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PHYSICO-CHEMICAL STUDIES
ON POLYMER COMPOSITES

A

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IN

THE FACULTY OF SCIENCE (CHEMISTRY)

BY

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

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

Dt.: -09-2006
Place: Rajkot.

(Mr. Niral M. Mehta)

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

Date : -09-2006
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ACHIEVEMENTS

LIST OF PAPERS ACCEPTED, COMMUNICATED AND PRESENTED

(A) Papers published

1. **"Preparation, mechanical and electrical properties and moisture absorption study of novel bisphenol-C-formaldehyde treated and untreated jute composites", N. M. Mehta, S. I. Mavani and P. H. Parsania, J. Polym. Mater., 22, 205-212, 2005.**
2. **"Fabrication and evaluation of some mechanical and electrical properties of jute-biomass based hybrid composites", N. M. Mehta and P. H. Parsania, J. Appl. Polym. Sci., 100, 1754-1758, 2006.**
3. **"Synthesis and physico-chemical study of halogenated aromatic cardo polysulfonates", B. G. Manwar, S. H. Kavthia, N. M. Mehta and P. H. Parsania, Ind. J. Eng. & Mater. Sci., 13, 155-161, 2006.**
4. **"Synthesis and physico-chemical study of novel bisphenol-C-formaldehyde-toluene diisocyanate-PEG-200 copolymer films", N. M. Mehta and P. H. Parsania, J. Polym. Mater. Inpress**
5. **"Synthesis, fabrication, mechanical, electrical and moisture absorption study of epoxy polyurethane-jute and epoxy polyurethane-jute-rice/wheat husk composites", S. I. Mavani, N. M. Mehta and P. H. Parsania, J. Appl. Polym. Sci. Inpress**
6. **"Synthesis and physico-chemical study of bisphenol-C-formaldehyde-toluene diisocyanate polyurethane-jute and jute-rice/wheat husk composites", S. I. Mavani, N. M. Mehta and P. H. Parsania, J. Appl. Polym. Sci., 101, 2363-2370, 2006.**
7. **"Ultrasonic velocity and acoustical parameters of poly (4,4'-cyclohexylidene diphenyloxy-4,4'-diphenylenesulfone) solutions at different temperatures", R. R. Amrutia, N. M. Mehta, F. D. Karia and P. H. Parsania, J. Sci. & Ind. Research. Inpress**

8. “Mechanical, electrical and water absorption evaluation of bisphenols-C-formaldehyde-acrylate-Jute/Glass/Jute-bamboo/ Glass-bamboo a value added composites”, P. J. Vasoya, N. M. Mehta and P. H. Parsania, Polym. Plast. Technol. & Eng, In press.
9. Mechanical, electrical and water sorption study of glass fiber reinforced phenolic-epoxy hybrid composites”, J. K. Joshi, S. T. Gadhia, N. M. Mehta and P. H. Parsania, J. Polym. Mater, In press.

(B) Papers communicated

1. “Effect of temperature on ultrasonic velocity and thermodynamic parameters of bisphenol-C-formaldehyde-acrylate resin solutions”, N. M. Mehta, F. D. Karia and P. H. Parsania, Fluid Phase Equilibria.
2. “Preparation and physico-chemical study of sandwich glass-jute-bisphenol-C-formaldehyde resin composites”, N. M. Mehta, P. J. Vasoya, V. A. Patel and P. H. Parsania, Ind. J. Eng. Mater. Sci.
4. “Synthesis and physico-chemical study of polyester polyol of epoxy resin of 1,1’-bis (3-methyl-4-hydroxy phenyl) cyclohexane and ricinoleic acid and its polyurethanes with polyethylene glycol in different proportions”, S. I. Mavani, N. M. Mehta and P. H. Parsania, J. Sci. & Ind. Research.
5. “Synthesis and physico-chemical characterization of halogenated partly aromatic cardo copolyesters”, N. B. Joshi, N. M. Mehta and P. H. Parsania, Eur. Polym. J.

(C) Papers presented at National/ International conferences/ symposia/ workshop:

1. National Seminar on “Polymer Research in India: Opportinity and Challenges”, Sept. 25, 2004 (Oral presentation), Allahabad.
2. International Conference on Polymers for Advanced Technologies-Macro-2004, Dec.14,-17, 2004 (Poster presentation), Thiruvananth-puram.

3. 9th National conference including one day international symposium on “Bioactive Heterocycles and Drug Discovery Paradigm”, by CDRI-Lucknow & DOC, Jan. 8-10, 2005, (Attended), Rajkot.
4. National Seminar on “Polymer, Surfactants & Gels”, by Indian Society for Surface Science and Technology, Maharaja Sayajirao University of Baroda, March 11-13, 2005, (Poster presentation), Baroda.
5. “Polymer Materials: Present Status and Future Prospects and Fourth Polymer Foundation Award Function” - Ahmedabad Textile Industry’s Research Association, Dec. 10-11, 2005, (Oral presentation), Ahmedabad.
6. “National Conference on Thermodynamics of Chemical & Biological Systems”, Guru Nanak Dev University, Dec. 28-30, 2005, (Poster presentation), Amritsar.
7. National Workshop on “E-resources in Chemical Synthesis and Natural Products”, Saurashtra University, March 2-3, 2006, (Attended), Rajkot.

GENERAL INTRODUCTION

India, endowed with an abundant availability of natural fibers such as jute, coir, sisal, rice husk, wheat husk, bamboo and vegetable fibers, etc., has focused on the development of natural fiber composites primarily to explore value-added application avenues. Such natural fiber composites are well suited as wood substitutes in the housing and construction sector. The development of natural fiber composites in India is based on two pronged strategy of preventing deplection of forest resources as well as ensuring good economic returns to the cultivators of natural fibers [1].

Natural fiber reinforced polymer composites are superior over synthetic composites in certain properties like enhanced biodegradability, combustibility, light-weight, ease of recyclability, etc. These advantages place the natural fiber composites amongst high performance composites having economical and environmental advantages with good physical properties [2, 3].

Hybrid composites can be prepared by combining two or more different types of fibers in common matrix. They offer a range of properties that can not be achieved with single kind of reinforcement. With careful selection of reinforcing fibers, cost of material can be reduced substantially and balance in performance and cost could be achieved via appropriate material design [4].

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1. S. Biswas, G. Srikanth and S. Nangia, in “News and Views”, “Development of natural fiber composites in India”, 2005.

2. M. S. Sreekala, M.G. Kumaran, S. Joseph and M. Jacob, “Oil-palm fiber reinforced phenol-formaldehyde composite: influence of fiber surface modification on mechanical performance”, Appl. Compos. Mater., **7**, 295, 2000.

3. A. K. Bledzki and J. Gassan, “Composites reinforced with cellulose based fibres”, Prog. In Polym. Sci., **24**, 221, 1999.

4. M. M. Thwe and K. Liao, Plastic, “Tensile behavior of modified bamboo-glass fiber reinforced hybrid composites”, Rubbers and Compos. **31**, 422, 2002.

Phenolic resins are well known for their fire retardance, low smoke density and toxic emission [5, 6] and are widely used in the construction and electrical industries [6]. It also is being used in specialized applications like airframe, transport, chemical industries, marine industries, aerospace application [7] and also in some engineering applications [8].

Polyurethanes are well known for their excellent adhesion, flexibility, high cohesive strength, low temperature performance and amenable curing speed. They effectively wet and readily form H-bonds with various substrates such as textile fibers, metals, plastics, wood, glass, etc. [9].

In plywood industries formaldehyde is used as a main raw material because of generic organic compound. Formaldehyde based adhesives have drawback of formaldehyde emission but due to cost effectiveness formaldehyde is preferable over the use of costly polyols with isocyanates [10].

Much research has been conducted to improve the properties of phenolic resin. Phenolic resin modified by boric acid is a thermosetting resin, with excellent performance such as thermal stability, mechanical strength, and electric properties.

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5. "Low-smoke resin fends fires effectively" in reinforced plastics, Elsevier Science Publishers, pp.36, June-1994.

6. "Phenolic GRP-Where is it today?" in reinforced plastics, Elsevier Science Publishers, pp. 30, June-1992.

7. S. Ramakrishna, Wintermantel and K. W. Leong "Biomedical applications of polymer composite materials", Compos. Sci. and Technol., 61, 1189, 2001.

8. H. Shen and S. Nutt "Mechanical characteristics of sort fiber reinforced phenolic foams", Composite Part: A, Appl. Sci. and Manuf., 34, 899, 2003.

9. Hardwood, Plywood and Veneer Association. 1995, ANSI / HPVA HP. 1 (1994).

10. Patent Co-operation Treaty (PCT). WO 053012 (2004) A.

Some reports have been appeared on synthesis and application of boron-containing phenol-formaldehyde resin [11, 12]. Recently research is being directed globally in producing low cost composites by using biomass or agriculture wastes in combination with jute fibers. Rice husk, wheat husk, sugarcane husk [13], coconut fibers [14], papaya fibers, cotton [15], etc. are the byproducts of the crops and vegetables [13-15].

Scientific community has focused their attention all over world on natural fiber reinforced low-cost, light weight composite materials. Where high strength is not a priority such composites are useful for low load bearing housing units in construction industries. They are relatively easy to process [16].

The literature survey on phenolic and metal containing phenolic resins based on bisphenols revealed that most of the work is confined on bisphenol-A and to some extent on bisphenol-C. A Comprehensive summary of the work to be incorporated in the thesis is summarized as under:

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11. J. G. Gao, Y. F. Liu and F. L. Wang, "Structure and properties of boron-containing bisphenol-A formaldehyde resin", Eur. Polym. J., **37**, 207, 2001.

12. Y. F. Liu, J. G. Gao and R. Z. Zhang, "Thermal properties and stability of boron-containing phenol-formaldehyde resin formed from paraformaldehyde", Polym. Deg. and Stability, **77**, 495, 2002.

13. C. N. Zarate, M. I. Aranguren and M. M. Reboredo, "Resol-vegetable fibers composites" J. Appl. Polym. Sci. **77**, 1832, 2000.

14. C. Y. Lai, S. M. Sapuan, M. Ahmad and N. Yahya, "Mechanical and electrical properties of coconut coir fiber-reinforced polypropylene composites", Polymer-Plastics Technol. and Eng., **44**, 619, 2005.

15. Eliton S. De Medeiros, Jose A. M. Agnelli, J. Kuruvilla, H.De Carvalho, H. C. Mattoso, "Mechanical properties of phenolic composites reinforced with jute/cotton hybrid fabrics", Polym. Compos., **26**, 1, 2005.

16. R. Kozlowski, M. Wladyka and M. Helwig, "Composites based on ligno-cellulosic raw material", Mol. Cryst. Liq. Cryst., **418**, 131, 2004.

CHAPTER 1 : Literature survey on bisphenol-C, phenolic resins and natural fiber reinforced composites

CHAPTER 2 : Syntheses of bisphenol -C based resins and their characterization

CHAPTER 3 : Fabrication of composites based on BCF resin and their physico-chemical characterization

CHAPTER 4 : Synthesis of polyurethanes and their characterization

CHAPTER 5 : Ultrasonic velocity and allied parameters of BCFA solutions

CHAPTER 6 : A brief review of the work done

CHAPTER 1 : Literature survey on bisphenol-C, phenolic resins and natural fiber reinforced composites

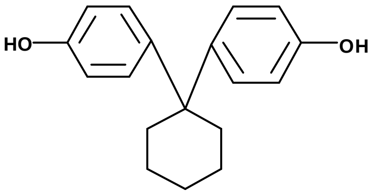
This chapter of the thesis describes the up to date literature survey on syntheses and characterization of phenolic resins, properties and applicability of natural fibers and applications of composites in different fields of science and in routine life.

CHAPTER 2 : Syntheses of bisphenol-C based resins and their characterization

This chapter is further subdivided into six sections

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

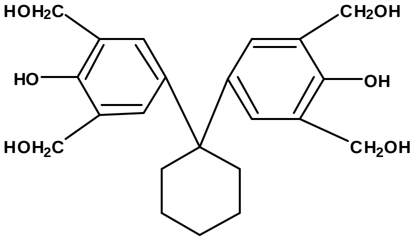
Bisphenol-C was synthesized by Friedel-Crafts condensation of phenol and cyclohexanone by using a mixture of HCl-CH_3COOH (2:1 v/v) as a catalyst at 50-55^o C for 4h and was repeatedly recrystallized from methanol-water system prior to its use.



I

Section-II : Synthesis of bisphenol- C- formaldehyde resin (BCF)

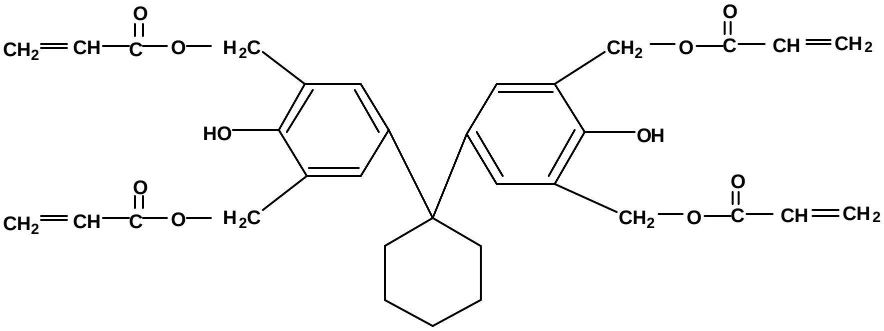
Bisphenol-C-formaldehyde resin (BCF) was synthesized by condensing bisphenol-C and formaldehyde by using alkali as a catalyst at 70°C for 1h. A creamish solid product was repeatedly purified from methanol-water system prior to its use.



II

Section-III : Synthesis of bisphenol- C- formaldehyde-acrylate resin

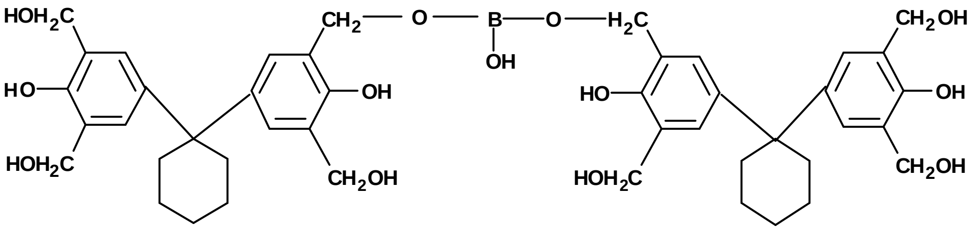
Bisphenol-C-formaldehyde - acrylate (BCFA) was synthesized by condensing bisphenol -C-formaldehyde (BCF) resin and acrylic acid by using 1, 4-dioxane as a solvent and phenothiazine as a catalyst at 80°C for 6 h. The solid greenish brown product was purified repeatedly from MEK-water system prior to its use.



III

Section-IV : Synthesis of boron containing BCF resin

Boron containing bisphenol-C-formaldehyde resin (BCFB) was synthesized by condensing bisphenol-C, formaldehyde and boric acid in 1:4:1 mole ratio by using alkali as a catalyst at 70°C for 1 h. A creamish solid product was repeatedly purified from methanol-water system prior to its use.



IV

Section-V : IR spectral characterization of resins

Formation of different linkages in the resin is supported by IR spectral data.

Section-VI : Thermal analysis of resins

Thermal analysis of polymers is an important tool in predicting the behavior of polymers under varied temperature conditions and also helpful in evaluating the strength of various bonds in polymer backbone chain and hence the mechanism of the degradation pattern. The physico-chemical properties of cured resin depend upon the degree of curing and extent of cross-linking density.

Thermogravimetry can precisely describe the degradation of polymers under varying temperature range and atmosphere. Various kinetic parameters provide usefulness of the potentially unstable nature of material under investigation. Thermal stability and kinetic parameters such as n, A, E_a and ?S* of the resins have been evaluated and interpreted in this section.

CHAPTER 3: Fabrication of composites based on BCF resin and their physico-chemical characterization

This chapter is further subdivided into three sections.

Section-I: fabrication of composites

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

Jute, glass and hybrid composites of wheat husk, rice husk, sugarcane, papaya fiber, coconut fiber, jamun fiber and bamboo fiber in combination with jute and glass fibers are prepared by hand lay up compression molding under pressure of 30.4 MPa and at appropriate temperature. Physical properties of jute fibers are modified by alkali treatment and malenization.

Section-II : Mechanical and electrical properties of composites

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

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

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

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

CHAPTER 4 : Synthesis of polyurethanes and their characterization

Section – I : Introduction

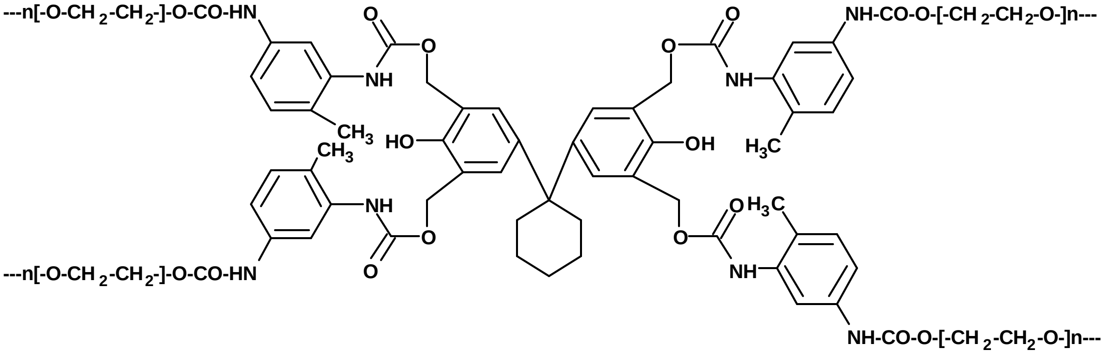
Modern technology can not be satisfied with single structured materials to fulfill economical needs of mankind. To make economic production of desired articles with desired combination of properties, it is often necessary to use complex structured materials.

Hybrid coating materials resulting from intercross linking network (ICN) mechanism enhance thermal stability, hydrophobicity and impact behaviors as compared to those of blending technique [17].

Polyurethanes are well known for their excellent adhesion, flexibility, high cohesive strength, low temperature performance and amenable curing speed. They effectively wet and readily form H-bonds with various substrates such as textile fibers, metals, plastics, wood, glass, etc [9].

Section - II : Synthesis of polyurethane resin

Into a 250 ml beaker, 0.002M BCF was dissolved in 15ml MEK at room temperature. To this solution 0.005M TDI in 5ml MEK was added and the resultant solution was stirred manually for 15 min and to this pre polyurethane, 0.001/0.002 M PEG-200 in 5ml MEK was added drop wise with stirring. After completion of the PEG-2OO addition, the mixture was stirred for 10 min. and poured into a leveled 15cm x 15cm glass mold. The solution was allowed to dry with controlled evaporation of MEK at room temperature. After 24 h, the film was removed from the mold.



V

Section – III : Spectral characterization of polyurethane resin

Formation of polyurethane linkages in the resin is supported by IR spectral data.

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17. X. Song, “Miscibility, morphology and fracture toughness of tertafunctional epoxy resin/poly (styrene-co-acrylonitrile) blends”, J. Mater. Sci., **35**, 5613, 2000.

Section – IV : Density measurements of polyurethane films

The densities of polyurethane films are determined by floatation method and discussed in light of composition of PEG-200.

Section – V : Thermo-mechanical and electrical properties of polyurethane films

Thermal data of materials provide wealth of informations on physico-chemical changes occurring in the system during heating. Polyurethane films are analyzed by TGA/DSC at the heating rate of 10°C / min in an N_2 atmosphere. The glass transition temperature, thermal stability and kinetic parameters of the polyurethane films are determined and discussed. The tensile strength, electric strength and volume resistivity of polymer films are determined according to standard test methods and interpreted in terms of PEG-200 concentration, degree of resin cure, etc.

Section - VI: Chemical resistance study of polyurethane films

The chemical resistance of the films was determined against water and 10% each of aqueous acids, alkalis and salt solution at room temperature by change in mass method at the interval of 24 h.

Section - VII: Surface coating and its chemical resistance

This section describes the surface coating application of polyurethane resin on different substrates such as copper, tin, mild steel and glass .The chemical resistance of coated samples is tested against water, acid and alkali at room temperature for varying time interval and interpreted in light of nature of substrate.

CHAPTER 5: Ultrasonic velocity and allied parameters of BCFA solutions

Recently ultrasonic has become the subject of extensive research because it finds applications in numerous fields of science like consumer industries, medical fields, engineering, process industries, etc.[19].

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19. J. A. Szpunar and D. C. Hinz, "Ultrasonic velocities in textured metals", J. Mater. Sci., **24**, 45, 1990

Knowledge of acoustical properties of solutions furnishes a wealth of informations on molecular interactions occurring in the solutions, the nature and the strength of interactions. The density, viscosity and ultrasonic velocity measurements of BCFA resin solutions in different solvents at 30^o, 35^o and 40^o C are determined. Various acoustical parameters such as isentropic compressibility ($?_s$), specific acoustical impendance (Z), Rao's molar sound function (R), Van der wals constant (b), internal pressure (p), classical absorption coefficient $(a/f^2)_{cl}$, viscous relaxation time (T), solvation number (S_n), free volume (V_f) and intermolecular free length (L_f) are determined and discussed in light of effect of solvent, temperature, concentration, etc.

CHAPTER-6: A brief review of the work done

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

Signature of the guide **Signature of the candidate**

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General Introduction

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

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

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

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

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

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

[A] LITERATURE SURVEY ON BISPHENOL-C

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

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

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

They have also proposed the following mechanism:

1. The addition of phenol to ketone

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

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1. I.G. Farbenind; "Condensation of ketones with phenols", Fr. Patent 647,454, 1929; C.A. Vol.**23** p. 2540, 1929.
2. I.G. Farbenind; Ger. Patent 467,728 (1927); C.A. Vol. **23**, 1929.
3. M. E. McGreal, V. Niendert and J. B. Niedert, "Condensation of ketones with phenols", J. Am. Chem. Soc., **33**, 2130, 1939.

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

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

Bender et al. [7] have reported the preparation of bisphenols by irradiating a mixture of ketone and phenol at 20-100^o C with ß –rays or ultraviolet in the presence of 37% aq. HCl or 70% H_2SO_4 as condensing agent and stirring at 30-37^oC. 1, 1'-Bis (4-hydroxy phenyl) cyclohexane (m.p. 186-189^o C) was obtained in 93% yield from 1 mol cyclohexanone and 4 mol phenol.

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

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4. J. E. Johnson and D. R. Musell, "Bis (hydroxy phenyl) cyclohexane compositions", U.S. 2,538,725 (1951); C.A. Vol. **45**, p.4412 1951.
5. J. E. Johnson and D. R. Musell, "Diphenol compound composition for coccidiosis", U.S. 2,535,014 (1950); C.A. Vol.**45**, p.2635 1951.
6. H. L. Bender,L. B. Conte and F. N. Apel "Bisphenols", U.S. 2,858,342 (1958); C.A. Vol.**53**, p.6165, 1959.
7. H.L.Bender, L.B.Conte and F.N.Apel, "Diphenol compound composition for coccidiosis control", U.S. 936,272 (1960); C.A. Vol.**45**, p.2635, 1951.
8. Farbenfabriken, " Bisphenols", Ger. 1,031,788 (1958); C.A. Vol.**54**, p.19, 603. 1960.

Freudewald et al. [9] have reported the condensation of phenol (94 g) with cyclohexanone (98 g) in the presence of 2 g EtSH and anhydrous HCl (4.7 g) and heating at 70^oC in closed system for 3 h to give 97% yield of 1,1'-bis(4-hydroxy phenyl) cyclohexane.

Rao et al. [10] have reported a convenient method for the preparation of bisphenols. Cyclohexanone was treated with PhOH at 40^oC and with o-cresol at room temperature in the presence of HCl and AcOH to give 1, 1'-bis (4-hydroxy phenyl) cyclohexane and 1,1'- bis(3-methyl-4-hydroxy phenyl) cyclo-hexane, respectively.

Garchar et al. [11-14] have studied optimization reaction conditions for the synthesis of 1,1'-bis (R, R'-4-hydroxy phenyl) cyclohexane by condensing cyclohexanone (0.05 mol) and phenol, o-cresol, and 2,6-dimethyl phenol (0.1 mol) in the presence of varying mixture of hydrochloric acid and acetic acid (2:1 v/v) at four different temperatures : 40^o, 50^o, 60^o, 70^oC.

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9. Freudewald, E. Joachim, Konarad and M. Frederic,"p-Phenylphenol", Fr. 1,537,574 (1968); C.A. Vol.**71**, 21868, 1969.
10. M. V. Rao, A. J. Rojivadiya, P. H. Parsania and H. H. Parekh, "Convenient method for the preparation of the bisphenols", J. Indian Chem. Soc., **64**, 758-759, 1987.
11. H. H. Garchar, H. N. Shukla and P. H. Parsania, "Kinetics of formation of 1, 1'-bis (3-methyl-4-hydroxy phenyl) cyclohexane", Indian Acad. Sci. (Chem. Sci), **103**, 149-153, 1991.
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-hydroxy phenyl) cyclo- hexane", Asian J. Chemistry, **6**, 87-91, 1994.
14. H. H. Garchar and P.H.Parsania, "Optimization reaction conditions for synthesis of 1,1'-bis (4-hydroxy phenyl) cyclohexane", Asian J. Chemistry, **6**, 135-137, 1994.

They have reported optimum catalyst concentration (10-15 ml), time (30-90 min) and temperature (55-70°C) for obtaining yields greater than 80%. They have also synthesized chloro, bromo and nitro derivatives and screened for their potential antimicrobial and antifungal activities against different microbes. Some of these compounds are significantly found active against B. subtilis, S. pyogens and A. niger. The nitro compounds are found to be the most active antifungal agents.

[B] LITERATURE SURVEY ON PHENOLIC RESINS

Phenol formaldehyde condensation polymers often referred as phenolic resins, were the first true synthetic polymers to gain commercial acceptance. They have maintained a prominent position in the polymer market to the present time. About 70% of all the thermosetting polymers produced are made up of phenol, urea and melamine-formaldehyde polymers, with phenolics enjoying the lion’s share.

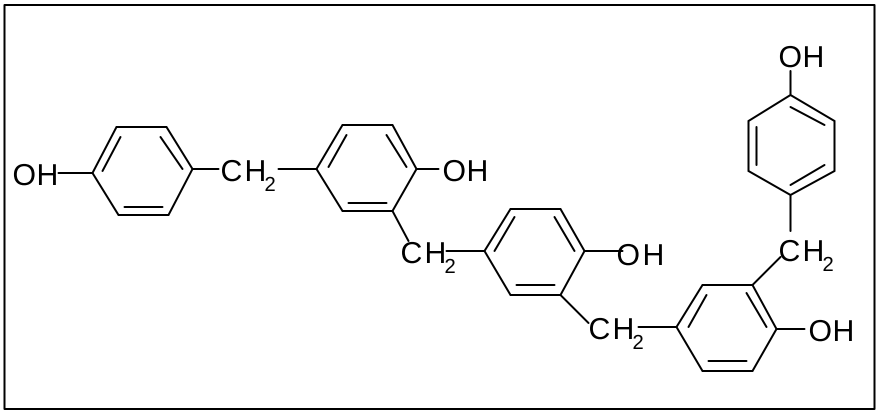
The ability of formaldehyde to form resinous substance had been observed by chemists in the second half of the 19th century. In 1859 Butlerov described formaldehyde polymers, while in 1872 Adolf Bayer reported that phenols and aldehydes react to give resinous substances. In 1899 Arthur Smith took out British patent 16274, the first dealing with phenol–aldehyde reaction was investigated, mainly for purely academic reasons, but on occasion, in the hope of commercial exploitation. In due course Leo Hendrik Baekeland discovered techniques of controlling and modifying the reaction that useful products could be made. The first of his 119 patents on phenol–formaldehyde plastics was taken out in 1907, and in 1910 the general Bakelite Company was formed in United States. Within a very few years the material had been established in many fields, in particular for electrical insulation.

Although phenolic resins have been known widely utilized for over 60 years and their detailed chemical structures remained to be established.

Phenolic resin chemistry has been discussed in detail elsewhere [15-19].

Novolacs:

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



In the other hand the novolacs are sometime reffered as two stage resins as it is necessary to add some curing agents that will enable additional methylene bridge to be formed.

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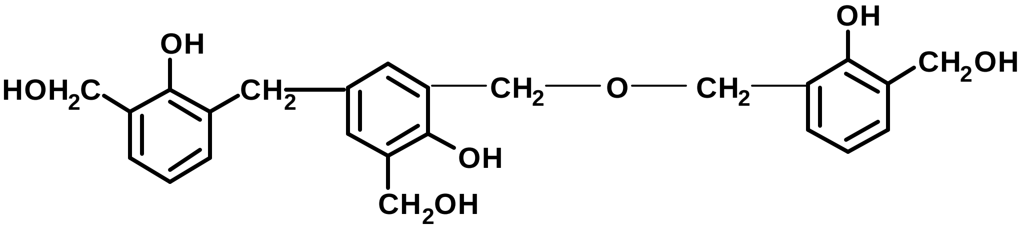
15. A. A. K. Whitehouse, E. G. K. Pritchett and G. Barnett, “Phenolic Resins”, Liffe, London (1967).
16. P. Robitschek and A. Lewin, “Phenolic-Resins” Liffe, London (1950).
17. R. W. Martin, “The Chemistry of Phenolic Resins”, John Wiley, New York (1956).
18. N. J. L. Megson, “Phenolic Resin Chemistry”, Butterworth, London (1958).
19. T. S. Carswell, “Phenoplast”, Inter science, New York (1947).

