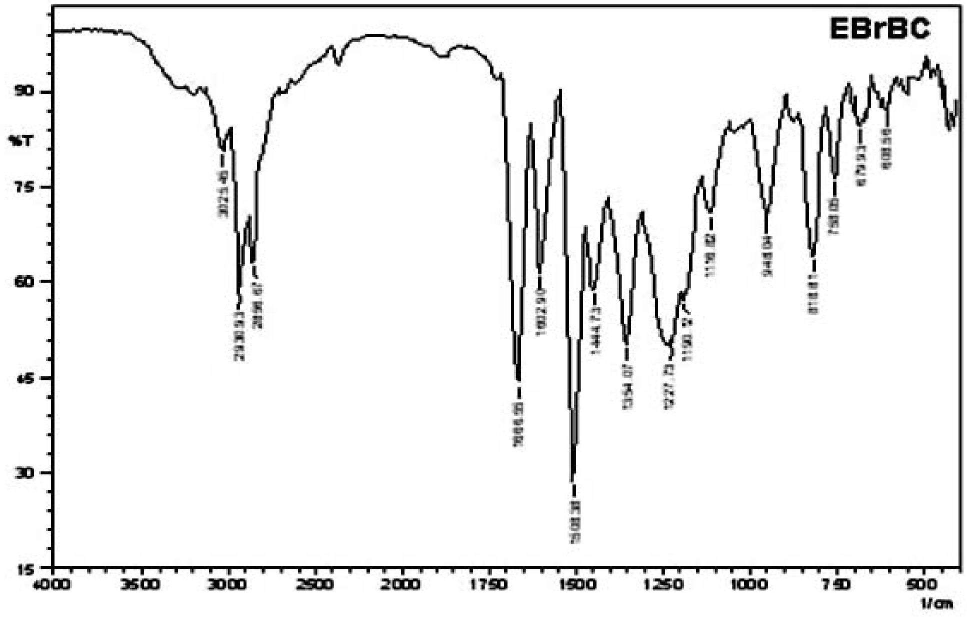


Fig.3.2: IR spectrum (KBr pellet) of EBrBC

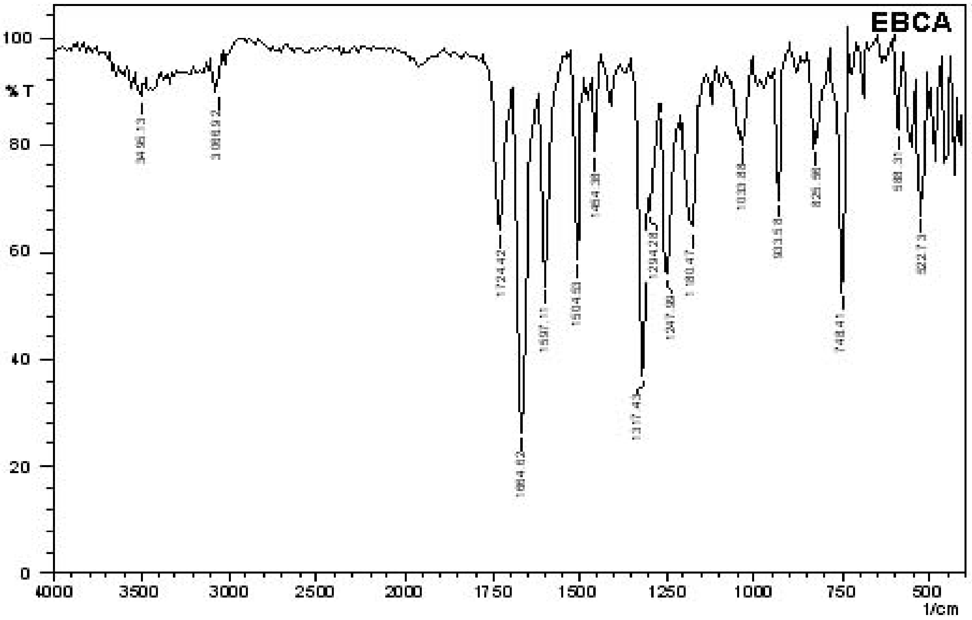


Fig.3.3: IR spectrum (KBr pellet) of EBCA

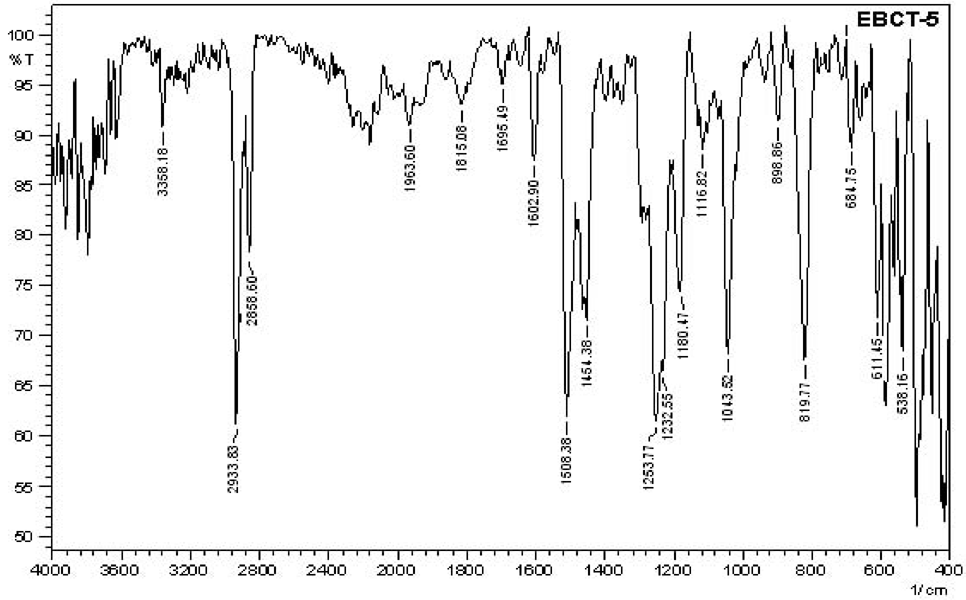


Fig.3.4: IR spectrum (KBr pellet) of EBCT-5

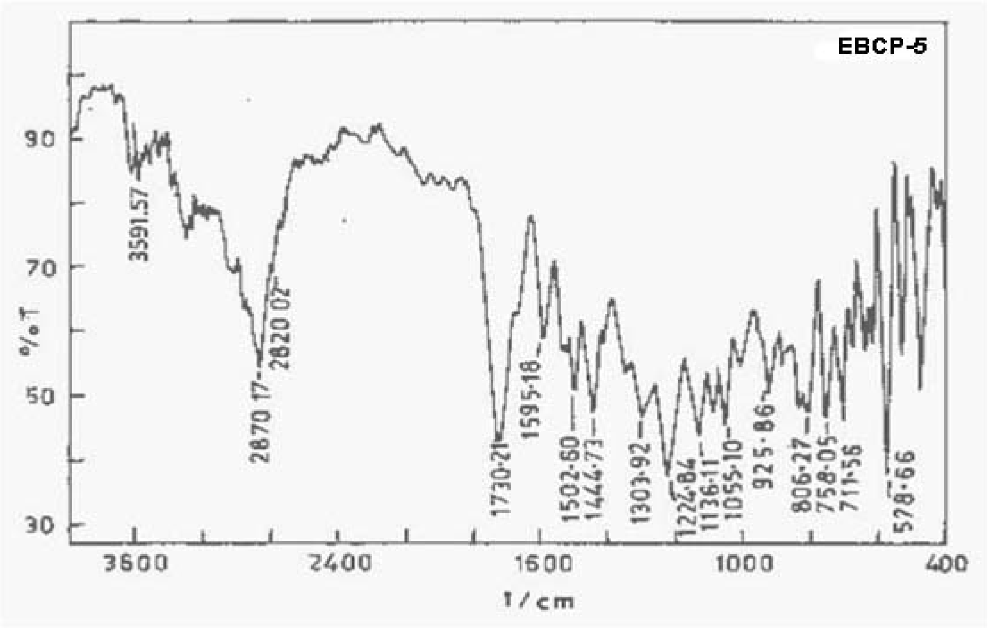


Fig.3.5: IR spectrum (KBr pellet) of EBCP-5

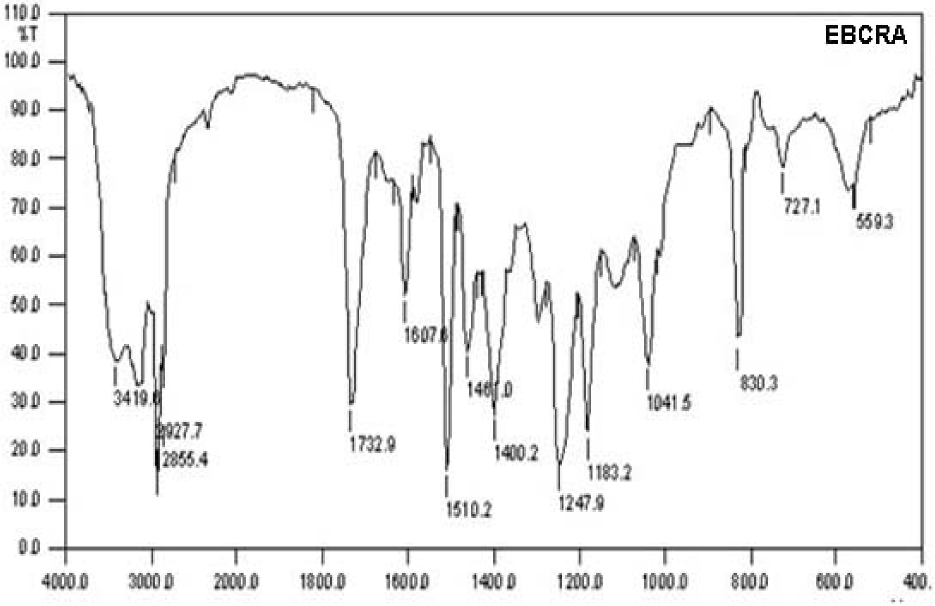


Fig.3.6: IR spectrum (KBr pellet) of EBCRA

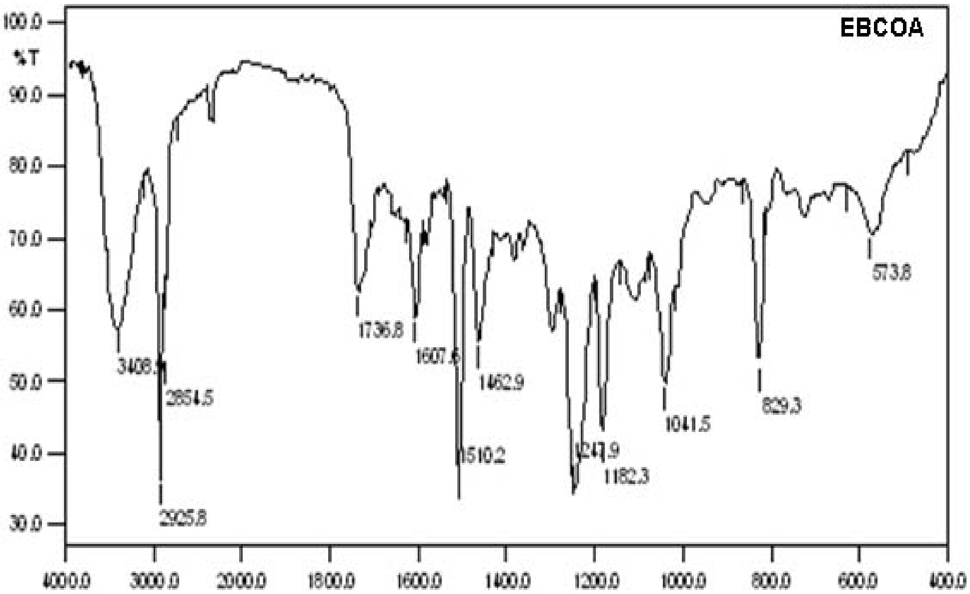


Fig.3.7: IR spectrum (KBr pellet) of EBCOA

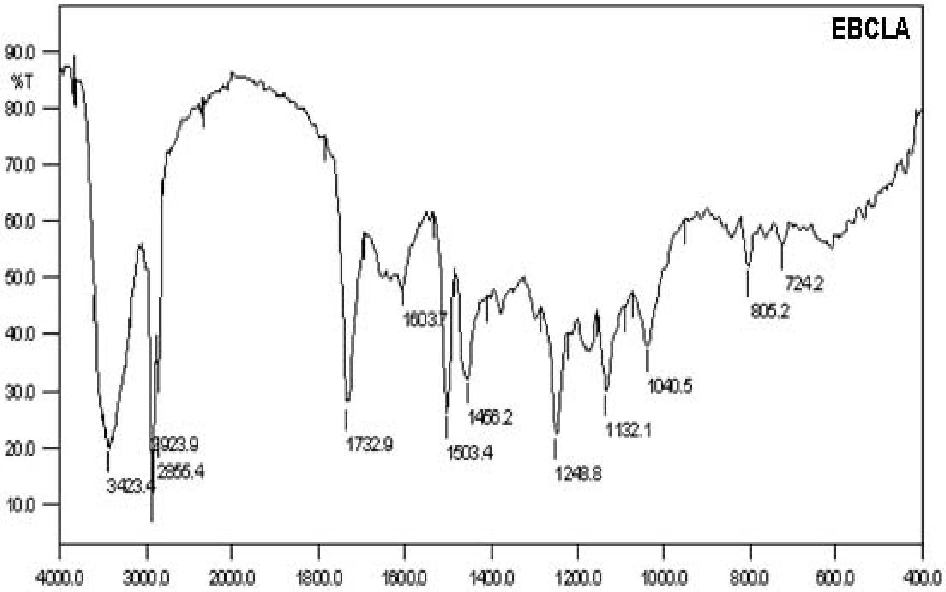


Fig.3.8: IR spectrum (KBr pellet) of EBCLA

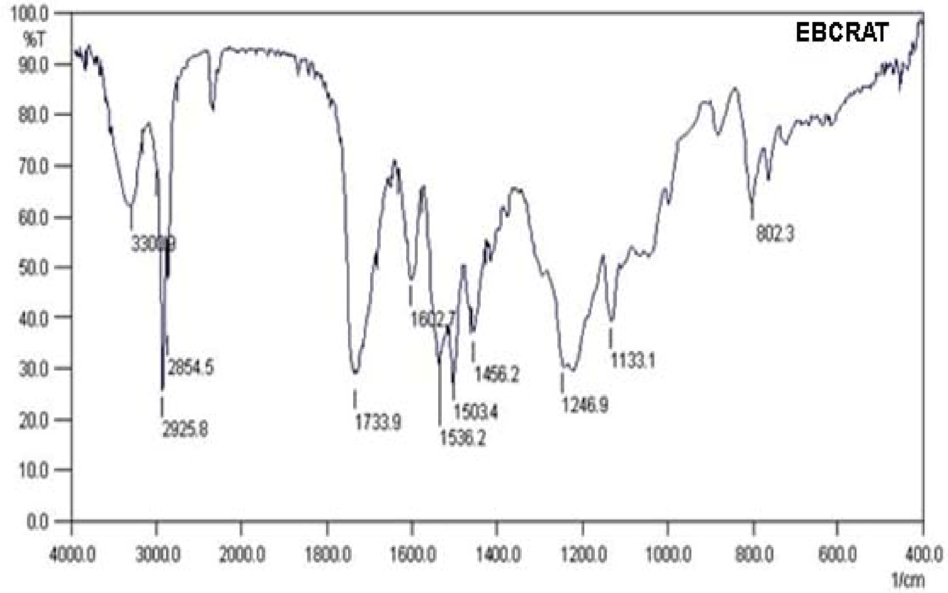


Fig.3.9: IR spectrum (KBr pellet) of EBCROAT

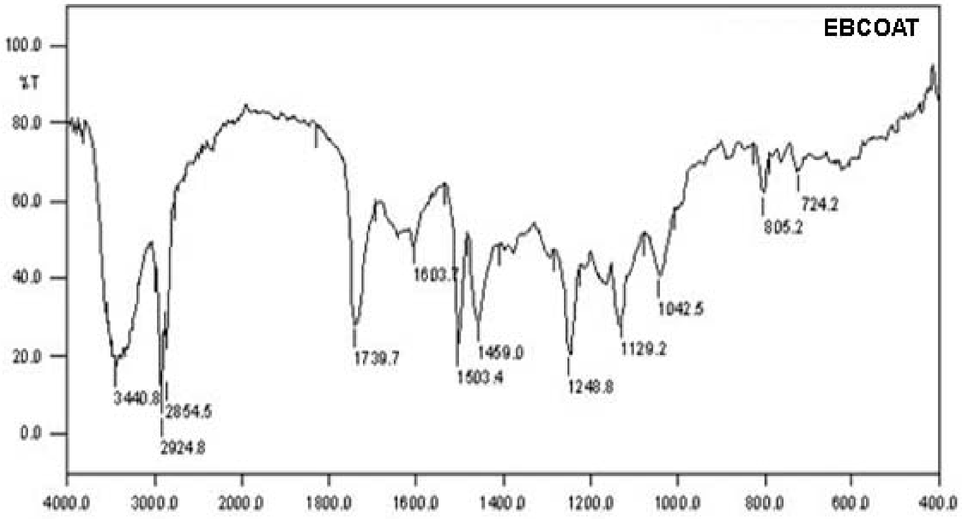


Fig.3.10: IR spectrum (KBr pellet) of EBCOAT

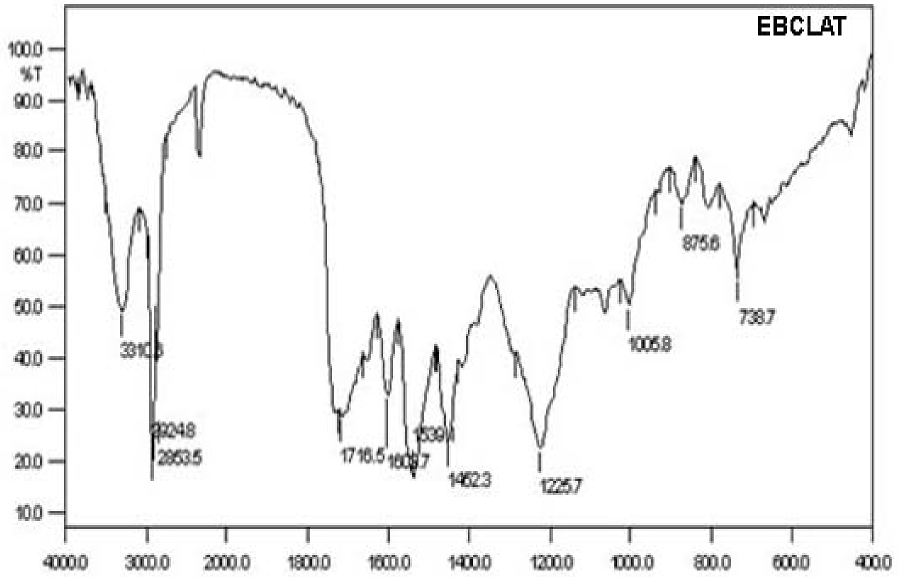


Fig.3.11: IR spectrum (KBr pellet) of EBCLAT

3.2: Epoxy equivalent, hydroxyl and acid values

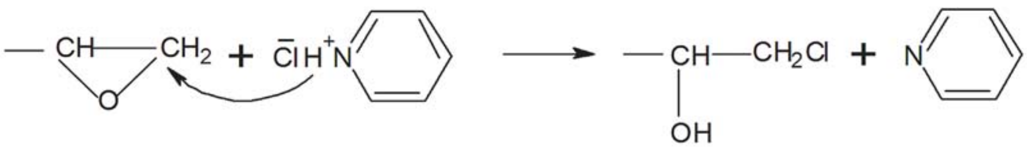
[A] Epoxy equivalent of epoxy resins

Epoxy content is reported in terms of “epoxide equivalent” or “epoxy equivalent weight” and is defined as the weight of resin in grams, which contain 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 877 807 cm^{-1} for terminal epoxy groups; from 848 to 775 cm^{-1} for internal epoxy groups; and from 769 to 752 cm^{-1} for triply substituted epoxy group [1.] The epoxide equivalent may be determined from changes in intensity as related to change in molecular weight using the absorption band of the epoxy group at 912 or 862 cm^{-1} in comparison to aromatic bands at 1610 cm$^{-1.}$

Greenlee [2] has described the method for epoxy equivalent. The epoxide content of the complex epoxide resins were determined by heating a 1 g sample 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 [3] 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 [1] 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:

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

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 EBC is 600.

[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 the reaction progresses acid is consumed to form ester and at the end of the reaction the acid value is low, which signifies the completion of the ester reaction.

Acid values of polyester polyols were determined according to standard reported method [4]. Into a 250 ml stoppered flask, 1g EBCRA /EBCLA /EBCOA 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

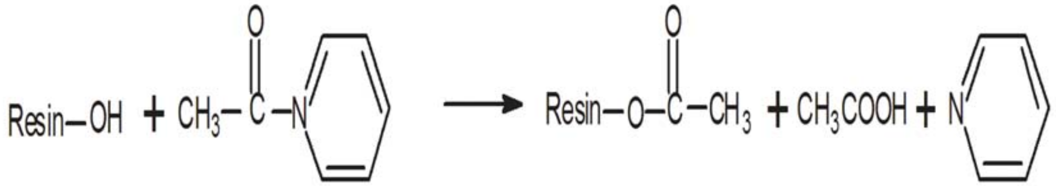
W = Weight of sample in grams

The average of three measurements of each of polyester polyols is reported in Table 3.1

[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 EBCRA/EBCLA/EBCOA 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 [4]:

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

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 Table-3.1. From Table-3.1 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.

TABLE-3.1: Acid and hydroxyl values of epoxy polyester polyols

Time, h	Acid value, mg KOH/g			Hydroxyl Value, mg KOH/g		
	EBCRA	**EBCOA**	**EBCLA**	**EBCRA**	**EBCOA**	**EBCLA**
3	120.5	112.4	105.30	687	423	368
4	92.9	88.90	81.8	709	445	396
5	45.6	42.60	50.7	763	478	420
6	18.9	20.6	15.4	786	504	454
7	09	12	11	814	543	473
8	40	07	06	847	583	511

---

1. R. E. Burge, Jr. and B. P. Geyer "Analytical Chemistry of Polymers" (G. M. Hline, ed.) Vol. XII/1, Interscience New York, (1959).
2. S. O. Greenlee; (Devoe & Raynolds Co. New York) "Phenol aldehyde and epoxide resin compositions", U.S. Pat. 2,502,145 (1949); C.A. 44, 5614, (1950).
3. J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss "Organic analysis (J. Mitchell Jr., ed.)", 1, 127, Interscience, New York, (1953).
4. ASTM-D-1639-61.

CHAPTER – 4

THERMAL ANALYSIS

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.

---

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

---

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).

Kinetic study of thermal decomposition of epoxy resins containing flame retardant components has been 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 behavior 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.

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.

---

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. Phys. 43 (12), 1548-1555, (2005).

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 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

---

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).
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).

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. Non-isothermal kinetic analysis of the degradation reaction implied that all the polymers undergo degradation in at least two steps, except in the case of ethynyl phenyl azo resin, which showed apparent single step degradation.

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 multistep 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 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.

---

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," J. Thermal Ana.and Calorim. 102 (2), 605-608, (2010).

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 (E). 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% weightloss (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)

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 EBCT-5, EBCT-20, EBCRAT and EBCLAT

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 and TG thermograms of EBCT-5, EBCT-20, EBCLAT, and EBCRAT were scanned at 10°C heating rate in nitrogen atmosphere. DSC thermograms of EBCT-5, EBCT-20, EBCLAT, and EBCRAT are presented in Figs. 4.1-4.4, respectively. Observed DSC transitions are presented in Table-4.1. The endothermic transition for EBCT-5 at 70°C and EBCT-20 at 64.°C is due to melting transition of uncrossed linked EBCT. The exothermic transition for EBCLAT at 184.9 °C and EBCRAT at 190.7 °C is due to some physical transformation in the sample, which is further confirmed by no weight change in their TG thermograms at those temperatures.

TG thermograms of EBCT-5, EBCT-20, EBCLAT, and EBCRAT are presented in Figs. 4.5 and 4.6. 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 Fig. 4.5, it is observed that EBCT-5 and EBCT-20 followed apparently single step decomposition reaction, whereas EBCLAT and EBCRAT (Fig. 4.6) followed two steps and three steps decomposition reactions, respectively. EBCT-5, EBCT-20, EBCLAT, EBCRAT are thermally stable up to about 309, 318, 260 and 215°C, respectively. From Table-4.1, it is clear that thermal stability is increased slightly with TEA concentration confirming increase in degree of cross-linking. EBCT-5 and EBCT-20 have practically almost same thermal stability (309-318°C), T_{max}(367.9°C) and the % weight loss involved in the decomposition reaction(68.7%).

---

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).

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. Details of calculation schemes are presented in Tables-4.2-4.5 and the plots of $\Delta \ln \frac{dW}{dt}$ against $\Delta \ln W$ are presented in Figs. 4.7-4.10. Derived least squares 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 EBCT-5 and EBCT-20 followed approximately one and half orders degradation kinetics. EBCLAT followed second (first step) and first (second step) degradation kinetics. First, second and third step decomposition reaction of EBCRAT followed .43, 0.75 and 1.12, respectively.

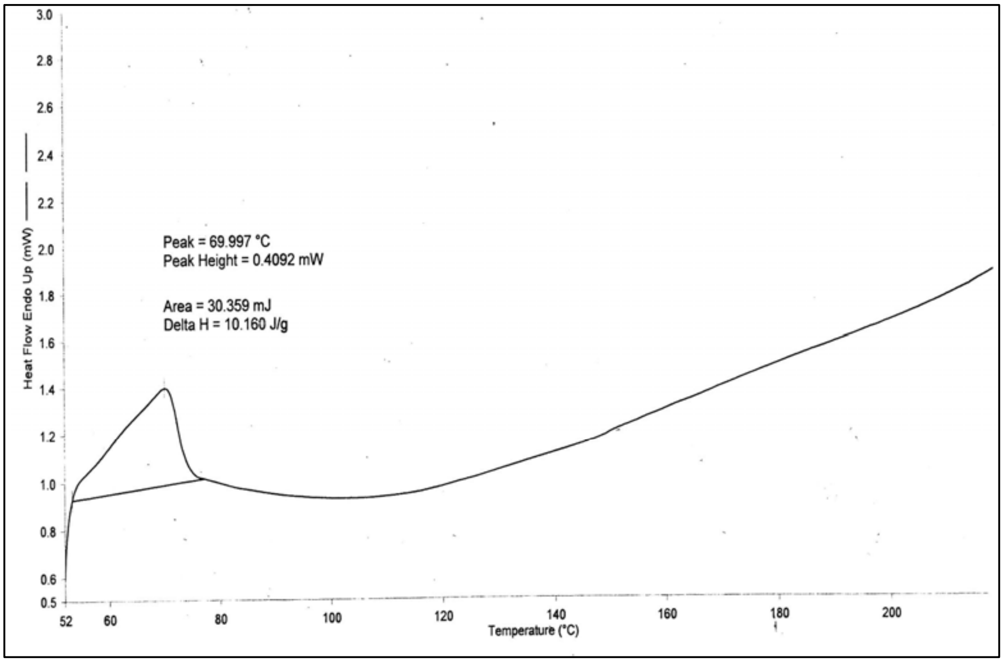


Fig. 4.1: DSC thermogram of EBCT-5 at the heating rate of 10^0C/min in an N_2 atmosphere.

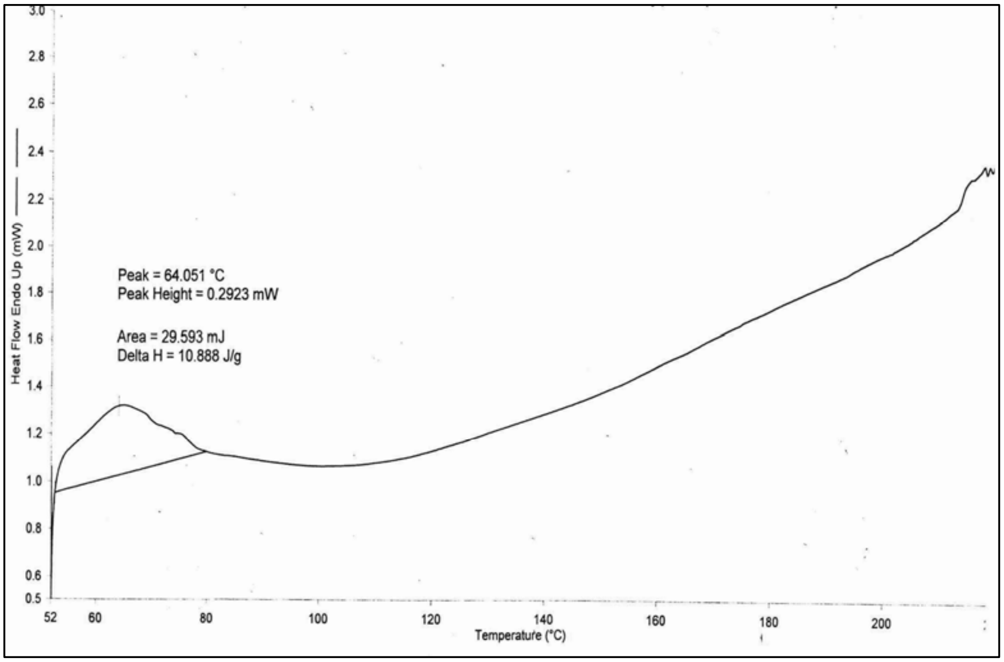


Fig. 4.2: DSC thermogram of EBCT-20.at the heating rate of 10^0C/min in an N_2 atmosphere

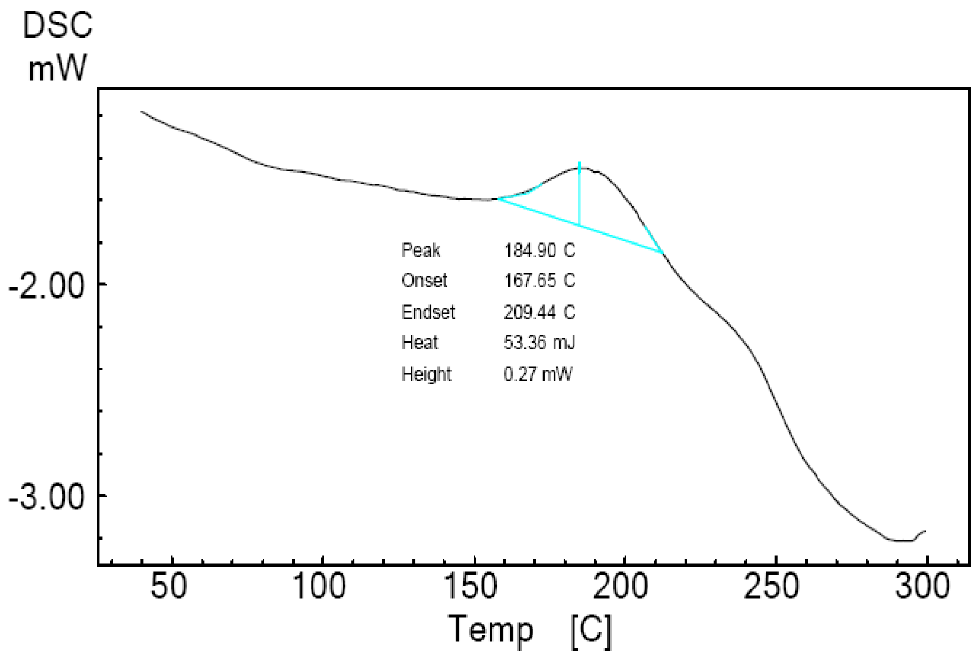


Fig. 4.3: DSC thermogram of EBCLAT at heating rate of 10^{0}C /min in an N_2 atmosphere.

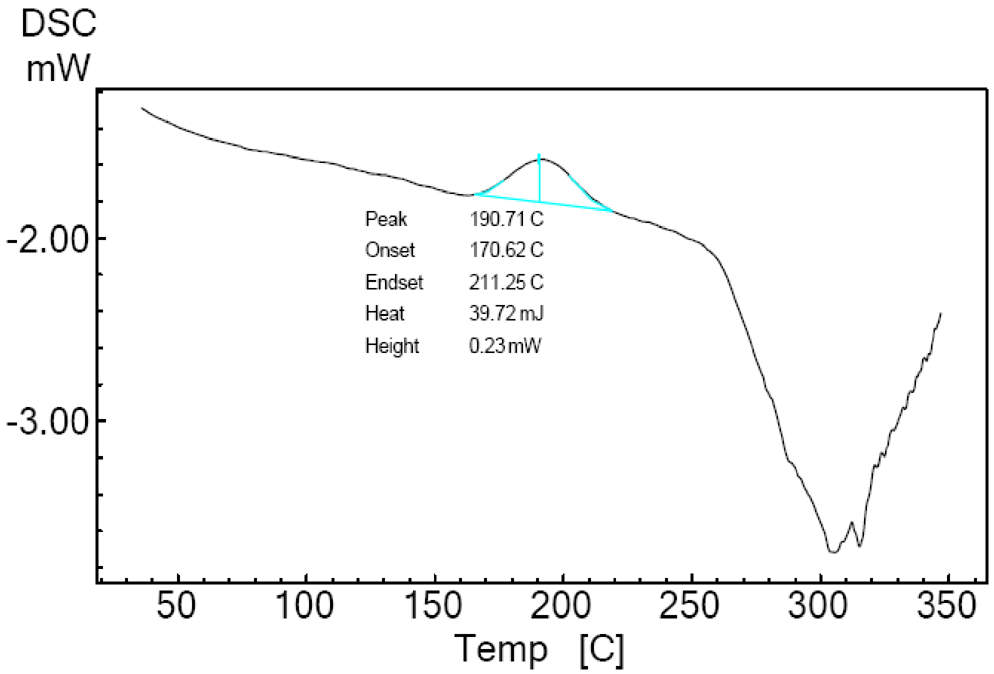


Fig. 4.4: DSC thermogram of EBCRAT at heating rate of 100C /min in an N2 atmosphere

Table-4.1: DSC and TGA data of resins of EBCT-5, EBCT-20, EBCLAT and EBCRAT

Sample	DSC transin °C	IDT, °C	Tmax, °C	Decompn. range, °C	% wt loss	% Residue at 450 °C
EBCT-5	72.6 (endo)	309	367.9	308-407	68.7	11
EBCT-20	71.1 (endo)	318	367.9	318-422	68.1	7
EBCLAT	184.9 (exo)	260 500	407.2 530.1	260-470 500-585	30.3 11	29
EBCRAT	190.7 (exo)	215 340 515	299.9 426.2 560.20	215-320 340-470 515-600	21.5 42.5 21.1	34

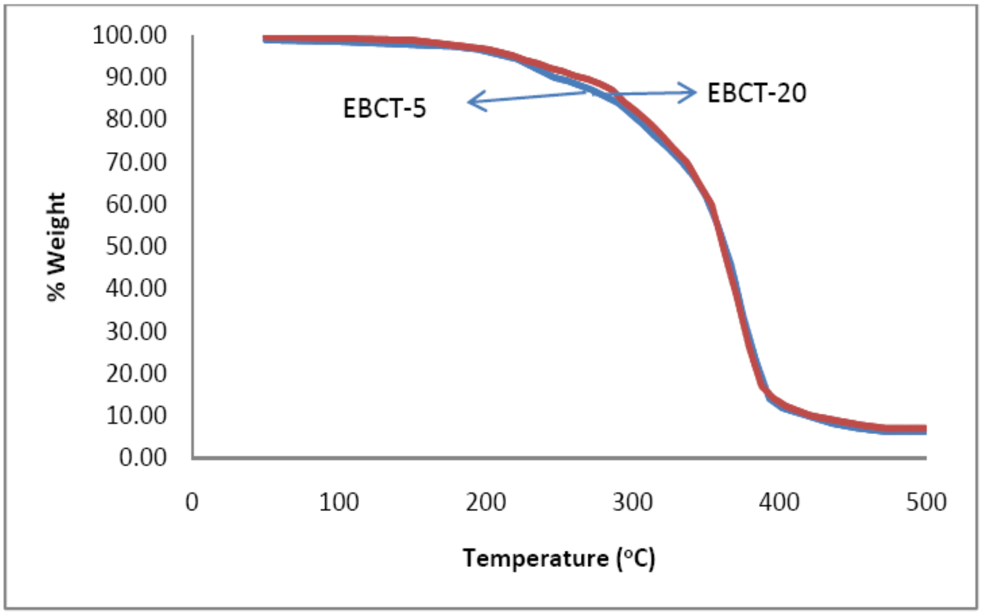


Fig. 4.5: TG thermograms of EBCT-5 and EBCT-20 at heating rate of 10^0C /min in an N2 atmosphere

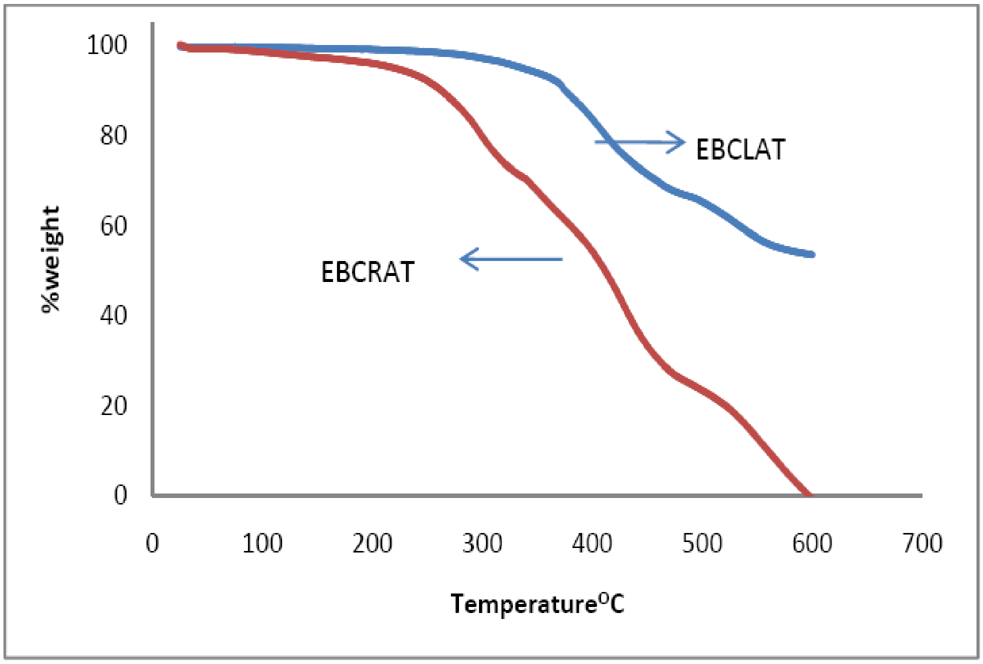


Fig. 4.6: TG thermograms of EBCLAT and EBCRAT at heating rate of 100C /min in an N2 atmosphere

Table- 4.2: Calculation scheme for EBCT-5

1000/T	%Wtloss	W	lnW	dW/dt	lndW/dt	ΔlnW	ΔlndW/dt
1.64	4.182	29.574	55.426	4.015	1.430	-0.0521	0.1967
1.63	5.091	32.389	52.611	3.962	1.627	-0.0622	0.2128
1.62	6.298	35.56	49.44	3.900	1.840	-0.0732	0.2014
1.61	7.703	39.051	45.949	3.827	2.041	-0.0854	0.1754
1.6	9.18	42.813	42.187	3.742	2.217	-0.0990	0.1678
1.59	10.857	46.791	38.209	3.643	2.384	-0.1145	0.0817
1.58	11.781	50.925	34.075	3.528	2.466	-0.1324	0.0694
1.57	12.628	55.152	29.848	3.396	2.535	-0.1537	0.0301
1.56	13.014	59.405	25.595	3.242	2.566	-0.1799	-0.0121
1.55	12.857	63.619	21.381	3.062	2.553	-0.2134	-0.0590
1.54	12.12	67.727	17.273	2.849	2.494	-0.2591	-0.1136
1.53	10.819	71.669	13.331	2.590	2.381	-0.3267	-0.1799

Table- 4.3: Calculation scheme for EBCT-20

1000/T	%Wtloss	W	lnW	dW/dt	lndW/dt	ΔlnW	ΔlndW/dt
1.62	34.892	6.31	55.108	4.0093	1.8421	-0.0591	0.1673
1.61	38.053	7.459	51.947	3.9502	2.0094	-0.0703	0.1640
1.6	41.58	8.788	48.42	3.8799	2.1734	-0.0825	0.1464
1.59	45.415	10.174	44.585	3.7974	2.3198	-0.0958	0.0825
1.58	49.489	11.049	40.511	3.7016	2.4023	-0.1106	0.0500
1.57	53.729	11.616	36.271	3.5910	2.4524	-0.1270	0.0193
1.56	58.055	11.842	31.945	3.4640	2.4717	-0.1458	-0.0110
1.55	62.39	11.713	27.61	3.3182	2.4607	-0.1678	-0.0420
1.54	66.654	11.231	23.346	3.1504	2.4187	-0.1941	-0.0750
1.53	70.772	10.419	19.228	2.9564	2.3436	-0.2269	-0.1120
1.52	74.675	9.315	15.325	2.7295	2.2316	-0.2698	-0.1549

Table- 4.4: Calculation scheme for EBCLAT (Step-I)

1000/T	%Wtloss	W	lnW	dW/dt	lndW/dt	ΔlnW	ΔlndW/dt
1.43	23.56	2.524	8.24	2.1085	0.926	0.138	0.058
1.44	22.34	2.675	9.46	2.2468	0.984	0.125	0.043
1.45	21.08	2.791	10.72	2.3717	1.027	0.113	0.027
1.46	19.80	2.868	12.00	2.4850	1.054	0.103	0.012
1.47	18.50	2.902	13.30	2.5880	1.065	0.094	-0.004
1.48	17.19	2.890	14.61	2.6819	1.061	0.085	-0.020
1.49	15.88	2.833	15.92	2.7674	1.041	0.078	-0.036
1.5	14.60	2.732	17.20	2.8450	1.005	0.070	-0.053
1.51	13.34	2.590	18.46	2.9154	0.952	0.063	-0.071
1.52	12.14	2.413	19.66	2.9786	0.881	0.056	-0.089
1.53	11.00	2.207	20.80	3.0351	0.791	0.050	-0.108

Table- 4.4: Calculation scheme for EBCLAT (Step-II)

1000/T	%Wtloss	W	lnW	dW/dt	lndW/dt	ΔlnW	ΔlndW/dt
1.205	44.33	1.186	1.37	0.3170	0.170	0.24	0.104
1.21	43.95	1.315	1.75	0.5570	0.274	0.21	0.087
1.215	43.55	1.435	2.15	0.7667	0.361	0.19	0.071
1.22	43.11	1.542	2.59	0.9525	0.432	0.17	0.056
1.225	42.64	1.630	3.06	1.1185	0.488	0.15	0.041
1.23	42.15	1.699	3.55	1.2681	0.529	0.14	0.027
1.235	41.63	1.745	4.07	1.4036	0.556	0.12	0.014
1.24	41.10	1.769	4.60	1.5269	0.570	0.11	0.001
1.245	40.55	1.771	5.15	1.6395	0.571	0.10	-0.011
1.25	39.99	1.752	5.71	1.7423	0.560	0.09	-0.022
1.255	39.43	1.714	6.27	1.8365	0.539	0.09	-0.031
1.26	38.86	1.662	6.84	1.9226	0.508	0.08	-0.038
1.265	38.30	1.599	7.40	2.0014	0.469	0.07	-0.043