Resols:

A resol is produced by reaction a phenol with an excess of formaldehyde under basic conditions. In this case the formation of phenol – alcohols is rapid but their subsequent condensation is slow. Thus there is a tendency for polyalcohols, as well as monoalcohols, to be formed. The resulting polynuclear polyalcohols are of low molecular weight, while a solid resol may have only three to four benzene rings per molecule. Heating of these resins will result in cross-linking via the uncondensed methylol groups or by some complex mechanism. It is also called as one stag resin.



Phenolic resin is one of the earliest synthetic resins to possess excellent fire retardance and low smoke density and toxic emission [20-22] and widely used in the construction and electrical industries[22].

The technical development of the first fully synthetic resins, phenol-formaldehyde (PF) resin formed from the reaction of phenol with formaldehyde proceeded very rapidly after the discovery of bakeland [23].

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20. Y. Zaks, J. Lo, D. Raucher and E. M. Pearce," Some structure-property relationships in polymer flammability: Studies of phenolic-derived polymers", J Appl Polym Sci., **27**, 913-921, 1982.
21. "Low smoke resin fends fires effectively" in reinforced plastics, Elsevier Science Publishers, pp. 36, June – 1994.
22. "Phenolic GRP- Where is it today?" in reinforced plastics, Elsevier Science Publishers, pp. 30, June – 1992.
23. A. Knop and W. Scheib, "Chemistry and Applications of Phenolic resins"; Springer-Verlag, Berlin, 1979.

However the understanding of the basic chemistry of the resins lagged far behind. The structural peculiarities of resins are attributed to the polyfunctional nature of phenol (i.e. more than one site for aromatic substitution reactions). Under different sets of conditions such as temperature, pH and catalyst, for example, the resin will exhibit differences in their isomeric compositions, chain length and so forth.

The specific details of the structure of phenol-formaldehyde resin have a substantial effect on the nature, extent, and rate of curing [24-30].

Development in the late 1970's saw these traditional systems supplemented by a new range of phenolic resole resins, which were designated to cure at low temperature and pressure through the use of acid-base catalysts. From that time up to the present day these resins and their catalysts have been the subject of development and refining so that now all the processes normally used for composite production are commercially viable, i. e.

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24. Chem. Eng. News. **31**, 2771, 1953.
25. A. Knop, L. A. Pilato, "Chemistry: Applications and performance, future-directions", Springer-Verlag: Berlin, 1985.
26. A. W. Christiansen, L. Gollob, "Differential scanning calorimetry of phenol-formaldehyde resols", J. Appl. Polym. Sci., **30**, 2279-2287, 1985.
27. M. Grenier, F. Loustalot, S. Larroque, D. Grande and P. Grenier, "Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics", Polymer, **37**, 1363-1367, 1996.
28. A. Pizzi and A. Stephanon, "On the chemistry, behavior, and cure acceleration of phenol-formaldehyde resins under very alkaline conditions", J. Appl. Polym. Sci., **49**, 2157-2168, 1993.
29. G. Asterloq-Aierbe, J. M. Echeverrie, A. Vazqueq and I. Mondragon, "Influence of the amount of catalyst and initial pH on the phenolic resol resin formation", Polymer, **41**, 3311-3317, 2000.
30. P. Luukko, L. Alvila, T. Holopainen, J. Raino and T. T. Pakkanen, J. Appl. Polym. Sci., "Effect of alkalinity on the structure of phenol-formaldehyde resol resins", **82**, 258-269, 2001.

Hand Lamination
Resin Transfer Moulding (RTM)
Warm Press Moulding
Filament Winding
Continuous Lamination
Vacuum Injection Moulding
Pultrusion
Spray Deposition
Vacuum Bag

In addition to the above, novel delayed action catalyst technology has now caused prepregs to become available based on these phenolic resins, which offer a high strength system with low temperature and fast cure.

Phenolic resins are the polycondensation products of the phenol and formaldehyde. Phenol and formaldehyde can combine to give substituted phenols under different conditions and different ratios. Numerous articles can be found in literature on chemistry and reaction of resols. Saunders [31], Knop and Scheib [32] gave a detailed compilation of chemistry of phenolic resins. The reaction listed in Fig. 1.1 broadly represents the reactions taking place in the phenol-formaldehyde system. The main reaction under basic conditions is substitution of hydrogen with methylol group at para and ortho positions of phenols [33]. Substitutions can take place at any or all of the three positions shown in figure.

In addition, there are a large number of possible reactions with different combinations of unsubstituted and substituted phenols. The probability of dimmer formation, although low under basic conditions, is not negligible.

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31. K. J. Saunders “Organic Polymer Chemistry”2nd ed.; Chapmann and Hall : Network pp. 316-339, 1988.
32. A. Knop and W. Scheib “Chemistry and application of Phenolic Resins; Springer-Verlag; Berlin/Heidelberg/New York pp. 29-57, 1979.
33. J. C. Woodbrey, H. P. Higginbottom and H. M. Culbertson, J. Poym. Sci., Part A: Polym. Chem., **3**, 1079-1106, 1965.

Variously substituted dimmers could be formed by condensation of substituted phenols with another molecule of same type (self condensation) or by condensation with differently substituted or even unsubstituted phenol (cross –condensation). Moreover, the presence of oxy methylene species are formed from formaldehyde in solution [33], which could form long straight chains before substitution at ortho and para positions of phenols. The linkages between phenols can therefore be of different lengths.

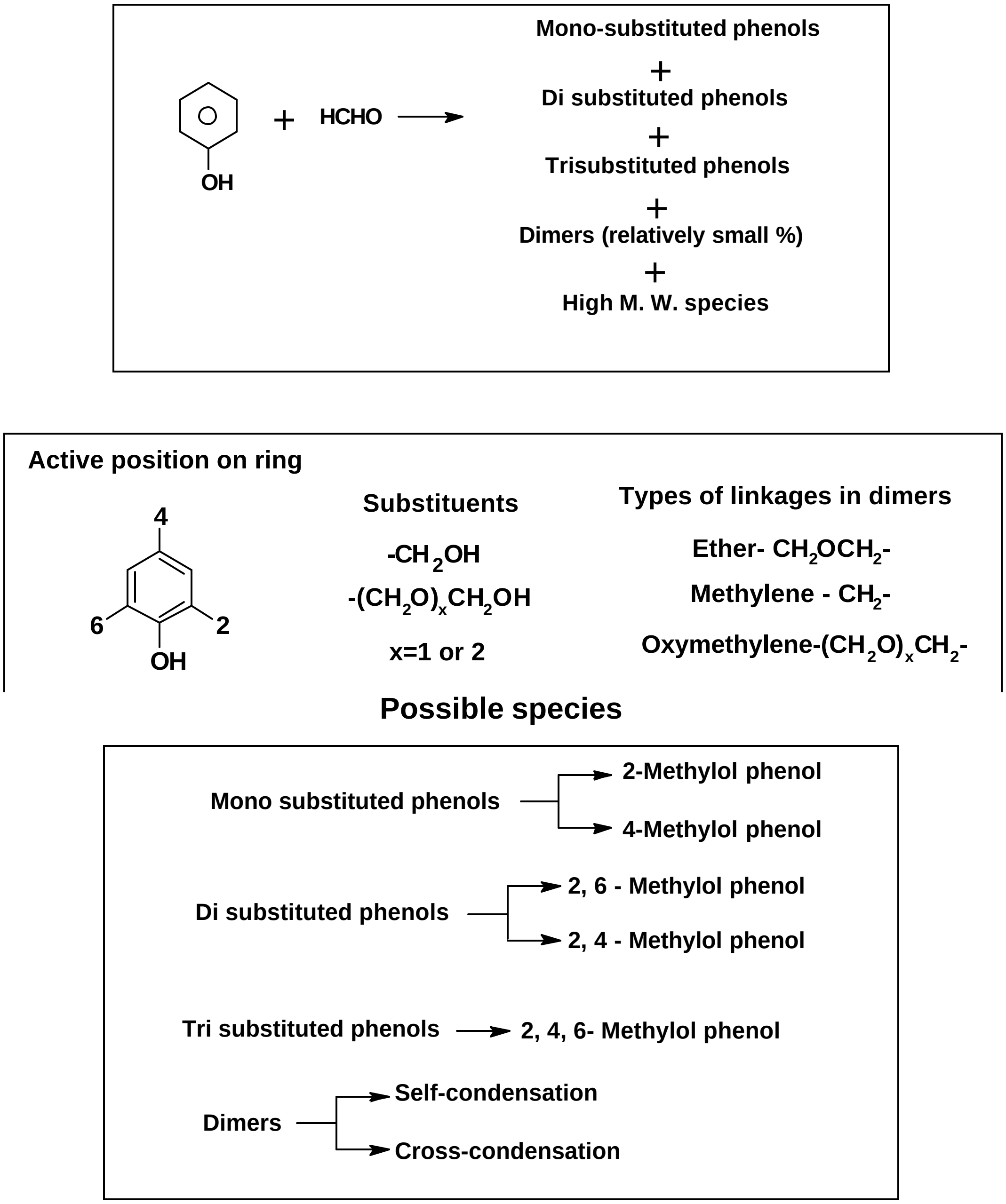

Fig. 1.1 Chemistry of resol resin systems starting from phenol and formaldehyde [34].

Chemistry of Cure

The cure of phenol formaldehyde resins take place either at elevated temperatures (~150 – 200^{o}C) or at lower temperature (~60^{o} C) with the aid of a strong acid catalyst. The chemistry of cure has been proposed on the basis of work done with simpler systems. In particular, pure mononuclear methylol phenols have been used in place of complex mixtures that make up the resin [35].

Fundamentally this approach is justified because the functional groups generally undergo the same reactions in both monomeric and polymeric species. The cure proceeds through polycondensation reactions of the variously substituted phenols. As illustrated in Figure 1.2, there are 2 possible routes for the condensation reactions (I and II). The reaction is believed to proceed through carbanium ions formed at substituent methylol groups [31]. An ether linkage is formed when a carbanium ion reacts with methylol groups of substituted phenol, while a methylene linkage is formed if it reacts with an unsubstituted position of substituted or unsubstituted phenol. Preferential ether linkage is expected when there are few unsubstituted ortho and para positions available for attack by carbanium ions.

Thus, ether and methylene bridge arise out of competitive reactions. It has been found that while the methylene bridges are generally stable, the ether bridges undergo number of ill-defined reaction at temperatures above 150^{o}C. One of the reactions is the breakdown of ether bridges to form methylene bridges with loss of formaldehyde (reaction III in Fig. 1.2). The temperatures at which these reactions occur are not well known.

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34. K. P. Singh and G. R. Palmese, "Enhancement of phenolic polymer properties by use of ethylene glycol as diluent", J. Appl. Polym. Sci., **91**, 3096-3106, 2004.
35. S. So and A. Rudin, "Analysis of the formation and curing reactions of resole phenolics", J. Appl. Polym. Sci., **41**, 205-219, 1990.

Some report it as~150 [31- 33], while others quote temperatures as high as 220° C [36, 37]. The formaldehyde, formed as a result of reaction III in Fig.2 and that is already present in the resin, causes further substitution at the active positions of phenols. Cross-linking takes place when the phenols undergo condensation reactions at more than two positions. The mechanisms and specific rates of many of the above reactions are known to markedly depend on factors such as pH, type of catalyst and temperature.

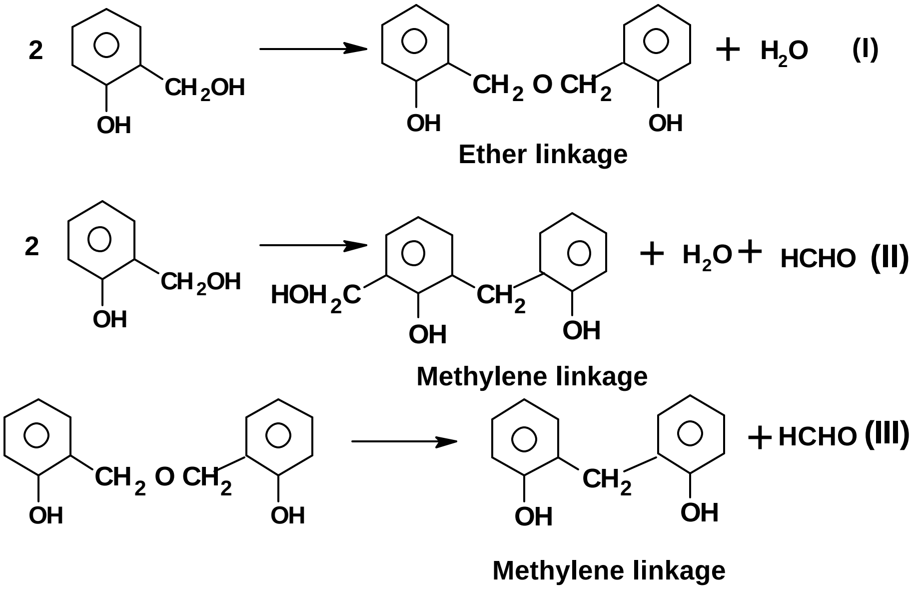

Fig. 1.2 Chemistry of cure of resol resins [20]

Unmodified phenolic resin is a brittle material with limited applications. Much research has been conducted to improve the properties of phenolic resins. The polyester phenolic copolymer has been synthesized to improve the mechanical properties and heat resistance [38].

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36. P. W. King, R. H. Mitchell and A. R. Westwood," Structural analysis of phenolic resole resins", J. Appl. Polym. Sci., **18**, 1117-1130, 1974.
37. L. A. Igonin, M. M. Mirakhmedov, K. I. Turchaninova, A. N. Shabalin, and D. A. Nauk, SSSR **141**(**6**), 1366-1368, 1961.
38. A. Matsumoso, K. Hasegawa, K. Fakuda and K. Otsuki, "Study on modified phenolic resin and modification with p-hydroxyphenylmaleimide/acrylic ester copolymer", J. Appl. Polym. Sci., **44**, 1547-1556, 1992.

One modification of phenolic resin by boric acid which give thermosetting resin with excellent performance such as Mechanical strength, thermal stability, electrical properties and shielding of neutron radiation.

Some reports have appeared on the synthesis and application of boron-containing phenol-formaldehyde resin [39-42]. In that work boron-containing resin was synthesized by formalin method [39, 40].

Formaldehyde contained phenolic resins are best with wood based cheap composites due to the excellent adhesion with cellulosic materials.

Arndt Karl [43] 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 filler [such as CaO, $Ca(OH)_2$ $CaSO_4$ or $CaCO_3$] and an additive such as sand were suitable for use as building material.

Vikram Sarabhai Space Center [44] has reported phenolic resin prepared by treating HCHO with bisphenol/cardanol mixture in presence of basic catalyst.

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39. America Potash Chem. Corp. British patent 957611:1994.
40. J. G. Gao, Y. F. Liu and F. L. Wang, "Structure and properties of boron-containing bisphenol-A formaldehyde resin", Eur. Polym. J., **37**, 207-212, 2001.
41. Y. F. Liu, J. G. Gao and R. Z. Zhang, "Thermal properties and stability of boron-containing phenol-formaldehyde resin formed from paraformaldehyde", Polym. Deg. and Stability, **77**, 495-501, 2002.
42. J. G. Gao, Y. F. Liu and F. L. Wang, Polym. Mater. Sci. and Engg, **11**, 31-50, 1995.
43. Arndt Karl "Phenol-HCHO resins for building materials" Ger. 1, 544, 609 (1965); C. A. **73**, 4516, 1970.
44. Vikram Sarabhai Space Center "Phenolic resins", Ind. **137**, 274 (1973); C. A. 92, 59687, 1980.

Resole type phenolics possess exceptional adhesive properties and have high rigidity, dimensional stability and exceptional heat and fire resistance due to highly cross linked aromatic structure [45-47]. Phenolic resin generates chemical bonding with lignocellulosic reinforcement leading to strong forces between fiber and resin. Thus high compatibility in the system between fiber and polymer is achieved [48].

Kazak et. al have reported the fiber reinforced phenolics and improved techniques of their properties via post curing. They have reported the thermo-mechanical behavior and effects of post curing on a range of glass-phenolics and provides a relationship that allows prediction of the Tg over broad range of post cure times and temperatures using dynamic mechanical analysis. In their study they used phenolic-furan copolymer and a rubber modified resol [49]. Hew-Der-Wu et al. [50] have described the study of phenoxy resin toughened phenolic resin. They have studied the rheological behavior of phenoxy /phenol solution and mechanical properties.

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45. A. K. Bledzki, S. Reihmaine and J. Gassan, "Properties and modification methods for vegetable fibers for natural fiber composites", J. Appl. Polym. Sci., **59**, 1329-1343, 1996.
46. P. S. Achari and R. Ramaswamy, "Reactive compatibilization of a nitrile rubber/phenolic resin blend: Effect on adhesive and composite properties" J. Appl. Polym. Sci., **69**, 1187-1191, 1998.
47. K. R. Harikumar, K. Joseph and S. Thomas, J. Reinforced Plast Compos. **4**, 346, 1999.
48. M. S. Sreekala, S. Thomas and N. R. Neelakantan, J. Polym. Engg., **16**, 265, 1997.
49. G. Stephen, Kuzak and A. Shanmugam "Dynamic Mechanical Analysis of Fiber Reinforced Phenolics", J. Appl. Polym. Sci. **73**, 649-656, 1999.
50. Hew-Der-Wu, Chen-Chi M. Ma and Jia-min Lin "Processability and properties of phenoxy resin toughened phenolic resin composites" National Science Council, Taiwan, May-1996.

[C] NATURAL FIBER REINFORCED COMPOSITES

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

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

History

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

The 12th century Mongols made the advance weapons of their day with bows that were smaller and more powerful than their rivals. These bows were composite structures made by combining cattle tendons, horn, bamboo, which bonded with natural pine resin. The tendons were placed on the tense of the bow, the bamboo was used as a core, and sheets of horn were laminated the compression side of the bow. The entire structure was tightly wrapped using the rosin adhesive. The 12th century weapons designers certainly understood the principles of composite design. In the recent time some of the old museum pieces were strung and tested. They were about 80% as some modern composite bows [51].

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

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

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

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

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

First composites industry began in earnest in the late 1940s and developed in 1950s. Most of the composites processing methods used today like molding, filament winding, hand lay-up technique, resin transfer molding, vacuum bagging were all developed and used in production between 1946 and 1950. Some products manufactured from composites during this period included: boats bodies (corvette), truck parts, aircrafts component, underground storage tank, buildings and many familiar products.

Composites typically use thermoset resins, which begin as liquid polymers converted to solid during the molding process. This process known as crosslinking is irreversible. Because of this, these polymers are known as thermosets and can not be melted and reshaped.

The benefit of composite materials have fueled growth of new application markets such as transportation, constructions, corrosion resistance, marine infrastructure, consumer products, electrical, aircraft and aerospace application and business equipments.

The benefits of using composites materials include:

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

Compare a ¼ inch diameter steel rod to a ¼ inch diameter glass fiber composites rod. The steel rod will have higher tensile strength and compressive strength, but weight is more. If the fiber glass rod were increased in diameter to the same weight as steel rod, it would be stronger [52]. Automotive industries in Europe show large interest in NFC (Natural Fiber Composite) that can be used in load bearing elements of cars. Some of the beneficial points for using composites over conventional ones are below [53].

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52. “Composites Fabricators Association” – The Composites Industry Overview-2003.
53. U. Gayer and Th. Schuh, “Automotive applications of Natural Fiber Composites”, First International Symposium on ligno-cellulosic Composites – UNESP- Sao Paulo State, 1999.

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

Different types of fibers for reinforcement and study of their properties

Natural cellulose based fibers are gaining attention as their application is diversified into engineering end uses such as building materials and structural parts for motor vehicles [54, 55], where light weight is required. There are at least 1000 types of plant that bear usable fibers [56].

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54. A. Maguno, 2nd International wood and natural fiber composites symposium, Kassel, Germany, 29-1, June 28-29, 1999.
55. H. A. Al-Qureshi 2nd International wood and natural fiber composites symposium, Kassel, Germany, 32-1, June 28-29, 1999.
56. J. Robson, J. Hague, G. Newman, G. Jeronimidis and M. P. Ansell, Report No. EC/ 431/ 92 to DTI LINK, Structural Composites Committee, January – 1993.

India, endowed with an abundant availability of natural fibers such as jute, coir, sisal, pineapple, ramie, bamboo, banana, etc. have focused on the development of natural fiber composites. Primarily explore value-added application avenues. Such natural fiber composites are well suited as wood substitutes in the housing and construction sector [57].

In order to save a crop from extinction and to ensure a reasonable return to the farmers, non-traditional outlets have to be explored for the fiber. One such avenue is in the area of fiber-reinforced composites. Such composites can be used as a substitute for timber as well as in number of less demanding applications [57].

The estimated global tonnage of fibrous raw material from agricultural crops is provided in Table 1.1[58]. Jute, sisal, banana and coir, the major sources of natural fibers are grown in many parts of the world. Some of them have aspect ratios (ratio of length to diameters) > 1000 and can be woven easily. These fibers are extensively used for cordage, sacks, fishnets, matting and rope and as filling for mattresses and cushions. Cellulosic fibers are obtained from different parts of plants, e. g. Jute and remie are obtained from stem; sisal, banana and pineapple from the leaf; cotton from seeds; coir from fruit, vegetables. The properties of some of the natural fibers are compared in Table1.2 [59]. Jute is an attractive natural fiber for reinforcement in composites because of its low cost, renewable nature and much lower energy requirement for processing. Apart from much lower cost and renewable nature of jute and much lower energy requirement for the production of jute (only 2% of that of glass) makes it attractive as a reinforcing fiber in composites [59].

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57. S. Biswas, G. Srikanth and S. Nangia "Development of Natural Fiber Composites in India"-Composites 2001 convention and Trade show, Composites Fabricators Association. October 3- 6, 2001, Tampa – FL, USA.
58. R. Kozlowski, A report on "Green Fibers and Their Potential in Diversified Application", Institute of Natural Fibers, Poland, 2003.
59. S. Nangia and S. Biswas "Jute composite: Technology and business Opportunities" in News and Views, 2003.

Table-1.1: Estimated global tonnage of fibrous raw materials from agricultural crops

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

Table-1.2: Properties of selected natural fibers and glass fiber

Property	Jute	Banana	Sisal	Pineapple	Coir	Glass
Width or Diameter (mm)	---	80-250	50-200	20-80	100-450	7-8
Density (gm/cc)	1.3	1.35	1.45	1.44	1.15	2.5
Volume Resistivity at 100 volts	---	6.5-7	0.4-0.5	0.7-0.8	9-14	9-10
Micro-fibrillar angle (Degree)	8.1	11	10-22	14-18	30-49	---
Cellulose Content (%)	61	65	67	81	43	---
Lignin Content (%)	12	5	12	12	45	---
Elastic Modulus(GN/m^2)	---	8-20	9-16	34-82	4-6	85.5
Tenacity (MN/m^2)	440-553	529-754	568-640	413-1627	131-175	4585
Elongation (%)	1-1.2	1.0-3.5	3-7	0.8-1.6	15-40	5.7

The comparison of mechanical properties for jute and glass fibers [59] is given in Table 1.3. Jane L. O'Dell has reported the comparative properties of lignocellulosic fibers with glass and carbon fibers [60]. The comparisons of properties of different fibers are given in Table-1.4.

The attractive features of natural fibers like jute [61-63], sisal [64], coir [65, 66], and banana [67] are their low cost, light weight, high specific modulus, renewability and biodegradability. Many plant fibers have lots of applicable part as commercialized materials are concerned. One of the common and very critical environmental solutions is biodegradable nature of all these natural fibers, which increases their demand in world composite manufacture markets.

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60. Jane L. O'Dell, "Natural fibers in Resin Transfer Molded Composites" The fourth International Conference on Wood Fiber-Plastic Composites, Forest Products Society, Madison, 1997.
61. M. K. Sridhar, G. Basavarappa, S. G. Kasturi and N. Balasubramaniam, "Mechanical properties of jute / polyester composites", Indian J. Tech. **22**, 213-218, 1984.
62. P. Kumar "Mechanical behavior of jute fiber and their composites", Indian J. Tech., **24**, 29-32, 1986.
63. A. N. Shah and S. C. Lakkad "Mechanical properties of jute reinforced plastics", Fiber Sci. Tech., **15**, 41-45, 1981.
64. E. T. N. Bisanda and M. P. Ansell "The effect of silane treatment on the mechanical and physical properties of sisal-epoxy composites. Compos. Sci. Tech., **41**, 165-78, 1991.
65. S. V. Prasad, C. Pavithran and P. K. Rohatgi "Alkali treatments of coir fibers for coir-polyester composites", J. Mater. Sci., 18, 1443-1449, 1983.
66. J. Rout, M. Mishra, S. K. Nayak, S. S. Tripathy and A. K. Mohanty "Effect of surface modification of coir fiber on physico-mechanical behavior of coir-polyester composites In: A. K. Ghosh, editor. Polymers beyond AD 2000, 1999 P. 489-91.
67. L. A. Pothan, S. Thomas and N. R. Neelakantan "Short banana fiber reinforced polyester composites: Mechanical, failure ageing characteristics", J. Reinforced Plastics, **16**, 744-751, 1997.

Table-1.3: Mechanical properties of glass and jute fibers

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

Table-1.4: Comparison of properties of different fibers

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

Plant fibers are composed of cellulose, hemicellulose and lignin. Other components, usually regarded as surface impurities, are pectin and wax substances (Table 1.5) [68].

Diversified uses of green fibers

Global trends towards sustainable development have brought to light natural, renewable, biodegradable raw materials. Science and technology continue in extending their use in textile and other industries.

Recent achievements and new applications of green fibers and associated products, bast fibrous plants can provide from the background for following conclusions:

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

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[68] L. Y. Mwaikambo and Martin P. Ansell, “Chemical modification of hemp, sisal, jute and kapok fibers by alkalization”, J. Appl. Polym. Sci., **84**, 2222-2236, 2002.

Table-1.5: Important chemical composition of some selected fibers

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

Different methods for modification of natural fibers

All the polymers and composites containing natural fibers as reinforced materials absorb moisture in humid atmosphere and when immersed in water. Natural fibers including jute fiber absorb more moisture as compared to synthetic fibers. There is, however, a major drawback associated with the application of natural fibers for reinforcement of resin matrices. Due to presence of hydroxy groups and other polar groups in various constituents of natural fiber, the moisture uptake is high (approx. 12.5% at 65% relative humidity at 20^oC) by dry fiber [56]. The higher cellulosic content (64 to 65%) and that of hemicellulose (16-17%) are responsible for high OH groups, which make jute fibers more susceptible to moisture uptake [69].

Environmental performance of such composites is generally poor due to delamination under humid condition. With increase in relative humidity up to 70%, the tenacity and young's modulus of jute increases but beyond 70%, a decrease is observed. Thus, it is essential to pre-treat the fiber so that its moisture absorption is reduced and the wettability by the resin is improved [56].

In order to develop composites with better mechanical performance and environmental performance, it is necessary to impart hydrophobicity to the natural fibers by chemical reaction with suitable coupling agents or by coating with appropriate resins. Such surface modifications of fiber does not only decreases moisture absorption, but also concomitantly increases wettability of fibers with resin and improve the interfacial bond strength, which are critical factors for obtaining better mechanical properties of composites.

The compatibility of fiber surface with interacting chemicals such as resin depends on the smoothness or roughness of the fiber. Rough surfaces increase the number of anchorage points, thus offering a good fiber-resin mechanical interlocking [70].

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69. A. K. Bledzki and J. Gassan, "Composites reinforced with cellulose based fibres", Prog. Polym. Sci., **24**, 221-249, 1999.
70. P. Hedenberg, "Licentiate thesis, Chalmers University of Technology, Goteborg, Sweden, 1996.

The performance and stability of fiber-reinforced composite materials depends on the development of coherent interfacial bonding between fiber and matrix. In natural fiber-reinforced composites there is a lack of good interfacial adhesion between the hydrophilic cellulose fibers and hydrophobic resins due to their inherent compatibility [71].

The elementary unit of cellulose macromolecules (Fig.1) is anhydro-D-glucose, which contains three alcohol hydroxyls (-OH). These hydroxyls form hydrogen bonds inside the macromolecule itself (intramolecular) and between other cellulose macromolecule (intermolecular) as well as with hydroxyl groups from the air. All vegetable fibers are of hydrophilic in nature; their moisture content reaches 8-12.6% (Table 1.6) [72]. An important characteristic of vegetable fibers is their degree of polymerization (DP). The cellulose molecules of each fiber differ in their DP. The fibrils of cellulose macromolecules form spirals along the fiber axis [72].

The strength and stiffness of fibers correlates with angle between the axis and fibril of the fiber [72, 73]. The smaller this angle is, the higher are the mechanical properties (Table 1.7) [72].

Reinforcing fibers can be modified by physical and chemical methods. Chemical and physical modifications of natural fibers are usually performed to correct the efficiencies which described above of these materials, especially to impart bonding and adhesion, dimensional stability. Physical treatments change the structural and surface properties of fiber and influence mechanical bonding with matrix.