Table- 4.5: Calculation scheme for EBCRAT (Step-I)

1000/T	**%Wtloss**	**W**	**lnW**	**dW/dt**	**lndW/dt**	**ΔlnW**	**ΔlndW/dt**
1.725	22.2707	3.227	3.829	1.343	1.172	0.129	0.011
1.73	21.742	3.263	4.358	1.472	1.183	0.115	0.007
1.735	21.2109	3.287	4.889	1.587	1.190	0.103	0.004
1.74	20.6787	3.299	5.421	1.690	1.194	0.094	0.000
1.745	20.1469	3.300	5.953	1.784	1.194	0.085	-0.003
1.75	19.6167	3.292	6.483	1.869	1.191	0.078	-0.005
1.755	19.0894	3.274	7.011	1.947	1.186	0.072	-0.008
1.76	18.5661	3.248	7.534	2.019	1.178	0.067	-0.010
1.765	18.0479	3.214	8.052	2.086	1.168	0.062	-0.013
1.77	17.5358	3.174	8.564	2.148	1.155	0.057	-0.015
1.775	17.0308	3.128	9.069	2.205	1.140	0.053	-0.017
1.78	16.5339	3.076	9.566	2.258	1.124	0.050	-0.018
1.785	16.0459	3.020	10.054	2.308	1.105	0.046	-0.020
1.79	15.5675	2.960	10.533	2.354	1.085	0.043	-0.022
1.795	15.0994	2.896	11.001	2.398	1.063	0.041	-0.023
1.8	14.6424	2.830	11.458	2.439	1.040	0.038	-0.025
1.805	14.197	2.761	11.903	2.477	1.016	0.036	-0.026
1.81	13.7637	2.690	12.336	2.513	0.990	0.034	-0.027
1.815	13.3429	2.619	12.757	2.546	0.963	0.031	-0.028
1.82	12.9352	2.546	13.165	2.578	0.935	0.030	-0.029
1.825	12.5408	2.473	13.559	2.607	0.905	0.028	-0.030
1.83	12.16	2.400	13.940	2.635	0.875	0.026	-0.031
1.835	11.7929	2.327	14.307	2.661	0.845	0.024	-0.031
1.84	11.4399	2.255	14.660	2.685	0.813	0.023	-0.032
1.845	11.1008	2.184	14.999	2.708	0.781	0.021	-0.033
1.85	10.7757	2.114	15.324	2.729	0.748	0.020	-0.033
1.855	10.4646	2.045	15.635	2.750	0.716	0.019	-0.033

Table- 4.5: Calculation scheme for EBCRAT (Step-II)

1000/T	%Wtloss	W	lnW	dW/dt	lndW/dt	ΔlnW	ΔlndW/dt
1.395	64.32	3.971	7.778	2.051	1.379	0.129	0.038
1.400	63.25	4.126	8.848	2.180	1.417	0.117	0.032
1.405	62.15	4.261	9.950	2.298	1.450	0.107	0.027
1.410	61.03	4.376	11.074	2.405	1.476	0.098	0.021
1.415	59.89	4.468	12.212	2.502	1.497	0.090	0.015
1.420	58.74	4.537	13.357	2.592	1.512	0.082	0.010
1.425	57.60	4.582	14.500	2.674	1.522	0.075	0.004
1.430	56.46	4.602	15.636	2.750	1.526	0.069	-0.001
1.435	55.34	4.598	16.759	2.819	1.526	0.064	-0.006
1.440	54.24	4.570	17.863	2.883	1.519	0.059	-0.011
1.445	53.16	4.518	18.943	2.941	1.508	0.054	-0.016
1.450	52.11	4.444	19.995	2.995	1.492	0.050	-0.022

Table- 4.5: Calculation scheme for EBCRAT (Step-III)

1000/T	%Wtloss	W	lnW	dW/dt	lndW/dt	ΔlnW	ΔlndW/dt
1.210	88.063	2.875	11.937	2.480	1.056	0.078	-0.013
1.215	87.0899	2.839	12.910	2.558	1.043	0.071	-0.018
1.220	86.1379	2.787	13.862	2.629	1.025	0.065	-0.024
1.225	85.2117	2.721	14.788	2.694	1.001	0.059	-0.030
1.230	84.3156	2.641	15.684	2.753	0.971	0.053	-0.036
1.235	83.4542	2.548	16.546	2.806	0.935	0.048	-0.042
1.240	82.6322	2.443	17.368	2.855	0.893	0.044	-0.049
1.245	81.8541	2.326	18.146	2.898	0.844	0.039	-0.056
1.25	81.1246	2.200	18.875	2.938	0.789	0.035	-0.063
1.255	80.4485	2.0671	19.552	2.973	0.726	0.031	-0.070

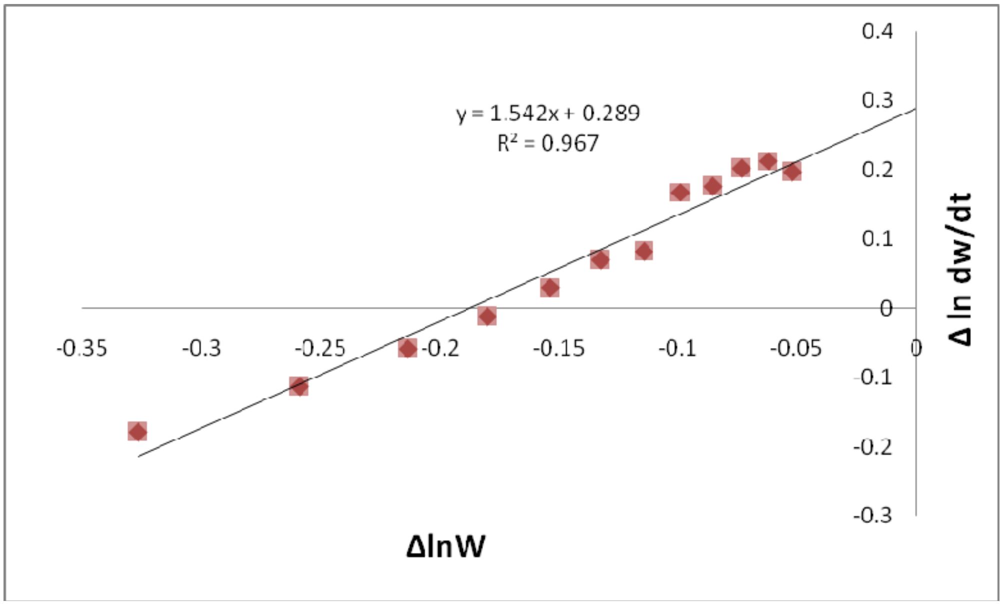


Fig. 4.7. The Anderson-Freeman plot for EBCT-5

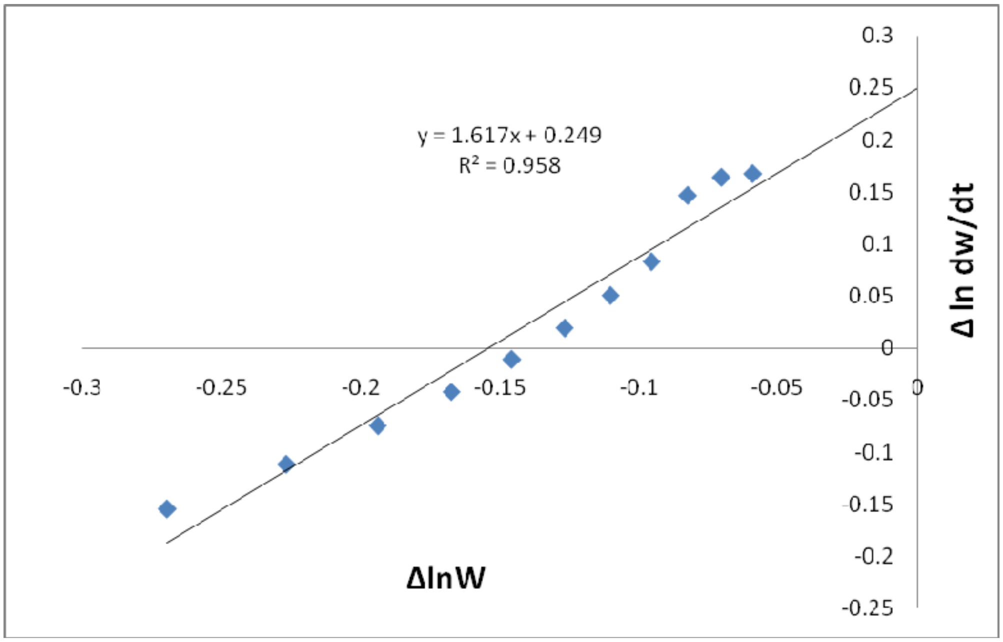
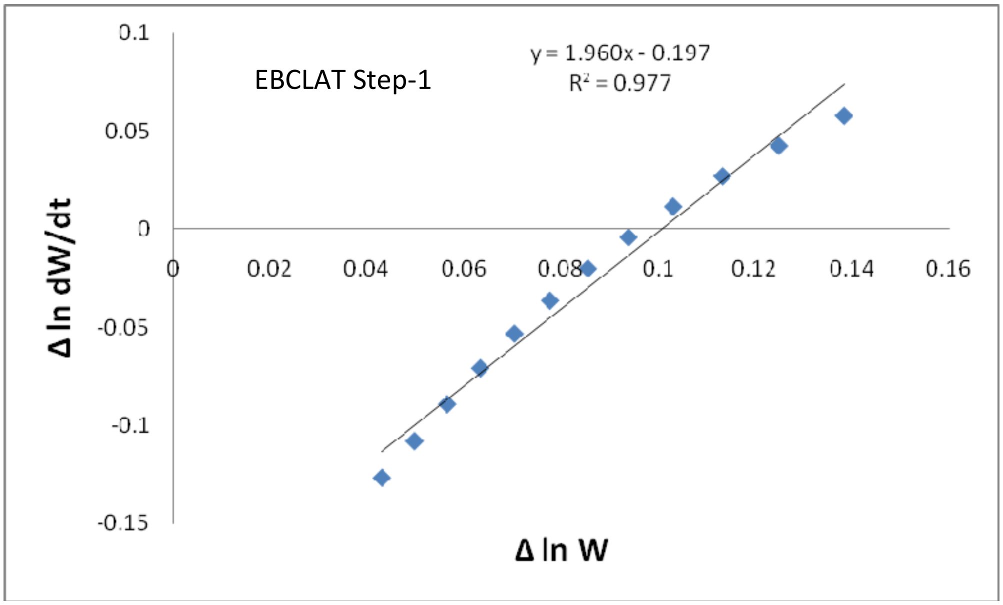


Fig. 4.8. The Anderson-Freeman plot for EBCT-20



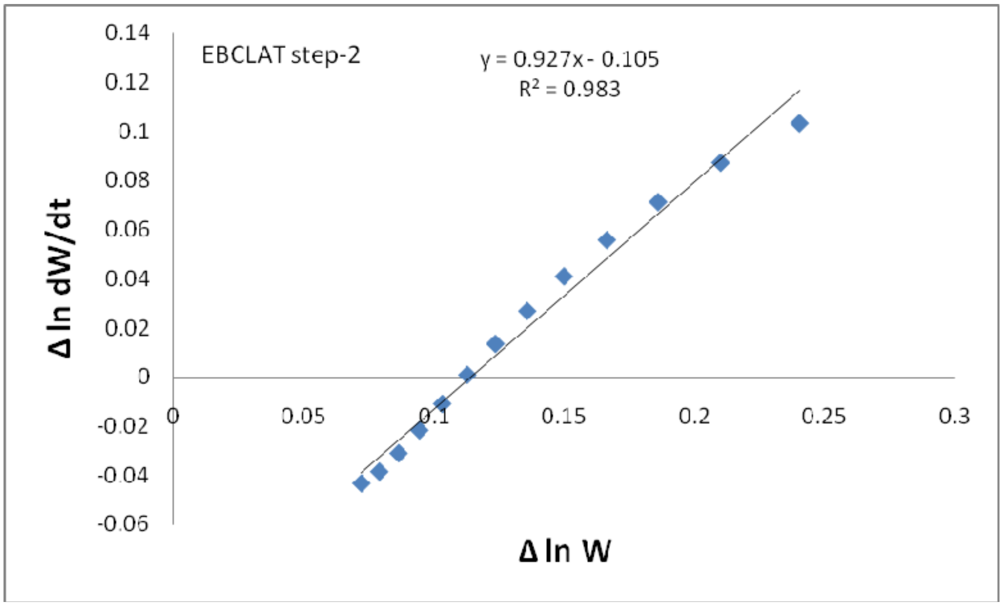


Fig. 4.9. The Anderson-Freeman plots of EBCLAT for steps-I and II.

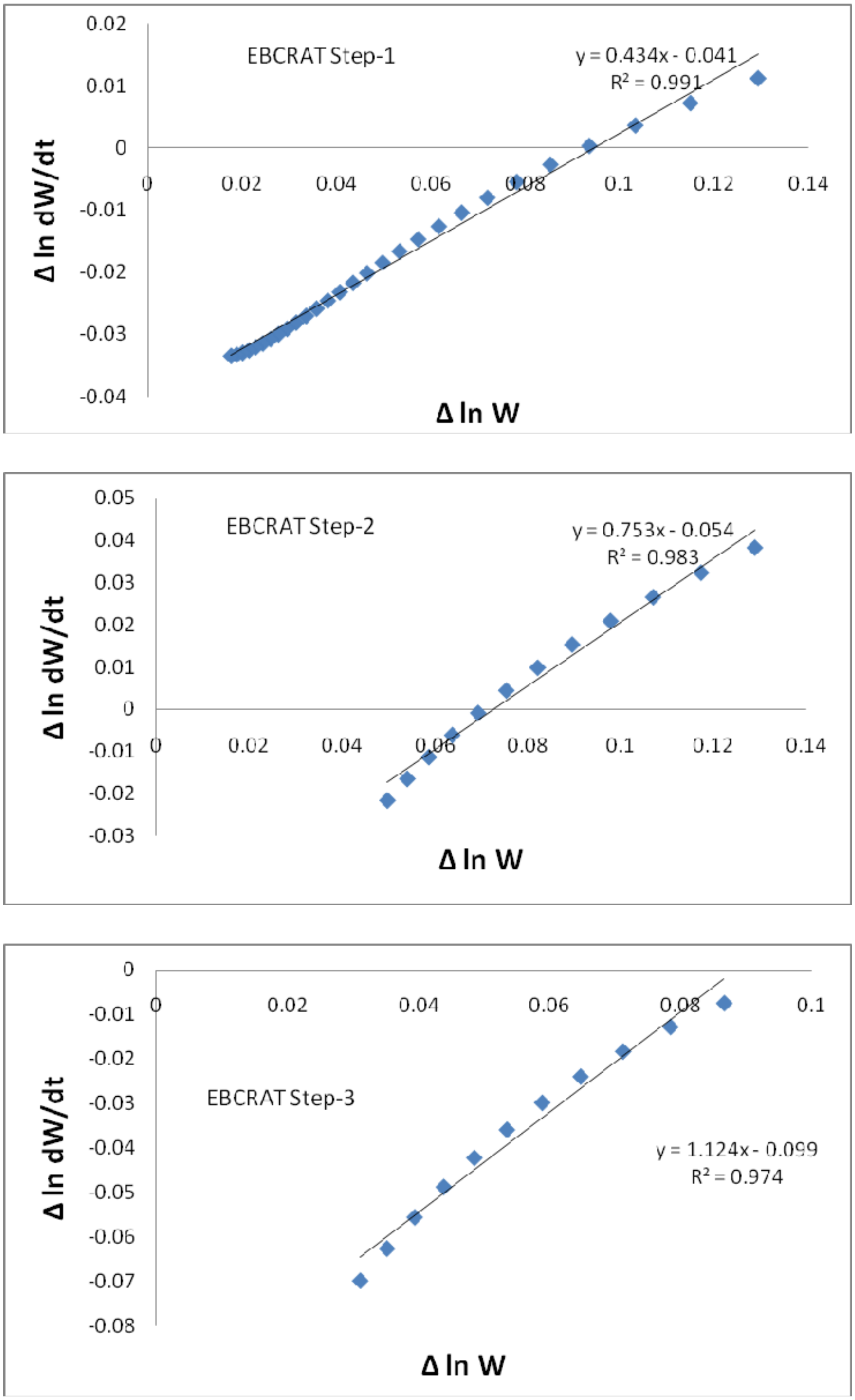


Fig. 4.10. The Anderson-Freeman plots of EBCRAT for Steps-I –III.

Table-4.6. DSC and TGA data of resins of EBCT-5, EBCT-20, EBCLAT and EBCRAT

Sample	**E, kJ**	**A, S^{-1}**	**n**	**Δs^* JK^{-1} mol^{-1}**	**R^2**
EBCT -5	240.3	$4.44 x 10^{17}$	1.54	86.57	0.967
EBCT -20	207.0	$7.47 x 10^{14}$	1.44	33.46	0.958
EBCLAT	163.8 174.6	$2.67 x 10^{10}$ $1.23 x 10^{9}$	1.96 0.93	- 52.2 - 79.2	0.977 0.983
EBCRAT	68’2 89.8 164.6	6.8×10^{3} 1.8×10^{4} 9.89×10^{7}	0.43 0.75 1.12	-176.9 -170.2 -100.4	0.991 0.983 0.974

CHAPTER-5

COMPOSITE FABRICATION

CHAPTER-5

COMPOSITE FABRICATION

5.1 General Introduction

There are many processes, which are applicable for fabrication of composites such as, Wet filament winding, Hand lay-up technique ,Automated tape placement, Resin transfer molding, Pultrusion, Injection molding, Vacuum aging ,Machine finishing. Among all the processes, hand lay-up technique is the cheapest process and all the composites reported in this Chapter are fabricated by this technique. Many researchers have reported the fabrication of composites by hand lay-up technique since 1978 onwards [1-7].

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

---

1. M. Cormack and E. William, “Fabrication and joining of polymer-matrix composites, Flight-vehicle materials, structures, and dynamics assessment and future directions”. J. Appl. Polym. Sci. 1, 348-356, (1994).
2. M. A. Hayat and S. M. A. Suliman, “Mechanical and structural properties of glass reinforced phenolic laminates”. Polym. Test., 17, 79-85, (1998).
3. J. Sinke, “Manufacturing of glare parts and structures”. Appl. Compos. Mater. 10, 293-305, (2003).
4. S. R. Dyer, L. V. J. Lassila, M. Jokinen and P. K. Vallittu, “Effect of cross-sectional design on the modulus of elasticity and toughness of

fiber-reinforced composite materials". J. Prosthetic Dentistry. 94, 219-226, (2005).

Mechanical properties

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

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

Electrical properties

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

---

5. P. Thomas, K. Dwarkanath, P. Sampathkumaran, S. Seetharamu and Kishore, "Influence of moisture absorption on electrical characteristics of glass-epoxy polymer composite system". Proceedings of the International Symposium on Electrical Insulating Materials. 3, 612-615, (2005).
6. A. K. Bledzki, A. Jaszkiewicz "Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibers –

A comparative study to PP". Compos. Sci. and Technol. 70, 1687–1696, (2010).

7. C. Gonzalez-Murillo, M. P. Ansell "Co-cured in-line joints for natural fiber composites". Comp. Sci. and Technol., 70, 442–449, (2010).

When assessing a potential insulating material, information on the following properties will be required.

Experimental

Solvents and chemicals used were of laboratory grade and purified prior to their use [8]. 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, ground nut, wheat straw, banana and sugarcane fibers were collected from local farms and were used after appropriate treatments.

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^{o}C by using 25/75mm brass electrodes and a Hewlett Packard high resistance meter in air at 25^{o}C and 500 V DC applied voltage after charging for 60 Sec, respectively. Measurements were carried out in four to five times and the mean values were considered.

5.2 Fabrication of Jute and Glass Fiber Composites of EBC

Glass, jute and their hybrid composites (15cmx15cm) of epoxy resin of bisphenol-C (EBC) were fabricated by hand layup technique using phthalic anhydride (PA) as a curing agent. A 70% matrix material (EBC) of reinforcing fibers (woven glass and jute fabrics) was used (Table-5.1). Required quantity of matrix material was dissolved in 110-130 ml methyl ethyl ketone (MEK) and applied to jute/glass fabrics with the help of a smooth brush and prepregs were allowed to dry in the sunlight for about 15 min. Ten such prepregs were stacked one over the other and pressed between the two preheated stainless steel plates under the hydraulic pressure of 27.58 MPa and at 150^{O}C for 6h and 12h at room temperature. Silicone spray was used as a mold releasing agent. The composites are designated as EBC-J-PA and EBC-G-PA. Similarly alternate Glass-Jute-Glass (EBC-GJG-PA) and Jute-Glass-Jute (EBC-JGJ-PA) composites were prepared.

Table-5.1 Fiber-matrix and hardener (PA) compositions for epoxy jute, glass and their hybrid composites

Composite	Wt. of Fabric ,g	Wt. of resin, g	Wt. of hardener, g
J-EBC-PA	90	63	12.6
G-EBC--PA	40	28	5.6
JGJ-EBC- PA	67(45J+22G)	46.9	9.38
GJG -EBC--PA	60(35G+25J)	42	8.4

---

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

Table-5.2 Mechanical and electrical properties of the composites

Composite	Tensile strength, MPa	Flexural strength, MPa	Electric strength, kV/mm	Volume resistivity, ohm-cm
J-EBC-PA	47	31	1.0	$1.2x10^{9}$
G-EBC--PA	43	36	1.9	$4.2x10^{13}$
GJG-EBC-PA	27	19	1.6	$8.7x10^{11}$
JGJ-EBC- PA	21	22	1.3	$4.0x10^{11}$

Mechanical and electrical properties of the composites are of paramount importance for various high performance applications. Tensile strength, flexural strength, electric strength and volume resistivity data of J-EBC-PA, G-EBC-PA, JGJ-EBC-PA and GJG-EBC-PA are reported in Table 5.2 from which it is clear that hybrid composites have intermediate mechanical and electrical properties than those of parent composites. Mechanical and electrical properties of the composites depend on the fiber content, fiber orientation, humidity, interfacial bonding, additives like fillers, compatibilizers and impact modifier and mode of testing, etc. Fiber-matrix interfacial bonding in natural fiber reinforced polymer composites is of paramount importance for potential applications in various fields.

5.3 Fabrication of Jute and Jute-Biofiber Reinforced Composites

For composites preparation, 70%matrix materials of reinforcing fibers were used (Table-5.3). Thus, required quantity of EBCRA/EBCLA/EBCOA was dissolved into a 500 ml beaker containing 110-130 ml MEK at room temperature. To this solution required quantity of toluene diisocyanate (30 % of matrix material) in 20 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 20 min at room temperature. The resultant polyurethane solution was applied to two/ten sheets and remaining solution was used to impregnate wheat/coconut/groundnut/banana/ground nut chopped fibers (2-5 mm). Impregnated fibers was sandwiched uniformly between two jute prepregs and placed between two Teflon sheets. The Teflon sheets were placed between two preheated stainless sheets and pressed under 27.58 MPa pressure at 150^0C for 4h and 12h at room temperature. Hereafter sandwich composites are designated as J-EBCRAT, J-EBCLAT, J-EBCOAT, JSC-EBCRAT, JSC-EBCLAT and JSC-EBCOAT, JW-EBCRAT, JW-EBCLAT, JW-EBCOAT, JCN-EBCRAT, JCN-EBCLAT, JCN-EBCOAT, JGN-EBCRAT, JGN-EBCLAT, JGN-EBCOAT, JBN-EBCRAT, JBN-EBCLAT, and JBN-EBCOAT.

Table-5.3 Compositions for jute-biofiber reinforced polyurethanes of epoxy polyester polyols based sandwich composites

Composite	Wt. of fibers, g		Epoxy polyester polyol, g	TDI, ml
	Jute	Biofiber		
J-EBCRAT	80	-	56.0	16.8
J-EBCLAT	85	-	59.5	16.2
J-EBCOAT	84	-	58.8	17.6
JSC-EBCRAT	20	20	28	6.9
JSC-EBCLAT	23	23	32.2	8.0
JSC-EBCOAT	22	22	30.8	7.6
JW-EBCRAT	25	50	45.0	11.1
JW-EBCLAT	24	50	44.0	10.9
JW-EBCOAT	25	48	43.0	10.8
JCN-EBCRAT	22	40	37.2	9.2
JCN-EBCLAT	20	40	36.0	8.9
JCN-EBCOAT	23	40	37.8	9.3
JGN-EBCRAT	24	50	44.0	10.9
JGN-EBCLAT	25	50	45.0	11.1
JGN-EBCOAT	24	50	44.0	10.9
JBN-EBCRAT	23	23	32.2	8
JBN-EBCLAT	23	23	32.2	8
JBN-EBCOAT	23	23	32.2	8

J: Jute; W: Wheat fibers; CN: Coconut fibers, GN: Groundnut fibers and BN: Banana fibers

For high performance applications mechanical and electrical properties of the composites are of paramount importance. A comparative tensile strength, flexural strength, electric strength and volume resistivity of the jute and jute-biofiber sandwich composites are reported in Table 5.4. It is observed that J- ECRAT has better tensile strength as compared to J-ECLAT and J-ECOAT because of hydroxyl group in RA, which has participated in polyurethane formation and contributed high degree of crosslink density. J-ECOAT is stiffer than those of J-ECRAT and J-ECLAT as judged from flexural strength. Similar observation is also observed in sandwich composites. Low mechanical properties of the sandwich composites is mainly due to random orientation of the sugar cane fibers, which causes discontinuous load transfer from fiber to matrix. Jute-coconut sandwich bio-composites possess 2-3 times more tensile strength than those of jute-wheat sandwich biocomposites due to more interfacial bonding. Jute-coconut biocomposites showed better tensile property because of better fiber-matrix interface adhesion. JW-ECRAT showed slight improvement in flexural property but JW-ECLAT, JW-ECOAT did not show improvement in flexural property probably due to brittle nature of polyurethanes and less stiffness of wheat husk. Considerable improvement in flexural property is observed in jute-coconut biocomposites mainly due to better stiffness of coconut fibers. Low mechanical properties of the sandwich composites is mainly due to random orientation of the wheat and coconut fibers, which cause discontinuous load transfer from fiber to matrix. Jute-coconut sandwich composites showed almost double electric strength than those of jute-wheat sandwich composites. Better volume resistivity of jute-coconut sandwich composites is due to less polar nature of coconut fibers as compared to wheat fibers. From Table-5.4, it is clear that all the sandwich biocomposites possess almost identical electric strength but JGN-EBCRAT and JGN-EBCOAT possess almost ten to twenty times volume resistivity as compared to remaining biocomposites due to partial charge neutralization among polar group present in fibers and matrix materials. Thus, fairly good mechanical and electrical properties of bio-composites may be useful for low load bearing application for housing units and in electrical and electronic appliances.

Table-5.4 Mechanical and electrical properties of jute-biofiber reinforced polyurethanes of epoxy polyester polyols based sandwich composites

Composite	Tensile strength, MPa	Flexural strength, MPa	Electric strength, kV/mm	Volume Resistivity, Ω cm
J-EBCRAT	35.	16	1.7	9.8×10^{12}
J-EBCOAT	29.4	34	1.8	1.5×10^{12}
J-EBCLAT	25	12	1.9	3.9×10^{12}
JSC-EBCRAT	21.5	17	1.7	3.3×10^{11}
JSC-EBCLAT	12.9	19	2.3	4.3×10^{13}
JSC-EBCOAT	9.6	60	2.6	4.3×10^{11}
JW-EBCRAT	5.7	10	0.64	9.8×10^{7}
JW-EBCLAT	12.6	12	0.62	1.7×10^{8}
JW-EBCOAT	13.6	14	0.67	1.5×10^{8}
JCN-EBCRAT	17.8	27.5	1.6	7.2×10^{11}
JCN-EBCLAT	29.7	9.9	1.4	3.3×10^{13}
JCN-EBCOAT	27.6	39.9	1.5	3.8×10^{11}
JGN-EBCRAT	31.4	57.5	1.3	1.4×10^{12}
JGN-EBCLAT	26.9	31.5	1.4	2.2×10^{11}
JGN-EBCOAT	19.5	22.9	1.4	1.1×10^{12}
JBN-EBCRAT	35.3	16.2	1.4	1.2×10^{11}
JBN-EBCLAT	29.8	35.6	1.3	1.3×10^{11}
JBN-EBCOAT	14.2	45.7	2.1	1.2×10^{13}

The most important problem 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 pendant hydroxyl and polar groups in various constituents of the natural fibers resulting in poor wettability and also moisture absorption of the fibers is too high, giving rise to poor interfacial bonding with the hydrophobic matrix polymers. The properties of the composites 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 modifier and mode of testing, degree of cross linking, etc. Overall low mechanical properties confirmed poor interfacial bonding between fiber and matrix material, brittle nature of polyurethanes and also low degree of cross-linking density. Thus moderate mechanical and fairly good electrical properties of the sandwich composites signify their importance for low load bearing housing units and in electrical and electronic appliances.

5.4 Filled jute-polyurethane composites

Particulate fillers have played a vital role in the development of commercial uses for polymers. Originally they were mainly seen as cheap diluents and hence the name fillers however their ability to modify many properties soon began to be realized and they are used for many purpose today. The term functional filler is often used to describe materials that do more than provide cost reduction. Example of functional filler includes carbon black and precipitated silica.

Some of the main reasons for using particulates filler are cost reduction, Improved processing, density control, optical effects such as translucency, thermal conductivity, control of thermal expansion, electrical properties e.g. antistatic, magnetic properties, improve mechanical properties notably hardness, stiffness and, flame retardancy. Of course, no single filler provides all of these benefits each type improve some properties, while having no, or even detrimental effect on others. Thus a great deal of care to go into optimizing filler performance for a particular application and a multidisciplinary approach is required if one is to master the subject.

For composites preparation, 70% matrix materials of reinforcing fibers were used (Table-5.5). Thus, required quantity of resin was dissolved into a 500ml beaker containing 110-130 ml MEK at room temperature. To this solution required quantity of triethyl amine (30 % of matrix material) in 20 ml MEK was added dropwise through a dropping funnel over a period of 10 min with stirring and added aluminum trioxide in varying proportion as a filler. The reaction mixture was stirred manually for about 20 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 15 min. Six such prepregs were staked one over the other, placed between two Teflon sheets and then placed between two preheated stainless steel plates and pressed under 27.58 MPa pressure at 150^0C for 6h and 12h at room temperature. Hereafter sandwich composites are designated as J-EBrBCT-AO-2, J-EBrBCT-AO-4, J-EBrBCT-AO-6, J-EBrBCT-AO-8, J-EBrBCT-AO-10; J-EBCT-AO-2, J-EBCT-AO-4, EBCT-AO-6, EBCT-AO-8 and EBCT-AO-10 Numerical figures indicate the amount of filler in the composites.

Tensile and flexural strengths of the filled composites are reported in Table-5.6 from which it is observed that tensile strength increased, while flexural strength decreased with filler content in case of J-EBC-AO-2 to J-EBC-AO-10. Tensile strength increased and flexural strength decreased up to 6% filler content in case of halogenated epoxy resin and then remained constant. A considerable tensile property is improved, while flexural property decreased by the use of halogenated epoxy resin. Composites may find their applications in building construction especially for low load bearing applications.

Table-5.5 Compositions for jute fiber reinforced filled epoxy resin composites

Composite	Jute fabric, g	EBC, g	TEA, ml	Al_2O_3, g
J-EBCT-AO-2	75	52.5	15.8	1.05
J-EBCT-AO-4	75	52.5	15.8	2.10
J-EBCT-AO-6	75	52.5	15.8	3.15
J-EBCT-AO-8	75	52.5	15.8	4.20
J-EBCT-AO-10	75	52.5	15.8	5.25
J-EBrBCT-AO-2	80	56	16.8	1.12
J-EBrBCT-AO-4	80	56	16.8	2.24
J-EBrBCT-AO-6	80	56	16.8	3.36
J-EBrBCT-AO-8	80	56	16.8	4.48
J-EBrBCT-AO-10	80	56	16.8	5.60

Table-5.6 Tensile and flexural properties of jute fiber reinforced filled epoxy resin composites.

Composite	Tensile strength, MPa	Flexural strength, MPa
J-EBCT-AO-2	29.9	46.0
J-EBCT-AO-4	36.6	44.4
J-EBCT-AO-6	39.9	38.9
J-EBCT-AO-8	41.5	37.2
J-EBCT-AO-10	45.5	33.0
J-EBrBCT-AO-2	41.9	51.7
J-EBrBCT-AO-4	42.2	33.3
J-EBrBCT-AO-6	45	25.4
J-EBrBCT-AO-8	45.1	25.4
J-EBrBCT-AO-10	45.2	25.0

5.5 Diffusivity (Dx)

Absorbed water in composites influences mechanical behavior, and long-term durability of the polymer matrix composites. Water absorption in composites is proved to be Fickian as well as non-Fickian in character [9]. Assuming one-dimensional diffusion, water absorption in semi-infinite plate exposed to same environment is given by

$$\%Mt = \frac{W_m - W_d}{W_d} \times 100 \qquad ---.1$$

Where M_t = % water content at time t, W_m = Weight of moist material and W_d =Weight of the dry material. Diffusivity is related with water uptake with the passage of time as under,

$$Mt = \frac{4Mm}{h} \sqrt{\frac{t}{\pi}} \sqrt{D_x} \qquad --.2$$

Where M_m = Equilibrium water content in the sample, D_x = Diffusivity and t = time

---

9. Collings, T. A. Handbook of Polymer-Fiber Composites, Jones F R, Ed. Longman Scientific and Technical, UK, 366-371(1994).

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

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

Diffusivity in different environments was determined according to Eqns. 2 and 3.

5.6 Water uptake study of Jute-EBC and Glass-EBC composites

Water uptake study of the composites was carried out at 35^0C in water, 10% aq HCl and 10% aq NaCl and also in boiling water. The percentage weight gained by the composites in water, 10 % aq. HCl and 10 % aq. NaCl solutions with the passage of time ($t^{1/2}$) is shown in Figs.5.1-5.6. The % weight gained by each composite increased, reached maximum and then practically remained constant, when equilibrium was established in each of the environment. The equilibrium water content and the equilibrium time for each of the composites in water, 10 % aq. NaCl, 10 % aq. HCl environments are recorded in Table 5.7. The observed trend in % equilibrium water content in studied environments is HCl > H_2O > NaCl. High equilibrium water content in the composites is due to the presence of hydrophilic groups in the matrix and reinforcing materials and may also due to microcraks and voids formed because of brittle nature of polyurethane resins. From Table-5.7, it is clear that composites possess excellent hydrolytic stability even under harsh environmental conditions without any damage. Excellent hydrolytic stability of the composites in studied environments signifies their usefulness in marine applications.

The effect of boiling water on the % water absorption with the passage of time is shown in Figs.5.7 and 5.8 from which it is evident that the water absorption in composites is the maximum after 6h and remained almost constant. The equilibrium water absorption time is reduced drastically without damage to the composites. Thus, composites possess excellent hydrolytic stability against boiling water.

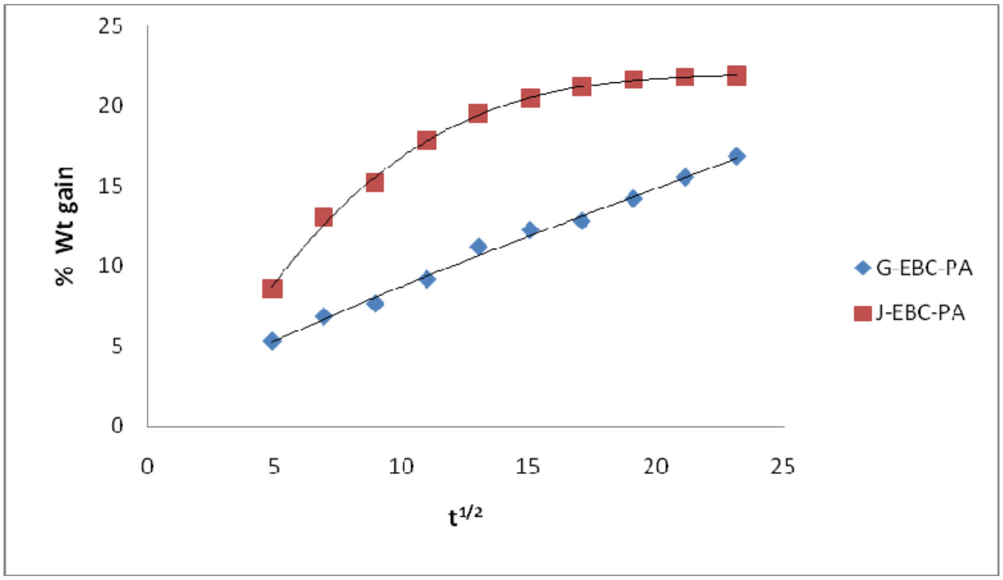


Fig. 5.1: The plots of % weight gain against $t^{1/2}$ for J-EBC-PA and G-EBC-PA composites in water at 35°C.

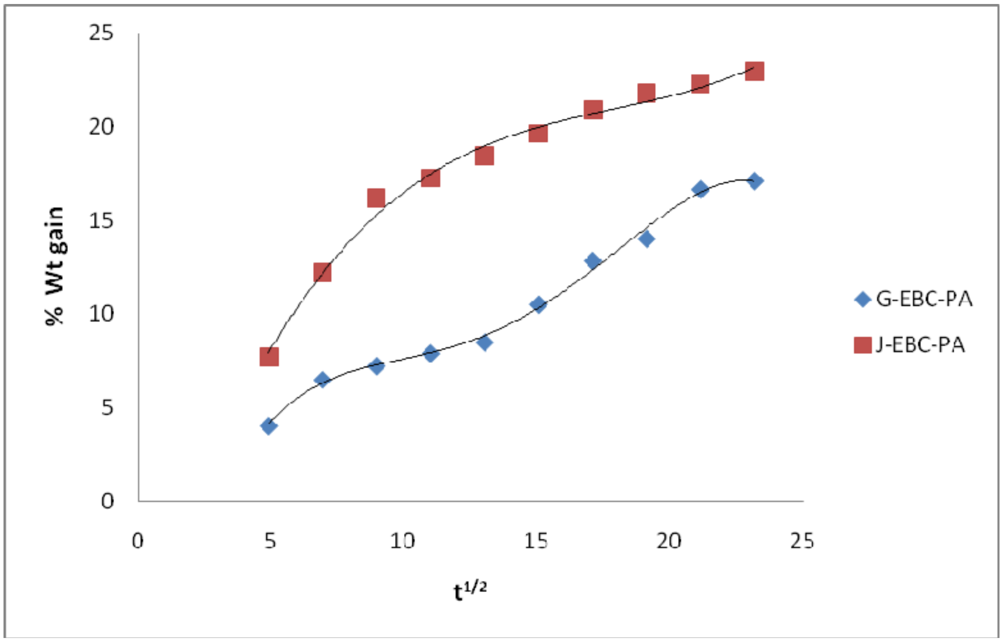


Fig. 5.2: The plots of % weight gain against $t^{1/2}$ for J-EBC-PA and G-EBC-PA composites in 10 % aq. HCl at 35°C.

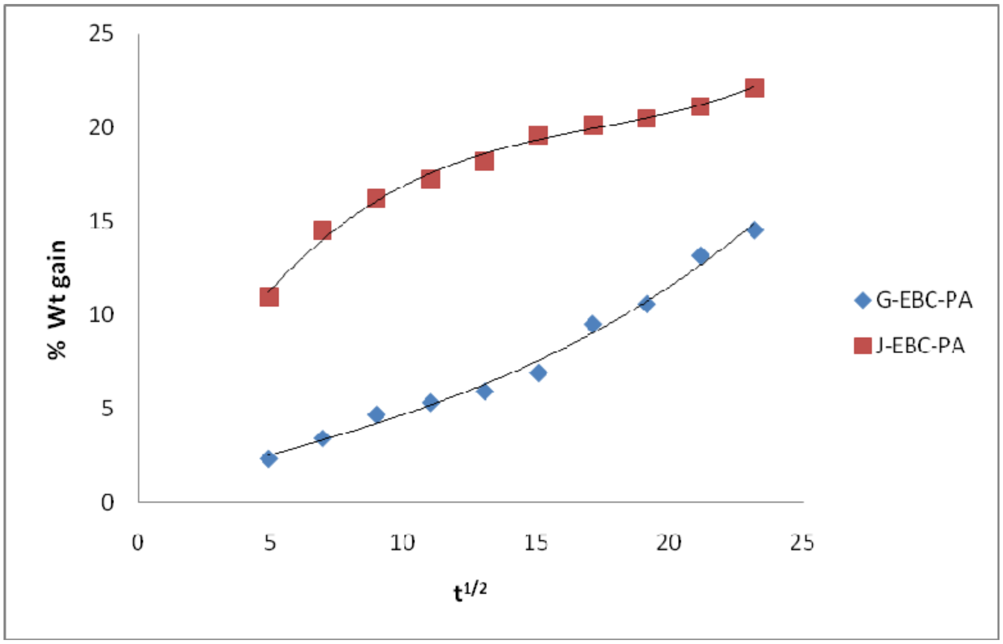


Fig. 5.3: The plots of % weight gain against $t^{1/2}$ for J-EBC-PA and G-EBC-PA composites in 10 % aq. NaCl at 35^{O}C.

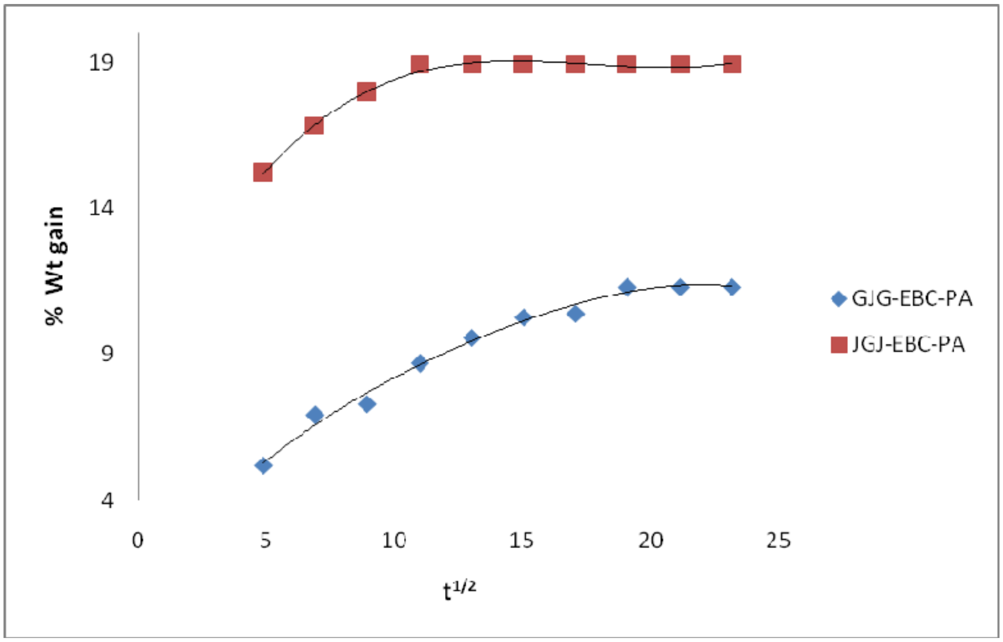


Fig. 5.4: The plots of % weight gain against $t^{1/2}$ for GJG-EBC-PA and JGJ-EBC-PA composites in water at 35^{O}C.