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71. K. Oksman and C. Clemons, “Mechanical properties and morphology of impact modified polypropylene-wood flour composites”, J. Appl. Polym. Sci., **67**, 1503-1511, 1998.
72. A. K. Bledzki, S. Reihmane and J. Gassan, “Properties and Modification methods for Vegetable fibers for natural fiber composites”, J. Appl. Polym. Sci. **59**, 1329-1336, 1996.
73. S. C. O. Ugbolue, Text. Inst. **20**(**4**), 1-43, 1990.

Table- 1.6: Structure parameters of vegetable fibers [72]

Fiber	Cell length (µm)	Spiral angle(Deg)	Moisture content (Wt. %)
Jute	2.3	8.0	12.6
Flax	20.0	10.0	10.0
Hemp	23.0	6.2	10.8
Ramie	154.0	7.5	8.0
Sisal	2.2	20.0	11.0
Coir	0.8	45.0	8.0

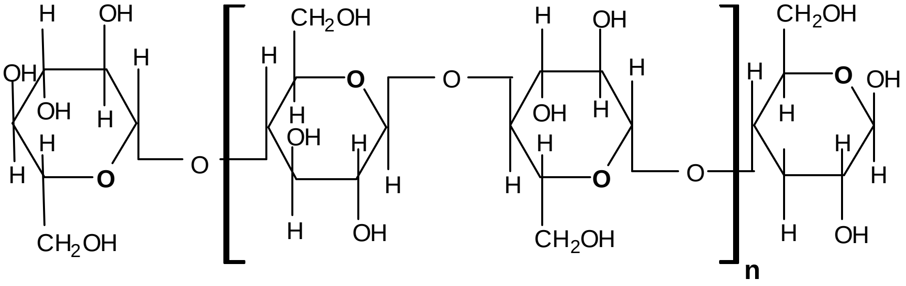

Fig. 1.3 Macromolecules of cellulose [74]

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74. J. I. Kroschwitz, “Polymers: Fibers and Textiles”, Wiley, New York, 1990.

Table-1.7: Comparative values of cellulose and with conventional reinforcing fibers [73]

Fiber	Density (g/cm^3)	Elongation to break (%)	Tensile strength (MPa)	Young's modulus (GPa)
Jute	1.45	1.5	550	13
Flax	1.50	2.4	1100	100
Hemp	---	1.6	690	---
Ramie	1.50	1.2	870	128
Sisal	1.45	2.0	640	15
Coir	1.15	15.0	140	5
E-Glass	2.50	2.5	2000-3000	70
S-Glass	2.50	2.8	4570	86
Aramide	1.40	3.3-3.7	3000-3150	63-87
Carbon	1.70	1.4-1.8	4000	230-240

Many authors have studied the mechanical analysis with various kinds of modifications. Some examples of different properties based studies by some authors are reported below:

Ray et al. [75, 76] have studied the mechanical and thermal analysis of vinylester-resin-matrix composites reinforced with untreated and alkali treated jute fibers and somewhat improvement are reported in the mechanical properties.

Sarkar et al. [77] have reported the mechanical properties of vinyl ester resin matrix composites by alkalization of jute fibers with 5% NaOH solution for 0, 2, 4, 6 and 8h at 30^o C and reported that modulus of jute fibers improved by 12, 68 and 79% after 4, 6 and 8 h of treatment, respectively. They have reported improvement in flexural strength with the treatment of alkalization of jute fibers.

Rana et al. [78] have studied the acetylation process for modification of jute at different time and temperature in absence of catalyst and solvent. They also studied the characterization of acetylated fibers by FTIR, DSC, TGA and SEM techniques. They have reported that thermal stability of acetylated jute was found to be higher than the untreated jute.

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75. D. Ray, B. K. Sarkar, S. Das and A. K. Rana, "Dynamic Mechanical and Thermal Analysis of Vinylester-resin-matrix Composites reinforced with Untreated and Alkali treated Jute fibers", Compos. Sci. and Technol. **62**, 911-917, 2002.
76. D. Ray, B. K. Sarkar, R. K. Basak and A. K. Rana, "Study of the Thermal behavior of Alkali Treated Jute fibers", J. Appl. Polym. Sci. **85**, 2594-2599, 2000.
77. B. K. Sarkar, D. Ray, A. K. Rana and N. R. Bose "Mechanical properties of Vinylester resin matrix Composites reinforced with alkali treated Jute fibers", Composites: Part A **32**, 119-127, 2001.
78. A. K. Rana, R. K. Basak, B. C. Mitra, M. Lawther and A. N. Banerjee, "Studies of acetylation of jute using simplified procedure and its characterization", J. Appl. Polym. Sci., **64**, 1517-1523, 1997.

Dash et al. [79] have been reported the weathering and thermal behavior of Jute-polyester composites by bleaching or delignification and they have reported that tensile modulus increased after bleaching. Overall thermal stability was found to be better than that of untreated one.

Frolini and Razera [80] have studied the properties of fibers and composites based on phenolic matrices by alkali and ionized air-treated jute fibers and jute fibers were characterized with respect to lignin, hemicellulose, ash and humidity contents. They also reported the water absorption study before and after treatment. The mechanical property and morphology aspects of the composites were evaluated by impact strength and SEM.

Mishra and Naik [81] have studied the effect of maleic anhydride on mechanical properties of natural fiber. They have reported that maleic anhydride treatment shows significant improvement in young's modulus, flexural modulus, impact strength and shore-D-hardness compared with the untreated fiber composites.

Lai et al. [82] have reported the effect of various treatments like alkali, permanganate, stearic acid for modification of coconut coir fibers. The various reactions between the modified fiber and polypropylene chains were used to improve interfacial adhesion between fiber and polymer using new bond.

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79. B. N. Dash, A. K. Rana, H. K. Mishra, S. K. Nayak and S. S. Tripathy, “Novel low-cost jute-polyester composites. III. Weathering and thermal behavior”, J. Appl. Polym. Sci. **78**, 1671-1679, 2000.
80. E. Frolini and I. A. T. Razera, “Composites based on Jute fibers and phenolic matrices: properties of fibers and composites”, J. Appl. Polym. Sci., **91**, 1077-1085, 2004.
81. S. Misra and J. B. Naik, “Effect of treatment of maleic anhydride on mechanical properties of natural fiber: Polystyrene composites”, Polymer-Plastics Technol. Eng., **44**, 663-675, 2005.
82. C. Y. Lai, S. M. Sapuan, M. Ahmad and N. Yahya, “Mechanical and electrical properties of coconut coir fiber-reinforced polypropylene composites”, Polymer-Plastic Technol. Eng., **44**, 619-624, 2005.

Bledzki et al. [83] have described the mercerization treatment on flax and hemp fibers and reported the effects of different mercerization parameters such as concentration of alkali (NaOH), temperature and duration along with tensile strength applied to the fibers on structure and properties of hemp fibers and flax fibers.

Gassan et al. [84] have studied the surface characteristics of corona and silane treated jute fibers by using dynamic contact angle (DCA), capillary rise and resin adsorption method as well as inverse gas chromatography (IGC). They have reported that corona treatment increases the polarity of jute fibers, whereas dispersive part was constant over the whole range of corona energy output.

Agarwal et al. [85] have reported the thermal conductivity and thermal diffusivity of treated and untreated polymer composites. They have studied the surface modifications of fibers by pre-alkali, potassium permanganate and peroxide treatments, which increased the fiber-matrix adhesion by increasing porosity and pore size of fiber surfaces. The increase in cross linking enhanced the thermal conductivity of composite of resin treated with peroxide compared to other composites.

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83. A. K. Bledzki, H. P. Fink and K. Specht, “Unidirectional hemp and flax EP and PP composites: Influence of defined fiber treatments”, J. Appl. Polym. Sci., **93**, 2150-2159, 2004.
84. J. Gassan, V. S. Gutowski and A. K. Bledzki, “About the surface characteristics of natural fibers”, **283**, 132-141, 2000.
85. R. Agarwal, N. S. Saxena, K. B. Sharma, S. Thomas and M. S. Sreekala, “Temperature dependence of effective thermal conductivity and thermal diffusivity of treated and untreated polymer composites”, J. Appl. Polym. Sci., **89**, 1708-1717, 2003.

Various surface treatments for natural fibers

Mercerization

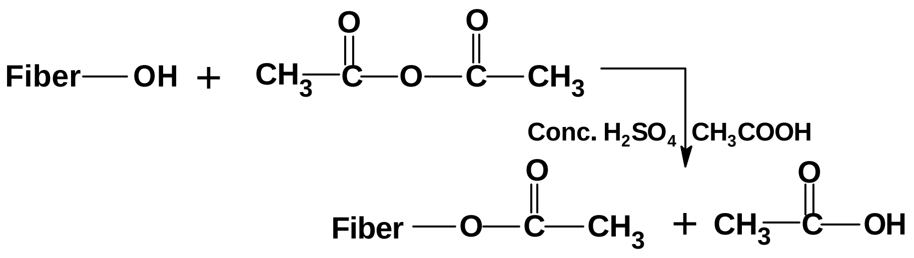
Mercerization leads to the increase in the amount of amorphous cellulose at the expense of crystalline cellulose. The important modification expected here is the removal of hydrogen bonding in the network structure. As a result of sodium hydroxide penetration into crystalline regions of parent cellulose (Cellulose I), alkali cellulose is formed. Then, after washing out unreacted NaOH, the formation of regenerated cellulose takes place [86].

$$\text{Fiber}-\text{OH} \qquad \text{NaOH} \longrightarrow \text{Fiber}-\text{O}^{-}\,\text{Na}^{+} + H_2O$$

The most popular esterification method is acetylation, which has already been developed in commercial scale, first in United States [87], than in Russia [88].

Acetylation [89]

At high temperature and longer reaction time, acetic anhydride is able to swell the fiber, making reactive chemical sites more accessible too and therefore, enhancing the reaction rate. Acetylated fiber was found to be brighter and lighter in color. Acetylation at the –OH groups from cellulose and lignin is shown in scheme



$$\text{Fiber}-\text{OH} + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[CH_3COOH]{\text{Conc. } H_2SO_4} \text{Fiber}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Acetylation

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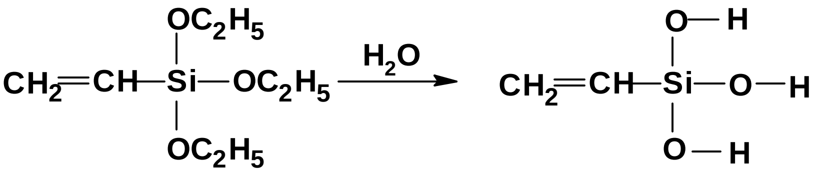
86. R. Kozlowski, M. Wladyka and M. Helwig, “Composites based on lignocellulosic raw materials”, Mol. Cryst. Liq. Cryst., **418**, 131– 151, 2004.
87. Kopper’s Acetylated wood. New Materials Technical Information No. (RDW-400), E-106 (1961).
88. Y. Otlesnov and N. Nikitina, Latvijas Laukasaimniecibas Akademis as Raksti, **130**, 50, 1977.

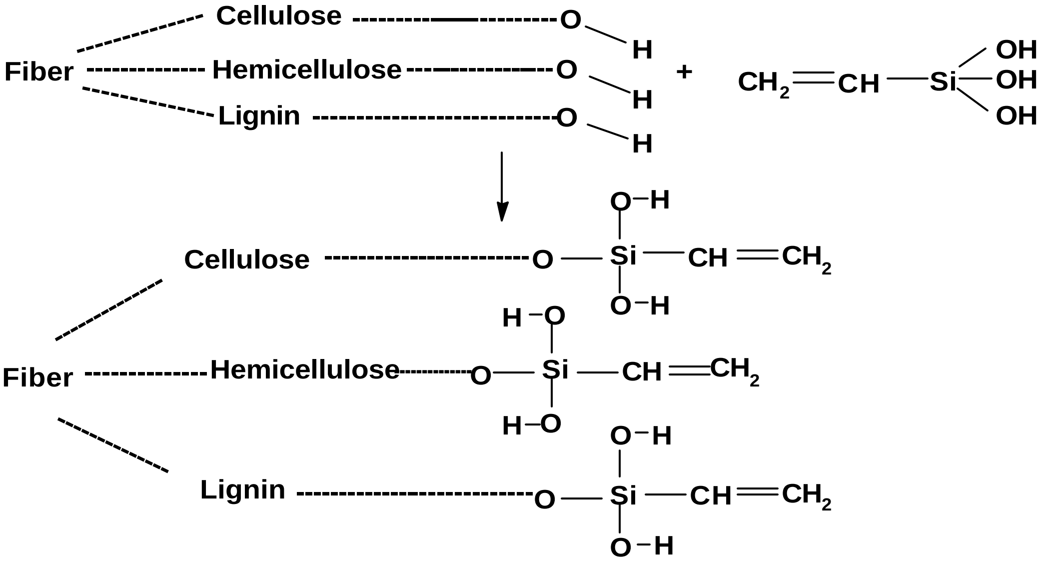
Silane treatment [89]

Alkoxy silanes are able to form bonds with hydroxyl groups. Silanes undergo hydrolysis, condensation and the bond formation stage. Silanols can form polysiloxane structures by reaction with hydroxyl group of the fibers. In presence of moisture hydrolyzable alkoxy group leads to the formation of silanols.



Silane treatment

Hypothetical reaction of fiber and silane



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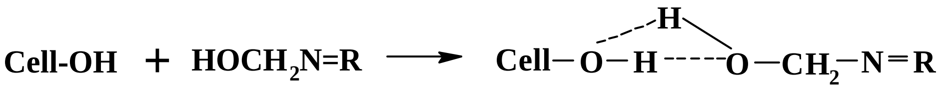
89. M. S. Sreekala, M. G. Kumaran, S. Joseph and M. Jacob, "Oil palm fiber reinforced phenol formaldehyde composites: Influence of fiber surface modification on mechanical performance", Appl. Compos. Mater., **7**, 295-309, 2000.

Treatment with compounds which contain Methylol groups [90]

Chemical compounds which contain methylol groups ($-CH_2OH$) form stable, covalent bonds with cellulose fibers. Those compounds are well known and widely used in textile chemistry.



$$\text{Cell-OH} + \text{HOCH}_2\text{N=R} \longrightarrow \text{Cell}-\text{O}-\text{H}\cdots\text{O}-\text{CH}_2-\text{N}=\text{R}$$

Permanganate treatment

This treatment leads to the formation of cellulose radical through MnO_3^- ion formation [89].

$$\textbf{Cellulose}-\textbf{H} + \textbf{KMnO}_4 \xrightarrow{\textbf{H-transfer}} \textbf{Cellulose}-\textbf{H}-\textbf{O}-\textbf{Mn}-\textbf{O}^-\,\textbf{K}^+$$

Permanganate treatment

The radical enhances the chemical interlocking at the surfaces.

TDI treatment [90]

Isocyanates have functional groups –N=C=O, which are very susceptible to reaction with the hydroxyl groups of cellulose and lignin in fiber

$$-\text{N}=\text{C}=\text{O} + \text{HO}-\text{Fiber} \longrightarrow -\overset{\text{H}}{\overset{|}{\text{N}}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-\text{Fiber}$$

Malenization [69]

Two schemes are proposed for malenization of fibers with maleic anhydride. First intramolecular malenization and other is intermolecular malenization. By maleic anhydride, the formation of ring like structure results within same cellulose molecules or between two adjacent –OH groups of neighbouring cellulose molecules:

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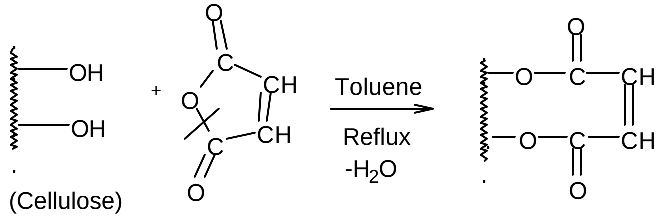
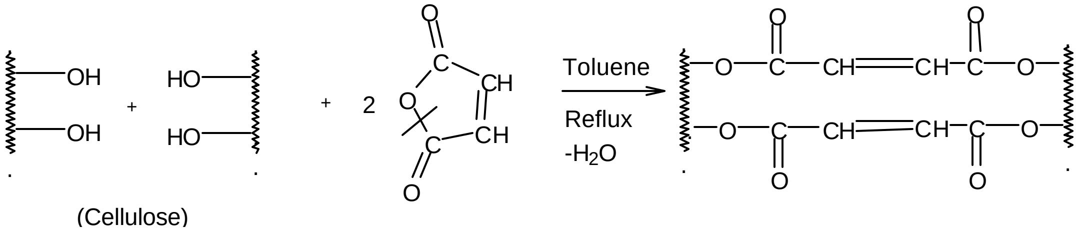
90. J. George, S. S. Bhagawan and S. Thomas, “Improve interactions in chemically modified pineapple leaf fiber reinforced polypropylene composites”, Compos. Interfaces, **5**, 201-213, 1998.





Many researchers have fabricated composites of various types of resins like polyester, phenolic resin, polyurethane resin, vinylester, epoxy resin, polypropylene by using various natural and synthetic fibers as a reinforcing material.

Feih et al. [91] have reported the influence of fiber/matrix interface strength on fiber. Cross - over bridging in a crack along fibers is investigated. Four different composite systems (commercial glass fiber with two different sizing and two matrix resins) resulting in strong and weak interfaces were manufactured in their study. Bridging-laws were derived from the experimental results and correlated with chemical interface characteristics and micro-mechanical model. Composites with different matrix resins showed large variations in bridging behavior even if their transverse strength was similar.

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91. S. Feih, J. Wei, P. Kingshott and B. F. Sorenson, “The enfluence of fiber sizing on the strength and fracture toughness of glass fiber composites”, Composites: Part A, **36**, 245-252, 2005.

Hine et al. [92] have studied the effect of hydrostatic pressure on mechanical properties of glass fiber–epoxy unidirectional composites. An investigation has been carried out to show the effect of hydrostatic pressure up to 850MPa on the mechanical properties of pure epoxy and unidirectional (UD) E-glass/Epoxy laminates. Compression tests on pure epoxy samples showed that the compressive Young's modulus increased significantly with increasing pressure, while the compressive strength show a modest increase with increasing pressure.

Joseph et al. [93] have fabricated composites were of banana and glass fibers by using phenol-formaldehyde resin matrix. They reported that the interlocking between banana fiber and phenol-formaldehyde resin is higher than that between glass and phenol-formaldehyde resin. Finally experimental tensile strength were compared with the theoretical prediction.

Sweeting and Liu [94] have measured the thermal conductivity of fiber - reinforced composites. Testing was performed on F-593 carbon-epoxy laminates and thermal conductivity curves for service temperature range were determined. Espert et al. [95] have studied the comparison water absorption study in natural cellulosic fiber from wood and one - year crops in polypropylene

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92. P. J. Hine, R. A. Duckett, A. S. Kaddour, M. J. Hinton and G. M. Wells, "The effect of hydrostatic pressure on the mechanical properties of glass fiber/epoxy unidirectional composites", Composites: Part A, **36**, 279-290, 2005.
93. S. Joseph, M. S. Sreekala, Z. Oommen, P. Koshy and S. Thomas, "A comparison of mechanical properties of phenol formaldehyde composites reinforced with banana fibers and glass fibers", Compos. Sci. and Technol., **62**, 1857-1871, 2002.
94. R. D. Sweeting and X. L. Liu, "Measurement of thermal conductivity for fiber-reinforced composites", Composites: Part A, **35**, 933-944, 2004.
95. A. Espert, F. Vilaplana and S. Karlsson, "Comparison of water absorption in natural cellulosic fibers from wood and one year crops in polypropylene composites and its influence on their mechanical properties", Composites: Part A, **35**, 1267-1276, 2004.

composites in water at 23, 50 and 70° C. The process of moisture absorption of water was found to follow the kinetics and mechanism by Fick's theory in their study. They reported the decrease in tensile properties of composites, which showing a great loss in mechanical properties of water saturated samples compared to dry samples. The morphology change was shown by Scanning Electron Microscopy (SEM) study. Bhattacharya et al. [96] have fabricated wood fiber – polypropylene composites sheets without any modification of fibers or polymer. Formability was studied by varying different forming parameters such as V-bending, matched-die forming (dome), pressure forming and deep draving (Cup).

Kishi et al. [97] have fabricated the composites of natural/plant fibers by using bisphenol-A epoxy resin at 130° C in silicon coated mold in presence of 4, 4' – diamine diphenyl methane as a catalyst for 4h at 150°C. They have reported the better adhesive property of resin with plant fibers by the dynamic mechanical analysis. Carvalho and Silva [98] have studied the improvement in mechanical properties by fiber orientation influence. They have investigated mechanical properties as a function of fiber content and its orientation. They have manufactured polyester-jute composites of long unidirectional flax fiber (0-50% w/w) and randomly distributed short flax fiber (0-30% w/w). The tensile and impact properties were determined and from that they reported the unidirectional fiber composites shown good mechanical properties than the randomly aligned samples of composites.

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96. D. Bhattacharya, M. Bowis and K. Jayaraman, "Thermoforming wood fiber-polypropylene composite sheets", Compos. Sci. and Technol., **63**, 353-365, 2003.
97. H. Kishi, A. Fujita, H. Miyazaki, S. Matsuda and A. Murakami, "Natural fiber reinforced wood-based epoxy composites", in proceeding of 8th Polymers for Advanced Technologies International Symposium, Budapest, Hungary, September-2005.
98. L. H. Carvalho and S. M. L. Silva, "Influence of fiber orientation on the mechanical properties of polyester/jute composites", 3rd Brazil MRS Meeting, "Symposium on improving fatigue and mechanical behavior in structure component", October-2004.

Kaynak et al. [99] have studied the effects of matrix and interface modification on the mechanical behavior of short carbon fiber-reinforced diglycidylether of bisphenol-A (DGEBA)-based epoxy composite. The fibers were treated using a silane-coupling agent (SCA) and the epoxy matrix was modified with hydroxyl-terminated polybutadiene (HTPB). HTPB modification of the matrix also has an effect on improving the mechanical properties, especially increasing the toughness.

World's big automotive manufacturers are also replacing the composite materials instead of heavy metals and other costly materials in automotive parts. Plant fibers based composites are currently used in the interior of passenger cars and truck cabins. Trim parts in Brazilian trucks, made of a mixture of jute, coffee wastes and polypropylene bags, show that recycling sometimes can lead to advanced applications. Another well established field of application is the use of coconut fibers bonded with natural latex for seat cushions.

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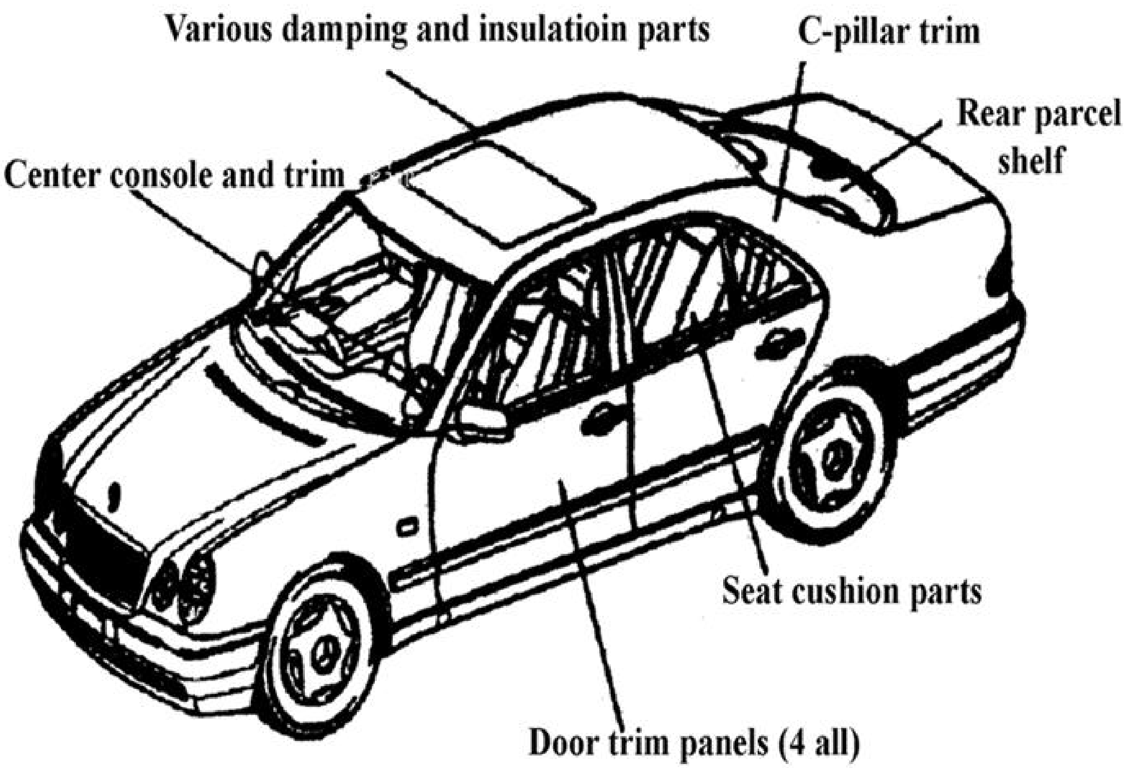
99. C. Kaynak, O. Orgun and T. Tincer, "Matrix and interface modification of short carbon fiber-reinforced epoxy", Polymer Testing, **24**(**4**), 455-462, 2005.



Plant fiber composites applications in the current Mercedes-Benz-E-Class

An important step towards higher performance applications was achieved with the door panels of the Mercedes-Benz-E-Class. The wood fiber materials previously used for the door panels was replaced by a plant fiber-reinforced material consisting of a flax/sisal fiber mat embedded in an epoxy resin matrix. A remarkable weight reduction of about 20% was achieved, and the mechanical properties, important for passenger protection in the event of an accident, were improved. [100]

Furthermore, the flax/sisal material can be molded in complicated 3-dimensional shapes, thus making it more suitable for door trim panels than the previously used materials.

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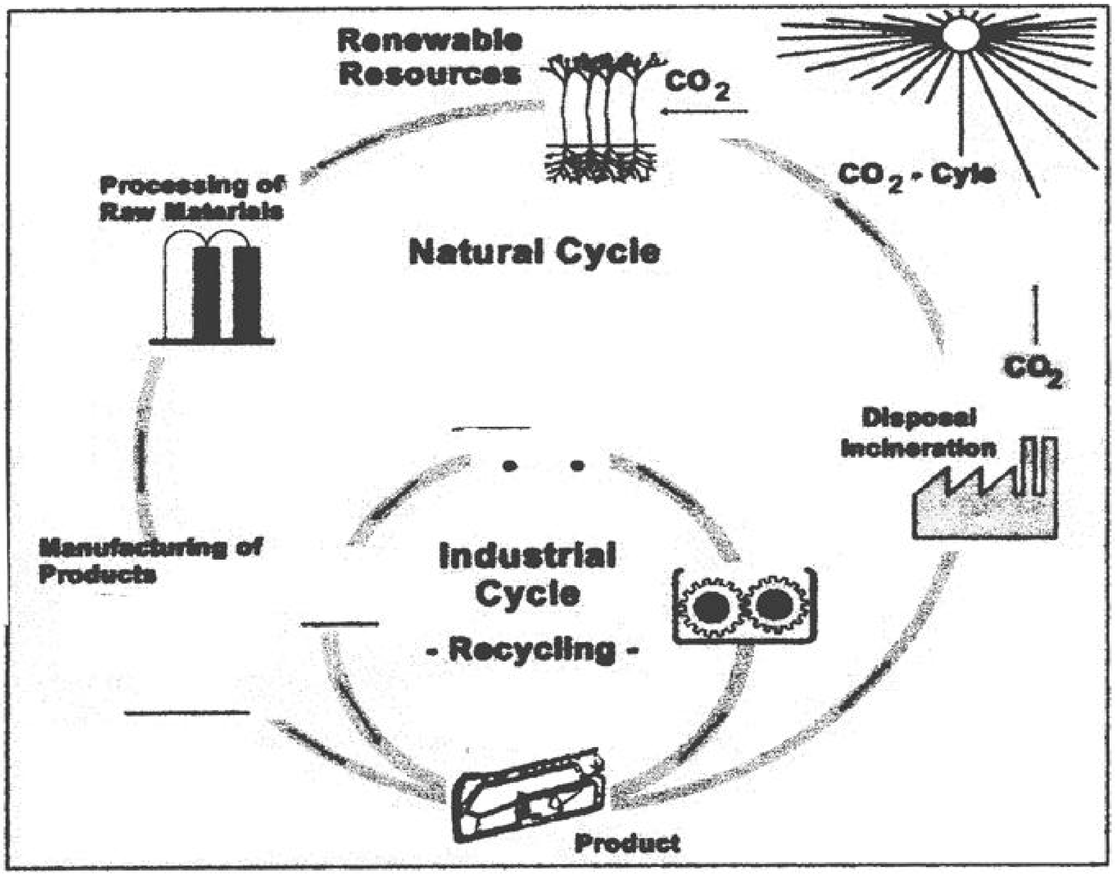
100. Thomas G. Schuh, A. G. Daimler-Chrysler and Stuttgart, “A review on renewable materials for automotive applications”, 1999.



Interaction between natural and industrial cycles

The above chart shows industrial and natural life cycle of a product made from renewable resources. Because the CO_2 emission produced by EMBED incineration at the end of the technical cycle is compensated through photosynthesis during growth, the total CO_2 balance is zero and the emissions thus do not contribute to that greenhouse effect.

For atmospheric solution which creates by the industries and the appropriate use of the agriculture wastes and plants, which are easily available in high quantity in many parts of the world. The all over scientific group in the world, which are working on composites concentrate on plant fibers and agriculture waste materials at present. Which indicates the fruitful results can be obtained by the natural fiber composites.

Composites based on glass fibers

Glass-reinforced polymer (GRP) composites are often used in the construction of a wide variety of maritime craft, such as yachts, fishing trawlers, coastal patrol boats, passenger ferries, naval mine hunting ships and submarines. GRP is also being used increasingly in light-weight structures on off-shore oil drilling platforms. The growing popularity of GRP composites over metallic materials traditionally used in ships and drilling platforms, such as steel and aluminium alloy, is due to their light weight, excellent corrosion resistance and in the case of naval vessels, their low magnetic signature and good acoustic damping properties.

Most GRP composites used in naval and other vessels are made of either polyester or vinyl esters. These resins attribute low ignition times when exposed to a high temperature fire and release large quantities of heat, smoke and toxic gases. These properties of GRP composites are not preferable for passenger vessels, navalships, submarines, offshore platforms [101-103].

Literature survey reveals that several publications and patents described the synthesis and different types of characterization of glass composites and with different types of reinforcements.

Gellert and Turley [104] have studied the seawater immersion ageing in glass-fiber polymer laminates. They compared the water uptake behavior of glass fiber composites for the polyester, phenolic and vinylester GRPs and neat

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101. J. R. Brown and Z. Mathys, “Reinforcement and matrix effects on the combustion properties of glass reinforced polymer composites”, Compos., **28** A, 675-681, 1997.
102. C. S. Smith, “Design of marine structures in composite materials”, Elsevier Applied Science; London, 1990.
103. A. P. Mouritz and Z. Mathys, “Mechanical properties of fire damaged glass reinforced phenolic composites”, Fire and Mater., **24**, 67-71, 2001.
104. E. P. Gellert and D. M. Turley, “Seawater immersion ageing of glass-fiber reinforced polymer laminates for marine applications”, Composites Part A, **30**, 1259-1267, 1999.

resins castings, and losses in mechanical properties determined for GRPs. The phenolic GRP displayed anomalous uptake behavior considered to relate to both interface and matrix absorption. Water uptake by the polyester and vinylester laminates appeared to be affected initially by suppression from fiber barrier effects then later by enhancement from interface effects. Flexural strength fell by 15-21% for the water saturated polyester and vinylester GRPs, and 25% for the phenolic GRP. An experimental study on the behavior of glass-epoxy composites at low strain rates was carried out by Saniee et al. [105]. Their article is concerned with the rate dependency of mechanical behavior of RE200 glass/epoxy, at low strain rates. With this regard, several tensile tests were carried out by employing a 600 kN Instron testing machine. The experiments were conducted at strain rates ranging from 0.0001 to 0.11s^{-1} with specimens having different fiber orientations. Based on the results obtained in this research work, longitudinal strength and stiffness increased 24.7% and 4.2%, respectively, by increasing the strain rate from 0.0001 to 0.11s^{-1}. This implies that certain mechanical properties of some polymer matrix composites could be rate dependent, even at low strain rates.

Thwe and Liao [106] have reported the effects of environmental ageing on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites. Short bamboo fiber reinforced polypropylene composites (BFRP) and short bamboo-glass fiber reinforced polypropylene hybrid composites (BGRP) were fabricated by using compression molding method. They have reported that by incorporating up to 20% (by mass) glass fiber, the tensile and flexural modulus of BGRP were increased by 12.5 and 10%, respectively; and tensile and flexural strength were increased by 7 and 25%, respectively, compared to those of BFRP. The Sorption behavior of both the

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105. F. Fereshteh– Saniee, G. H. Majzoobi and M. Bahrami, "An experimental study on the behavior of glass-epoxy composites at low strain rates", J Mater. Process. Technol.,**162**, 39-48, 2005.
106. M. M. Thwe and Kin Liao, "Effects of environmental ageing on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites", Composites Part A, **33**, 43-54, 2002.

composites was studied by immersing samples in water for up to 1200 h at 25^oC. Compared to BFRP, a 4% drop in saturated moisture level seen in BGRP. Thus it is shown that the durability of bamboo fiber reinforced polypropylene can be enhanced by hybridization with small amount of glass fibers.

Temperature dependence of thermo-physical properties of untreated glass oil-palm-fiber reinforced phenol- formaldehyde composites were reported by Singh et al. [107]. Thermo-physical properties such as effective thermal conductivity (?$_e$) and effective thermal diffusivity (?$_e$) of untreated reinforced phenol-formaldehyde with different weight percentages of oil-palm-fiber are measured simultaneously using the transient plane source (TPS) technique between 80 to 120°C. The composites investigated contain 20, 30 and 50 weight percentage of oil-palm-fiber. Maximum values of ?$_e$ and ?$_e$ are observed at 100°C, which lie in the vicinity of glass transition temperature (T_g) of these composites. Efforts are also made to predict the weight percentage of oil-palm-fiber (OPF) and temperature dependence of ?$_e$ and ?$_e$ through the development of an empirical model.

Ghosh et al. [108] have fabricated glass-jute hybrid composites and studied on some morphological and thermal properties of the composites. Three-ply composite laminates based on glass fibers (E-glass or N-glass chopped strand mats, CSM) and jute (J) fabric as reinforcing agents and amine cured epoxy resin as the matrix material were studied employing differential

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107. K. Singh, N. S. Saxena and S. Thomas, "Temperature dependence of thermo-physical properties of untreated glass oil-palm-fiber reinforced phenol-formaldehyde composites", J. Sci. and Ind. Res., **62**, 903-916, 2003.
108. P. Ghosh, N. R. Bose and R. K. Basak, "Thermal and morphological characteristics of some FRP composites based on different fiber reinforcements and epoxy resin as the matrix material", J. Polym. Mater., **18**, 179-188, 2001.

scanning calorimetry (DSC), thermo gravimetric analysis (TGA) and scanning electron microscopy (SEM). Mechanical strength and reinforcing effect were much higher for use of glass CSM than jute fabric as the reinforcing agent in making the composite laminates. For each of the cured epoxy resin and laminates based on glass CSM and jute fabric and for each of the glass-jute hybrid laminates, Examination of the epoxy resin and the relevant 3-ply composite laminates by TGA indicated enhancement of degree of thermal stability for the matrix epoxy resin on reinforcement with glass fibers and lowering in the stability on reinforcement with jute fibers. Analysis by SEM indicated that spread of the matrix (epoxy) resin and its adhesion with the reinforcing fibers were much uniform and improved for use of jute fabric than glass CSM as the reinforcing agent.

The mechanical properties and chemical resistance of short glass-fiber-reinforced epoxy composites was reported by Kaushik et al. [109]. Epoxy-short glass fiber composites were prepared by directly blending two-pack system of Araldite (CY-230) and hardener (HY-951) with short glass fibers. The short glass fiber content was varied from 2% to 10% by weight of the total matrix. These composites were then characterized for morphology using scanning electron microscopy, mechanical properties, that is, tensile and flexural properties and resistance toward various chemicals. The epoxy-glass fiber composites showed improved tensile and flexural properties but increased dispersion among the properties with increasing fiber content. Several reasons to explain these effects in terms of reinforcing mechanisms were discussed. These composites were stable in most chemicals but were completely destroyed in concentrated sulfuric acid, nitric acid, and pyridine.

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109. A. Kaushik, J. Kaushik and P. Singh, “The mechanical properties and chemical resistance of short glass-fiber-reinforced epoxy composites”, Int. J. Polym. Mater., **55**, 425-437, 2006.

Priya and Rai [110] have reported the mechanical performance of bio-fiber/glass-reinforced epoxy hybrid composites. The degree of mechanical reinforcement that can be obtained by the introduction of glass fibers in bio-fiber (silk fabric)-reinforced epoxy composites has been assessed experimentally. The addition of a relatively small amount of glass fabric to the silk fabric reinforced epoxy matrix enhances the mechanical properties of the resulting hybrid composites. It has also been observed that the properties increase with the increase in the weight fraction of reinforcement content to the maximum extent. The water uptake of hybrid composite was observed to be less than that of unhybridized composites.

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110. S. P. Priya and S. K. Rai, 'Mechanical performance of biofiber/ /glass-reinforced epoxy hybrid composites', J. Indus. Res., **35**, 217-228, 2006.

AIMS AND OBJECTIVES

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

Following are the aims and objectives of the present work:

I. To collect literature on syntheses and characterization of monomers, resins, and their applications.
II. To synthesize and modify resins and their characterizations by various techniques.
III. To fabricate glass, jute and sandwich composites based on agricultural wastes.
IV. To evaluate mechanical and electrical properties of the composites.
V. To study water absorption behavior of the composites in various environments.
VI. To study coating and chemical resistance of the resins.
VII. To study acoustical properties of the resin solutions at different temperature.

This chapter is further subdivided into six sections

SECTION-I : SYNTHESIS OF 1,1'-BIS (4-HYDROXY PHENYL) CYCLOHEXANE [BISPHENOL- C]

SECTION-II : SYNTHESIS OF BISPHENOL- C- FORMALDEHYDE RESIN (BCF)

SECTION-III : SYNTHESIS OF BISPHENOL-C-FORMALDEHYDE-ACRYLATE RESIN

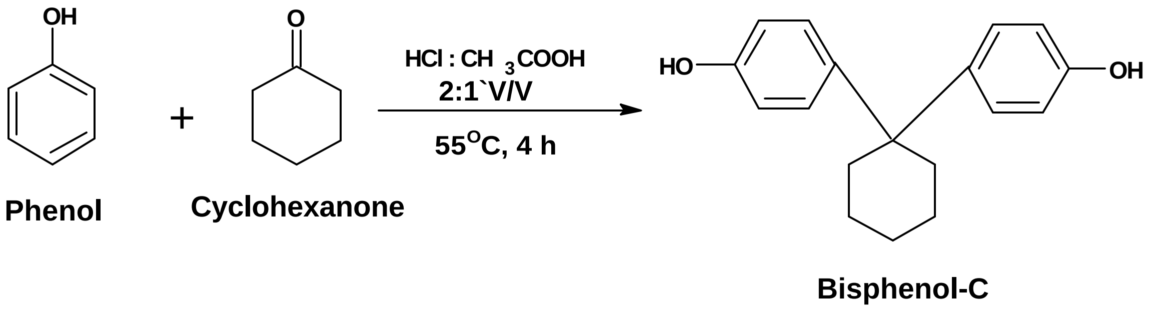
SECTION-IV : SYNTHESIS OF BORON CONTAINING BCF RESIN

SECTION-V : IR SPECTRAL CHARACTERIZATION OF RESINS

SECTION-VI : THERMAL ANALYSIS OF RESINS

SECTION-I : SYNTHESIS OF 1, 1'-BIS (4-HYDROXY PHENYL) CYCLOHEXANE [BISPHENOL- C]

1, 1'- Bis (4-hydroxy phenyl) cyclohexane of general structure (I) here after designated as BC was synthesized according to reported methods [1, 2].



I

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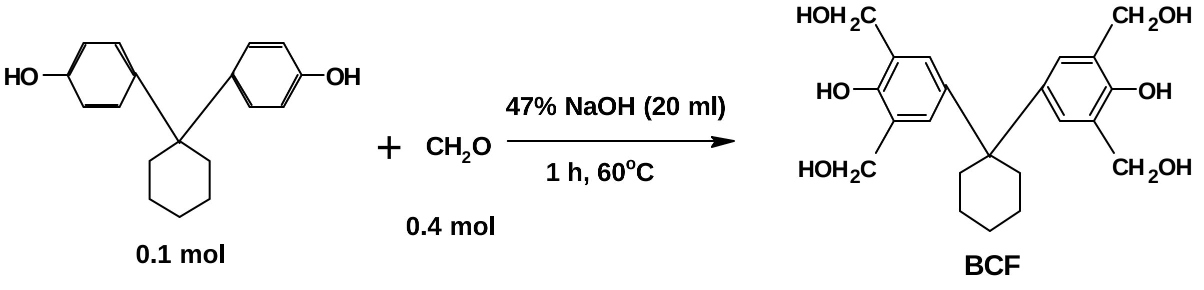
1. M. V. Rao, A. J. Rojivadia, P. H. Parsania and H. H. Parekh, “A convenient method for the preparation of bisphenols”, J. Ind. Chem. Soc., **4**, 758-9, 1987.
2. H. H. Garcher, H. N. Shukla and P. H. Parsania, “Kinetics of formation of 1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane”, Indian Acad. Sci.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

Thus, cyclohexanone (0.5 mol, 49 g) was treated with phenol in the presence of mixture of HCl : CH_3COOH (2:1 v/v, 100:50 ml) as a Friedel-Craft catalyst at 55°Cfor 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution. The resinous material was removed by filteration through cotton plug. The yellowish solution so obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50°C. BC was further recrystallized repeatedly from benzene and methanol water systems. The process was repeated to get pure, white, shining crystals of ~81% yield, m. p. of BC was 186°C.

SECTION-II : SYNTHESIS OF BISPHENOL-C-FORMALDEHYDE RESIN (BCF)

1, 1'- Bis (4-hydroxyphenyl) cyclohexane-formaldehyde resin (BCF) (II) was synthesized according to reported method [3].



II

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

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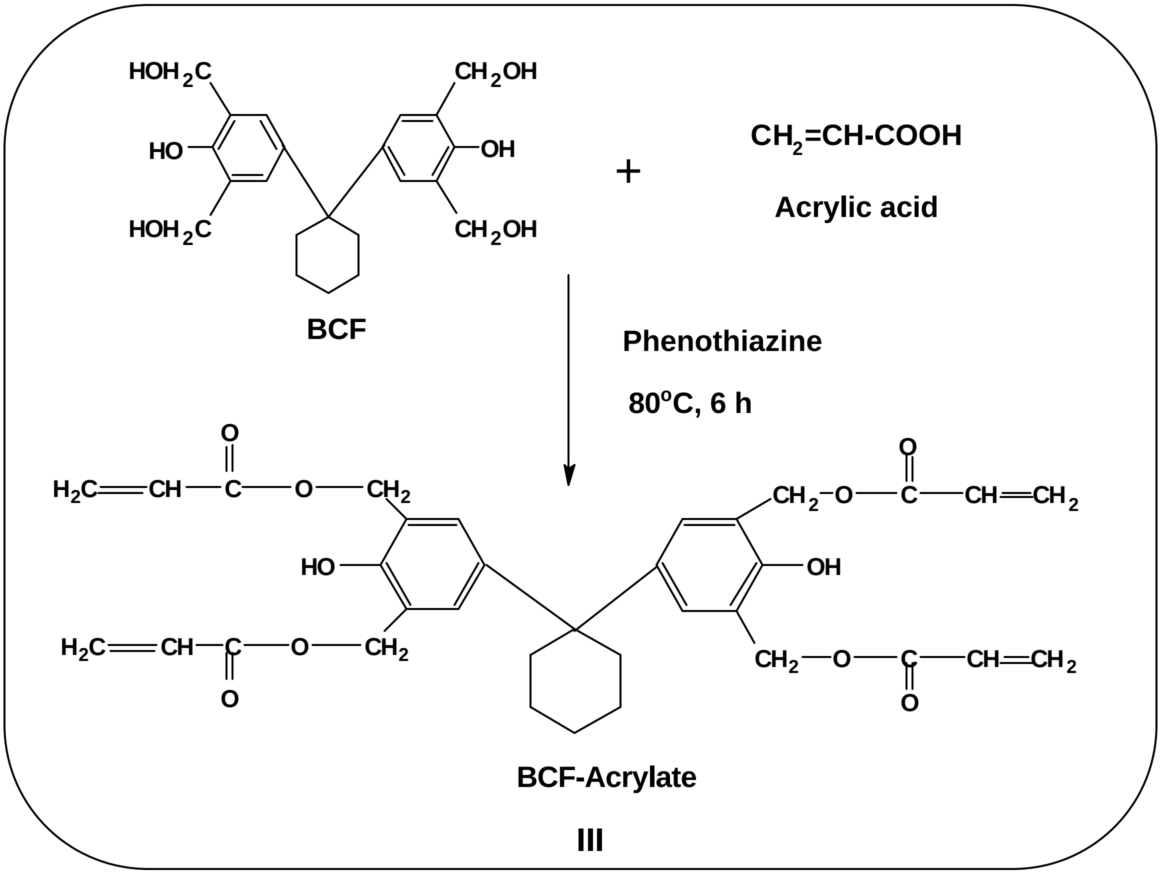
3. M. R. Sanariya and P. H. Parsania, "Synthesis of new bisphenol-C-formaldehyde and bisphenol-C-formaldehyde epoxy resins", J. Polym. Mater., **17**, 261-266, 2000.

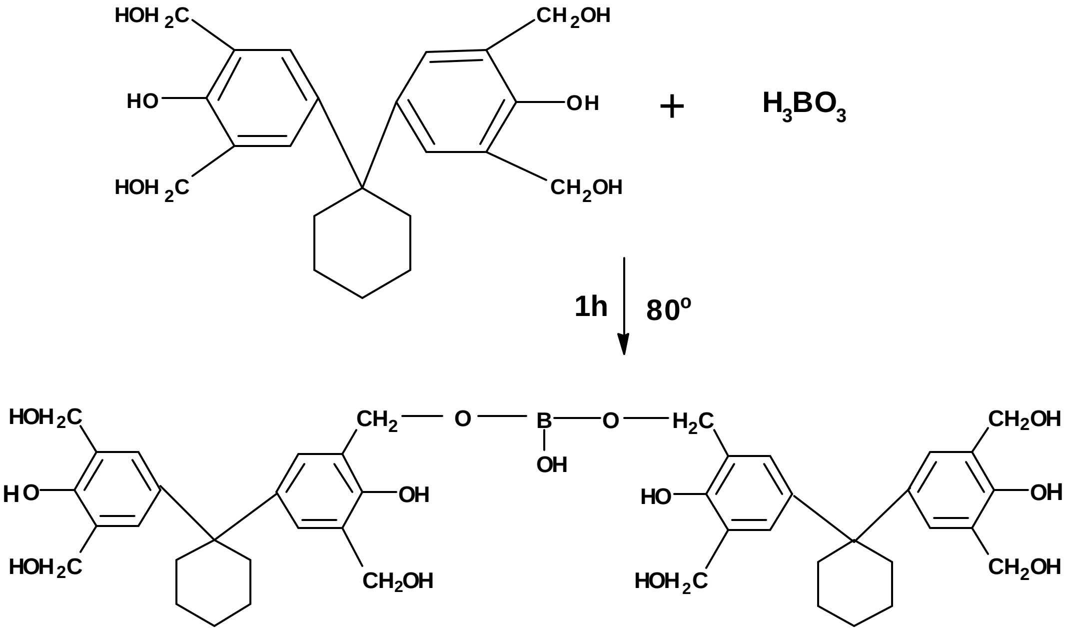
SECTION-III : SYNTHESIS OF BISPHENOL-C-FORMALDEHYDE-ACRYLATE RESIN (BCFA)

Bisphenol-C-formaldehyde-acrylate resin was synthesized by condensing bisphenol-C-formaldehyde (BCF) resin (0.01 mol / 38.8 g) and acrylic acid (0.04 mol /28.8 ml) by using 1,4-dioxane as a solvent and phenothiazine as a catalyst at 80^o C for 6h. Brownish green solid product was obtained, which was purified repeatedly from MEK-water system prior to its use.



SECTION-IV : SYNTHESIS OF BORON CONTAINING BCF RESIN (BCFB)

Into a 3 necked flask equipped with a stirrer, thermometer and a condenser, BC (0.01 mol / 26.8 g), aq. formaldehyde (0.04m / 44ml) and 47% NaOH (20 ml) solution were charged and the mixture was heated at 55^{o}C for about 45 min and then (0.01 mol/ 0.62 g) boric acid was added, heated up to 80^{o}C for 30 min[4]. A light yellow solid was obtained, washed well with hot water, dried at 50^{o}C and was repeatedly purified from methanol-water system.



BCF-B

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4. J. Gao, L. Xia, Y. Liu, “Structure of a boron-containing bisphenol-F-formaldehyde resin and kinetics of its thermal degradation”, Polym. Deg. and Stability, **83**, 71-81, 2004.

SECTION-V : IR SPECTRAL CHARACTERIZATION OF RESINS

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 wavenumber 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 wavenumbers from 4000 to 400 cm^{-1} has just the right energy to correspond to stretching and bending vibrations in molecules. Electromagnetic radiation with this energy is known as infrared radiation because it is just below the “red region” of visible light. (Infra is Latin word for “below”).

The intensity of an absorption band depends on the size of dipole moment change associated with the vibration. In other words, depends on polarity of the vibrating bond. Intensity of the absorption bond 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 (KBr pellets) of all resins were scanned on Shimadzu-8400 FT-IR spectrometer over the frequency range from 4000-400 cm $^{-1}$. The IR spectra of resins are shown in Figs. 2.1 to 2.3. The characteristic absorption bands (cm^{-1}) for each system besides the normal modes of alkane, alicyclic and aromatic groups are reported in Table 2.1.

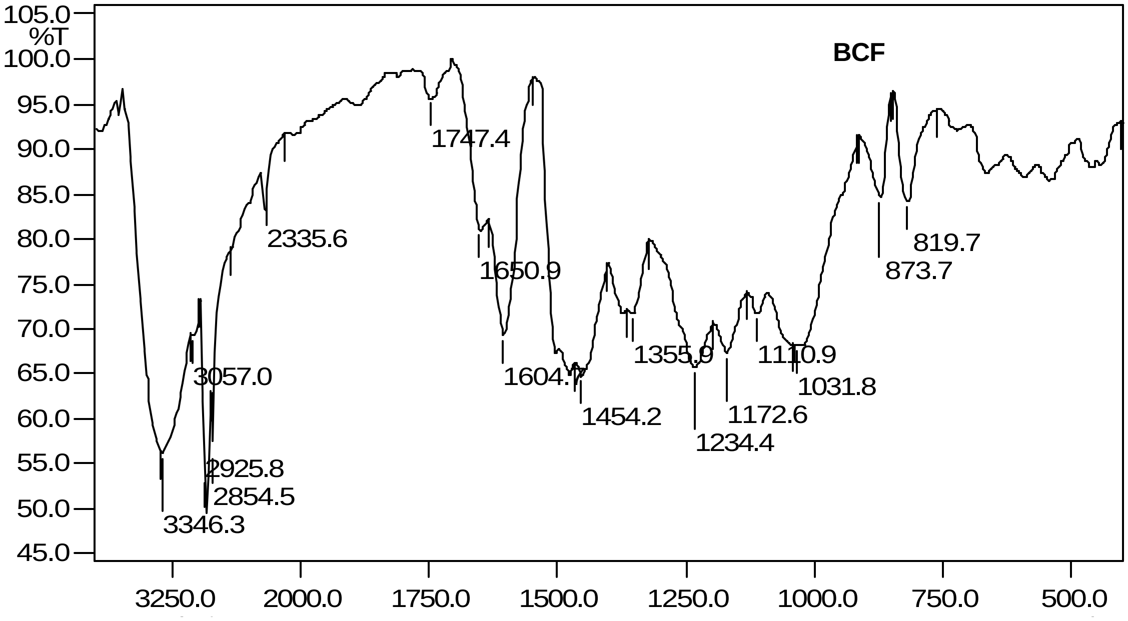

Figure 2.1 IR (KBr) spectrum of BCF

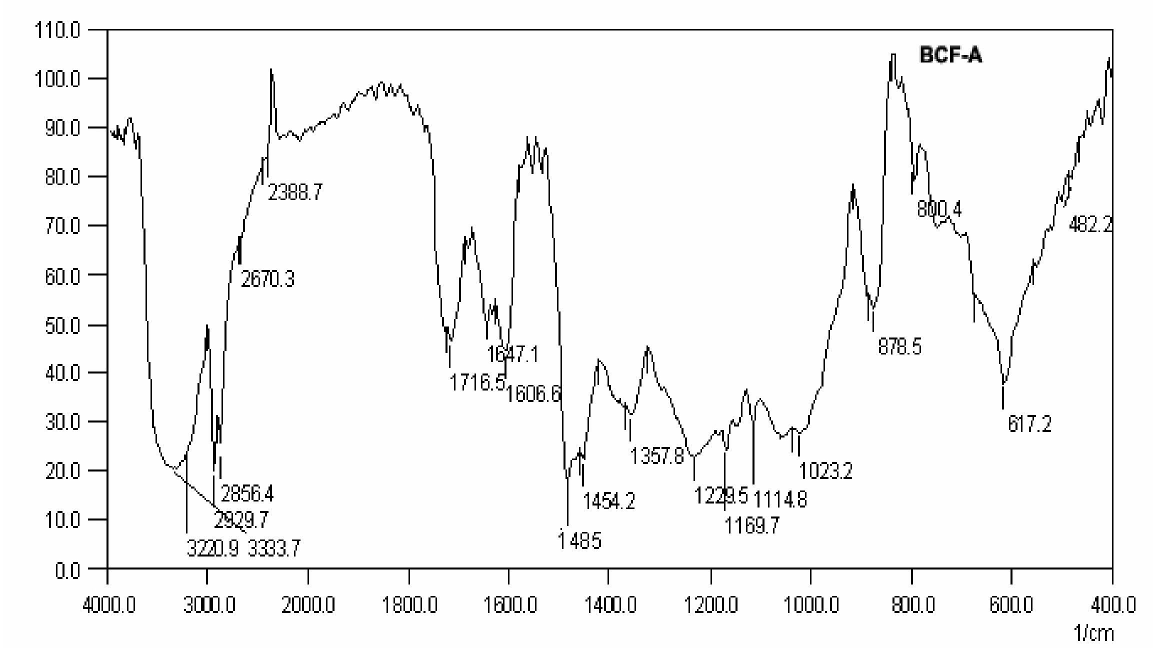

Figure 2.2 IR (KBr) spectrum of BCF-A

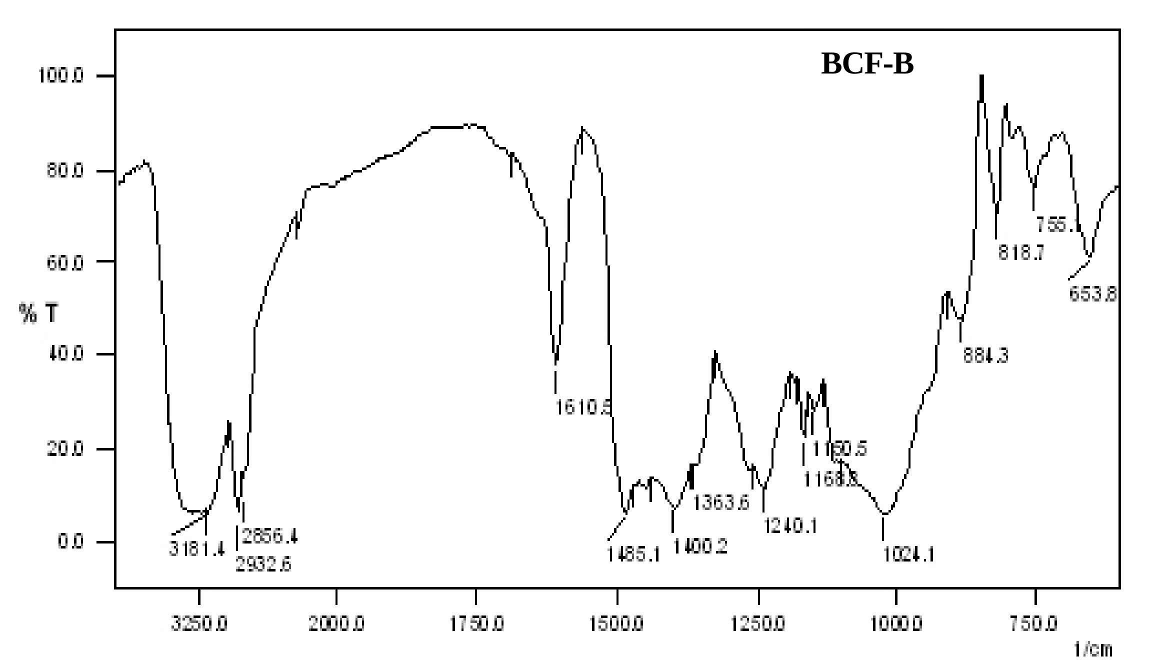

Figure 2.3 IR (KBr) spectrum of BCF-B

Table 2.1 The characteristic absorption frequencies of the resins

Resin	Absorption Frequency, cm^{-1}	Type
BCF	3346.3	-OH str.
	3057.0	Ar. –CH str.
	2925.8	C-H str. (asym.) (alkane)
	2854.5	C-H str. (sym.) (alkane)
	1604.7	Ar. C=C str.
	1234.4	$-CH_2$ (rocking)
	1110.9	C-O
BCF-A	3333.7	-OH str.
	2929.7	Alk. C-H str. (asym.)
	2856.4	C-H str. (sym.)
	1716.5	-C=O str. (ester)
	1606.6	Ar. -C=C str.
	1485	C=C-H
	1114.8	Ar. C-H i.p. def.
BCF-B	3181.4	-OH str.
	2932.6	-C-H str. (asym.) (alkane)
	2856.4	-C-H str. (sym.) (alkane)
	1610.5	Ar. -C=C- str.
	1240.1	$-CH_2$ (rocking)
	1150.5	-C-O
	1485.1	-B-O str.