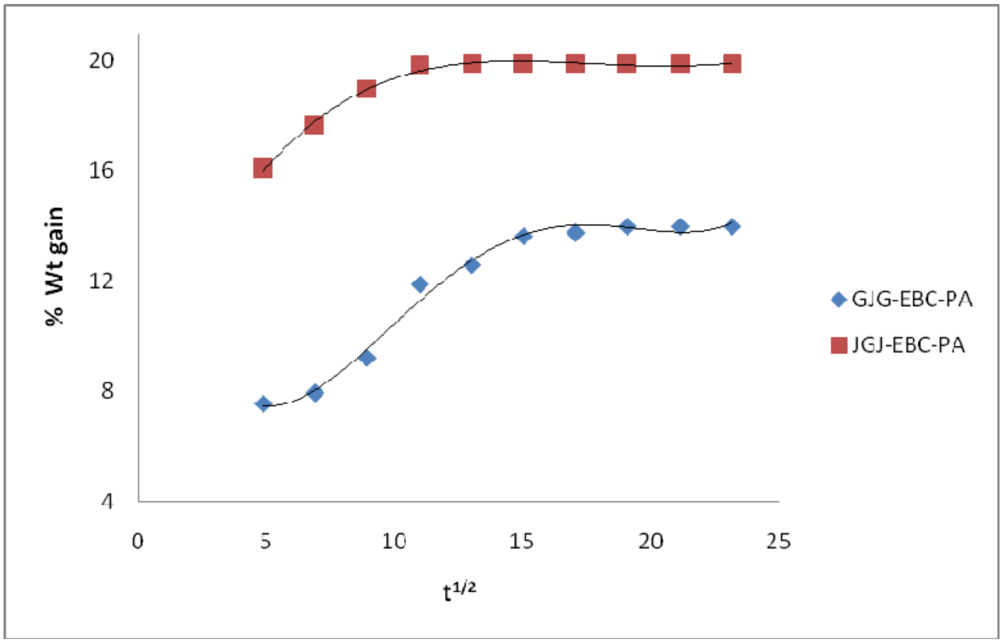


Fig. 5.5: The plots of % weight gain against $t^{1/2}$ for GJG-EBC-PA and JGJ-EBC-PA composites in 10 % aq. HCl at 35°C.

.

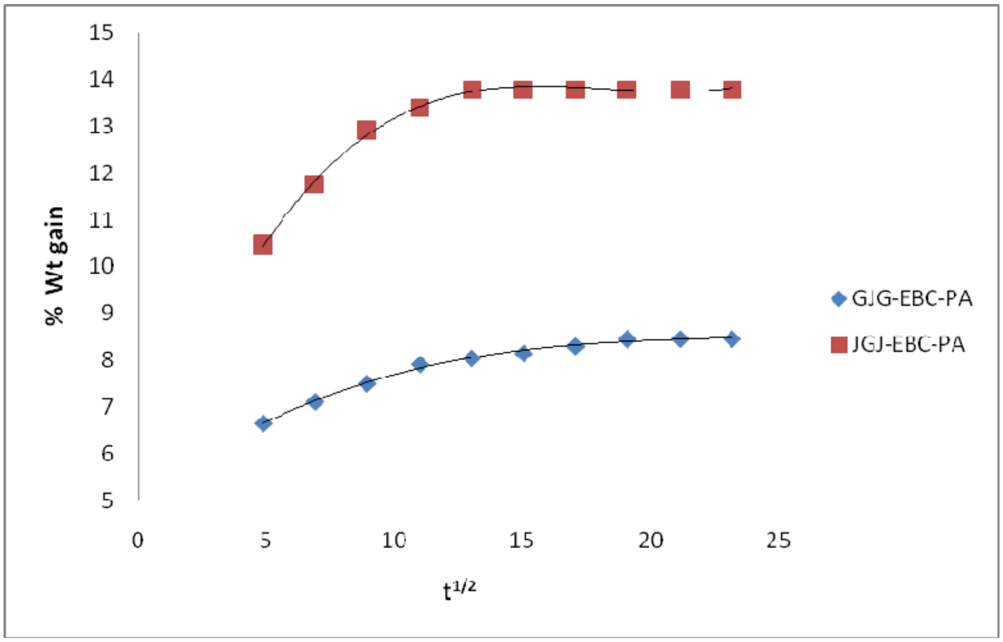


Fig. 5.6: The plots of % weight gain against $t^{1/2}$ for GJG-EBC-PA and JGJ-EBC-PA composites in 10 % aq. NaCl at 35°C.

Table-5.7: Equilibrium water content and diffusivity data of epoxy jute, glass and their hybrid composites in different environments at 35^{O}C and in boiling water

Composite	%, Equilibrium water content at room temperature			Diffusivity(D_x), 10^{-11}, m^2/s			% Eqm. water content in boiling water
	H_2O	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl	
J-EBC-PA	23.3	22.7	24.3	1.40	1.59	1.26	20.4
G-EBC--PA	16.7	13.9	19.1	5.56	6.34	7.71	15.6
JGJ-EBC-PA	18.9	13.8	19.9	2.32	3.56	2.33	13.8
GJG-EBC-PA	11.3	8.5	14.0	3.58	0.57	4.34	10.1

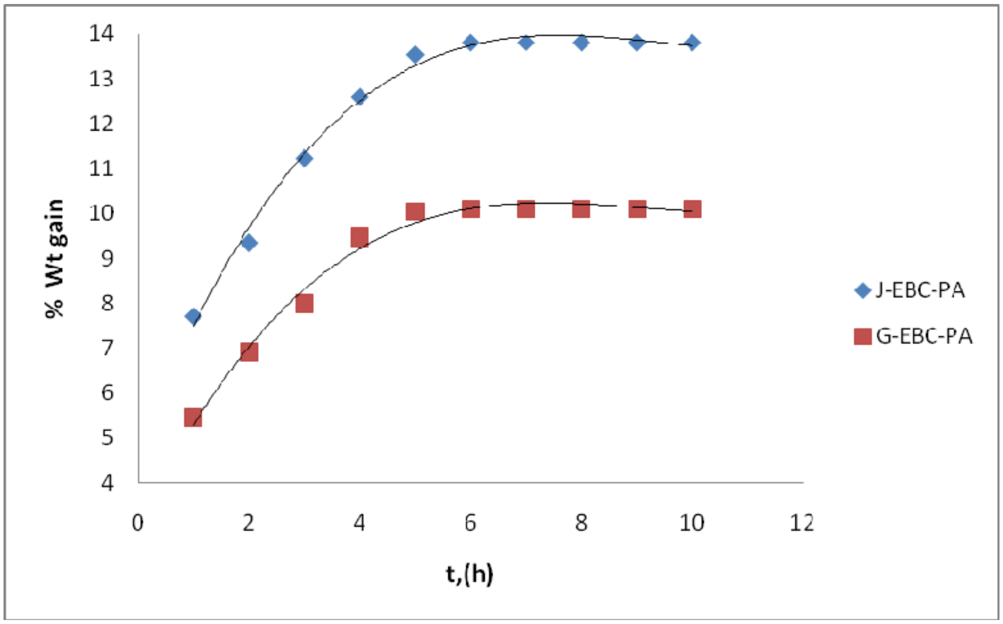


Fig.5.7: The plots of % weight gain against time for J-EBC-PA and G-EBC-PA composites in boiling water.

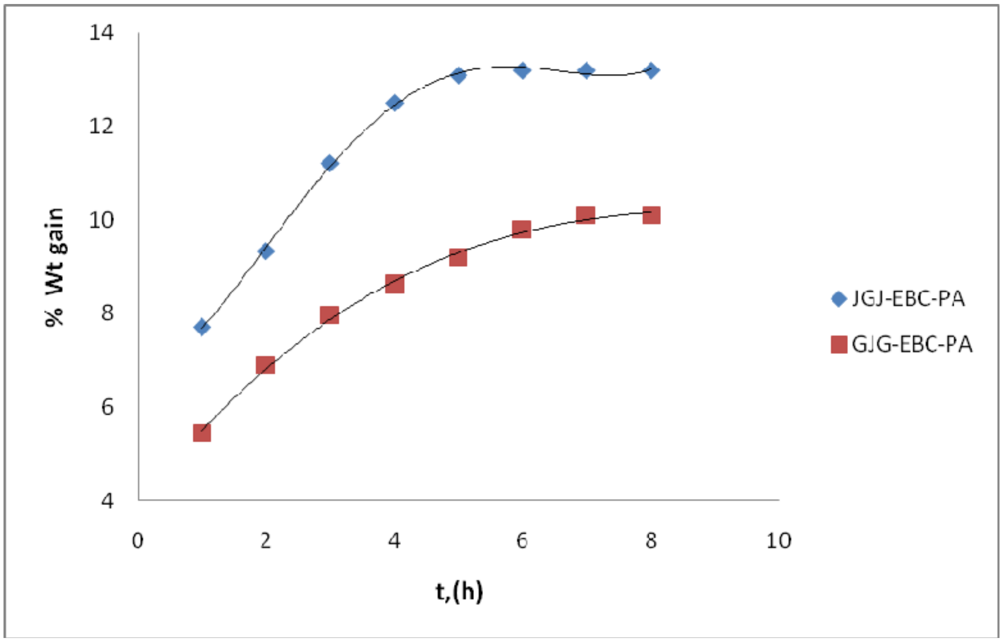


Fig.5.8: The plots of % weight gain against time for GJG- EBC- PA and JGJ-EBC- PA composites in boiling water.

5.7 Water uptake study Jute-biofiber reinforced polyurethane composites

Water uptake study of the Jute-biofiber reinforced polyurethane composites were carried out at 35^0C in water, 10% aq HCl and 10% aq NaCl and also in boiling water. The percentage weight gained by the composites in water, 10 % aq. HCl and 10 % aq. NaCl solutions with the passage of time ($t^{1/2}$) is shown in Figs. 5.9-5.26 The % weight gained by each composite increased, reached maximum and then practically remained constant, when equilibrium was established in each of the environment. The equilibrium water content and the equilibrium time for each of the composites in water, 10 % aq. NaCl, 10 % aq. HCl environments are recorded in Table 5.8. The observed trend in % equilibrium water content in studied environments is HCl > H_2O > NaCl. High equilibrium water content in the composites is due to the presence of hydrophilic groups in the matrix and reinforcing materials and may also due to microcraks and voids formed because of brittle nature of polyurethane resins.

From Table 5.8, it is observed that sandwich composites have considerably low diffusivity probably due to random orientation of fibers. The presence of strong electrolytes in water affects water structure and hence diffusivity. The solvated ions affect the diffusivity. Smaller is the size greater is the diffusivity. Absorption of water in composites causes swelling of fibers till the cell walls are saturated with water and beyond that water exists as free water in the void structure [10, 11] leading to composites delamintion or void formation.

---

10. J. Gassan, and A. K Bledzky, “The influence of fiber-surface treatment on the mechanical properties of jute-polypropylene composites”. Composites. 28, 1001-1005, (1997).
11. S. Das,, A. K., Saha, P. K., Choudhary, R. K., Basak, B. C., Mitra, T. Todd, and S. Lang. “Effect of steam pretreatment of jute fiber on dimensional stability of jute composite”. J. Appl. Polym. Sci. 76, 1652-1661, (2000).

Absorbed water causes weakening of interfacial adhesion and hydrolytic degradation of both matrix and fibers [12-14] and hence deterioration of tensile strength. Cracking and blistering of fibers cause high water absorption, while degradation causes leaching of small molecules [15].

The effect of boiling water on the % water absorption with the passage of time is shown in Figs. 5.27-5.32 from which it is evident that the water absorption in composites is the maximum after 6h and remained almost constant. The equilibrium water absorption time is reduced drastically without damage to the composites. Thus, composites possess excellent hydrolytic stability against boiling water.

---

12. S. Pavlidou, and C. D. Papaspyrides,"The effect of hygrothermal history on water sorption and interlaminar shear strength of glass/polyester composites with different interfacial strength". Composites Part A. 34, 1117-1124 (2003).
13. S. Lin-Gibson, V. Baranauskas, J. Riffle and, U. Sorathia, "Cresol novolac-epoxy networks processability and properties". Polymer**.** 43, 7389-7394, (2002).
14. C. S. Tyberg, K. Bergeron, M. Sankarapandian, P. Shih, A. C. Loos, D. A. Dillard, J. E. McGarth, J. S. Riffle, and U. Sorathia, "Structure-property relationships of void-free phenolic-epoxy matrix materials". Polymer. 41, 5053-5061, (2000).
15. L. R. Bao, A. F. Yee, "Effect of temperature on moisture absorption in a bismaleimide resin and its carbon fiber composites". Polymer. 43, 3987-3997, (2002).

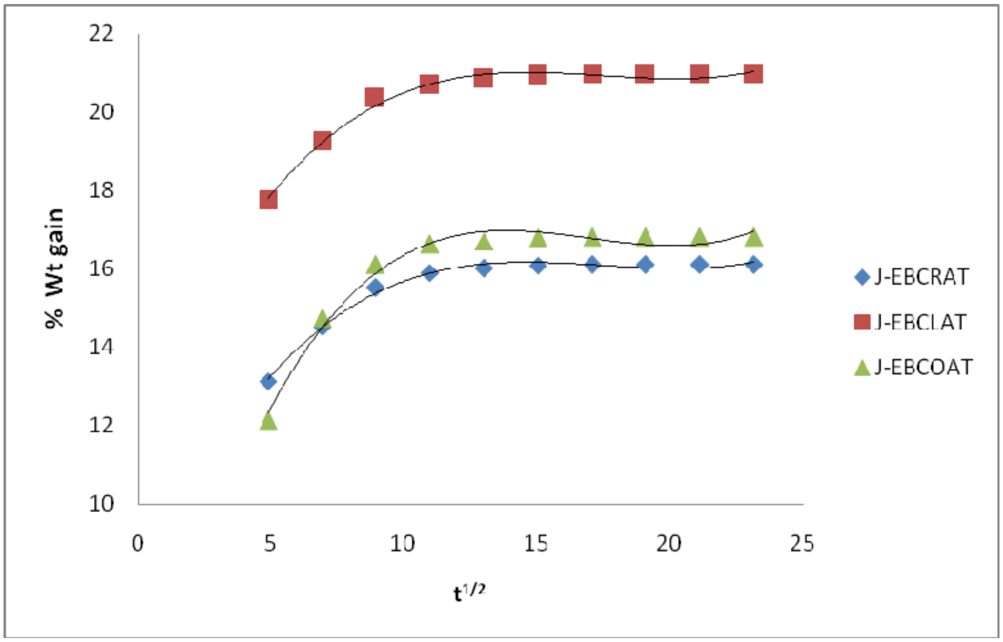


Fig.5.9: The plots of % weight gain against $t^{1/2}$ for J-EBCRAT, J-EBCLAT and J-EBCOAT composites in water at 35^{O}C.

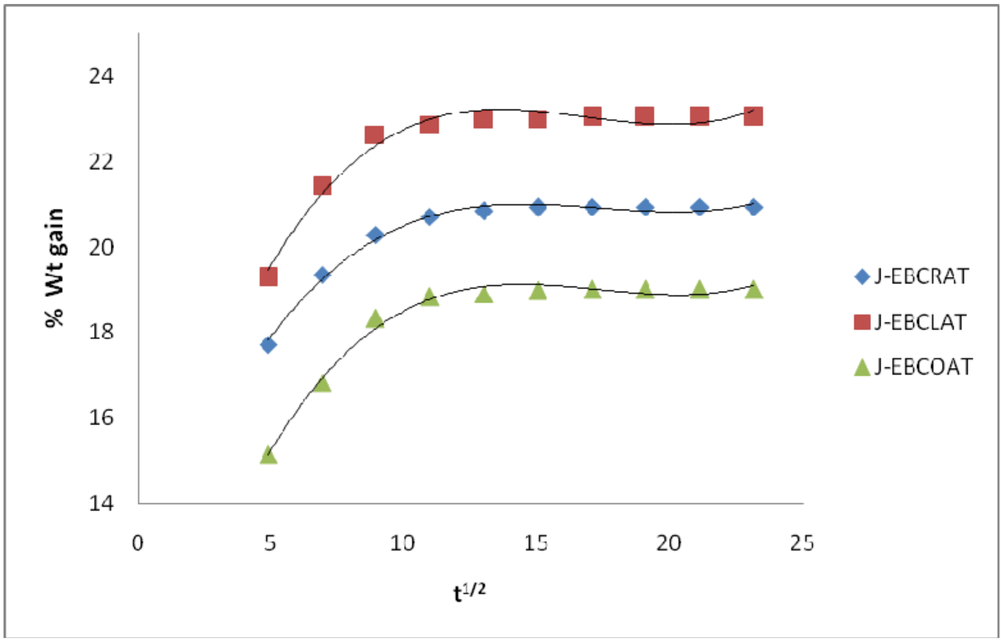


Fig.5.10:The plots of % weight gain against $t^{1/2}$ for J-EBCRAT, J-EBCLAT and J-EBCOAT composites in 10 % aq. HCl at 35 ^{0}C.

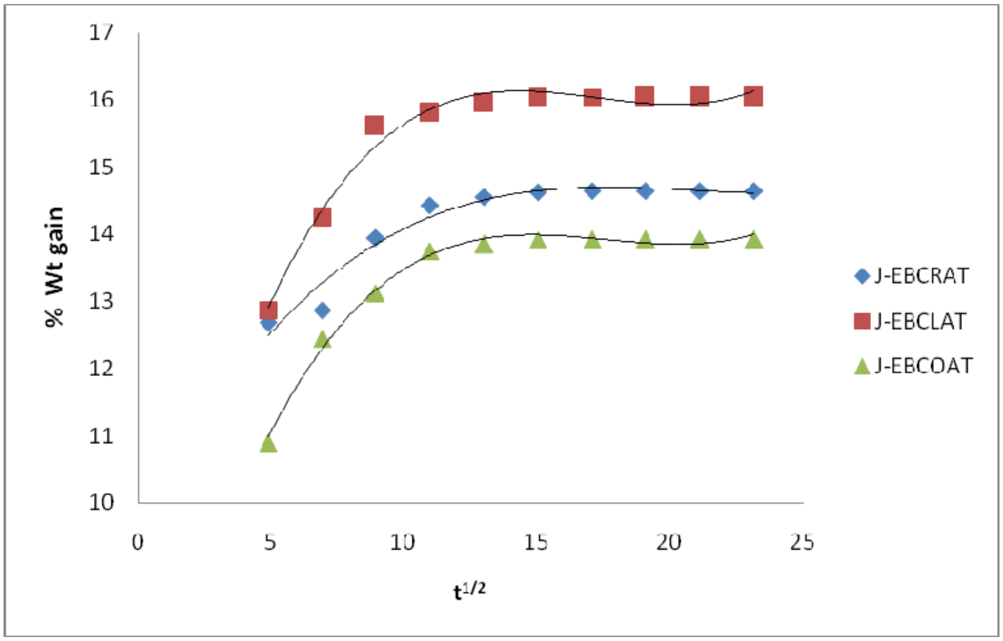


Fig.5.11: The plots of % weight gain against $t^{1/2}$ for J-EBCRAT, J-EBCLAT and J-EBCOAT composites in 10 % aq. NaCl at 35^{0}C.

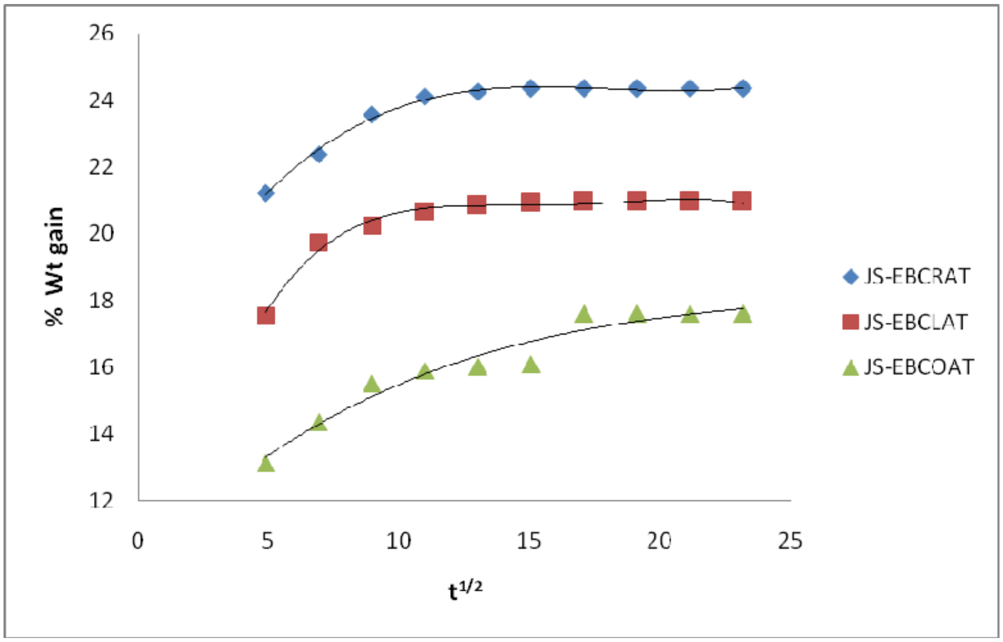


Fig.5.12: The plots of % weight gain against $t^{1/2}$ for JS-EBCRAT, JS-EBCLAT and JS-EBCOAT composites in water at 35^{O}C.