SECTION-VI: THERMAL ANALYSIS OF RESINS

This section describes the thermal analysis of resins. Synthetic polymers are highly useful in the rapidly developing fields such as space exploration, terrestrial, transportation, modern communications, energy saving, environmental protection, public health, microbiology, medicine, etc. A major driving force for the growth and interest in the studies of thermally stable polymers is attributed to their extensive applications in aeronautics and in supersonic appliances. Considerable research work has been undertaken [5] 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.

Various performance properties of the polymers depend on temperature. An imbalance of toughness and stiffness occurs below and above a specific temperature range depending on the molecular structural feature of the material. Thermal analysis is the best tool for understanding the molecular architecture, decomposition mechanism, degradation pattern, etc. It is very important also for predicting their utility under various environmental conditions especially for high temperature applications. Scientific studies help to reveal the molecular structure such as the sequence and arrangement of repeating units and side groups in the polymers as well as the nature of the chain ends of the cross links between chains. The kinetics of degradation is very useful in determining the strength of various bonds in polymer structure [6].

The thermal studies throw light on molecular architecture of polymers such as degree of polymerization, orientation, crystal perfection, percentage crystallinity,

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5. R. T. Conley, “Thermal stability of polymers”, Marcell Dekker, New York, 1973.
6. H. C. Anderson, J. Appl. Polym. Sci., **6**, 484, 1962.

the extent of chain branching, strength of various bonds holding together polymer molecules, on the kinetic of depolymerization, on the effects of time, temperature, pressure, etc., and on the rates and products of degradation. 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.

Literature survey shows that many researchers have reported the thermal studies of different polymer and resins.

Kinetic study of thermal decomposition of epoxy resins containing flame retardant components was reported by Wang and Shi [7]. Hyperbranched polyphosphate ester (HPPE) and phenolic melamine (PM) were blended in different ratios with a commercial epoxy resin to obtain a series of flame retardant resins. The thermal decomposition mechanism of cured ester was studied by thermogravimetric analysis and in situ Fourier-transform infrared spectroscopy. The degradation behaviors of epoxy resins containing various flame retardant components were found to be greatly changed. The incorporation of phosphorus and nitrogen compounds improved the thermal stability at elevated temperature. The kinetics of thermal decomposition was evaluated by Kissinger, Flynn-Wall-Ozawa and Horowitz-Metzger methods. The results showed that the activation energy at lower degree of the degradation decreased by the incorporation of flame retardant components, while increased at higher degree of the degradation.

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7. Q. Wang and W. Shi, “Kinetics study of thermal decomposition of epoxy resins containing flame retardant components”, Polym. Deg. and Stability, **91**, 1747-1754, 2006.

Laza et al. [8] 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 have been studied 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 studied by the Barontini et al. [9]. They have investigated the thermal degradation behavior of electronic boards manufactured using tetrabromobisphenol A and diglycidyl ether of bisphenol A epoxy resins. Qualitative and quantitative information was obtained on the products formed in the thermal degradation process, and the bromine distribution in the different product fractions was determined. The more important decomposition products included hydrogen bromide, phenol, polybrominated phenols, and polybrominated bisphenol A species.

Wang et al. [10] 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.

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8. J. M. Laza, J. L. Vilas, M. T. Garay, M. 5RGUtguez and L. M. / Hyn, “Dynamic mechanical properties of epoxy-phenolic mixtures”, J. Polym. Sci., Part B: Polym. Physics, **43**, 1548-1557, 2005
9. F. Barontini, K. Marsanich, L. Petarca and V. Cozzani, “Thermal degradation and decomposition products of electronic boards containing BFRs”, Ind. and Eng. Chem. Res., **44**, 4186-4193, 2005
10. M. Wang, L. Wei and T. Zhao, “Cure study of addition-cure-type and condensation-addition type phenolic resins”, Eur. Polym., J., **41**, 903-917, 2005

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.

Thermal degradation of crosslinked resins in controlled atmospheres have studied by Bouajila et al. [11]. In their study they involved the thermal degradation of phenolic resins in controlled atmospheres (inert and oxidizing). Their aim was to characterize volatile organic compounds (VOC) and inorganic compounds released during heat treatment. The methods used were thermogravimetry coupled with thermodesorption/gas chromatography/mass spectrometry (TG/TCT/GC/MS) and thermogravimetric analysis coupled with infrared (TGA/IR). At the end of the heat cycle, residues were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (solid state ^{13}C NMR (CP/MAS).

The studies on thermal characterization of thermoset matrix resins have reported by Kandola et al. [12]. They have studied the thermal degradation behavior

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11. J. Bouajila, G. Raffin, S. Alamercery, H. Waton, C. Sanglar and M.F.Grenier-Loustalot, "Phenolic resins (IV) - Thermal degradation of crosslinked resins in controlled atmospheres", Polym. and Polym. Compos., **11**, 345-357, 2003.
12. B. K. Kandola, A. R. Horrocks, P. Myler and D. Blair, "Thermal characterization of thermoset matrix resins", ACS Symposium Series, **797**, 344-351, 2001.

of a range of commercially available phenolic, epoxy and polyester resins by simultaneous DTA-TGA under a flowing air atmosphere. Thermal analytical transitions of these resins are correlated with their degradation mechanisms cited in literature. Furthermore, TGA studies have also shown that all resins, after decomposition, are completely oxidized and little or no char residue are left above 550°C. Introduction of an inherently flame-retardant cellulosic fibre, Visil (Sateri, Finland), in combination with melamine phosphate - based intumescents (with and without dipentaerythritol) has been made to each resin as a char-promoting system. TGA results of the individual components and their mixtures have indicated that these additives do indeed increase char formation and there is evidence of chemical interaction between different components. A means of increasing the flame retardancy of rigid composites is proposed.

Nair et al. [13] have reported the thermal characteristics of addition-cure phenolic resins. The thermal and pyrolysis characteristics of four different types of addition-cure phenolic resins were compared as a function of their structure. Whereas the propargyl ether resins and phenyl azo functional phenolics underwent easy curing, the phenyl ethynyl- and maleimide-functional ones required higher thermal activation to achieve cure. All addition-cure phenolics exhibited improved thermal stability and char-yielding properties in comparison to conventional phenolic resole resin. The maleimide-functional resins exhibited lowest thermal stability and those crosslinked via ethynyl phenyl azo groups were the most thermally stable systems. Propargylated novolac and phenyl ethynyl functional phenolics showed intermediate thermal stability. The maximum char yield was also given by ethynyl phenyl azo system. Non-isothermal kinetic analysis of the degradation reaction implied that all the polymers undergo degradation in at least two steps, except in the case of ethynyl phenyl azo resin, which showed apparent single step degradation. The very low pre-exponential factor common to all polymers implied the significance of volatilisation process in the kinetics of degradation.

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13. C. P. Reghunadhan Nair, R. L. Bindu and K. N. Ninan, “Thermal characteristics of addition-cure phenolic resins”, Thermal Deg. and Stability, **73**, 251-263, 2001.

The usefulness of DSC and TGA in various fields of chemistry is described in Table 2.2

Table 2.2 The usefulness of DSC and TG in various fields of chemistry

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

Contd…

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

Effect of various operating parameters

1. Atmosphere

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

2. Container geometry

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

3. Container material

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

4. Sample size

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

5. Rate of heating

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

Thermo gravimetric analysis (TGA)

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

There are three types of thermogravimetry

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

Most of the studies of polymers are generally carried out with dynamic thermogravimetry. Normally the sample starts losing weight at a very slow rate up to a particular temperature and there after, the rate of loss becomes large over a narrow range of temperature. After this temperature, the loss in weight levels off. TGA curves are characteristic for a given polymer because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at rates that are function of the polymer structure. The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to evaluation of volatile products in the formation of heavier reaction products.

Pyrolysis of many polymers yields sigmoidal TG curves. The weight of the sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction is completed. The shape of the curve depends on the kinetic parameters: reaction order n, frequency factor A and activation energy E_a. The values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation [14, 15]. Reich and Levi [16] have described several temperature characteristics for qualitative assessment of relative thermal stability of polymers:

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

With dynamic heating T_0 and T_{10} are some of the main criteria of the thermal stability of a given polymer 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 two important assumptions that thermal and diffusion barriers are negligible and that Arrhenius equation is valid. Since small quantities of materials are employed in TG studies, thermal and diffusion barriers would be negligible.

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

$$\frac{dC}{dt} = kf(C) \qquad \ldots 2.1$$

where C = Degree of conversion, t = time, k = rate constant, f(C) = a temperature independent function of C.

The constant k is generally assumed to have the Arrhenius form

$$K = Ae^{-E/RT} \qquad \ldots 2.2$$

C is defined as the conversion with respect to initial material

$$C = 1 - \frac{W}{W_0} \qquad \ldots 2.3$$

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14. D. W. Levi, L. Reich and H. T. Lee; Polymer Eng. Sci., 5, **135,** 1965.
15. H. L. Friedman, U. S. Dept. Com., Office. Tech., 24 PP (1959); cf. C. A. 55, 26, 511, 1961.
16. L. Reich and D. W. Levi, Macromol. Rev. Eds. Peterlin Goodman Wiley Interscience, New York, 173, 1968.

Where W_0 = Initial weight of the material and W = weight of the material at any time. The residual weight fraction is given by

$$\frac{W}{W_0} = (1 - C)$$

and the rate of conversion is given by

$$\frac{dC}{dt} = -\left(1/W_0\right)\frac{dW}{dt} \qquad \ldots 2.4$$

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

$$f(C) = (1 - C)^n \qquad \ldots 2.5$$

where, n = order of the reaction.

Upon substituting Eqns. 2.2 and 2.5 into Eqn. 2.1

$$\frac{dC}{dt} = Ae^{-E_a/RT}(1 - C)^n$$

or

$$\frac{dC}{dT} = \left(\frac{A}{\text{ß}}\right)\left(e^{-E_a/RT}\right)(1 - C)^n \qquad \ldots 2.6$$

where β = Rate of heating.

Methods of single heating rate

1. Freeman – Carroll [17] and Anderson-Freeman [18] method

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

$$\frac{\ln(dC/dt)}{\ln(1-C)} = n - \frac{E_a}{R}\left[\frac{?\,(1/T)}{?\ln(1-C)}\right] \qquad \ldots 2.7$$

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17. E. S. Freeman and B. Carroll, J. Phys. Chem., **62**, 394, 1958.

18. D. A. Anderson and E. S. Freeman, J. Polym. Sci., **54**, 253, 1961.

A Plot of L.H.S. against $\frac{\Delta(1/T)}{\Delta \ln(1-C)}$ for equal interval of Δ(1/T) would yield a straight line with slope equal to –E/R and the intercept equal to n. Using Eqn. 2.7, Anderson-Freeman derived Eqn. 2.8:

$$\Delta ln\left(\frac{dC}{dt}\right) = n?\ln(1-C) - \frac{E_a}{R}?\left(\frac{1}{T}\right) \qquad \text{...2.8}$$

According to Eqn. 2.8, the plot of $\Delta ln\left(dC/dt\right)$ against $\Delta 1n(1-C)$ for equal intervals of $?\left(1/T\right)$ would be a straight line with slope equal to n and the intercept equal to $-(E/R)?\left(1/T\right)$

2. Sharp-Wentworth method [19]

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

$$\log\left[\frac{dC/dt}{1-C}\right] = \log\left(A/ß\right) - \frac{E_a}{2.303R}.\frac{1}{T} \qquad \text{…2.9}$$

The plot of log $\left(\frac{dC/dt}{1-C}\right)$against 1/T would be a straight line, with slope equal to –(*E/2.303 R*) and intercept equal to $\log(A/b)$.

3. Chatterjee method [20]

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

$$n = \frac{\log\left(-\frac{dW}{dt}\right)_1 - \log\left(\frac{dW}{dt}\right)_2}{\log W_1 - \log W_2} \qquad \text{…2.10}$$

Where, W_1 and W_2 are the sample weight.

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19. J. H. Sharp and S. A. Wentworth, Anal. Chem., **41**, 2060, 1969.

20. P. K. Chatterjee, J. Polym. Sci., A-**3**, 4253, 1965.

4. Horowitz and Metzger method [21]

The value of E can be determined from a single TG curve according to Horowitz and Metzger:

$$\ln\left[\ln\left(1-C\right)^{-1}\right] = \frac{E}{RTs^{2}}? \qquad \text{…2.11}$$

where Ts = Temperature at which the rate of decomposition is maximum and q = T – Ts.

The frequency factor A and entropy change ?S can be determined respectively according to Eqns. 2.12 and 2.13.

$$\ln E - \ln\left(RTs^{2}\right) = \ln A - \ln ß - \frac{E}{RTs} \qquad \text{…2.12}$$

$$A = \frac{k_{b}T}{h}e^{?S/R} \qquad \text{…2.13}$$

where k_b is Boltzmann constant

Uses of multiple heating rates

(1) Anderson [22] method

Anderson [22] and Friedman [23] have developed the methods based on multiple heating rates. These methods are based on the fact that as the heating rates are increased, TG curves tend to shift to higher temperatures, since at lower temperature decomposition occurs for shorter times.

The relation is $\ln R_t = \ln A + n\ln\left(1-C\right) - \frac{E}{RT}$ …2.14

where $R_t = ß\,dC/dt$

The plot of $\ln R_t$ against 1/T at various fixed degree of conversion would be a straight line with slope equal to –E/R at a fixed degree of conversion. In order to evaluate the values of n and A, Eqn. 2.15

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21. H. H. Horowitz and G. Metzger, Ana. Chem., **35**, 1464, 1963.
22. H. C. Anderson, J. Polym. Sci., **C6,** 175, 1964.
23. H. L. Friedman, J. Polym. Sci., **C6**, 183, 1964.

can be employed by considering 1/T = 1/To when ln $R_t = 0$

$$\frac{E}{RTo} = \ln A + n\ln(1\text{-}C) \qquad \text{…2.15}$$

According to Eqn. 2.15, the plot of E/RT_0 against ln (1-C) would be a straight line with slope equal to n and intercept equal to ln A.

(2) Friedman method [23]

Friedman [17] has developed following Eqn. 2.16:

$$\ln\left(\frac{dC}{dt}\right) = \ln A + n\ln(1\text{-}C) - \frac{E}{RT} \qquad \text{… 2.16}$$

According to Eqn. (2.16), the plot of ln dC/dt against 1/T at various values of fixed degree of conversion would be a straight line with slope equal to –E/R and

$$\text{Intercept} = \ln A + n\ln(1\text{-}C) \qquad \text{…2.17}$$

The intercept obtained from the first graph can be plotted against ln(1-C), the slope and the intercept of which yield the values of n and A, respectively.

(3) Ozawa method [24]

Ozawa has developed the following Eqn. 2.18:

$$\log\int_0^C \frac{dC}{(1-C)^n} \approx \log\frac{AE}{RT} - \log b - 2.315 - 0.4567\left(\frac{E}{RT}\right) \qquad \text{…2.18}$$

The plot of log *b* against 1/T would be a straight line for the fixed values of conversion; the slope is equal to –0.4567(E/R).

Experimental

TG thermograms of BCFA and BCFB were scanned on a Universal V 1.12 E TA instrument at the heating rate of 20^0C/mm in nitrogen atmosphere.

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24. T. Ozawa, Bull. Chem. Soc. Jap., **38**, 1881, 1965.

Results and Discussions

Thermal analysis of materials is very important in predicting their utility under various environmental conditions, in understanding molecular architecture, decomposition mechanisms and high temperature applications. Thermogravimetric analysis provides a means to estimate kinetic parameters of thermal decomposition reactions [25]. Thermal methods are based upon the relationship between temperature and some properties of a system such as mass, heat of reaction or volume, etc [26, 27].

TG-thermograms of BCFA and BCFB are presented in Figs 2.4 and 2.5, respectively. From TG thermograms it is found that BCFA and BCFB resins involved two steps degradation. BCFA is found to be thermally stable up to about 186^{o}C, while BCFB is thermally stable upto about 157^{o}C. The energy of activation (Ea), frequency factor (A), temperature of maximum weight loss (T_{max}) and entropy change (?S*) are determined according to Anderson-Freeman method [18] (Eqn. 2.8) and are reported in Table 2.5. The detail calculation for BCFA and BCFB are reported in Tables 2.3 and 2.4, respectively. The plots of $\Delta \ln {dW}/{dt}$ against $\Delta \ln W$ are presented in Fig. 2.6. Both resins followed first order degradation kinetic. A large and negative magnitude of ?S* confirmed that transition state is more in orderly state than neat resins.

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25. Jovan Mijovic, "Cure kinetics of neat vs reinforced epoxies", J. Appl. Polym. Sci., **31**, 1177-1187, 2003.
26. W. W. Wendlant, "Thermal methods of analysis", 2nd Ed. Willey, New York, 1974; T. Meisel and K. Seytold, Crit. Rev. Ana. Chem., **12**, 267, 1981.
27. R. C. Mackenizie, "Differential thermal analysis", Vol **1** and **2**, Academic Press, New York, 1970.

Table 2.3 The calculation scheme for BCFA by Anderson-Freeman method

10^3/T	% wt. loss	dw/dt	Active Wt.	lnW	ln dw/dt	?lnW	?lndw/dt
STEP-2							
1.34	33.15	8.23	43.97	3.783	2.108	0.052	-0.122
1.33	35.39	9.30	41.73	3.731	2.230	0.064	-0.095
1.32	37.97	10.23	39.15	3.667	2.325	0.078	-0.067
1.31	40.92	10.94	36.20	3.589	2.392	0.096	-0.037
1.30	44.24	11.35	32.88	3.492	2.426	0.012	-0.007
1.29	47.89	11.44	29.23	3.375	2.437	0.144	0.025
1.28	51.82	11.16	25.30	3.230	2.412	0.177	0.057
1.27	55.93	10.54	21.19	3.053	2.355	0.217	0.090

Table 2.4 The calculation scheme for BCFB by Anderson-Freeman method

10^3/T	% wt. loss	dw/dt	Active Wt.	lnW	ln dw/dt	?lnW	?lndw/dt
STEP-2							
1.44	30.57	6.15	50.91	3.930	1.816	0.031	-0.183
1.43	32.17	7.38	49.31	3.898	1.999	0.044	-0.176
1.42	34.28	8.80	47.20	3.854	2.175	0.058	-0.160
1.41	36.93	10.33	44.55	3.797	2.335	0.074	-0.142
1.40	40.10	11.91	41.38	3.723	2.477	0.093	-0.120
1.39	43.76	13.42	37.72	3.630	2.597	0.114	-0.095
1.38	47.83	14.77	33.65	3.516	2.692	0.140	-0.069
1.37	52.21	15.84	29.27	3.376	2.762	0.169	-0.040
1.36	56.77	16.50	24.71	3.207	2.803	0.206	-0.011
1.35	61.37	16.68	20.11	3.001	2.814	0.251	0.024
1.34	35.84	16.29	15.64	2.749	2.791	0.313	0.064

Table-2.5: Kinetic parameters of BCFA and BCFB resins derived according to Anderson- Freeman method

Resin	**n**	**T_{max}, ^oC**	**Ea, kJ**	**A, S^{-1}**	**?S*, J deg^{-1}**
BCFA	1.28	500.2	141	3.15×10^7	-109.3
BCFB	0.92	469.23	172	1.58×10^{10}	-57.25

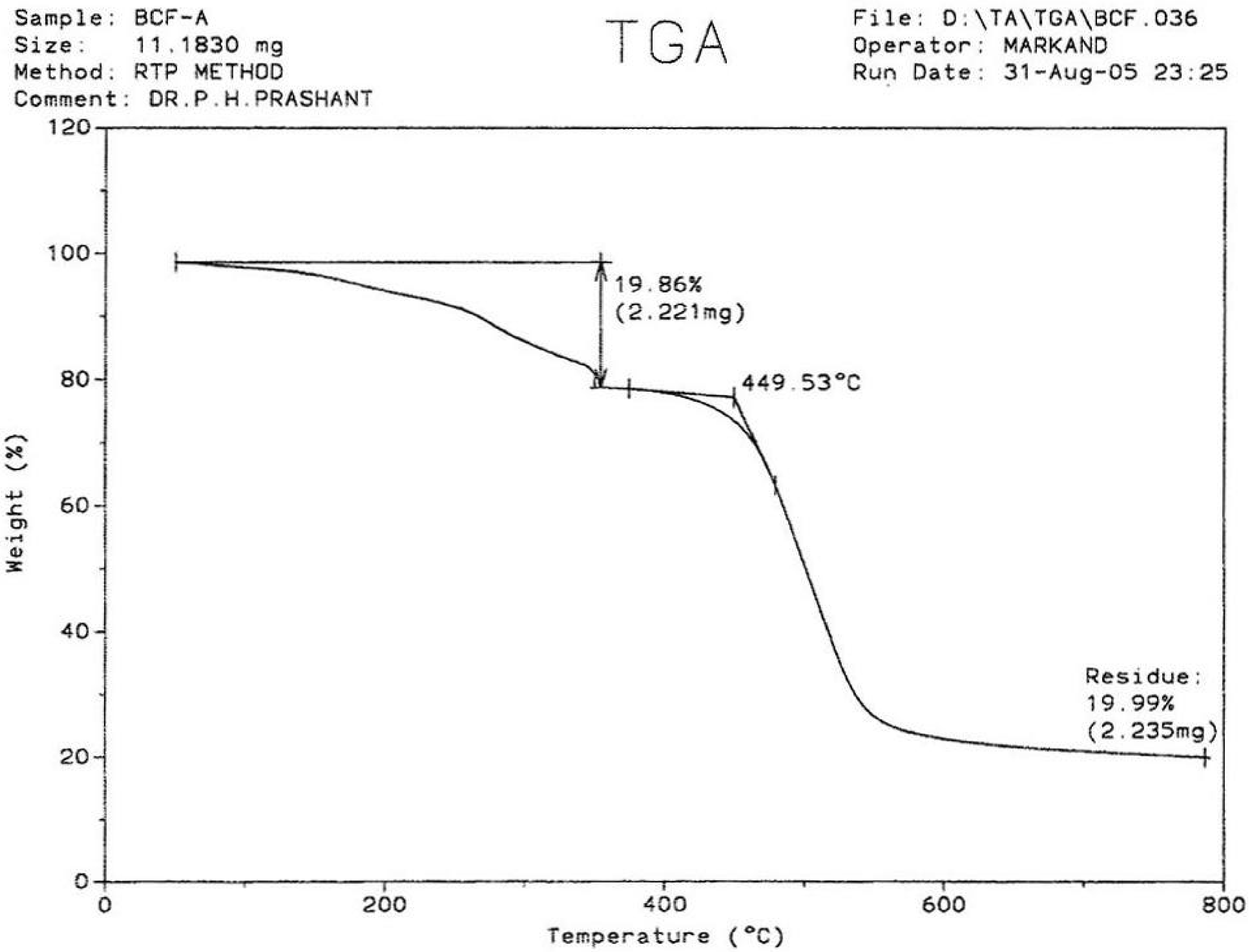


Fig. 2.4 TG thermogram of BCFA at the heating rate of 20°C/min in an N_2 atmosphere

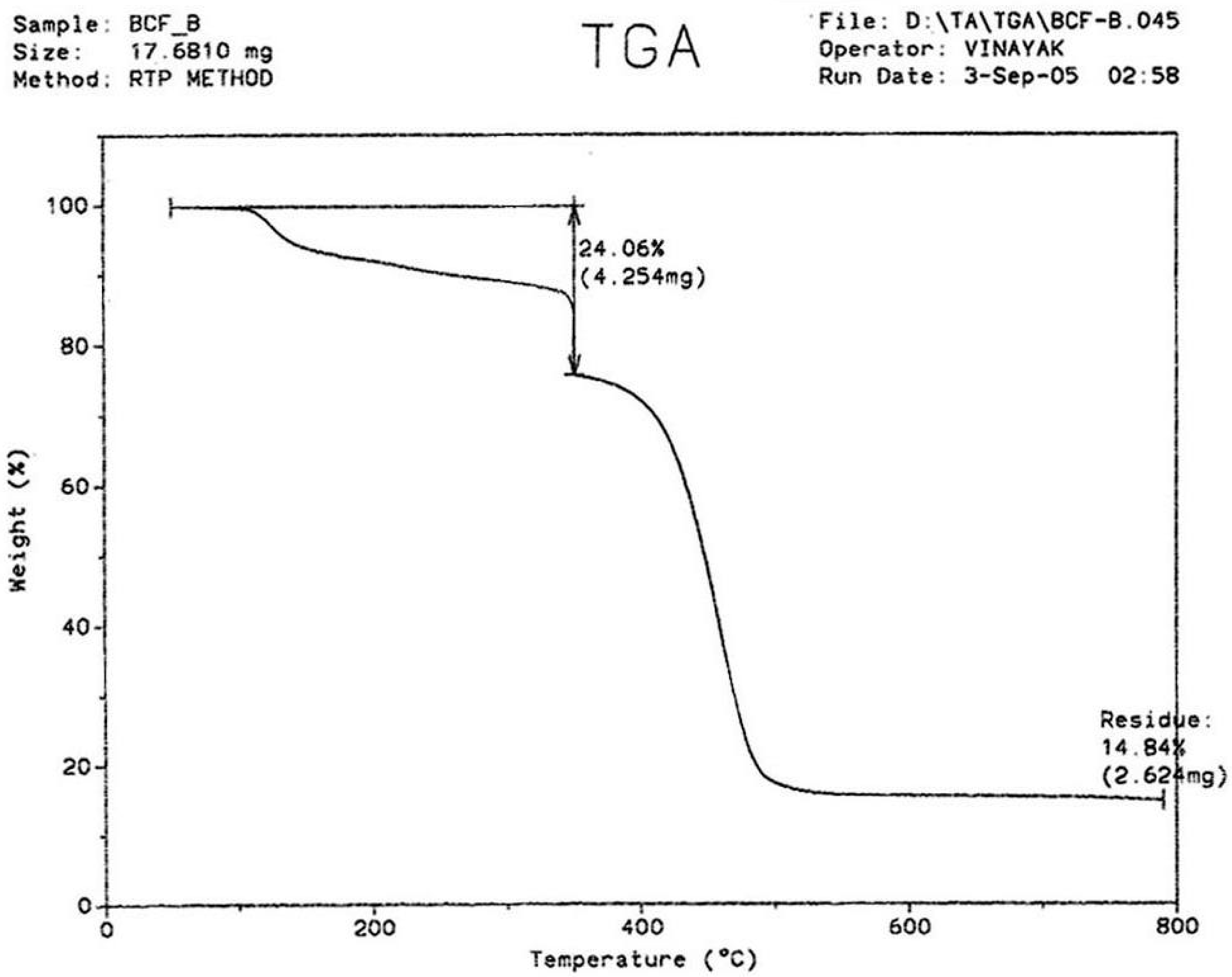
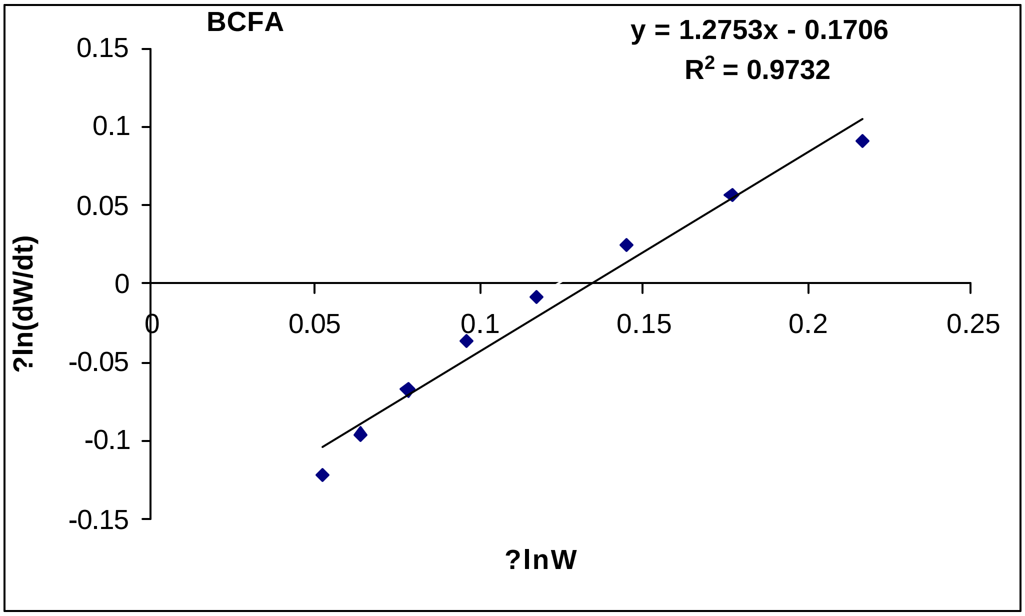


Fig. 2.5 TG thermogram of BCFB at the heating rate of 20^oC/min in an N_2 atmosphere



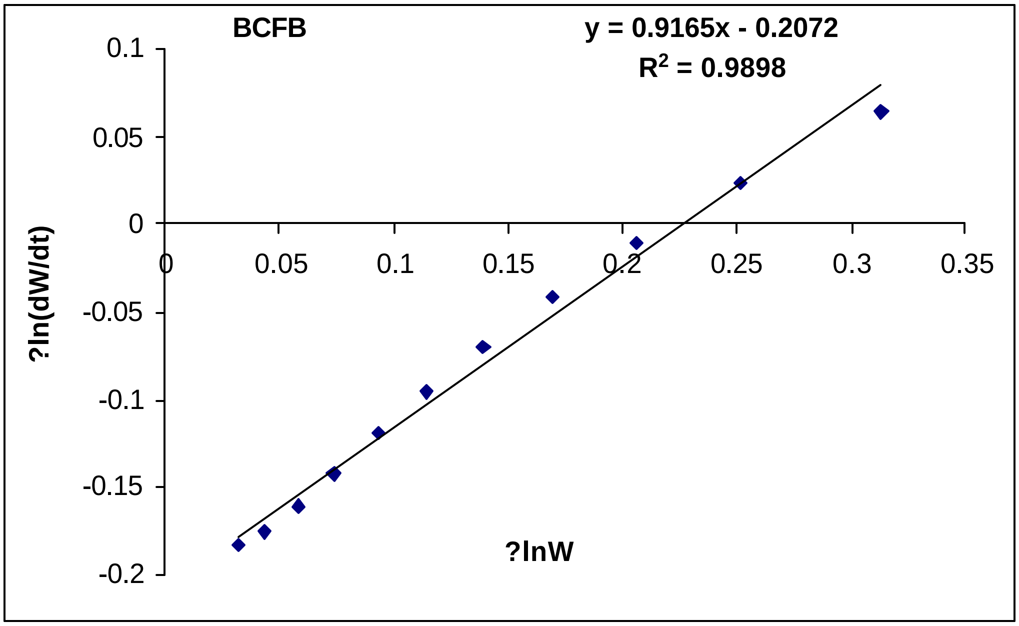


Fig. 2.6 The Anderson-Freeman plots of BCFA and BCFB

This chapter of the thesis describes the up to date literature survey on the composites based on jute, glass and natural fibers. The fabrication process, mechanical and electrical properties, chemical resistance and boiling water studies of bisphenol-C-formaldehyde based composites are well documented in this chapter.

This chapter is further subdivided into three sections:

SECTION-I : FABRICATION OF COMPOSITES

SECTION-II: MECHANICAL AND ELECTRICAL PROPERTIES OF COMPOSITES

SECTION-III: CHEMICAL RESISTANCE AND BOILING WATER STUDY OF COMPOSITES

SECTION-I : FABRICATION OF COMPOSITES

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

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

Among all the process, hand lay-up technique is the cheapest process and all the composites reported in this chapter are fabricated by this technique.

In literature 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 such as for manufacturing hardboard, construction devices, partition board, interior, medium density fiber boards, panels, packaging, etc. than any other techniques. Many composite industries and research institutes which are working on composites in India using hand lay-up technique for fabrication of composites.

Woven jute fibers (Brown jute, Corchorus Capsularis) used in present study was collected from the Indian Jute Industries' Research Association (IJIRA Kolkata). Bisphenol-C-formaldehyde (BCF) resin [8] was synthesized and recrystallized / purified according to our recent publications.

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1. Carignani and Giancarlo, "GRP expanded plastic composites", Kunstst Ger plast, **68**, 8-17, 1978.
2. P. K. Pal, **"**Jute reinforced plastics: a low cost composite material", Plast. and Rubber Proc. and Appl., **4**, 215-222, 1984.
3. Mc Cormack and E. William, "Fabrication and joining of polymer-matrix composites", Flight-Vehicle Materials, structures, and dynamics– assessment and future directions", **1**, 348**-**356**,** 1994.
4. M. A. Hayat and S. M. A. Suliman, "Mechanical and structural properties of glass reinforced phenolic laminates**",** Polym. Test.,**17**, 79-85, 1998.
5. J. Sinke, **"**Manufacturing of GLARE parts and structures", App. Compos. Mater., **10**, 293, 2005.
6. S. R. Dyer, L. V. J. Lassila, M. Jokinen and P. K. Vallittu, **"**Effect of cross-sectional design on the modulus of elasticity and toughness of fiber-reinforced composite materials**",** J. Pros. Dentistry., **94**, 219-232, 2005.
7. P. Thomas, K. Dwarkanath, P. Sampathkumaran, S. Sitharamu and Kishore, "Influence of moisture absorption on electrical characteristics of glass-epoxy polymer composite system", Proceedings of the International Symposium on Electrical Insulating Materials**, 3**, 605, 2005.
8. N. M. Mehta, S. I. Mavani and P. H. Parsania, "Preparation, mechanical properties and moisture absorption study of novel Bisphenol-C-formaldehyde-treated and untreated jute composites", J. Polym. Mater., **22**, 205-212, 2005.

Alkali and malinization of jute

Woven jute matrices of 15cm x 15cm were soaked in a 5% NaOH solution at 30°C for 8 h. The fibers were washed several times with distilled water to remove residual NaOH from the fiber surface, neutralized with dilute acetic acid and finally washed well with distilled water to pH 7. The fibers then dried in an oven at 100°C for 4 h. Alkali treatment can remove natural and artificial impurities and produce a rough surface topography. In addition, alkali treatment leads to breakdown of fiber bundles into smaller fibers. This increases the effective surface area available for wetting by the matrix resin.

Alkali treated fibers were subjected to 5% solution of maleic anhydride in xylene and concentrated sulfuric acid as a catalyst and refluxed for 5 h. The fibers were washed and dried in an oven at 80°C for 4 h [9].

3.1 Fabrication process of jute and glass composites

BCF (60% of jute fibers/glass fibers) was dissolved in 100 ml acetone and applied to the woven matrices (15cm x 15 cm and 5cm x 5 cm) of jute with the help of a smooth brush. The prepregs were allowed to dry in sunlight. Ten such prepregs were stacked one over other and subjected to hydraulic pressure of 30.4 MPa at 150°C for 2h and at room temperature for 12h. Silicon spray was used as a mold releasing agent. The edges of the specimens were sealed with BCF. Fibers and resin contents in the composites are reported in Table 3.1.

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9. S. V. Prasad, C. Pavithran and P. K. Rohatgi, J. Mater. Sci., **18**, 1443, 1983.

Table - 3.1: Fiber and BCF contents in jute/glass composites

Size, cm x cm	Types of composite	Wt. of Jute/glass, g	Wt. of BCF, g
15x15	Jute	54.90	32.94
	Treated jute	65.0	39.00
5 x 5	Jute	3.5	2.1
	Treated jute	3.8	2.3
15x15	Glass	42.5	25.5
5 x 5	Glass	3.2	1.92

Table - 3.2: Fiber and BCF contents in glass-jute composites

Size, cm x cm	Types of composite	Wt. of Glass-jute, g	Wt. of BCF, g
15x15	Glass-jute (Glass + Jute)	51.91 (8.07 + 43.84)	25.35 (4.03+21.32)
5 x 5	Glass-jute (Glass + Jute)	6.60 (0.91+5.69)	3.96 (0.45+2.84)

3.2 Fabrication process of glass- jute composite

Silane treated epoxy glass fabric (7 mil) used in the present study was collected from Unnati Chemicals-Ahemdabad.

BCF (50% of jute and glass fibers) was dissolved in 100 ml acetone and applied to the woven matrices (15cm x 15 cm, 5cm x 5 cm) of jute and glass with the help of a smooth brush. The prepregs were allowed to dry in sunlight. Ten such prepregs containing 2 upper layers of glass and 8 inner layers of jute matrices were stacked one over other and subjected to hydraulic pressure of 30.4 MPa at 150^oC for 2h and at room temperature for 12h. Silicon spray was used as a mold releasing agent. The edges of the specimens were sealed with BCF. Fiber and BCF contents in the composites are reported in Table-3.2.

3.3 Fabrication process of sandwich composites

The agro wastes such as rice husk (RH), wheat husk (WH), cane sugar husk (CH) and jamun flower husk (JH) were collected from local market. Cane sugar fibers after extracting juice was soaked in hot water for 1h and then washed well with hot water till clear and transparent washing was obtained. All the agro waste fibers were dried either in open sunlight or in an oven at 50-60^oC. Ordinary sieves were used to separate fibers of different sizes. Agro waste fibers used in the sandwich composites have different sizes as under.

A matrix material (BCF) used in the fabrication of hybrid composites was 50% of jute mats (15cm x 15cm) and biomass (Rice, Wheat, Cansugar and Jamun fiber husk). BCF was dissolved in 100 ml acetone and applied to the jute mats with the help of a smooth brush and the remaining solution was mixed with biomass. The solvent was allowed to evaporate at room temperature for about 15 min. Resin coated biomass was sandwiched uniformly between two resin coated jute /glass mats and was placed between two stainless steel plates and subjected to hydraulic pressure of 30.4 MPa at 150^oC for 2 h. Silicon spray was used as a mold releasing agent. Fibers and resin contents in the sandwich composites are reported on Table-3.3.

Fiber size of different fibers

Types of fiber	Size, mm
Rice husk	2-3
Wheat jusk	6-8
Can sugar	6-8
Jamun fiber	1-2

Table - 3.3: Fibers and BCF contents in sandwich composites

Types of composites	Wt. of jute/ glass, g	Wt. of WH/RH/CH/JH, g	Wt. of BCF, g
Jute-WH	5.5	30	17.75 (2.75 + 15)
Jute-RH	5.5	40	22.75 (2.75+20)
Jute-CH	5.5	40	22.75 (2.75+20)
Jute-JH	5.5	40	22.75 (2.75+20)
Glass-WH	4.3	30	17.15 (2.15+15)

SECTION-II: MECHANICAL AND ELECTRICAL PROPERTIES OF COMPOSITES

The physico-chemical properties include the study of mechanical, electrical and chemical properties of polymeric materials. The effect of molecular weight upon physical properties in general, are among the most frequently studied and described by researchers, while the electrical properties of the polymeric material are most significant, particularly when polymers are subjected to high electrical field. Infect, most polymers are excellent electrical insulators, and display high electrical resistance. The small amount of conductivity is observed due to electrolytic motion of ionic impurities in the polymers. The knowledge of the mechanical and electrical properties of polymeric materials is the most useful in defining quality characteristics for tailor made engineering design for various applications. Natural fiber reinforced composites offer many advantages over the traditional construction materials namely steel and aluminium in respect of low density, low thermal conductivity, excellent corrosion and chemical resistance, high strength to weight ratio, better design flexibility, excellent fatigue and impact properties, improved acoustical performance and low maintenance. Natural fibers have already been recognized for their role in composites and can be advantageously utilized for the development of environment friendly composite materials with good physical properties [10]. The incentives of utilizing agro waste in the fabrication of composites are their low density, less abrasiveness to equipment, low cost, etc.

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

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10. A. K. Bledzki and J. Gassan, Ninth International Conference on Mechanics of Composite Materials , Riga, Latvia, 17-20 Oct., 1995.

- Type of reinforcing fiber
- Type of curing mechanism and density of curing
- Fiber-matrix adhesion
- Time and temperature of cure
- Molecular weight of polymer

Most plastic materials are considered to be electrical insulators i.e. they are able to withstand a potential difference between different points of a given piece of material with the passage of only small electrical current and low dissipation energy. When assessing a potential insulating material, information on the following properties will be required.

- Dielectric constant (specific inductive capacity, relative permeability) over a wide range of temperature and frequencies
- Power factor over a range of temperature and frequency
- Dielectric strength (usually measured in V/mil (1 mil=0.001 in) or (kV/cm)
- Volume resistivity (usually measured in O cm or O m)
- Surface resistivity (usually measured in O)
- Tracking and arc resistance

The electrical properties of polymer materials are of considerable importance where plastics are used in or near electrical equipments as insulating materials, supporting assemblies, connectors, housing, etc. The use of polymers in engineering as dielectrics is becoming increasingly important. The choice of polymeric dielectrics for each concrete case depends on its dielectric and other physical properties over a wide range of temperatures and electrical field frequencies. Investigations of dielectric properties are most important for studying polymer structure. Typical electrical properties of some selected plastic materials are reported in Table 3.4.

Table- 3.4 : Electrical properties of some selected polymers

Polymer	Volume resistivity (O cm)	Dielectric strength (KV/cm)	Dielectric constant		Power factor	
			60 Hz	10^6 Hz	60 Hz	10^6 Hz
PTFE	$>10^{20}$	180	2.1	2.1	<0.0003	<0.0003
PE	10^{20}	180	2.3	2.3	<0.0003	<0.0003
PS	10^{20}	240	2.55	2.55	<0.0003	<0.0003
PP	$>10^{19}$	320	2.15	2.15	0.0008	0.0004
PMMA	10^{16}	140	3.7	3.0	0.06	0.02
PVC	10^{17}	240	3.2	2.9	0.013	0.016
Nylon 66	10^{15}	145	4.0	3.4	0.014	0.04
PC	10^{18}	160	3.17	2.96	0.0009	0.01
Phenolic	10^{13}	100	5.0-9.0	5.0	0.08	0.04
Urea-Formaldehyde	10^{14}	120	4.0	4.5	0.04	0.3

Wu et al. [11] have reported electrical and mechanical characterization of hybrid CFRP sheets. Six types of specimens have been fabricated to investigate the mechanical properties. The experimental results indicate that the hybridization of several types of carbon fibers was an effective method for upgrading the mechanical properties of the HCFRP sheets.

Bosze et al. [12] have studied mechanical properties of a carbon fiber/E-glass fiber, polymer matrix pultruded composite. The tensile strength decreased as a function of temperature and the reported flexure strength [944 MPa], the flexure modulus [47.4 GPa] and the shear strength [55.3 MPa].

Arib et al. [13] have reported the mechanical and electrical properties of pineapple leaf composites of polypropylene resin. They have investigated the tensile and flexural behaviors of pineapple leaf fiber-polypropylene composites as a function of volume fraction. The tensile modulus and tensile strength of the composites were found to be increasing with fiber content in accordance with the rule of mixtures. The tensile modulus and tensile strength with a volume fraction 10.8% are 687.02 and 37.28 MPa, respectively. The flexural strength of the composites containing 5.4% volume fraction was found to be higher than that of pure polypropylene resin by 5.1%.

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11. Z. S. Wu, C. Q. Yang, Y. H. Tobe, L. P. Ye and T. Harada, **“**Electrical and mechanical characterization of hybrid CFRP sheets”, J. Compos. Mater. , **40**, 227-239, 2006.
12. E. J. Bosze, A. Alawar and S. Nutt, “A hybrid polymer matrix composite for electrical transmission line supports”, International SAMPE Technical Conference, Pages 267-278, 2004.
13. R. M. N. Arib, S. M. Sapuan, M. M. H. M. Ahmad, M. T. Paridah and H.M.D. and Khairul Zaman, **“**Mechanical properties of pineapple leaf fibre reinforced polypropylene composites”, Mater. and Designs, **27**, 391-396, 2006.

Khondker et al. [14] have studied the static and impact mechanical properties of jute fiber-based thermosetting composites. Tensile, three-point flexural and low-to-medium energy drop-weight impact tests were conducted and mechanical properties were evaluated to study their dependence upon surface modifications of the fiber materials due to bleaching and coating treatments. Full-bleaching (longer and rigorous) treatments improved interfacial bonding and tensile strength properties of the woven jute composites compared to unbleached and half-bleached counterparts. Unbleached (natural) jute composites have relatively better flexural strength due to reduced microstructural waviness or fiber crimping to facilitate flexural failure. With coated jute yarns, the tensile properties of the resultant flat braided composites slightly degraded, whereas the flexural properties showed clear improvements. There was a clear indication that natural woven jute composites could be more effective in applications requiring better impact damage resistance, energy absorption capability and improved progressive crushing behavior.

Hou et al. [15] have reported commercial vacuum-bag moldable phenolic prepreg system. The traditional single-vacuum-bag (SVB) process was unable to manage the volatiles effectively, resulting in inferior voidy laminates. However, a double-vacuum-bag (DVB) process was shown to afford superior volatile management and consistently yield void-free quality parts. Laminate consolidation quality was characterized by optical photomicrography for the cross sections and measurements of mechanical properties. A 40% increase in short beam shear strength, 30% greater flexural strength, 10% higher tensile and 18% higher compression strengths were obtained in composite laminates fabricated by the DVB process.

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14. O. A. Khondker, U. S. Ishiaku, A. Nakai and H. Hamada, “Tensile, flexural and impact properties of jute fibre-based thermosetting composites”, Plast., Rubbers and Compos., **34**, 450-461, 2005.
15. T. H. Hou, J. M. Bai and J. M. Baughman, “Processing and properties of a phenolic composite system”, J. Rein. Plast. Compos., **25**, 495-507, 2006.

Under a project of Advanced Composites Mission programme of Govt. of India, FRP pultruded profiles (industrial gratings, solid rods for electrical insulation, cable-trays, ladders, etc.) with excellent surface finish and flame retardancy as per international standards have been reported. The profiles developed have met all the desired properties, which are reported in Table- 3.5 [16]. The degree of fiber-matrix adhesion and its effect on the mechanical reinforcement of short henequen fibers and a polyethylene matrix was studied by Herrera-Franco and Valadez-* RQ]i lez et al. [17]. They have reported comparison of tensile properties of the composites, which showed that the silane treatment and the matrix-resin pre-impregnation process of the fiber produced a significant increase in tensile strength. They have also reported that the silane treatment produced a significant increase in flexural strength.

Chen et al. [18] have fabricated the composites by using bagasse, kenaf, ramie, and polypropylene (PP) fibers. A comparative study of these experimental composites was conducted in terms of mechanical properties, thermal properties, and wet properties. Composites tensile and flexural properties are measured using a desktop tensile tester. They have found that the uniform structures have higher tensile strength and modulus, as well as higher flexural yielding stress and modulus than the sandwich structures. In uniform composites found less water absorption but higher swelling rate than the sandwich composites.

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16. Composites in Civil Engineering, Science Tech Entrepreneur, March 2001.
17. P. J. Herrera-Franco and A. Valadez-* RQ]i lez, "A study of the mechanical properties of short natural-fiber reinforced composites", Compos. Part B: Eng., **36,** 597-612, 2005.
18. Y. Chen, O. Chiparus, L. Sun, I. Negulescu, D. V. Parikh and T. A. Calamari, "Natural fibers for automotive nonwoven composites", J. Ind. Text., **35**, 47-56, 2005.

Table- 3.5: Mechanical and chemical properties of FRP pultruded sections Vs other structural materials

Mechanical Properties	Pultruded FRP		Rigid PVC	Mild steel	Stainless steel	Wood
	Polyester	Vinyl ester				
Tensile strength (N/mm^2)	382	401	44	340	340	80
Flexural strength (N/mm^2)	468	508	70	380	380	12
Flexural modulus (N/mm^2)	22489	48260	2400	19600	1960000	700
Izod impact (kg-m/cm)	1.36	1.63	0.09	1.5	0.53	------
Specific gravity	1.80	1.80	1.38	7.8	7.92	0.52
Safe working temp. (^oC)	120	170	55	600	600	160

Mechanical and dimensional stability of rice husk (RH)-glass fiber (GF) hybrid polyester composites was studied by Rozman et al. [19]. Tensile, flexural, impact, and dimensional properties of the composites have been investigated. From the results, it was observed that GF imparted higher tensile, flexural, and impact properties. The presence of RH in the matrix produced composites with comparable tensile, flexural, and impact properties especially in the middle range of RH:GF ratios. Longer GF had a profound effect on the strength and toughness, while the shorter GF contributed the modulus of the composites. The incorporation of RH in the composites resulted in an increase in water absorption and thickness swelling. Overall, the study reported that RH together with GF produced composites with acceptable properties.

Rozman et al. [20] have also reported polyurethane composites produced with rice husk (RH) and polyethylene glycol, molecular weight (M_w) of 200 (PEG200), used as a polyol. The effect of % of RH (by weight), % of RH hydroxyl (OH) groups and RH size on the flexural, tensile and impact properties were investigated. They have studied that size played a significant role in the properties; smaller size RH produced composites with higher strength.

In order to study the dielectric properties of composites, an ideal contact should be satisfied the certain conditions.

(1) It should not induce a resistance to the flow of the current

(2) It should not react chemically with semi conducting material

(3) The contact properties should not be affected by variation of ambient conditions like illumination, temperature, electrical field, etc.

(4) The Ohm’s low should apply to the semiconductor with contacts

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19. H. D. Rozman, A. Hazlan and A. Abubakar, **“**Preliminary study on mechanical and dimensional stability of rice husk-glass fiber hybrid polyester composites”, Polym. Plast. Technol. Eng., **43**, 1129-1138, 2004.
20. H. D. Rozman, Y. S. Yeo, G. S. Tay and A. Abubakar, **“**The mechanical and physical properties of polyurethane composites based on rice husk and polyethylene glycol”, Polym. Test., **22**, 617-628, 2003.

The working voltage applied to an electrical insulating material must be much lower than the voltage, which causes the material rupture. Electrical discharge through a material at a minimum voltage called break down or disruptive voltage V_{br} [20]. In some cases voltage lower than the break down voltage give rise to a surface discharge that dose not penetrate deep into the bulk of a material. This is a surface or creeping, breakdown occurring at a surface break down voltage.

The basic characteristic of an electrical insulating material is its breakdown or dielectric strength E_{br} (also called electric strength), which is a minimum strength of the uniform electric field that causes dielectric breakdown. The calculation of breakdown strength calls for measuring the breakdown voltage of the material under test. The breakdown voltage (U_{br}) is proportional to the electric field strength (E_{br}) only if the field is uniform. Such a field exists between two electrodes, which have the shape of the bodies of revolution; the surface of these electrodes may be described by Rogovsky equations [21].

It is common practice to use electrodes of a simple shape in the form of discs with rounded edges or as spheres; the field produced between such electrodes is very nearly uniform under certain conditions in a uniform field.

$$E_{br} = \frac{U_{br}}{t} \quad \ldots \qquad 3.1$$

where, t is the thickness of the material. Thus, the determination of break down voltage allows calculation of dielectric strength with measure of the thickness of the specimen at the point of rupture. The dielectric strength is expressed in volts per mil (0.001 in) or volts per millimeter.

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

There are several factors affecting dielectric breakdown strength. In general, the breakdown voltage tends to decrease with increasing electrode area. Geometry and the material of the electrodes also affect the results. Such factors are

- Specimen thickness
- Temperature
- Amount of moisture
- Time of voltage application
- Extent of ageing
- Frequency of current

Dielectric strength determinations are used to determine uniformity of the material and the manufacturing process. Although such determinations are not adequate for design purposes, they do give some relative indication of amount of insulating material that will be required to support a certain voltage level. Flexible plastics characterized by high dielectric and mechanical strengths in thin sections are useful as insulating taps.

Technologies to produce advanced composites with elastomers, foams, thermoset and thermoplast matrix materials are shown in Tables 3.6 - 3.8.

Measurements

The tensile strength (IS: 11298-Pt-2-87) and flexural strength (ASTM D-790-92), electric strength (IEC-243-Pt-1-88) and volume resistivity (ASTM D-257-92) measurements were made on a Universal Tensile Testing Machine, Model No. 1185 at a speed of 50mm/min, a high voltage tester (Automatic Electric-Mumbai) in air at 27^{O}C by using 25/75mm brass electrodes and a Hewlett Packard high resistance meter at 500 V DC after charging for 60 sec, respectively. Each test was carried out in duplicate and average value is used. Test specifications for all the composites are reported in Table-3.9. Mechanical (tensile and flexural strengths) and electrical (electric strength and volume resistivity) properties of the composites are presented in Tables-3.10 and 3.11, respectively.

Table-3.6: Technologies to produce advanced composite structures [22]

Elastomer matrix	Pallet	Wet impregnation	Long fiber	Short fiber	Prepreg	Casting
Polyurethane		Yes	Possible	Yes	No	Yes
Rubber matrix		Yes	Possible	Yes	No	Yes
Foam matrix	**Pallet**	**Wet impregnation**	**Long fiber**	**Short fiber**	**Prepreg**	**Casting**
Polyurethane		Yes	Yes	Yes	No	Yes
Phenolic		Yes	Yes	Yes	No	Yes
Acrylic		No	No	No	No	Yes
PVC		No	No	Yes	No	Yes
Silicone		No	No	No	No	Yes
Polyethylene		No	No	Yes	No	Yes

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22. EADS – Report of Composites Atlantic Limited, 2000.

Table-3.7: Technologies to produce advanced composite structures with thermoset matrix [22]

Techniques	Pallet	Wet impregnation	Long fiber	Short fiber 1- 50 m/m	Prepreg with thermoset resin	Sheet transformation
Hand lay up autoclave		Yes	Yes	No	Yes	
Lay up resin and fiber by projection		Yes	No	Yes	No	
Molding with press		Yes	Yes	Yes	Yes	
Hand lay up with oven		Yes	Yes	Yes	Yes	
Compression molding BMC		No	No	Yes	Yes	
Compression molding SMC		No	No	Yes	Yes	
Filament winding		Yes	Yes	No	Yes	
RTM (Resin transfer molding)		Yes	Yes	No	No	
Pultrusion		Yes	Yes	No	Yes	
Rotomolding		Yes	Yes	Yes	No	
Braiding		Yes, After braiding	Yes	No	Yes	
Continuous lamination		Yes	Yes	No	Yes	Yes

Table-3.8: Technologies to produce advanced composite structures with thermoplast matrix [22]

Thermoplastic matrix & fiber	**Pallet**	**Wet impregnation**	**Long fiber**	**Short fiber**	**Prepreg with thermo-plastic resin**	**Sheet transformation**
Thermoplastic injection	Yes	No	No	Yes	Yes	
Filament winding		No	Yes		Yes	
Pultrusion		No	Yes		Yes	
Compression molding	Yes	No	Yes	Yes	Yes	Sheet
Vacuum forming		No	No	Yes	Yes	Sheet only
Braiding		No	Yes	No	Yes	
Continuous press lamination		No	Yes	Yes	Yes	Yes
Extrusion	Yes	No	No	Yes	Yes	Sheet

Table-3.9: Test specification data of the composites

Types of composites	Breaking load, N	Span length, mm	Puncture voltage, kV	Resistance, ?
Jute	54-114	65	5.4	4.2×10^{10}
Treated jute	78.8-94.2	52	3.6	5.4×10^{10}
Glass	296-402	58	6.1	1.2×10^{10}
Glass-jute	287-397	48	5.4	2×10^{10}
Jute-WH	41-84	42	2.9	1.4×10^{11}
Jute-RH	33-37	55	7.2	2.8×10^{10}
Jute-CH	96-118	60	6.4	3.8×10^{10}
Jute-JH	94-157	50	3.6	9×10^{10}
Glass-WH	93-99	47	4.9	1.3×10^{10}

Table - 3.10: Mechanical properties of the composites

Types of composites	Thickness, mm	Tensile strength, MPa	Flexural strength, MPa
Jute	3.67	36	19
Treated jute	3.30	24	30
Glass	1.69	250	251
Glass-jute	3.08	23	119
Jute-WH	3.17	17	29
Jute-RH	3.25	10	14
Jute-CH	3.39	12	48
Jute-JH	3.34	12	41
Glass-WH	1.88	31	23

Table - 3.11: Electrical properties of the composites

Types of composites	Electric strength, kV/mm	Volume resistivity, ohm.cm
Jute	1.41	2.14×10^{12}
Treated jute	0.92	2.7×10^{12}
Glass	3.21	2.86×10^{12}
Glass-jute	1.72	1.25×10^{12}
Jute-WH	1.21	1.15×10^{13}
Jute-RH	2.11	1.60×10^{12}
Jute-CH	1.89	2.09×10^{12}
Jute-JH	1.29	6.35×10^{12}
Glass-WH	1.15	1.96×10^{12}

Comparative mechanical properties of composites

Mechanical and thermal properties of composites depend on the fiber content, fiber orientation, additives like filler, compatibilizers and impact modifiers and mode of testing [23, 24]. The tensile strength (s) of the composites was calculated by measuring the load value (W) at the point of breaking and cross sectional area (A).

$$s = \frac{W}{A} \qquad \ldots 3.2$$

Flexural strength of the composites was determined according to Eqn. 3.3:

$$\text{Flexural strength} = \frac{1.5FL}{wt^2} \qquad \ldots 3.3$$

From Table-3.10 it is clear that the tensile strength decreased by 33%, while flexural strength increased by 57.9% on alkali treatment and malinization. The decrease in tensile strength and flexural strength after alkali treatment and malinization are due to change in chemical composition of the fibers. Alkali treatment can remove natural and artificial impurities and produce rough surface tropography. In addition, alkali treatment leads to breakdown of fiber bundle in smaller fibers. This increases the surface area of available for wetting by the matrix resin [25, 26].

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23. D. Ray, B. K. Sarkar, S. Das and A. K. Rana, " Dynamic mechanical and thermal analysis of vinylester resin matrix composites reinforced with untreated and alkali-treated jute fibers" Comp. Sci. and Tech., **62**, 911-920, 2002.
24. A. K. Rana, B. C. Mitra and A. N. Banerjee, "Short jute fiber – reinforced polypropylene composites: Dynamic mechanical study ", J. Appl. Polym. Sci., **71**, 531-539, 1999.
25. A. K. Bledzki and J. Gassan, "Composites reinforced with cellulose based fibers ", Prog. Polym. Sci., **24**, 221-257, 1999.
26. Y. Li, Y. Mai and L., Ye, "Sisal fiber and its composites: a review of recent developments ", Compos. Sci. and Technol., **60**, 2037-2051, 2000.

Comparative mechanical properties of glass and glass-jute composites

Tensile strength of glass-jute, glass and jute composites are reported in Table 3.10, from which it is observed that tensile strength of sandwich glass-jute composite has decreased, while flexural strength has improved substantially in comparison to jute and it is almost half of the glass composite indicating improvement in stiffness of the hybrid composite.