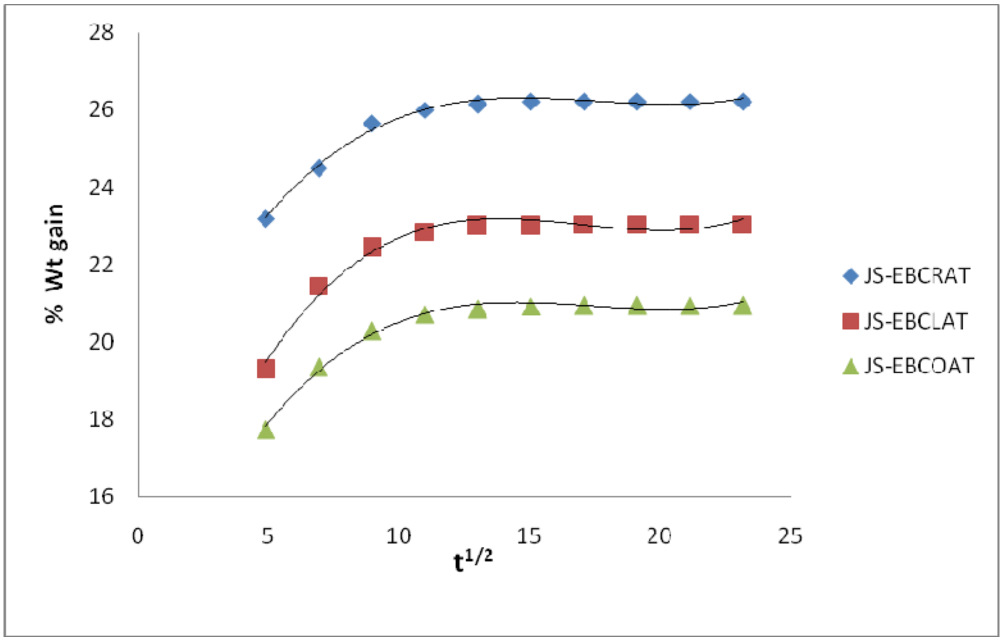


Fig.5.13: The plots of % weight gain against $t^{1/2}$ for JS-EBCRAT, JS-EBCLAT and JS-EBCOAT composites in HCl at 35^{O}C.

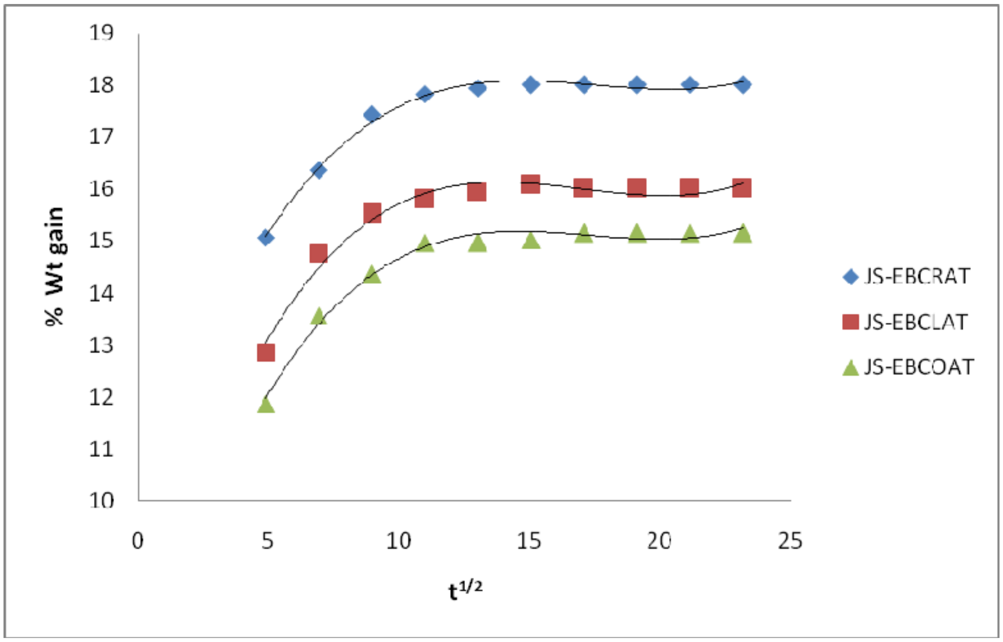


Fig.5.14: The plots of % weight gain against $t^{1/2}$ for JS-EBCRAT, JS-EBCLAT and JS-EBCOAT composites in NaCl at 35^{O}C.

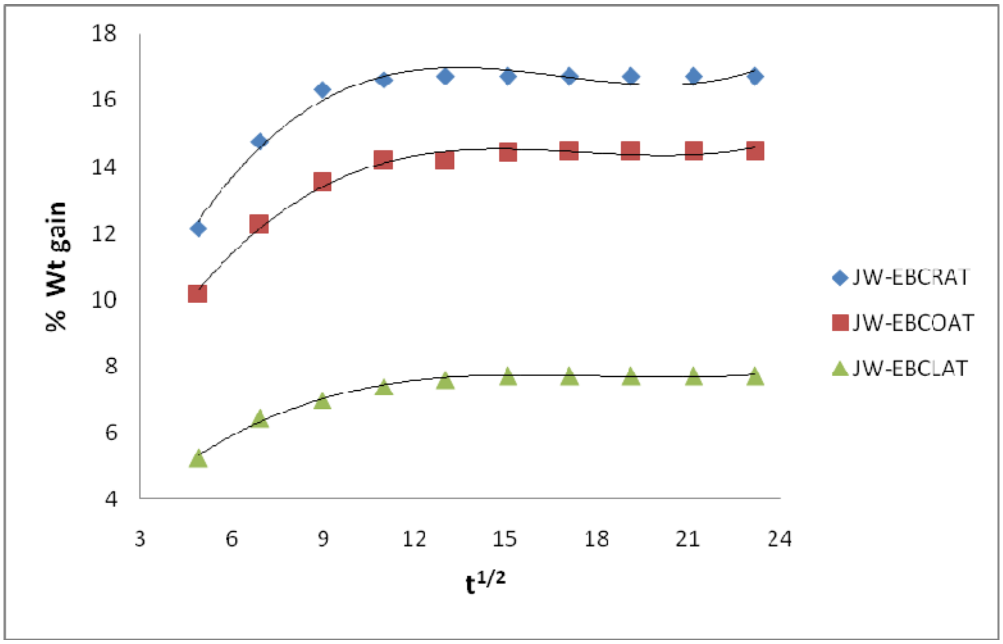


Fig.5.15: The plots of % weight gain against $t^{1/2}$ for JW-EBCRAT, JW-EBCLAT and JW-EBCOAT composites in water at 35°C.

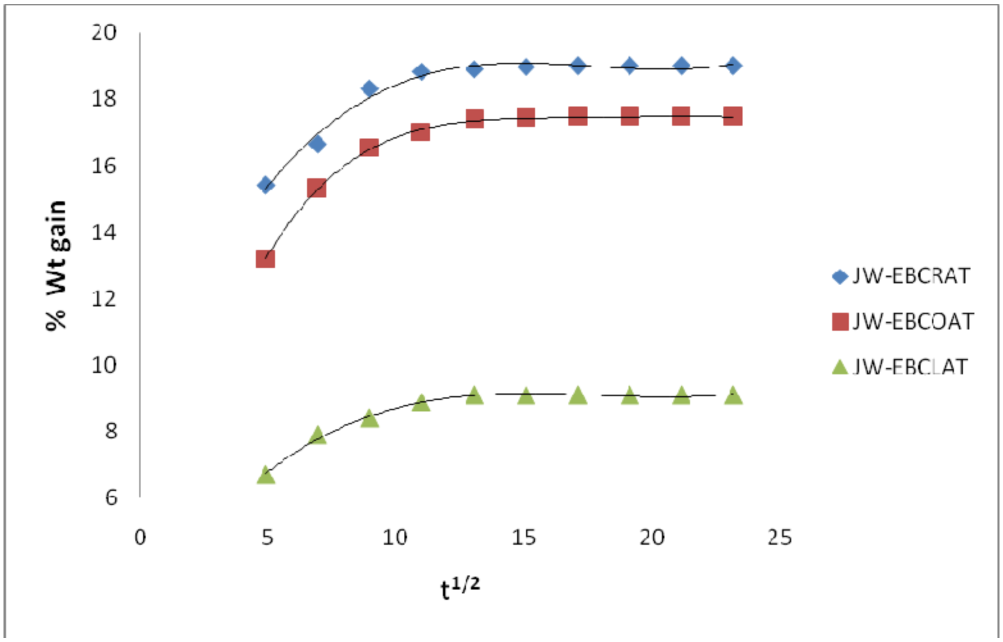


Fig.5.16: The plots of % weight gain against $t^{1/2}$ for JW-EBCRAT, JW-EBCLAT and JW-EBCOAT composites in 10 % aq. HCl at 35°C.

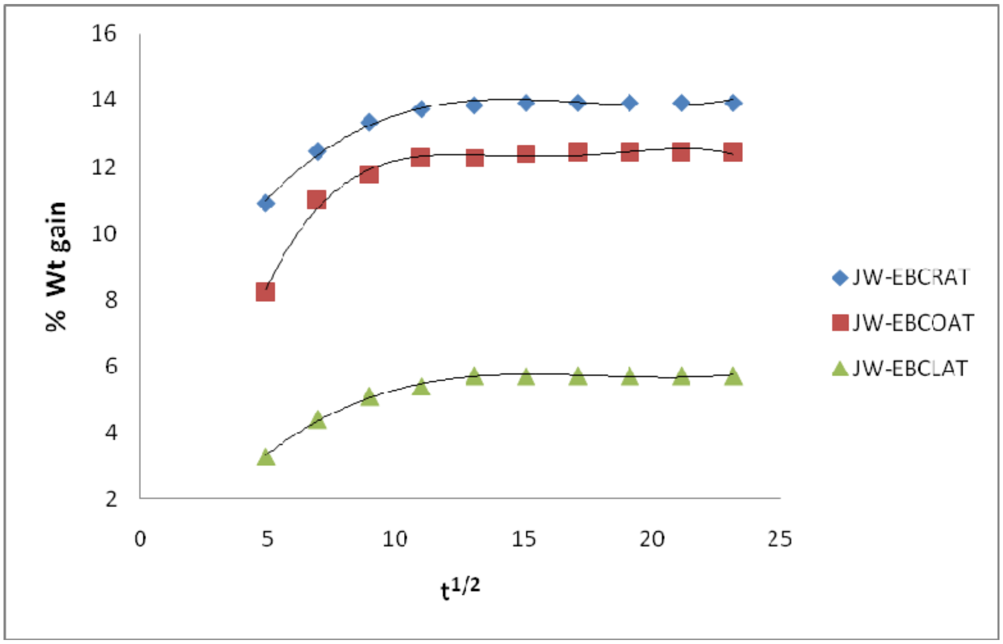


Fig.5.17: The plots of % weight gain against $t^{1/2}$ for JW-EBCRAT, JW-EBCLAT and JW-EBCOAT composites in 10 % aq. NaCl at 35^{0}C.

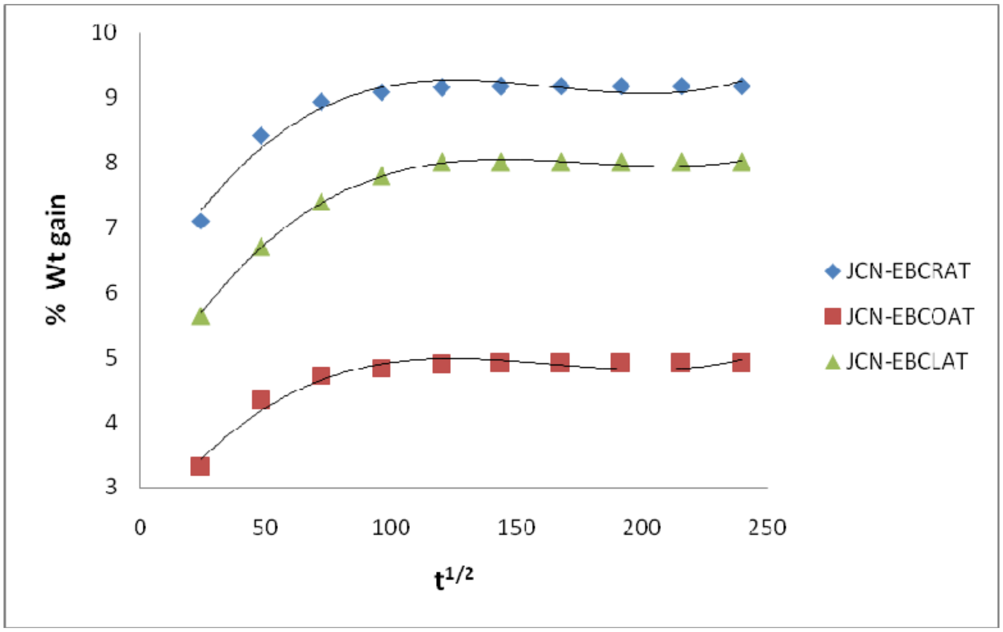


Fig.5.18: The plots of % weight gain against $t^{1/2}$ for JCN-EBCRAT, JCN-EBCLAT and JCN-EBCOAT composites in water at 35^{O}C.

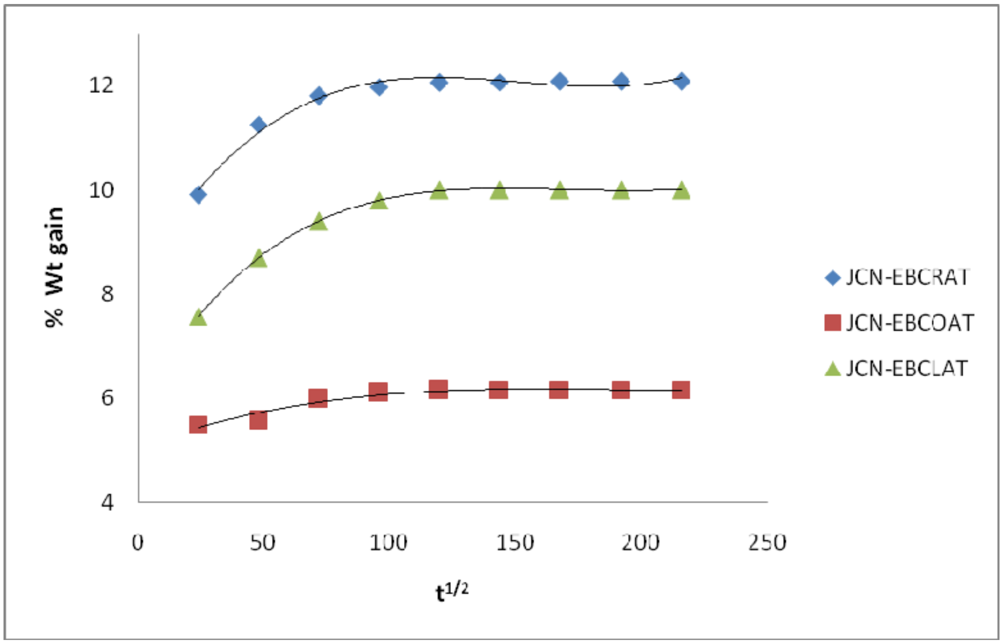


Fig.5.19: The plots of % weight gain against $t^{1/2}$ for JCN-EBCRAT, JCN-EBCLAT and JCN-EBCOAT composites in HCl at 35°C.

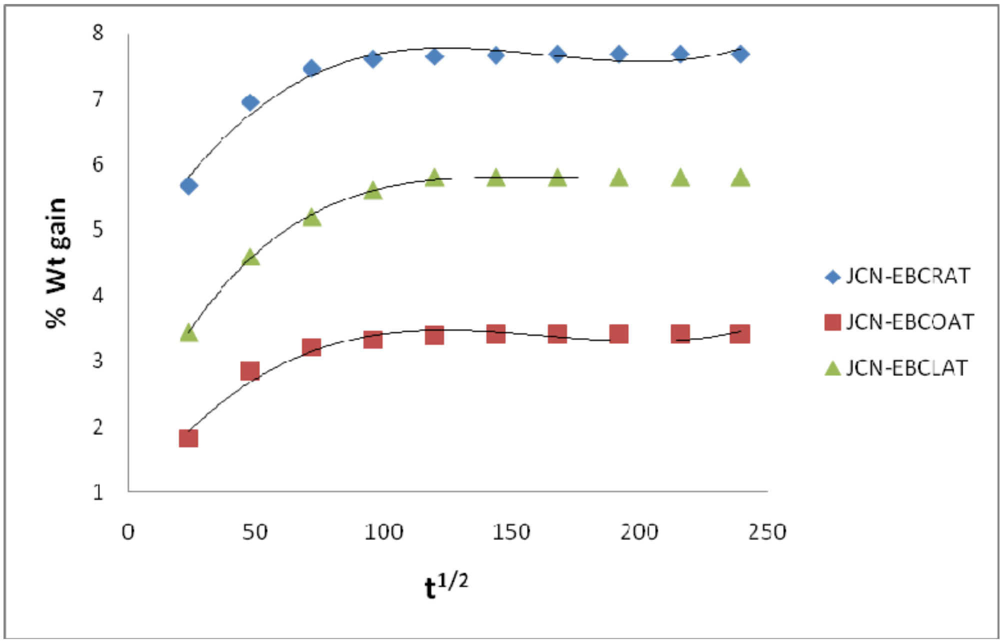


Fig.5.20: The plots of % weight gain against $t^{1/2}$ for JCN-EBCRAT, JCN-EBCLAT and JCN-EBCOAT composites in NaCl at 35°C.

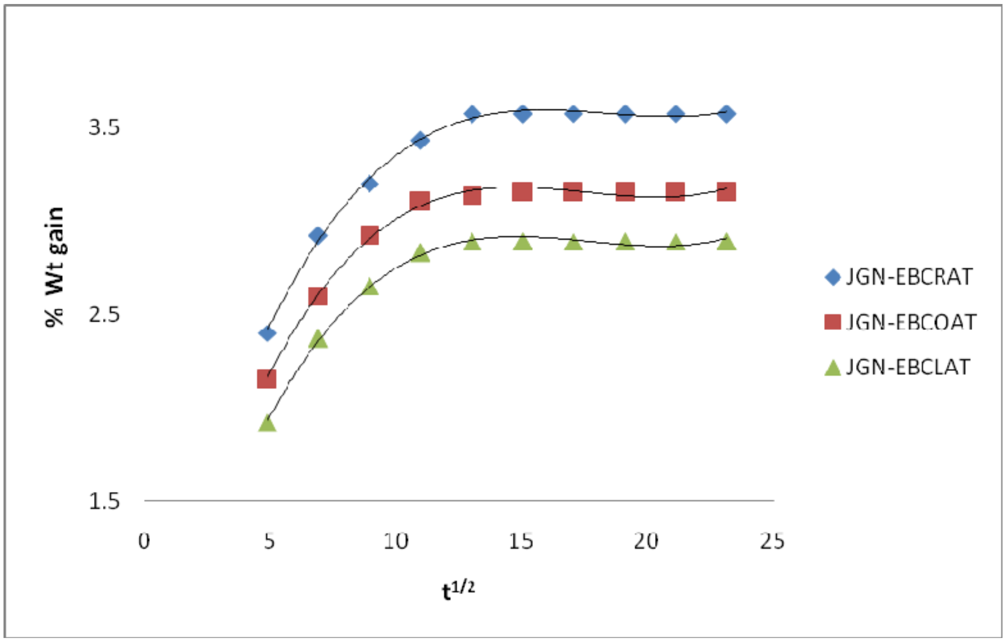


Fig.5.21: The plots of % weight gain against $t^{1/2}$ for JGN-EBCRAT, JGN-EBCLAT and JGN-EBCOAT composites in water at 35^{O}C.

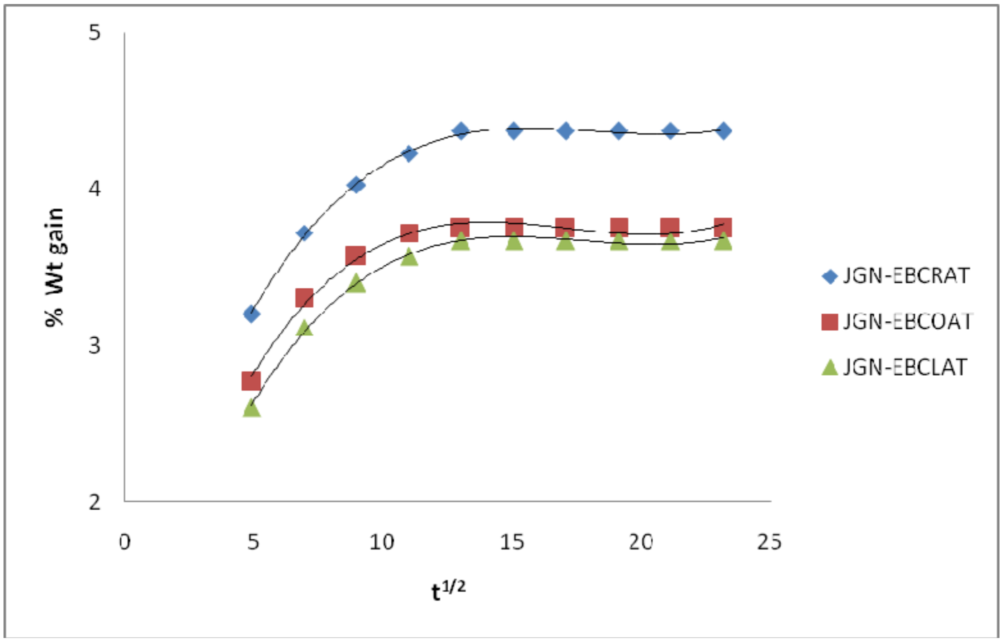


Fig.5.22 : The plots of % weight gain against $t^{1/2}$ for JGN-EBCRAT, JGN-EBCLAT and JGN-EBCOAT Composites in 10 % aq. HCl at $35\ ^{0}$C.