Mechanical properties of natural fiber composites are greatly influenced by adhesion characteristics of the fiber-matrix interface and that can be improved by compatibilizer. Hybridization of natural fibers with stronger and more corrosion resistant synthetic fibers such as glass or carbon fibers can also improve the stiffness, strength and moisture resistant behavior of the composite. Good fiber-matrix adhesion is required for effective stress transfer from matrix to fiber whereby maximum utilization of fiber strength in the composite is achieved. The decrease in tensile strength of hybrid glass-jute composite is attributed probably due to resin curing and poor glass-matrix-jute interface adhesion. Moreover tensile strength and stiffness of jute fiber (442 MPa and 55.5 MPa) are much lower than glass fiber (3400 MPa and 72 MPa), which may also change in tensile and flexural properties. Jute content (56.3 wt %) wt is 5.4 times higher than glass content (10 wt %) in the sandwich composite. Because of different nature of fibers and their strength, fiber content, matrix-fiber adhesion and nature of matrix attributed decrease in tensile strength and improvement in flexural strengths. Fairly good tensile strength of glass-jute composite indicated its usefulness for low load bearing applications. Tensile strength of glass-jute composites decreased due to poor glass-jute interfacial adhesion but flexural strength improved because of incorporation of strong and stiff glass fibers.

Comparative mechanical properties of hybrid composites

In hybrid composites, the performance depends on the selection of the constituent materials especially matrix materials and fiber loading. Jute fibers are mainly made up of cellulose, polyols and lignin. Jute fibers are hygroscopic and possess low wettability mainly due to hydroxyl groups of cellulose and lignin [27], while biomass mainly consists of cellulose and lignin to a lesser extent as compared to jute.

The tensile strength of hybrid composites: Jute-WH, Jute-CH, Jute-JH and Jute-RH has decreased by 53-72% as compared to Jute composite (Table -3.10). The decrease in tensile strength is mainly due to random orientation of sandwiched fibers indicating discontinuous stress transfer upon hybridization. Comparatively Jute-WH composite has almost two times tensile strength as compared to Jute-CH, Jute-JH and Jute-RH hybrid composites. Out of four biomass fibers selected, WH is found more effective in stress transfer as compared to remaining three husks. In glass and Glass-WH composites tensile strength of Glass-WH composite is only 12.4% than glass composite and flexural strength is 12.34% than glass composite. Thus, orientation of fiber, nature of fiber and nature of supporting mat for sandwiching biomass husk are very important in determining tensile properties of fabricated hybrid composites.

Flexural strength is the resistance of material under the bending mode. In a pure bending mode a rectangular beam made of homogeneous material undergoes maximum tensile stress on one surface through the thickness to maximum compressive stress on the other. If the tensile and compressive moduli are equal, the stress becomes zero at the midpoint of the thickness where tension reaches zero before compression starts building up at the midpoint.

Flexural strength of Jute-CH, Jute-JH, Jute-WH and Jute-RH and Glass-WH is shown in Table-3.10 from which it is clear that the flexural strength of Jute-WH (52.6%), Jute-JH (94.5%) and Jute-CH (152.6%) has increased to a greater extent upon hybridization, while for BCF-Jute-RH (26.3%) it is decreased.

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27. J. Gassan and A. K. Bledzki, “The influence of fiber-surface treatment on the mechanical properties of jute-polypropylene composites”, Composites, **28**, 1001-1011, 1997.

Flexural strength depends on matrix material and under tension the strength of composite is almost entirely provided by the reinforcement. The increase in the flexural strength indicates increase in resistance to shearing. The flexural property of hybrid fiber reinforced plastics is not only dependent on the hybrid composition but also on the arrangement of the material layers. The decrease in the flexural strength is the evident of reduction in the stiffness of the material. Thus tensile strength has decreased but the flexural strength has improved by 53-153% except Jute-RH composite. Under identical conditions except nature of husks selected, hybrid composites except Jute-RH possess excellent flexural strength as compared to Jute composite.

Comparative electrical properties of composites

Comparative electrical properties of untreated and treated jute composites

Electrical properties of the composites rely on area and geometry of the electrodes, sample thickness, temperature, humidity, time of voltage application, extent of ageing, frequency of current, impurities, degree of resin cure, nature of reinforcing agents, etc. Electric strength and volume resistivity of the composites were calculated by measuring puncture voltage and volume resistance, respectively.

From Table 3.11, it is clear that electric strength decreased by 34.7% and volume resistivity increased by 26.2%. The decrease in electric strength after alkali treatment and malinization are due to chemical composition, crystallinity, strength and surface modification of the fibers.

Comparative electrical properties of glass-jute composites

Electric strength and volume resistivity data of glass-jute hybrid composite along with glass and Jute composites are reported in Table 3.11. It is evident that electric strength of glass-jute hybrid composite is intermediate of glass and jute composites, while volume resistivity is almost half of the pure composites indicating considerable decrease in insulating property upon hybridization. Electric strength of material depends upon number of factors namely area and geometry of the electrodes, sample thickness, temperature, humidity, time of voltage application, extent of ageing and frequency of current, impurities, degree of resin cure, nature of reinforcing material, etc. The degree of cure and nature of reinforcing glass and jute fibers caused change in electric strength and volume resistivity of glass-jute composite.

Comparative electrical properties of hybrid composites

Comparative dielectric breakdown strength and volume resistivity of hybrid composites along with jute composite are shown in Table- 3.11 from which it is clear that there is no much change in dielectric breakdown strength is observed between jute composite and hybrid composites: Jute-CH, Jute-RH, Jute-WH and Jute-JH but volume resistivity of Jute-WH and Jute-JH composites has increased respectively 437.4% and 196.7% as compared to jute composite, while for Jute-CH and Jute-RH it is decreased by 2.3 to 25.2%. In Glass-WH composite volume resistivity is decreased 31.46% and dielectric breakdown strength is decreased 64.17% than glass composite.

Dielectric breakdown voltage of the material decreases with increase in electrode area and results are affected by geometry and the material of the electrodes. Factors like sample thickness, temperature, humidity, time of voltage application, extent of ageing and frequency of current inversely affect the breakdown strength. In present case, Jute - WH and Jute - JH composites possess superior volume resistivity as compared to Jute-RH and Jute-CH composites.

SECTION-III: CHEMICAL RESISTANCE AND BOILING WATER STUDY OF COMPOSITES

Chemical resistance study

It is sometimes stated that a given material has a good chemical resistance or alternatively the material may be stated to be poor or excellent in this respect. The resistant to chemicals (acid, alkali, salt and water) is determined by change in weight method. The key role plays for chemical resistance is diffusion and permeability of reagents through composite specimen. The diffusion of a reagent through the polymer mass swells the composite and changes the dimensions. The reagent deeply penetrates and eventually disintegrates the mass. Diffusion through a composite occurs by the small molecules passing through voids and other gaps between the polymer molecules.

The chemical stability of a plastic is evaluated by change in the mass, linear dimensions and mechanical properties of material in the state of stress free state and also by the tendency to splitting in the stress strain state after the samples have been exposed to reagents for a definite length of time [28, 29].

The chemical resistance of a polymeric material is as good as it's the weakest point. If it is intended that a polymeric material is to be used in the presence of a certain chemical environment then each ingredient must be unaffected by the chemical. In the case of a polymer molecule, its chemical reactivity will be determined by the nature of chemical groups present [30].

In commercial polymeric materials there are a comparatively limited number of chemical structure to be found and it is possible to make some general observations about chemical reactivity. Ester, amide and carbonate groups are susceptible to hydrolysis when such groups are present in the main chin. Their hydrolysis results in a reduction of molecular weight. When hydrolysis occurs in a side chain, the effect on molecular weight is usually insignificant. The presence of benzene rings adjacent to these groups may offer some protection against hydrolysis except, where organophilic hydrolysis agents are employed.

Hydroxyl groups are extremely reactive e.g. cellulose molecule and poly (vinyl alcohol). The –OH groups are highly susceptible to H-bonding. Benzene rings in the skeleton and on side groups can be subjected to substitution reactions [30].

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28. R. B. Seymour, "Treatise on Analytical Chemistry", 3, 341-391, Inter Science Publication, New York.
29. O. M. Dazornovasky, B. M. Tareev, I. O. Forsilova and L. I. Lybimov, "Testing and Electrical Insulating Materials", Mir Publishers, Moscow, 1982.
30. J. A. Brydson, "Plastics Materials"- 6th Ed. Butterworth-Heinemann Ltd. 1995.

Several other reagents such as oleic acid, methanol, benzene, toluene, aniline, mineral oil, transformer oil, olive oil, kerosene, gasoline, turpentine, 1% soap solution and other substances are being also used for specialized chemical resistances.

All polymers and composites absorb moisture in humid atmosphere and when immersed in water. Natural fibers absorb more moisture as compared to synthetic fibers. The effect of absorbed moisture is to degrade the properties especially tensile strength [31]. Recommended reagents for chemical resistance of plastics are presented in Table-3.12.

The most common methods used to determine chemical resistance are described below.

(1) Chemical resistance by change in mass method

According to this method the change in the mass of a test specimen after exposure of a chosen reagents at temperature of 20^0, 40^0, 60^0 and 100^0 is determined. The test duration is dependent on the time required for plastic specimen to attain sorption, equilibrium, or to loose stability in the test medium.

The specimens are weighed after 12, 24, 36, 48, 96 and 128h, and then after every seven days. The specimen that has passed the test may either loose or gain in mass. The chemical resistance of the material is determined by averaging the change in mass of several specimens. The test specimens for molded or extended plastics are in the form of a disc (50mm in diameter and 3mm in thickness). The specimens are cut from laminated or sheet plastics, the end faces of laminated specimens are coated with same binder as used in the production of material in questions. In case of rod samples, a length of rod should be 50 mm and diameter should be 50 mm. A reagent is taken in an amount of 8 ml per cm^2 surface area of plastic sample free from extractable substance and it is 20 ml per cm^2 surface area of extractable plastic sample.

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31. T. A. Collings, “Moisture Absorption – Fickian diffusion kinetics and moisture profiles”, in Handbook of Polymer-Fiber Composites, F. R. Jones, Ed., Longman Scientific and Technical, UK, pp 366-371, 1994.

Table-3.12: The reagents recommended for testing chemical resistance of plastics

Reagent	Concentration (%)
Sulfuric acid (1.84 g/cm^3)	3, 30, 100
Nitric acid (1.41 g/cm^3)	10, 40, 100
Hydrochloric acid (1.19 g/cm^3)	10, 100
Chromic acid	40
Acetic acid	5,100
Citric acid	10
Sodium hydroxide	1, 10, 60
Sodium chloride	3,10
Sodium hypochlorite	10
Sodium carbonate	2, 20
Hydrogen peroxide	3, 30
Ethyl alcohol	50, 96
Phenol	5

After loading the specimens in a bath, the reagent is mixed at least once in a day. After every seven days, specimens are removed from reagents one at a time, washed, wiped, dry and weighed. A percentage increase or decrease in the mass of a specimen is determined according to Eqn. 3.4:

$$?\,M = \frac{\left(M_2 - M_1\right)}{M_1} X100 \qquad \ldots 3.4$$

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

(2) Chemical resistance by change in linear dimensions

This method is based on change in linear dimensions of specimen after prolonged exposure to a reagent. The form, size and number of specimens and quantity of reagent must remain the same as in the change in mass method. Before testing, the thickness of central portion of the disc and two mutually perpendicular diameters of each specimen are measured after every seven days. The specimens are taken out from the bath, washed, wiped with a cloth and checked for dimensions at the same places. A change in any of the linear dimensions in percent (%) is determined according following equation.

$$?\,l = \frac{\left(l_2 - l_1\right)}{l_1} X100 \qquad \ldots 3.5$$

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

(3) Chemical resistance by change in mechanical properties

This method is based on stability of mechanical properties of plastics under prolonged exposure to reagent. The form, dimensions and number of specimens of plastic materials are chosen in compliance with the standard. After exposure to a reagent, the specimens are washed, wiped and tested for one or two characteristic properties such as tensile strength, flexural strength, impact strength, hardness, percentage elongation at break and mechanical stress in bending that causes a deflection equal to 1.5- fold thickness of specimen.

CHEMICAL RESISTANCE STUDY OF UNTREATED AND TREATED JUTE COMPOSITES

The moisture absorption by the composites was assumed by capillary action of the fiber ends towards the surface of the composites. Preweighed samples were immersed in distilled water, 10% HCl and 10% NaCl solutions at room temperature. Samples were periodically taken out from the solutions, wiped with tissue papers on both the sides, reweighed and re-immersed in the solutions. The process was repeated till equilibrium reached. For untreated and treated jute composites, percentage weight change with the passage of time (t) is shown in Figs. 3.1-3.3 for water, acid and salt, respectively. It can be seen from Figs. 3.1-3.3 that moisture uptake becomes nearly constant after 60, 179 and 174 h for untreated jute composites and 56, 47 and 98 h for treated jute composites in water, salt and acidic environments, respectively. The equilibrium moisture content and time for water, salt and acid environments are recorded in Table 3.13.

It is clear from Table 3.13 that % moisture uptake increases with time and remains almost constant at equilibrium for untreated fibers under specified environments. In case of MA treated fibers, % moisture content decreases with time and remains almost constant after reaching equilibrium for water and acid environment but in case of salt, it increases, reaches maximum and then decreases with time and becomes constant.

It is clear from Figs.3.1-3.3 that the drastic reduction in moisture uptake is due to replacement of hydrophilic –OH groups of jute fibers to water repellent ester groups. The decrease in % moisture uptake might be due to desorption of water, salt and acid. The π-electron of benzene ring and CH=CH of MA form weak H-bonding as compared to H-bonding with polar ester groups.

It is observed that the percentage moisture uptake by untreated jute composites is relatively higher than that of treated one. The malinization process is successfully implemented for jute fibers by maleic anhydride that produces water repellency by partial replacement of hydrophilic –OH groups by ester groups. It shows excellent moisture protection to composite, even specimens fully immersed in water, acidic and saline environments.

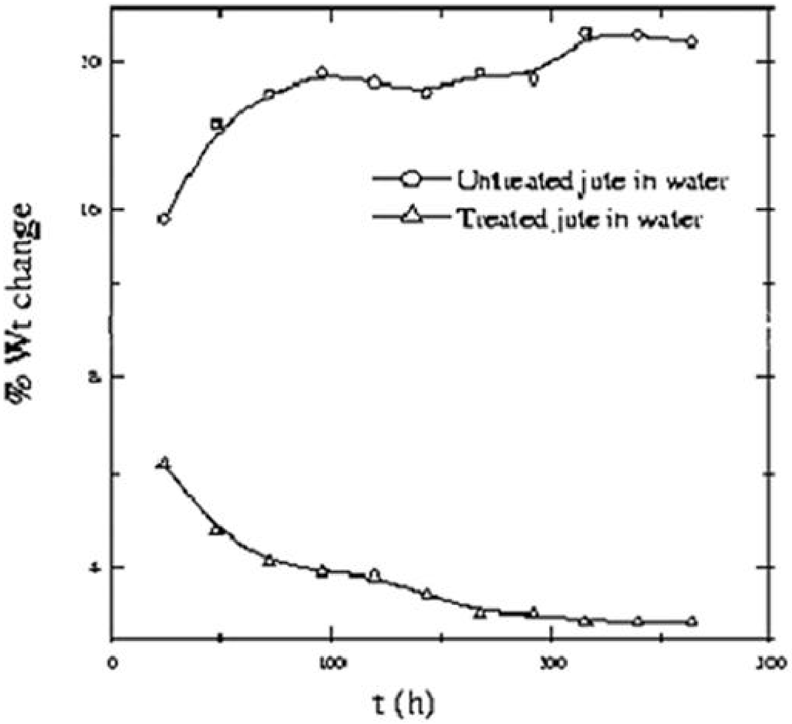

Fig. 3.1 The plots of % wt change with time for untreated and treated jute composites in water at room temperature

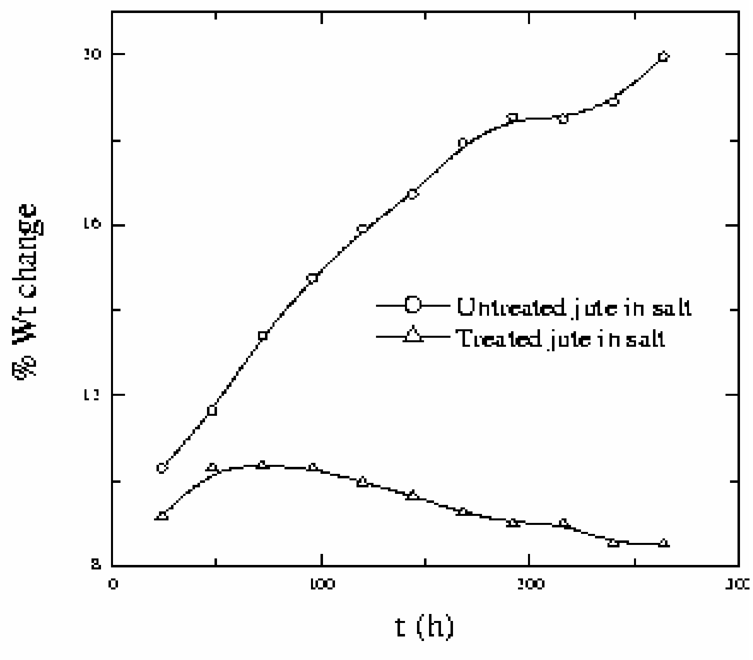

Fig. 3.2 The plots of % wt change with time for untreated and treated jute composites in salt at room temperature

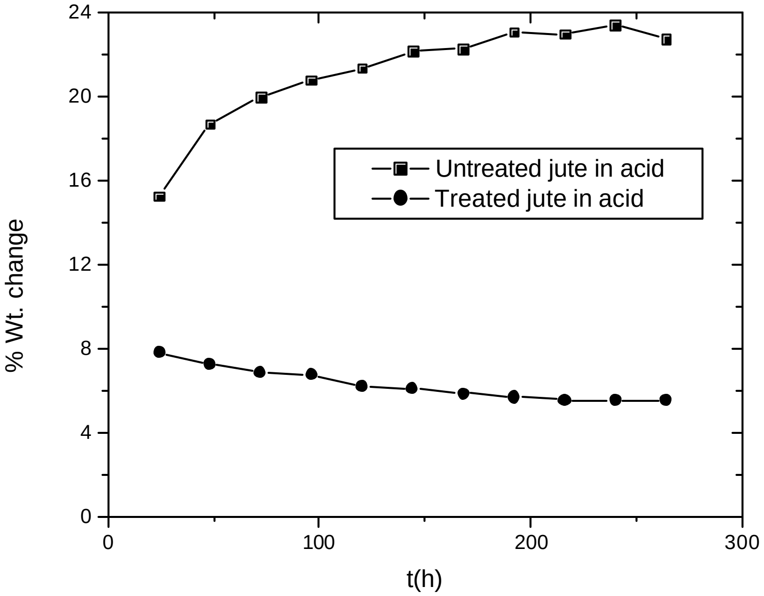

Fig. 3.3 **The plots of % wt change with time for untreated and treated jute composites in acid at room temperature**

Diffusivity (D_x)

With the consideration that moisture plays a significant role in influencing the mechanical behavior, long-term durability of the polymer and polymer matrix composites, we have carried out moisture absorption behavior in the different chemical environments by assuming one-dimensional diffusion only. For one-dimensional moisture absorption in semi-infinite plate exposed on both sides to same moisture environment, the total amount of moisture uptake [9] is given by

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

The moisture content can be determined by weight gain of the material. The percentage moisture content is defined as

$$M = \frac{W_m - W_d}{W_d} \mathbf{x}100 \qquad \ldots 3.6$$

Where M= % moisture content,

W_m = Wt. of moist material and

W_d =Wt. of dry material

Solving diffusion equation for weight of moisture, and rearranging the terms of percentage moisture content, following relation is obtained.

$$M = \frac{4M_m}{h} \sqrt{\frac{t}{p}} \sqrt{D_x} \qquad \ldots 3.7$$

Where M_m= Equilibrium moisture content of the sample,

D_x= Diffusivity and t = time

Diffusivity in a given environment can be determined according to following equation:

$$D_x = p \left(\frac{h}{4M_m} \right)^2 (slope)^2 \qquad \ldots 3.8$$

The diffusivity was determined by determining initial slope of % weight change against square root of time plots, which are shown in Figs. 3.4- 3.6 and reported in Table 3.13.

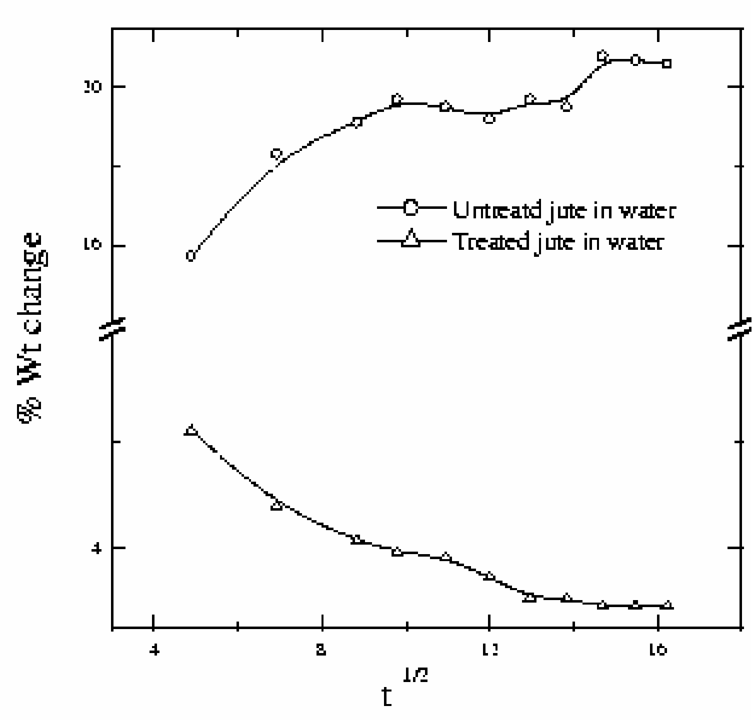

Fig 3.4 **The plots of %weight change against $t^{1/2}$ for untreated and treated jute composites in water at room temperature**

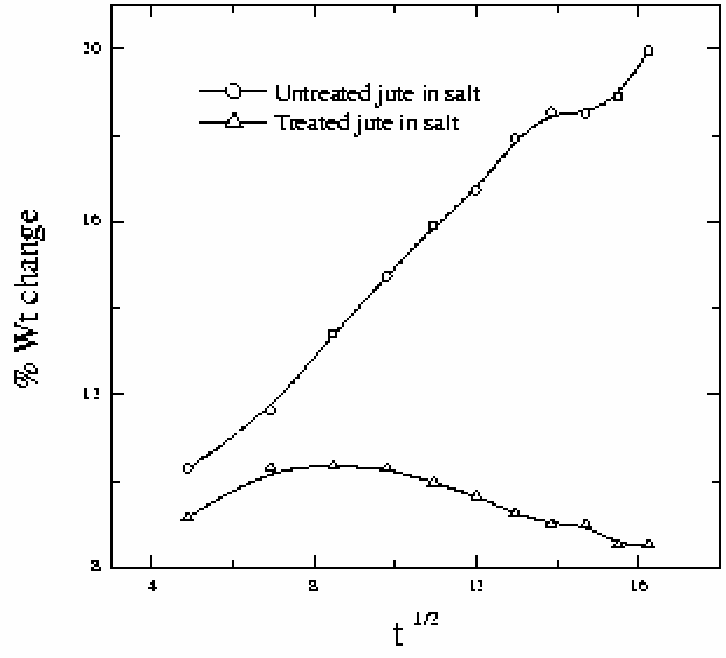

Fig 3.5 **The plots of %weight change against $t^{1/2}$ for untreated and treated jute composites in salt at room temperature**

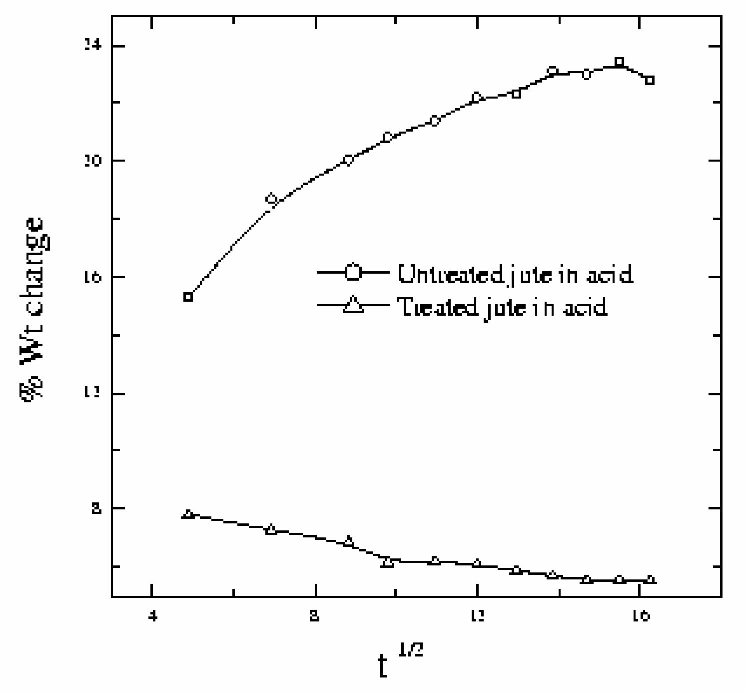

Fig 3.6 **The plots of %weight change against $t^{1/2}$ for untreated and treated jute composites in acid at room temperature**

Table- 3.13: Moisture uptake and diffusivity data of treated and untreated jute composites at room temperature

Properties	**Untreated jute composite**			**Treated jute composite**		
	Water	**Salt**	**Acid**	**Water**	**Salt**	**Acid**
Diffusivity (D_x) 10^{-13} m^2/s	3.04	7.45	1.76	0.56	2.01	0.81
% Moisture content at equilibrium	19.5	18.4	23.1	4.2	10.3	6.3
Time (h) for equilibrium Moisture	60.84	179.56	174.24	56.25	47.61	98.01

From Table 3.13, it is clear that diffusivity has decreased considerably on esterification of fibers.

On the basis of experimental findings it is concluded that malinization of jute fiber composites resulted in drastic reduction in moisture uptake and diffusivity in water, acid and alkali environments.

CHEMICAL RESISTANCE STUDY OF GLASS-JUTE COMPOSITE

The variation of moisture uptake against $\sqrt{t}$ for Glass-Jute-BCF composite in different environments is shown in Fig.3.7 from which it is evident that moisture uptake is maximum within 24h and then slightly decreased and reached equilibrium after 36h. The equilibrium time and equilibrium moisture content are recorded in Table-3.14. It is also evident from Fig.3.7 that moisture uptake is doubled in acidic environment as compared to salt environment. From Table 3.14, it is clear that drastic reduction in equilibrium time is observed but no much change in equilibrium moisture content is observed except salt environment, where considerably moisture content is reduced. The observed moisture content is due to the presence of hydrophilic group in jute fiber and uncured BCF. The π electrons of benzene ring form weak H-bonds with resin and OH groups of Jute. Hydrophilic groups undergo solvation in acid and salt environments. More solvation is expected in acidic environments as compared to salt and pure water environments. The work on glass composite showed that there was little moisture uptake (1.2 to 6.2% in water, -0.2 to -0.9% in 10% HCl and 6.9 to 8.9% in 10% NaCl) over a period of one month due to silane treatment of glass fibers [32].

The diffusivity of glass-jute hybrid composite in different environments was determined and is reported in Table 3.14. From which it is clear that diffusivity is maximum in water and minimum in acidic environment indicating effect of ionic hydration on diffusion rate.

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32. J. K. Joshi, S. T. Gadhia, and P. H. Parsania, “Physico-chemical properties of self cured bisphenol-C-formaldehyde and its glass composites”, J. Polym. Mater., **21**, 197-204, 2004.

Table- 3.14: Moisture uptake data of Glass-Jute-BCF hybrid composite

Property	Reagent		
	H_2O	10% NaCl	10% HCl
Glass-Jute-BCF			
% Equilibrium moisture content	18.02	11.87	24.24
Equilibrium time, h	36	36	36
Diffusivity, Dx, $10^{-11} m^2/s$	11.42	3.41	1.23

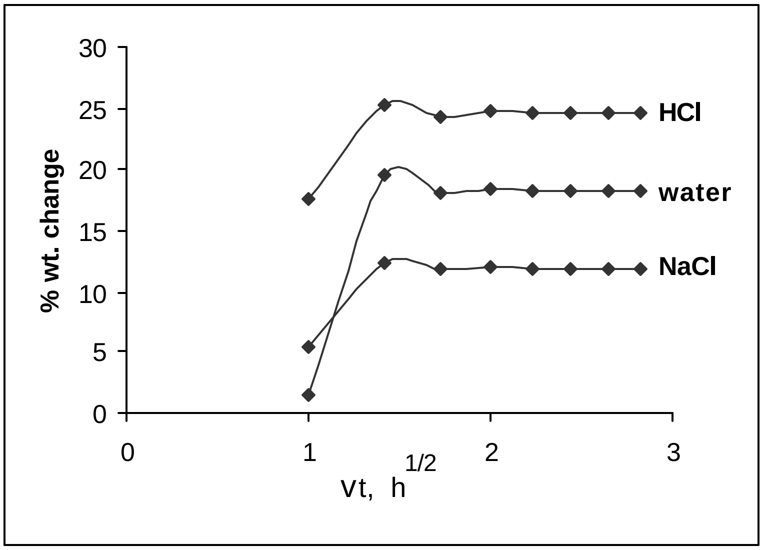

Figure 3.7 The plots of % wt change with time for glass - jute composite in water, 10% salt and 10% acid at room temperature

Due to solvation apparent molecular size has increased causing lowering in diffusivity. Moreover diffusivity is substantially increased upon hybridization. Thus, hybrid composite has much lower equilibrium moisture uptake time and much higher diffusivity in studied environments as compared to jute composite which is reported in Table 3.13.