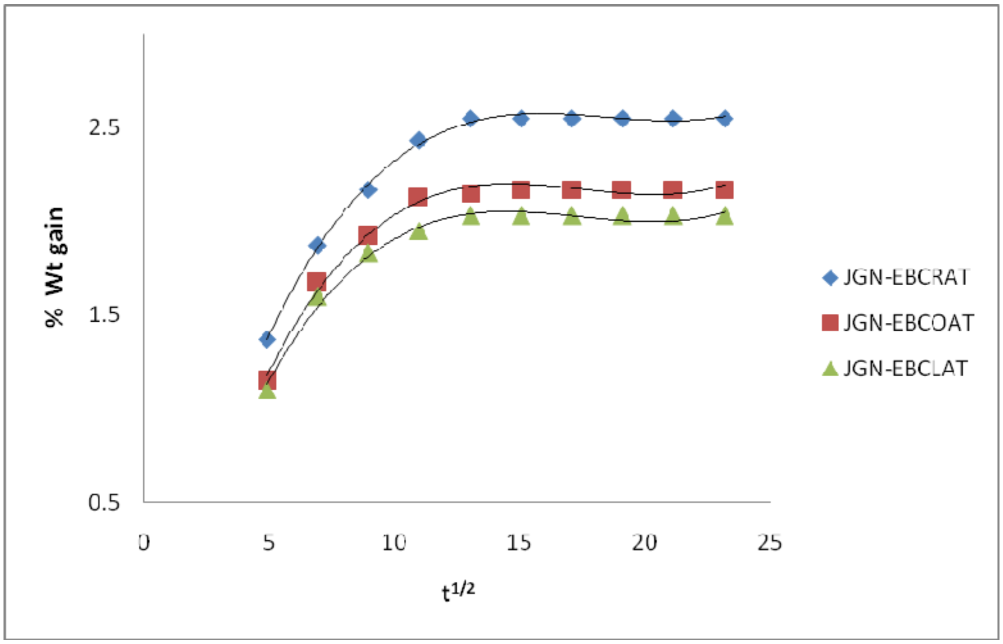


Fig.5.23: The plots of % weight gain against $t^{1/2}$ for JGN-EBCRAT, JGN-EBCLAT and JGN-EBCOAT composites in 10 % aq. NaCl at 35^0C.

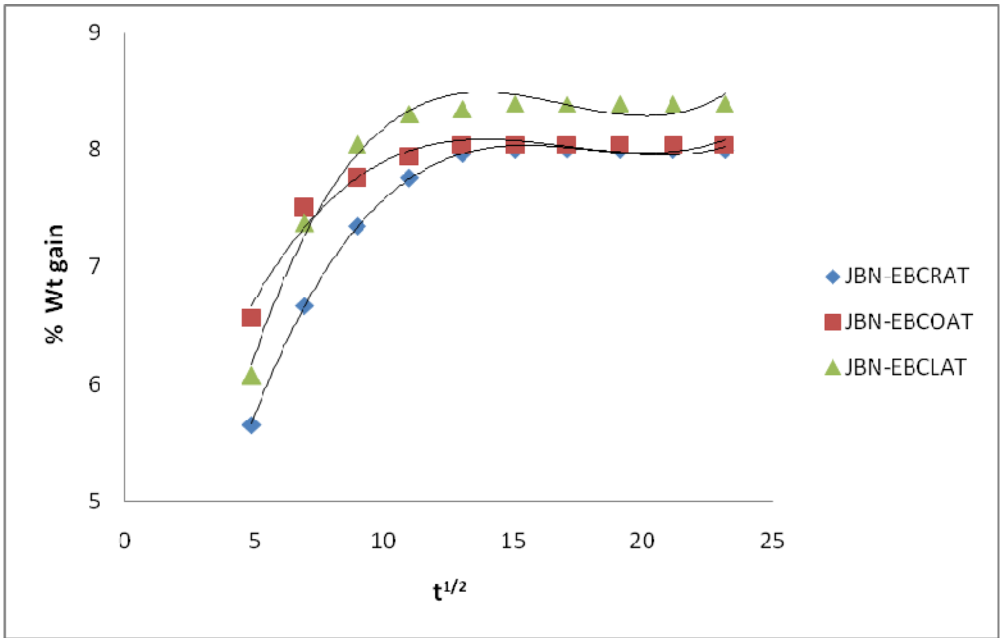


Fig.5.24: The plots of % weight gain against $t^{1/2}$ for JBN-EBCRAT, JBN-EBCLAT and JBN-EBCOAT composites in water at 35^OC.

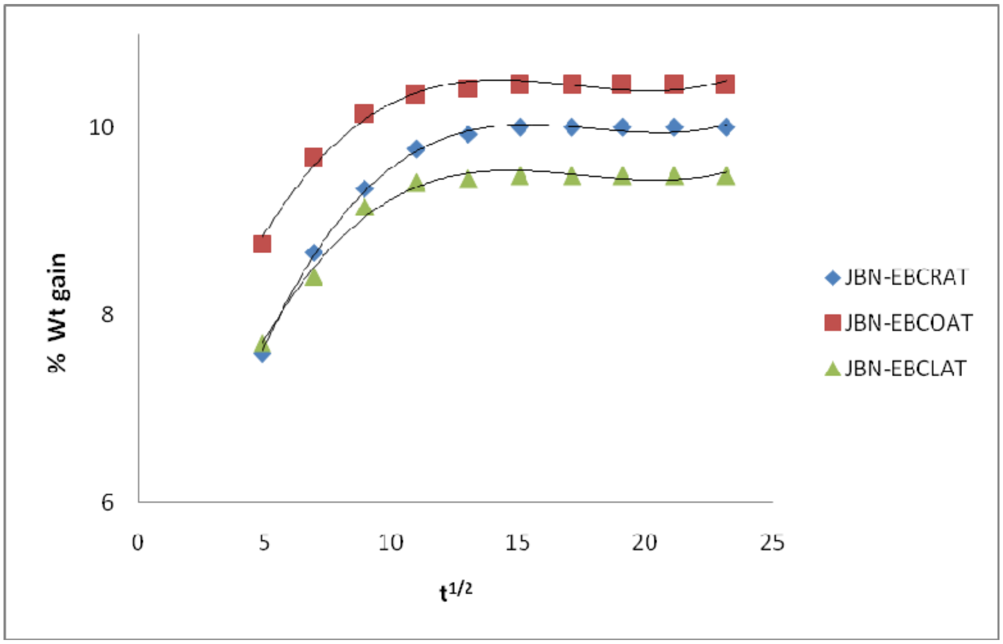


Fig.5.25: The plots of % weight gain against $t^{1/2}$ for JBN-EBCRAT, JBN-EBCLAT and JBN-EBCOAT composites in HCl at 35°C.

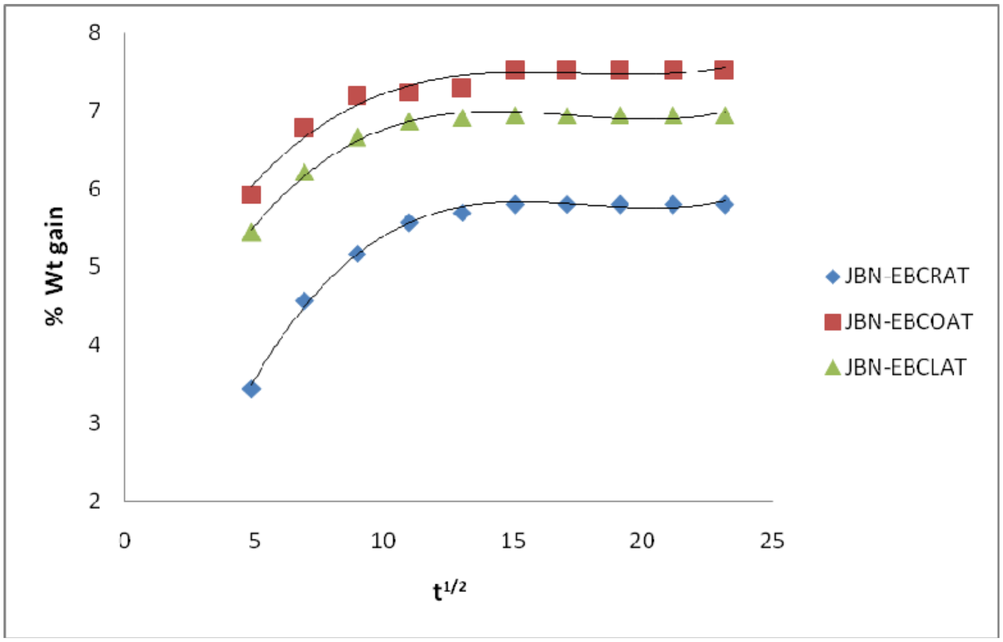


Fig.5.26: The plots of % weight gain against $t^{1/2}$ for JBN-EBCRAT, JBN-EBCLAT and JBN-EBCOAT composites in NaCl at 35°C.

Table-5.8 Equilibrium water content and diffusivity data of jute-biofiber reinforced polyurethanes of epoxy polyester polyols based sandwich composites in different environments at 35^{o}C and in boiling water.

Composite	%, Equilibrium water content at room temperature			Diffusivity(D_x), 10^{-11}, m^2/s			%, Eqm. water content in boiling water
	H_20	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl	
J-EBCRAT	16.1	14.7	20.9	7.3	9.7	4.3	20.7
J-EBCLAT	16.8	13.9	19.0	6.6	9.7	9.7	17.2
JSC-EBCOAT	21	16.0	23.0	2.4	3.5	2.3	20.7
JSC-EBCRAT	24.4	18.0	26.2	2.6	1.7	2.5	24.6
JSC-EBCLAT	17.6	15.2	20.9	5.8	3.4	1.7	15.8
JSC-EBCOAT	21	16.0	23.0	2.4	3.5	2.3	20.7
JW-EBCRAT	16.7	13.9	19	7.11	7.60	4.39	17.2
JW-EBCOAT	14.5	12.4	17.5	1.35	7.02	9.18	14.5
JW-EBCLAT	7.7	5.7	9.1	1.38	2.57	9.42	6.7
JCN-EBCRAT	9.2	7.7	12.1	1.6	2.25	1.05	9.2
JCN-EBCLAT	8.0	5.8	10	1.4	3.16	1.11	7.1
JCN- EBCOAT	4.9	3.4	6.2	3.22	6.67	1.35	5.0
JGN-EBCRAT	3.6	2.55	4.37	5.63	1.21	3.58	3.15
JGN-EBCLAT	2.9	2.0	3.7	6.27	1.34	5.04	2.75
JGN-EBCOAT	3.2	2.2	3.8	5.72	1.20	4.56	2.90
JBN-EBCRAT	8	5.8	10	3.7	7.23	2.42	7.1
JBN-EBCLAT	9.0	7.0	9.5	5.51	5.79	3.14	8.59
JBN-EBCOAT	8.04	7.51	10.5	5.2	2.55	2.62	8.20

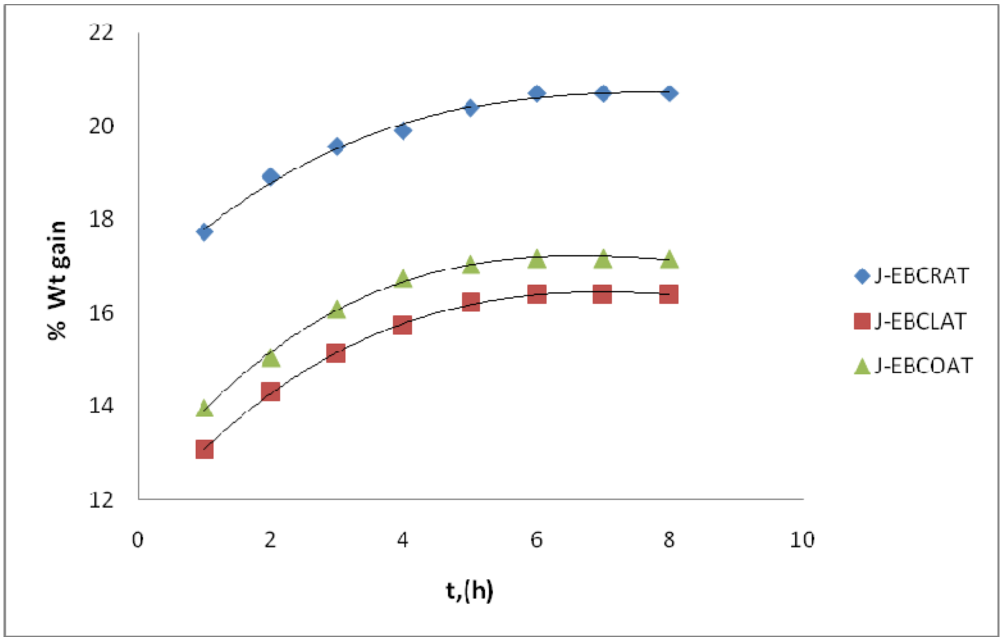


Fig.5.27: The plots of % weight gain against t, for J-EBCRAT, J-EBCLAT and J-EBCOAT composites in boiling water.

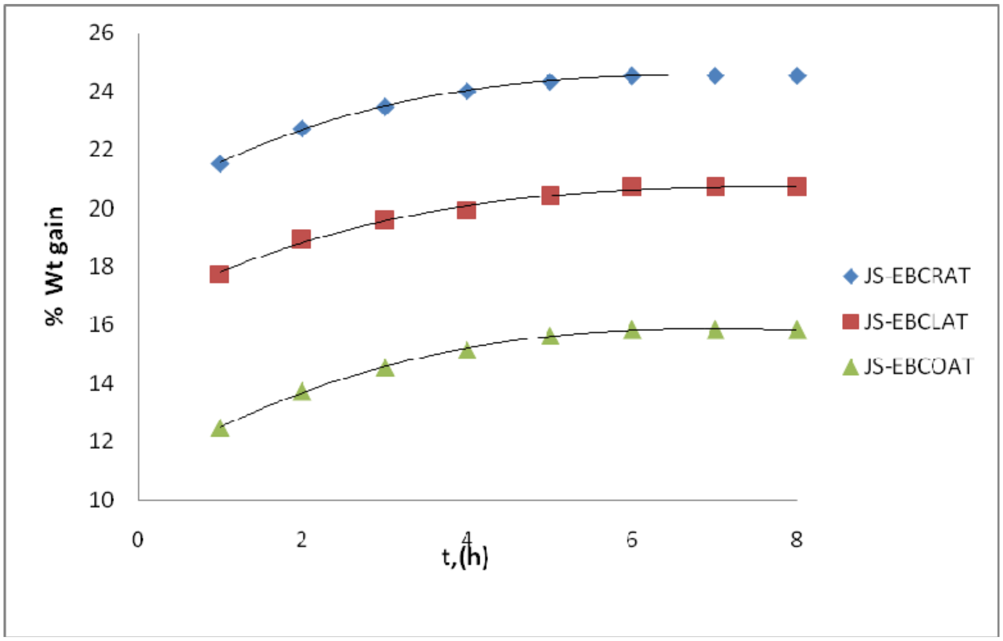


Fig.5.28: The plots of % weight gain against t, for JS-EBCRAT, JS-EBCLAT and JS- EBCOAT composites in boiling water.

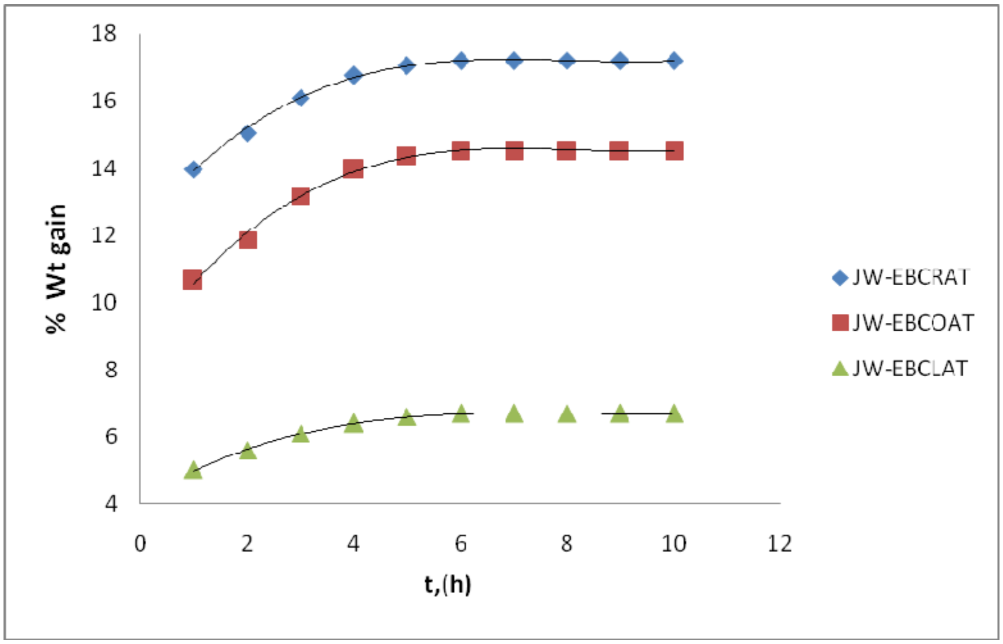


Fig.5.29: The plots of % weight gain against time for JW-EBCRAT, JW-EBCLAT and JW-EBCOAT composites in boiling water.

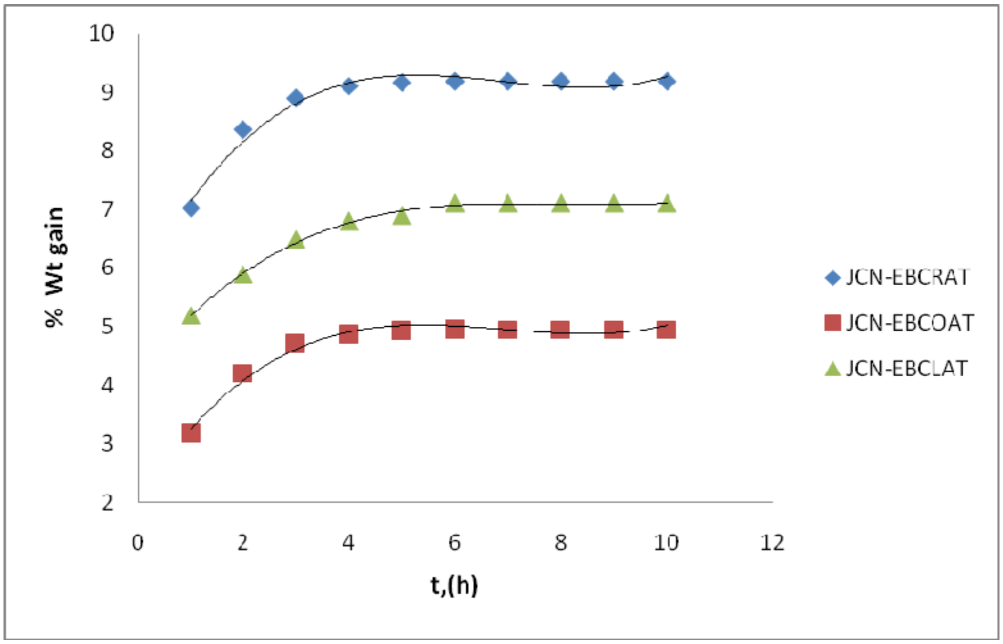


Fig.5.30: The plots of % weight gain against time for JCN-EBCRAT, JCN-EBCLAT and JCN- EBCOAT composites in boiling water.

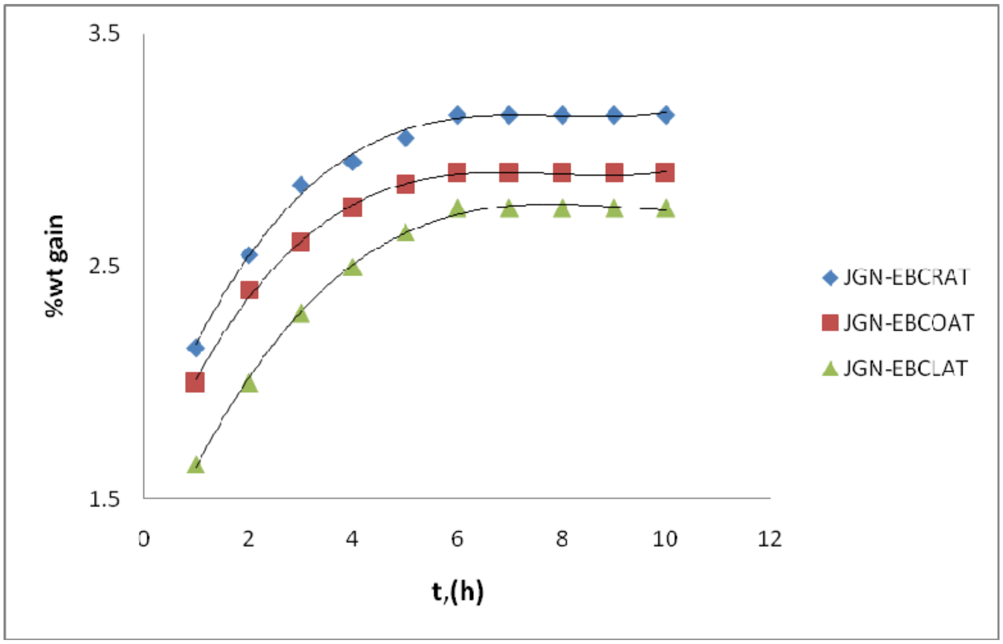


Fig.5.31: The plots of % weight gain against time for JGN-EBCRAT, JGN-EBCLAT and JGN-EBCOAT composites in boiling water.

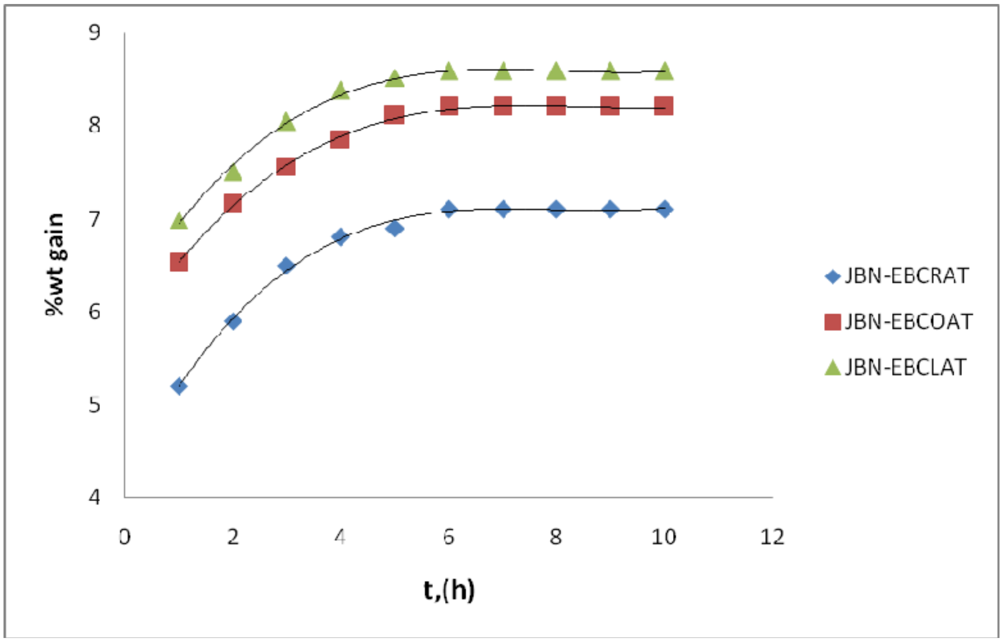


Fig.5.32: The plots of % weight gain against time for JBN-EBCRAT, JBN-EBCLAT and JBN- EBCOAT composites in boiling water.

CHAPTER-6

SURFACE COATING

CHEMICAL RESISTANCE

CHAPTER-6

SURFACE COATING

6.1 General introduction

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

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

Today coatings are not just used for decorative purposes but are used in almost ever facet of the human life. Applications of the sophisticated primers, surfaces and topcoats have greatly increased the life of coated article. Coatings have also triggered the development in the field of marine, automobile, architectural, maintenance and fiber optics coatings. Also specifically coating that control absorption or emission for temperature control, aircraft coatings that withstand the effect of UV radiation, absorption and the impact of air and dirt [1-2].

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

The diluents serve to adjust the viscosity of the paint. It is volatile and does not become part of the paint film. Anything else is in an additive.

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

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

Fillers serve to thicken the film, support its structure and simply increase the volume of the paint. Not all paints include fillers. Pigments that also function as fillers are called simply "pigments"; "fillers" are generally color-neutral and opaque. It is necessary to adjust the resulting off-white color with pigments to give the desired color. Common fillers are cheap and inert, such as talc, lime, baryte, bentonite clay, etc. Depending on the paint, most of the paint film may consist of filler and binder, the rest being additives. Typical additives include pigments, dyes, catalysts, thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, flatteners (de-glossing agents), and the like

6.2. Key developments in coating industries

Early chemists relied on natural products for varnishes based on fossilized resins and natural oil. The attempts have been made to modify the natural resins to produce synthetic natural products. Another key development of rubber and then phenolic resin followed by alkyd, urea and melamine formaldehyde resins. Other ‘Leap frog’ achievements came in around 1944-

---

1. J. H. Boatwright; Organic Coating; “Their Origin and Development”. R. B. Seymour and H. F. Mark, Elsevier. P-9, New York (1990).
2. Y. González-García , J. M. C Mol , T. Muselle , I. De Graeve , G. Van Assche , G. Scheltjens , B. Van Mele , H. Terryn” SECM study of defect repair in self-healing polymer coatings on metals”. Electrochemical and Surface Engineering. 13, 169–173, (2011).

silicone based paints and in 1947-epoxy resins. There after the coating industry was revolutionized by development of PVA and acrylic lacquers, powder coatings, water-borne paints, UV-cure coatings, cationic electro coatings and clear-over color top coats. The high degree of cross-linking in the cured structure produces hardness, strength, heat-resistance, electrical resistance and broad chemical resistance. These properties are important in coatings, adhesives and reinforcements. [3-4].

Polyurethanes are macromolecules or polymers formed by the reaction between a polyisocyanate and other polymer (commonly known as a polyol) that contains active hydrogens (OH, COOH….). The choice of raw materials, both polyols and polyisocyanates are very large enabling many combinations with wide varieties of properties. There have been many developments in the 60 or so years and today polyurethanes are used in a wide range of applications such as foams, elastomers and coatings. Polyurethanes were initially used to manufacture foams and plastic compounds, largely used in the Second World War II as thermal and sound insulation for German submarines leading to the development of new color stable coatings. Rapid progress followed, enabling car manufactures to use polyurethane coatings leading to the development of new color stable coatings Rapid progress followed, enabling car manufactures to use polyurethane coatings. In 1967, Matra produced an all- plastic car finished in a two- pack polyurethane topcoat. This was followed in 1968, by German Railways using two- pack polyurethane to coat locomotives and passenger carriages. In 1970 polyurethane coatings were introduced for vehicle repair applications. Nowadays polyurethane coatings are used in numerous industrial applications and on a wide variety of substrates:

---

3. R. D. Deanin, “Polymer Structure, Properties and Applications”, Cabners books, division of Cabners publishing company. Inc. (1972).
4. L. A. Sukhareva and N .Y. Abramova, ”Modification of polyurethanes with amides”.Polym.sci.series-C. 49,195-197, (2007).

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

The automotive industry is the largest user of polyurethane coatings, using 30% of total volume. The breakdown markets for polyurethane coatings in Western Europe are shown in the Table-6.1 below.

Table-6.1: European markets for PU coatings

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

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

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

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

Excellent mechanical properties

Due to the rapid elasticity of the urethane network, PU coatings can withstand extreme mechanical forces even at very low temperatures. Thus, they are used in coatings for aerospace.

Excellent chemical resistance

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

High reactivity

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

Under the ASTM D2794-93 norm, the American Society for Testing and Materials has classified the polyurethane coatings into six categories as described in Table-6.2.

Table-6.2: Classification of polyurethane

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

6.3. Two – component polyurethanes

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

This reaction allows a great deal of flexibility in terms of drying conditions. This is due to very reactive isocyanate group which is able to crosslink with hydroxylated resins over a wide range of temperatures or allowing air drying systems. The two component polyurethane system can achieve a very high performance level after drying. The drying time of two components polyurethane coating depends upon the type of the polyisocyanate used, which is shown in the Table-6.3. It is widely used to paint heat sensitive materials such as thermoplastics and heavy equipments such as tractors which cannot be coated by thermosetting paints.

Table-6.3: Relative drying times of two component PU coatings

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

Two pack polyurethane show very good resistance to water, aqueous chemicals and organic solvents. In case of water satisfactory formulations will show very good performance in immersion conditions. Thermal stability of these coatings is very good up to 180^0C. The most striking feature of the two pack polyurethane coatings is their excellent weatherability and chalk resistance in comparison with other finish coatings. The two pack polyurethane coatings give some excellent properties including long pot life, very good chemical and stain resistance, excellent non yellowing (aliphatic isocyanates), good mar resistance, long term flexibility, abrasion resistance, impact resistance, high gloss and in combination with the above properties relatively high solids can be obtained.

6.4 Polyurethanes for oven curing (1K PU)

This second family is similar to first one, but the isocyanate groups are protected by the blocking agents, which prevent the reaction with the hydroxyl groups at low temperatures. This allows the premixing of the two parts of the paint in a single pack with a very long shelf life. The blocking agent is released during the curing process. Depending upon the nature of the isocyanates and nature of the blocking agents, unblocking temperatures can be as high as 200^0C or as low as 100^0 to 120^0C. A catalyst such as dibutyl tin dilaurate (DBTL) would then also be added at levels between 0.5 and 1%. The basic rule of the formulation is the polyol must be non-yellowing on stoving and the solvents should have higher boiling points than those used in the two pack systems. The film possesses excellent hardness, abrasion resistance and solvent resistance.

6.5 Moisture cured polyurethanes

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

Formulations of moisture cure or one pack protective coatings provides products with many desirable properties. They are rapid drying even at low temperatures down to zero and below. They may also be applied at high humidities up to 1000%. This allows for application under extreme conditions such as in fog and onto damp (but not wet) substrates. High humidity is advantageous to the curing of one pack moisture cured polyurethanes, since high moisture contents accelerate the drying process. To ensure satisfactory drying the minimum relative humidity should be 30%.

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

This is widely used in open areas for painting large components which can not be placed in oven. Maintenance (offshore and marine topsides, motorway bridges, railway bridges and dock walls) and marine coatings are important markets for this type of technology. Now a day polyurethanes are widely used in the textile coatings, leather and paper industries. Polyurethanes are being suitable for these applications because specific properties can be obtained during the application or from the finished material, i.e. by chemical crosslinking.

Polyurethanes are distinguished by their very good adhesion to different substrates and by high flexibility even at low temperatures. Their thermoplsticity (uncrosslinked material) and resistance to most solvents are advantageous compared to the other polymers. Polyurethane products for textile coating were first marketed in the fifties. At first chintz articles were produced but soon tent roofs, tent floors, blinds, ironing board covers, light rain coats and other products were manufactured.

The typical properties for polyurethane textile coatings are as follows:

Leather like surface, warm comfortable touch, wash and cleaning stability, good adhesion between substrate and coating, high elongation and elasticity, good abrasion resistance, high flexibility at low temperature (without plasticizer), very good resistance to oils and fats, low specific weight,etc.

Mallu et. al [5] have synthesized interpenetrating polymer networks (IPNs) of polyurethane (PU)/ polyacrylates have been synthesized by sequential polymerization of castor oil, methylene diisocyanate (MDI), and acrylate monomers such as methyl acrylate (MA), methyl methacrylate (MMA), and ethyl acrylate (EA); with benzoyl peroxide (BPO) and ethylene glycol dimethyl acrylate (EGDM) as an initiator and cross linker, respectively and investigated the physico-mechanical properties, such as density, surface hardness, tensile strength, percentage elongation at break, and tear strength; and the optical properties, like total transmittance and haze of PU/polyacrylate IPNs. Microcrystalline parameters of IPNs have been computed by using wide angle X-ray scattering (WAXS) recordings.

, Cherian et al [6] have modified unsaturated polyester resins (UPRs) by reactive blending with polyurethane prepolymers having terminal isocyanate groups and studied the effect of blending on various properties.

---

5. P. Mallu, S. Roopa, H. Somashekarappa, R. Somashekar and Siddaramaiah, “Studies on physico-mechanical and optical properties, and WAXS of castor oil based polyurethane/polyacrylates interpenetrating polymer networks”. J. Appl. Polym. Sci. 95, 764-773, (2005).

.

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

Guhanathan et al [7] have prepared tricomponent interpenetrating polymer network (IPN) systems involving castor oil, toluenediisocyanate (TDI), acrylonitrile (AN), ethylene glycol diacrylate (EGDA), and general-purpose unsaturated polyester resin (GPR) with various compositions. The mechanical properties such as tensile, flexural, impact, and hardness for the IPNs with various compositions were determined. It was found that the tensile strength of the GPR matrix was decreased and flexural and impact strengths were increased upon incorporating PU/PAN networks. The swelling properties in water and toluene were also studied. The morphology of the IPNs was studied using SEM.

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

---

6. A. B. Cherian, B. T. Abraham, E. T. Thachil, “Modification of unsaturated polyester resin by polyurethane prepolymers”. J. Appl. Polym. Sci. 100, 449-456, (2006).
7. S. Guhanathan, R. Hariharan and M. Sarojadevi, “Studies on castor oil-based polyurethane/polyacrylonitrile interpenetrating polymer network for toughening of unsaturated polyester resin”. J. Appl. Polym. Sci. 92, 817-829, (2004).

polyurethane to glass surfaces was increased by using a thin layer of novolac primer.

Polus et. al [9] have prepared polyurethane coatings by the "prepolymer mixing" method in two steps. The synthesis of the urethane prepolymer was carried out in presence of stannous 2-ethyl hexanoate. The obtained prepolymer was exposed to the reaction with branched polyester polyols. This reaction was carried out in presence of the catalysts: DABCO, TEA and stannous 2-ethyl hexanoate. In the synthesis of polyurethanes the aliphatic diisocyanates with linear (TMDI) and cyclic (IPDI) structures were used. The polyurethanes obtained using these diisocyanates was oxidized. The changes in the quality were monitored by determining some properties of the cured coating, such as hardness, flexibility and scratch resistance.

Duffy et. al [10] have conducted studies on ternary blends consisting of poly(propylene oxide) and poly(methyl methacrylate co *n*-butyl methacrylate) blended with either poly(hexamethylene adipate) or poly(hexamethylene sebacate). These ternary blends formed the basis for preparation of high performance polyurethane-based hot-melt adhesives and coatings. Changes in polyester structure were found to strongly alter the miscibility behavior. Binary interaction parameters for the five polymer pairs were determined experimentally, permitting calculation of the phase behavior of the ternary polymer blends. Results predicted by the model are in excellent agreement with experimental observations. The influence of miscibility in the melt on the morphology development was also discussed.

---

8. E. A. Ismail and M. H. M. Hussain, “Improvement of polyurethane adhesion to glass using novolac primer”. J. Adhe. and Technol. 16, 1509-1513, (2002).
9. I. Polus, “Synthesis of polyurethane coating components with IPDI and TMDI”. J. Mater. Sci. 61, 238-240, (2003).
10. D. J. Duffy, H. D. Stidham, S. Sasaki, A. Takahara T. Kajiyama and S. L. Hsu, “Effect of polyester structure on the interaction parameters and morphology development of ternary blends: Model for high performance adhesives and coatings”. J. Mater. Sci. 37, 4801-4809, (2002).

Gite et. al [11] have synthesized polyurethane coatings from monoglycerides (MGs) of four oils (castor, linseed, soybean and sesame). These coatings were applied in the form of thin films on tin plates and analysed for various coating properties such as gloss, scratch resistance, flexibility properties and physico-chemical tests. A highly cross-linked product was obtained due to the higher functionality associated with MGs compared with their molecular weight. The trimer also imparted cross-linking due to its trifunctionality, and a hard yet flexible, tough, glossy polyurethane coating was obtained.

Wounters et. al [12] have prepared polyurethane coatings with different network compositions in well-defined model systems as well as commercially-available formulations. The properties, such as glass-transition temperature, hardness and surface free energy of the model network were tuned by the choice of the ingredients. All coatings were studied with respect to their bulk properties as well as their surface properties. It was found that by the addition of a fluorinated additive, the surface free energy of the coating was lowered by approximately 15mNm^{-1}, leaving the bulk properties intact. It was also shown that these polyurethane coatings were able to adapt their surface free energy in a reversible manner when exposed to water. The magnitude and rate of surface rearrangement was strongly dependent on the network density of the coating. The effect of coating properties on the biofilm and subsequent adhesion of diatoms was studied on a selection of the coatings used in this study.

---

11. V. V. Gite, R. D. Kulkarni, D. G. Hundiwale, U. R. Kapadi, “Synthesis and characterization of polyurethane coatings based on trimer of isophorone diisocyanate (IPDI) and monoglycerides of oils”. Surface Coatings International Part B: Coatings Trans. 89, 117-122, (2006).
12. M. Wouters, J. Zanten, T. Vereijken, D. Bakker, J. Klijnstra, “Fluorinated polyurethane coatings with adaptable surface properties”. Surface Coatings International Part B: Coatings Trans. 89, 23-30, (2006).

Shamekhi [13] have prepared novel polyurethane insulating coatings from the reaction of glycerin-terminated polyurethane prepolymers (GPUPs) and a blocked isocyanate curing agent (BIC). The polyols and curing agent were characterized by conventional methods, while the curing condition was optimized via gel content measurements. The curing kinetics of the polyurethane coating was investigated and the kinetic parameters derived. The crosslink densities of the samples were determined via the equilibrium swelling method, using the Flory–Rehner equation. The relationships between the crosslink density and the electrical, physical, mechanical and dynamic mechanical properties of the coatings were also studied.

Paul et. al [14] have measured the elastic properties of films made of red oxide primers and polyurethane-based synthetic enamel paints. The measurements included the modulus of elasticity, Poisson's ratio, and strain energy. If taken into account, these findings may ultimately lead to improved primer-paint systems for the surfaces.

Ni et. al [15] have reported synthesis of two series of polyesters of isomeric cyclohexane diacids. The first series of polyesters was synthesized with 1,4-cyclohexanedimethanol (CHDM) and three cycloaliphatic difunctional acids,1,4-cyclohexanedicarboxylic acid (1,4-CHDA), 1,3- cyclohexane dicarboxylic acid (1,3-CHDA), or hexahydrophthalic anhydride (HHPA). The second series was prepared with 1,4-CHDA and 1,3-CHDA with CHDM. Control polyesters with adipic, azelaic, and isophthalic acid (AA, AZA, IPA)

---

13. M. A. Shamekhi and H. Yeganeh, "Preparation and properties of novel polyurethane insulating coatings based on glycerin-terminated urethane prepolymers and blocked isocyanate" Polym. Inter. 54, 754-763, (2005).
14. K. C. Paul, A. K. Pal, A. K. Ghosh and N. R. Chakraborty, "Measurements of elastic properties of some coating materials". Surface Coatings International Part B: Coatings Trans. 87, 47-50, (2004).
15. H. Ni, J. L. Daum, P. R. Thiltgen, W. J. Simonsick, W. Zhong, A. D. Skaja and M. D. Soucek, "Cycloaliphatic polyester-based high-solids polyurethane coatings II. The effect of difunctional acid". Prog. in Org. Coat. 45, 49-58, (2002).

were prepared for comparison. All the polyesters were cross-linked with hexamethylene diisocyanate (HDI) isocyanurate, forming polyurethane films. General coatings, tensile, and viscoelastic properties were evaluated for the cured polyurethane films. In addition, fracture toughness and the mode of energy dissipation were investigated. The polyesters based on cycloaliphatic diacids have better solubility in MEK compared to the polyesters based on the aromatic or linear aliphatic diacids. The cycloaliphatic diacids based polyurethane coatings had intermediate mechanical and viscoelastic properties compared to polyurethane based on aromatic and linear aliphatic diacids. In addition, the cycloaliphatic diacids afforded polyurethane with a greater adhesion on aluminum substrate compared to the aromatic diacid IPA.

Narayan and Raju [16] have synthesized hydroxylated polyesters (HPs) with structural variation in the backbone used them in 2K polyurethane (PU) coatings. The HPs were characterized by gel permeation chromatography and differential scanning calorimetry. The potentialities of these HPs in coating formulation have been studied by developing two pack PU clear coats with diphenylmethane diisocyanate. The results indicated that the structural variation of diol and acetoacetylation help in significant reduction of viscosity of HPs that was also reflected in an increase in percent application solids of coatings. The tensile and dynamic mechanical properties of the coating free films along with supported film properties such as adhesion, scratch resistance, flexibility, impact and abrasion were determined. The dynamic data was used to calculate cross-link density (XLD) and elastically effective network chain (M_c).The results indicated that the structural variation of building block and acetoacetylation were two potential tools to enhance or maintain the coating properties at higher application of solids.

---

16. R. Narayan and K. V. S. N. Raju, “Properties of acetoacetylated hydroxylated polyesters based polyurethane coatings”. Prog. in Org. Coat. 45, 59-65, (2002).

6.6 Preparation of polyurethanes and surface coating

Polyurethanes of epoxy polyester polyols were prepared for surface coating on different substrates such as glass, tin, copper and aluminium plates and determined their chemical resistance in various reagents. The detail experimental procedure is as follows: Into a 50 ml beaker 2.4 g EBCRA / EBCLA / EBCOA was dissolved in 15 ml MEK at room temperature. Into a 50 ml conical flask, 0.7ml TDI was dissolved in 5ml MEK. This solution was added dropwise with manual stirring to polyol solution over a period of 5 min. The resultant solution was stirred with a glass rod for 20 min at room temperature and then applied to 10cm x 3cm glass/aluminium /tin/copper 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.

6.7 Chemical resistance study

Chemical resistance of coated substrates was tested against distilled water, 10% aq. HCl, 10% aq. Na_2CO_3, and 10% NaCl solutions at 35^0C. Into four different 100ml stoppered wide mouth bottles containing test solutions thermostated at 35^0C, 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 salt and saline environments without any physical and chemical change. The coating was removed within 24 h in acidic environment Thus, developed coating materials possess excellent hydrolytic stability against water, salt and saline solutions indicating their coating application in humid and saline environments but they failed in acidic environment due to chemical degradation.

CHAPTER-7

COMPREHENSIVE SUMMARY

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 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(4-hydroxyphenyl) cyclohexane 1-1'-bis(3, 5-dibromo-4-hydroxy phenyl) cyclohexane, epoxy resins, epoxy acrylate, epoxy polyester polyols: EBCRA, EBCLA, and EBCOA, polyurethanes of epoxy polyester polyols. Polyester polyols are highly soluble in common solvents. Epoxy resins were cured using 5-20% 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 spectroscopic techniques. 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 EBCT-5, EBCT-20, EBCRAT and EBCLAT 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 EBC, jute-biofiber reinforced epoxy resin sandwich composites, jute - polyurethane of epoxy resin reinforced composites. Tensile strength, flexural strength, and electric strength of all the composites have been determined according to standard test methods and discussed in light of nature of fibers, matrix materials, compositions ,orientation, etc. Water absorption behavior of all composites was studied in different environments. Good thermal behavior, mechanical and electrical properties of the composites signify their importance as low 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% 10% aq. Na_2CO_3 and 10% NaCl solutions at 35^0C. Coating remained intake in water salt and saline environments without any physical and chemical change. The coating was removed within 24 h in acidic environment Thus, developed coating materials possess excellent hydrolytic stability against water, salt and saline solutions indicating their coating application in humid and saline environments but they failed in acidic environment due to chemical degradation.