BOILING WATER STUDY

Boiling water study of composite is useful for understanding the interfacial adhesion of the matrices and matrix materials. Effect of temperature on water sorption was carried out at boiling temperature of water. Preweighed samples were immersed in boiling water. Samples were taken out from the solutions after every one hour, wiped with tissue papers on both the sides, reweighed and re-immersed in the water. The process was repeated till equilibrium reached.

Boiling water study of untreated and treated jute composites

The results of boiling water study of untreated and treated jute composites are shown in Table 3.15 and Figure 3.8. From Table 3.15, it is clear that in untreated jute composite maximum moisture absorption (25.31%) is observed up to 2 h and then it decreased up to 5 h (18.09%) and then remained constant.

Boiling water study of glass and glass-jute composites

Water sorption data for Glass-jute-BCF and Glass-BCF are shown in Table-3.16 and Fig.3.9 from which it is clear that maximum water content (18.26%) in Glass-jute reached within 1 h, decreased up to 14.40% within 2h, further increased up to 15.82% and reached equilibrium after 4 h.

In Glass-BCF water absorption increased up to 4h and reached equilibrium (9.13%). The water absorption behavior of glass-jute-composite is higher than jute composite and lower than glass composite, which indicate their usefulness even in harsh acidic and saline environments. The decrease in water absorption with time before saturation level is due to two reasons namely leaching of small molecules and desorption of solvated ions [33].

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33. L. R. Bao and A. F. Yee, “Effect of temperature on moisture absorption in bismaleimides resin and its carbon fiber composites”, **43**, 3987-3996, 2002.

Table- 3.15: % weight change with time for untreated jute and treated jute composites in boiling water

Time , h	Types of composites	
	Untreated jute	Treated jute
1	20.02	14.39
2	25.31	14.56
3	20.25	14.89
4	20.91	16.56
5	18.09	16.69
6	18.10	16.77
7	18.10	16.78
8	18.10	16.80

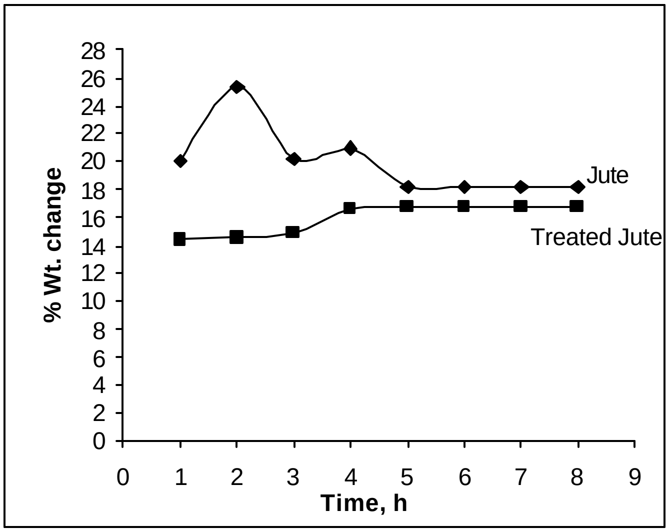


Figure 3.8 The plot of % weight change with time for untreated and treated jute composites in boiling water

Table- 3.16: Table of %weight change with time for glass and glass-jute composites in boiling water

Time , h	Types of composites	
	Glass	Glass-jute
1	8.37	18.26
2	8.54	14.40
3	8.76	15.82
4	9.15	15.16
5	9.13	15.29
6	9.13	15.27
7	9.13	15.27
8	9.13	15.27

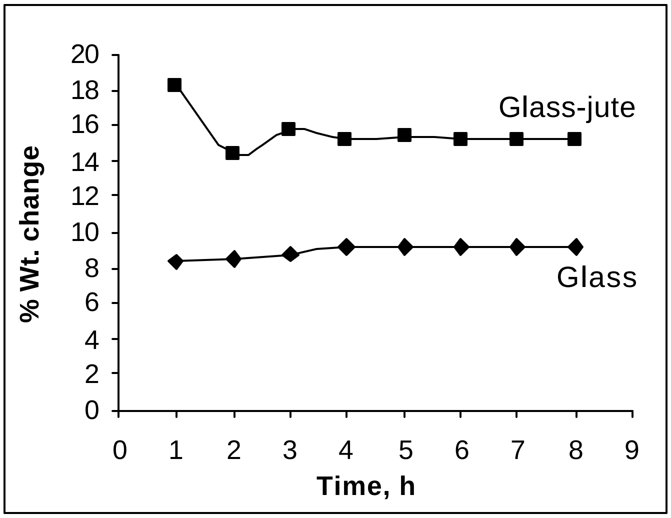
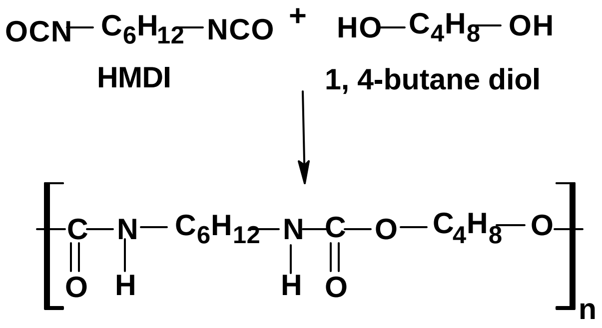


Figure 3.9 The plots of %weight change with time for glass and glass-jute composite in boiling water

This chapter of the thesis describes the up to date literature survey on polyurethane resins and its coating and adhesive applications with thermal and mechanical properties. The synthesis and preparation of the films with their thermo-mechanical analysis are well-documented in this chapter. The density and chemical resistance study of the films are also discussed with the PEG concentration in this study.

SECTION-I: INTRODUCTION

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



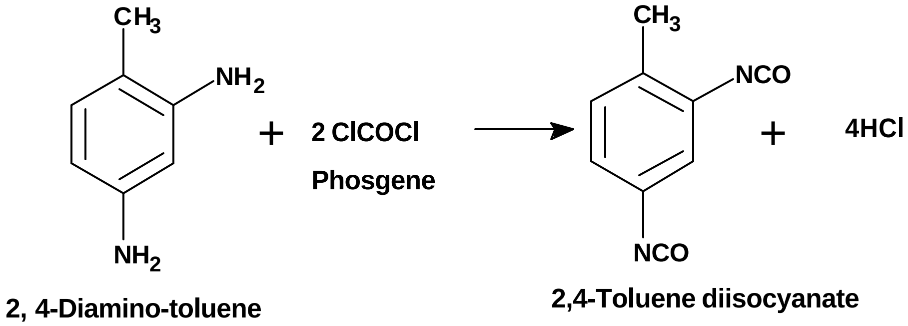
$$OCN-C_6H_{12}-NCO + HO-C_4H_8-OH \longrightarrow \left[-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-C_6H_{12}-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-O-C_4H_8-O- \right]_n$$

(I)

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

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

Polyurethane resins are very unique class of specialized materials, which are used industrially and on trade scale in virtually all sectors. Despite especially relatively high cost, their excellent durability, flexibility and resistance to corrosion, abrasion, water and chemicals make them suitable for range of high performance applications from paper coatings to the protection of equipment in industrial plants [1]. 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 (HDI) are frequently employed. They are prepared by the reaction of phosgene with the corresponding diamines, as shown in Scheme (II).



(II)

Polyurethanes are polymers that contain the urethane (carbamate) structure (-NH-CO-O-). Polyurethanes have revealed an unusual versatility; their chemistry, as well as chemistry of related intermediates (isocyanates among them), has been enormously developed and polyurethanes have one of the widest

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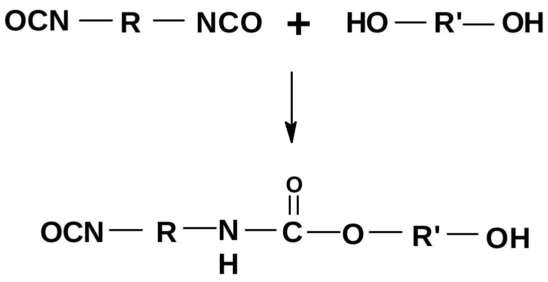
1. V. D. Athawale and K. R. Joshi, "Structure property relationship in polyurethane coatings synthesized from chemoenzymatically modified caster oil", J. Polym. Mater. **21**, 165-174, 2004.

ranges of polymer applications through out the world: Fibers, elastomers, foams, skins, adhesives, coating, etc. [2].

Polyurethane adhesives have developed reputation for reliability and high performance [3]. Polyurethane adhesive is widely used in footwear, packaging, automotive industries and furniture assembly [4].

Polyurethanes have been recognized as superior adhesives for metal bonding since the 1940s [5]. This characteristic of excellent adhesion to metal oxide surfaces has resulted in successful application of urethanes as structure adhesives, as primers for rubber to metal bonding and as vehicles for high performance paints.

The high reactivity of isocyanates with active hydrogens is the basis of urethane synthesis, polymerization proceeds by the reaction of a diisocyanate and diol to form a carbamate (or urethane) linkage (III):



$$\mathrm{OCN-R-NCO + HO-R'-OH} \longrightarrow \mathrm{OCN-R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O-R'-OH}$$

(III)

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2. X. Tassel, D. Barbry and L. Tighzert, "A New blocking agent of isocyanates", Eur. Polym. J., **36**, 1745-1751, 2000.
3. C. B. Vick and E. A. Okkoren, Forest Prod. J. **48**, 71, 1998.
4. S. D. Desai, A. L. Emanuel and V. K. Sinha, "Biomaterial based polyurethane adhesive for bonding rubber and wood joints", J. Polym. Res. **10**, 275-283, 2003.
5. S. Buchan, "Rubber to metal bonding" C. Lockwood, London, 206-211 1948.

The resulting polymer is rich in polar functional groups that are potentially capable of strong interaction with metal oxide surface to provide excellent adhesion [6-8]. In recent decades, a wide variety of PU have been synthesized and studied regarding compatibilization [9-11], miscibility [12], morphology, rheology and dynamic mechanical properties [13] and as well the gel formation [14].

Segmented PUs are regarded as multi-block copolymers of $(AB)_n$ type where A and B represent hard and soft segment repeat units, respectively. Usually, the hard-segment provides physical cross-links through H-bonding and filler like reinforcement to the soft segment, which plays a key role in imparting the

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6. S. S. Voyutski, "Autohesion and adhesion of high polymers", Wiley Interscience, New York, 197-198, 1963.
7. F. H. Sexsmith, Adhesives Age, June, 31-36, 1970.
8. M. M. Chehimi and J. F. Watts, J. Adhesion Sci. Technol. **6**(**3**), 377, 1992.
9. C. P. Papadopoulou and N. K. Kalfoglou, "Comparison of compatibilizer effectiveness for PET/PP blends: their mechanical, thermal and morphology characterization", Polymer. **40**, 905-919, 1999.
10. S. N. Jaisonkar and G. Radhakrishnan, "Effect of compatibilizer on morphology and mechanical properties of TPU/SAN blends", Polym. Eng. Sci. **40**, 621-629, 2000.
11. M. Ulenic-krump, P. Standler and T. Malovosik, Macromol. Symp. **149**, 131-138, 2000.
12. W. Wu, X. L. Luo and D. Z. Ma," Miscibility of the segmented polyurethane blends with chlorinated poly(vinyl chloride)", Eur. Polym. J. **35**, 985-995, 1999.
13. D. D. Jiang and R. F. Storey, "Gel formation between thermoplastic polyurethane and poly (ethylene-co-vinyl alcohol) during blend processing", Polym. Prep. (Am. Chem. Soc. Div. Polym. Chem), **41**, 1217-1224, 2000.
14. W. Y. Chiang and D. M. Ching, "Preparation and characterization of polyurethanes/allyl novolac resin simultaneous interpenetrating network", Eur. Polym. J., **31**, 709-120, 1995.

elasticity to PU materials [15]. The composition, concentration and NCO / OH molar ratio in the hard segment can affect the structure, organization and flexibility of the hard segment, and the segment micro-phase separation and mechanical properties of PU [16, 17].

Therefore the NCO / OH molar ratio is regarded as an efficient way to regulate the morphology and properties of PU s. The hard segment of PU is generally formed in a polyaddition reaction between diisocyanate and multifunctional alcohol or amine with low molecular weight [18].

There are three major types of polyurethane elastomers. One type is based on ether-or ester-type prepolymers that are chain-extended and cross-linked using polyhydroxy compounds or amines; alternately, unsaturated groups may be introduced to permit vulcanization with common curing agents such as peroxides. A second type is obtained by first casting a mixture of prepolymer with chain-extending and cross-linking agents, and then cross-linking further by heating. The third type is prepared by reacting a dihydroxy ester- or ether-type prepolymer, or a diacid, with a diisocyanate such as diphenylmethane diisocyanate and diol; these thermoplastic elastomers can be processed on conventional plastics equipment. In general, urethane elastomers are characterized by outstanding mechanical properties and resistance to ozone, though they may be degraded by acids, alkalis

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15. Z. S. Petrovic and J. Ferglson, “Polyurethane elastomers”, J. Prog. Polym. Sci. **16**, 695, 1991.
16. S. Desai, I. M. Thakore, B. D. Sarawae and S. Devi,” Effect of polyols and diisocyanates on thermo-mechanical and morphological properties of polyurethanes”, Eur. Polym. J., **36**, 711-720, 2000.
17. M. Debowski and A. Ballas, “Cast polyurethane elastomers obtained with N, N'-ethyleneurea and 1, 4-butanediol as chain extenders”, J. Appl. Polym. Sci. **75**, 728-736, 2000.
18. J. Huang and L. Zhang, “Effects of NCO / OH molar ratio on structure and properties of graft-interpenetrating polymer networks from polyurethane and nitrolignin”, Polymer, **43**, 2287-2298, 2002.

and steam. The growth in worldwide consumption in polyurethane is shown in the Table 4.1, which suggests continuing growth of polyurethane consumption.

Zuo et al. [19] have prepared polyurethane prepolymer by a reaction of polyester polyol and 2, 4-toluene diisocyanate and then end-capped with phenol. Soluble polyamide was prepared by two-step synthesis from 2,2'-bis (3,4-dicarboxyphenyl) hexafluoro propane dianhydride and 3,3' diamino- 4, 4' dihydroxy biphenyl. Cast films were obtained from blend solution of PU and PI. Dynamic analysis showed that lower glass transition temperature (Tg) of the films shifts to high temperature with increase of polyamide component.

Shufen et al. [20] have studied on the thermal behavior of polyurethanes. They have reported thermal decomposition mechanism of polyurethane under different environmental conditions, Thermal decomposition and combustion reaction of polyether-polyurethane and polyester-polyurethane in air and nitrogen atmosphere investigated by thermogravimetry analysis. Polyester-polyurethane was found to be more thermally stable than polyether – polyurethane.

Yeganeh et al. [21] have synthesized biodegradable elastomeric epoxy modified polyurethanes based on (?- caprolectone) and poly (ethylene glycol). 1,6-hexamethylene diisocyanate were used for preparation of isocyanate terminated PU, which were subsequently blocked with glycidol to prepare epoxy polyurethane. Optimum degradation rate and mechanical properties were obtained.

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19. M. Zuo and T. Takeichi, "Preparation and characterization of poly (urethane-amide) films prepared from reactive polyamide and polyurethane prepolymer", Polymer, **40**, 5153-5161, 1999.
20. Li. Shufen, J. Zhi, Y. Kaijin, Y. Shuqin and W. K. Chow, "Studies on thermal behavior of polyurethanes", Polymer Plast. Technol. Eng., **45**, 95-107, 2006.
21. H. Yeganeh, M. M. Lakouraj and S. Jamshidi, "Synthesis and properties of biodegradable elastomeric epoxy modified PUs based on poly (?– caprolectone) and poly (ethylene glycol)" Eur. Polym. J., **41**, 2370-2379, 2005.

Table-4.1: World consumption of polyurethanes by end-use market (%)

No.	Different application fields	Use in %
1	Furniture and mattresses	39
2	Automotive	16
3	Building	13
4	Refrigeration	7
5	Textile	6
6	Coating	7
7	Shoe	4
8	Other	8

Interpenetrating Polymer Network (IPN) is an important parameter for the adhesive strength. IPN is defined as combination of two polymer networks where atleast one polymer is synthesized or crosslinked in the presence of other. As physical blends and copolymerization the IPN is another way to combine two different polymers. It has been reported that polymeric materials with improved mechanical properties can be obtained via IPN structures [22-24].

IPNs form a special class of polymer blend in which the polymers are generally in a network structure. IPNs have especially known because of their unusual properties, mainly enhancement of tensile strength. This property enhancement is attributed to increased cross-linked density or due to permanent physical change entanglement in the IPNs [25].

Sung et al. [26] have studied the interpenetrating polymer network of 2-hydroxy ethyl methacrylate terminated polyurethanes (HPU) and polyurethanes (PU) with different ether type polyols, which prepared by solution polymerization. By this study they reported that compatibility of polymers in IPN formation depends on molecular weight of prepolymers. Water absorption of the IPNs was found to be mainly determined by the hard to soft segment ratio of materials. The maximum tensile strength occurred at 25 wt% HPU content for all the IPN systems.

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22. Y. C. Chou and L. J. Lee, Polym. Eng. Sci. **35**, 976, 1995.
23. A. Sam, D. J. Hourston, K. Manzoor and D. F. Williams, ”The stability of poly (ether urethane)/ polydimethyl siloxane inter penetrating polymer network”, J. Appl. Polym. Sci., **55**, 733, 1995.
24. P. Nayak, D. K. Mishra, D. Parida, K. C. Sahoo, M. Nanda, S. Lenka and P. L. Nayak, “Polymers from renewable resources: 1% interpenetrating polymer networks based on caster-oil polyurethane poly (hydroxyl ethyl methacrylates): Synthesis, chemical, thermal and mechanical properties”, J. Appl. Polym. Sci., **63**, 671, 1997.
25. D. S. Lee, D. S. Jung, T. H. Kim and S. C. Kim, J. Membr. Sci., **60**, 233, 1991.
26. T. Sung, T. Hseieh, K. H. Hseieh, G. P. Simon and C. Tiu, “Interpenetrating polymer networks of 2–hydroxyethyl methacrylate terminated polyurethanes and polyurethanes”, Polymer, **40**, 3153, 1999.

Li and Mao et al. [27] have studied on the damping properties of epoxy resin/polyurethane (EP/PU) semi-interpenetrating polymer networks (IPNs) by dynamic mechanical analysis (DMA) method. They reported that the semi IPNs have excellent damping properties at ordinary temperature when the weight composition of EP/PU was 70/30, tensile strength and elongation at break was maximum at this ratio. Applied to the cavitation corrosion resistant coating, the semi-IPNs show good cavitation corrosion resistance.

Bharadwaj et al. [28] have prepared polyurethane elastomers from caster-oil based polyol, poly (ethylene glycol) (PEG) of various molecular weights (200, 400 and 600) and toluene diisocyanate in the form of transparent sheets.

Rozman et al. [29] have studied the effect of isocyanate / glycol ratio, glycol type, and glycol mixture on impact strength, dimensional stability and thermal properties by using different molecular weight poly ethylene glycol and poly propylene glycol. The impact strength, dimensional stability and thermal behavior were investigated. The study revealed that as NCO / OH ratio was increased, impact strength increased. Thermal behavior was predominantly influenced by PPG 400.

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27. Y. Li and S. Mao, "Study on the properties and application of epoxy resin /polyurethane semi- interpenetrating polymer networks", J. Appl. Polym. Sci., **61**, 2059-2071, 1996.
28. V. Bharadwaj, K. Somani and S. Kansara, "The effect of chain length of polyethylene glycol properties of caster-oil based polyurethane elastomers", J. Macromol. Sci.- Pure Appl. Chem., A **39**, 115-129, 2002.
29. H. D. Rozman, G. S. Tay and A. Abubakar, "Oil palm empty fruit bunch- PU composite: The effect of isocyanate/glycol ratio, glycol type and glycol mixture on impact strength, dimensional stability and thermal properties", Polymer-Plast. Technol. Eng., **42**, 811-821, 2003.

Krol et al. [30] have developed a method for synthesis of urethane oligomers and linear polyurethanes with isocyanate and hydroxyl end groups arranged alternatively. 2,4–TDI, 2,6–TDI and 1,4–butanediol were used as the feedstock materials and polymerization process was carried out in THF solution at constant concentration. Complex mixtures of diisocyanate and hydroxyl compounds were obtained, which were then utilized as parent materials at further stages of the process. The mixture of urethane oligomers were produced where the molecular weights were gradually higher and molecular weight distribution was wider and wider.

Thermo-viscoelastic properties of phenolic resin / polymeric isocyanate binder systems were reported by Bakhtiyarov and Overfelt [31]. Thermo-viscoelastic properties of phenolic resin/polymeric isocyanate binder systems (i.e., ISOCURE Parts I and II) were reported. The effects of blend composition and the reaction between the binders on these properties of the systems were also considered in the study. The viscous properties of binders and their blends were measured using computer-controlled rotational viscometers (Brookfield HBDV-II + viscometer and HAAKE rotovisco 12 rheometer in the cone-and-plate mode). The elastic properties of the phenolic urethane polymer (the blend composition) were measured by means of a modified jet thrust technique based on measuring the thrust of a liquid jet. The viscosity of the blends increases both with time and with an increasing Part I content and may reach comparatively high values at high values of either parameter. This behavior was explained as a result of the rubbery nature of the phenolic urethane polymer, which was produced as a product of reaction between Part I and Part II. The use of the jet thrust method allowed determination of the relaxation time of various blends at different shear rates.

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30. P. Krol and B. Pilchpitera, “Study on the synthesis of urethane oligomers as intermediate products for the production of linear polyurethanes”, Eur. Polym. J. **37**, 251-262, 2001.
31. S. I. Bakhtiyarov and R. A. Overfelt, “Thermo-viscoelastic properties of phenolic resin / polymeric isocyanate binder systems”, Int. J. of Thermophysics, **23**, 221-229, 2002.

Morgan [32] has reported the study of fibers from polyurethanes based on halogen-substituted bisphenols. Fibers were prepared on an experimental scale by wet and dry spinning from eight, nonelastomeric polyurethanes based on halogen-substituted bisphenols. The fibers had properties suited to clothing textile uses. They were examined primarily for their potential in wash and wear fabrics. The fibers had moderate water absorption, low shrinkage in hot water, modest lowering of tensile properties under wet conditions, high tensile and work recoveries, and good stability to ultraviolet light. The polyurethanes from piperazines and 2,2-bis (4-hydroxy-3,5-dichlorophenyl) propane bischloroformate had unusually high thermal transitions and good solubility combined with ease of orientation and crystallization in fiber form. Fibers from the 2-methylpiperazine and homopiperazine urethanes were converted to fabrics. These fabrics exhibited a silk like handle; good wash wrinkle recovery, resistance to soil and bleach, stability to ironing at 200°C, and very low flammability.

Chen et al. [33] have reported a new method namely frontal polymerization, which was used by them for epoxy resin/ polyurethane hybrid networks synthesis. Frontal polymerization was thermally ignited at one end of the tubular reactor, and the resultant hot fronts propagated throughout the reaction vessel. Once initiated, no further energy was required for polymerization to occur. The dependence of the front velocity and front temperature on the catalyst concentration was thoroughly investigated. The samples were characterized with a Fourier transform infrared spectrometer, thermogravimetric analysis, and a scanning electron microscope. EP/PU hybrid networks synthesized by FP have the same properties as those synthesized by batch polymerization, but the FP method requires significantly less time and lower energy input.

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32. P. W. Morgan, “Fibers from polyurethanes based on halogen-substituted bisphenols”, J. Appl. Polym. Sci., **40**, 2037-2048, 1990.

33. S. Chen, Y. Tian, L. Chen and T, Hu, “Epoxy resin/polyurethane hybrid networks synthesized by frontal polymerization”, Chem. of Materials, **18**, 2159-2165, 2006.

Narayan et al. [34] have synthesized the polyurethane of polyesters and its characterization thermally and mechanically. In their study they were reported the synthesis of hydroxylated polyester (HP) based polyurethane polyols containing internal carboxyl group with different diisocyanates. These polyurethane polyols were partly acetoacetylated with ethyl acetoacetate to incorporate ß-ketoester in the polyurethane polyol backbone. The synthesized polyols were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance, and differrential scanning calorimetry. Polyurethane polyols and their acetoacetylated cousins were used to develop PUDs. Particle size of the reactive PUDs was evaluated by a particle size analyzer. PUDs were crosslinked with hexamethoxy methyl melamine and their film properties were studied by dynamic mechanical and thermal analyzers and thermogravimetric analyses. The effects of different diisocyanates and acetoacetylation on the stability of reactive dispersion and properties of the crosslinked films were evaluated.

A review on structures and moisture permeability of polyurethane films was reported by and Shibaya et al. [35]. In this study, moisture permeable segmented polyurethane films with different content of polytetramethyleneglycol (PTMG) and polyethyleneglycol (PEG) as soft segment were used. Three parameters of C_1, C_2 and higher order term ?H calculated by Mooney-Rivlin plots in the stress-strain relationship were measured. It was clarified that these mechanical parameters had relation with structure of films. Higher order term ?H and hydrogen bond concentration of urethane group by FTIR measurement decreased with increasing

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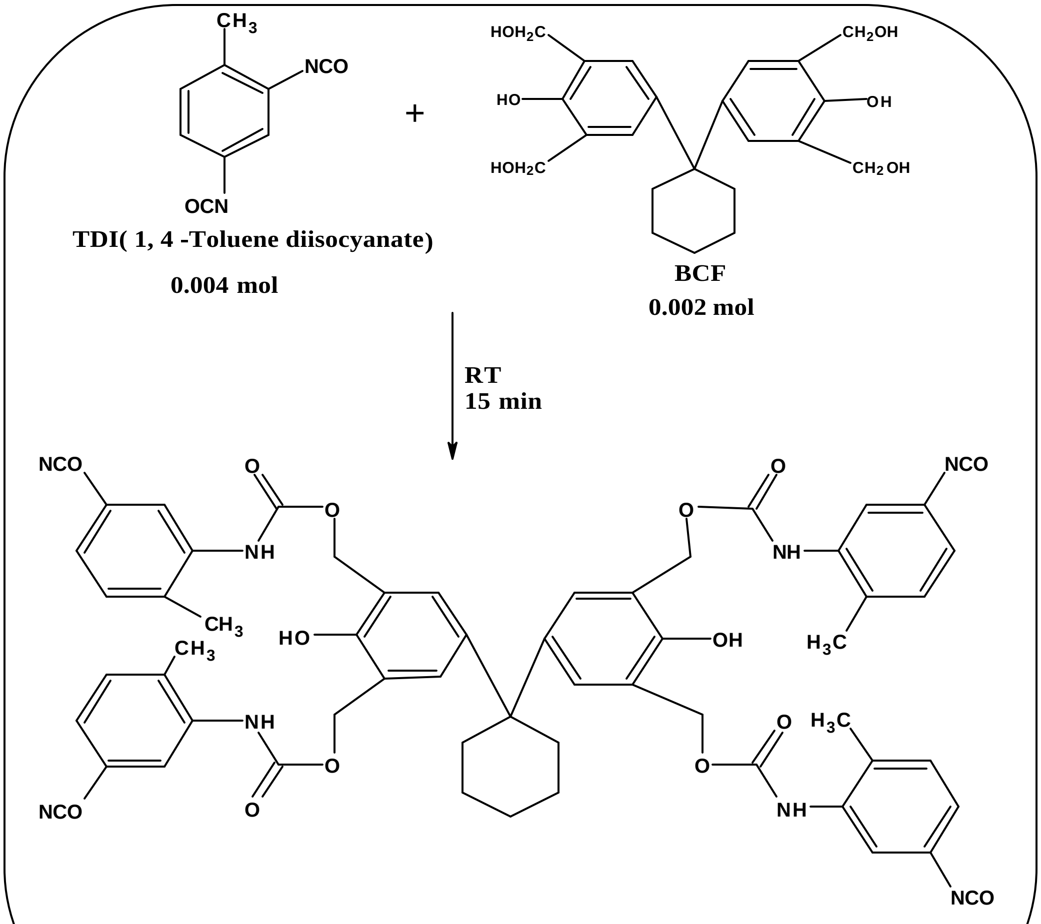
34. R. Narayan, D. K. Chattopadhyay, B. Sridhar, K. V. S. N. Raju, N. N. Mallikarjuna and T. M. Aminabhavi, “Synthesis and characterization of crosslinked polyurethane dispersions based on hydroxylated polyesters”, J. Appl. Polym. Sci., **99**, 368-376, 2006.
35. M. Shibaya, H. Dobashi, Y. Suzuki, H. Ishihara, M. Enomoto, N. Yoshihara and T. Kotani, “Structures and moisture permeability of polyurethane films”, J. Text. Machinery Soc. Japan, **58**, 51-59, 2005.

PEG content in soft segment. That is to say, aggregate structure of hard segment decreased with increasing PEG content. Low PEG content samples showed transverse orientation in relation to aggregate structure of hard segment at initial state of elongation process. Transverse orientation has correlation with magnitude of aggregate structure. In the case of soft segment, degree of molecular restraint evaluated by dynamic mechanical analysis decreased with increasing PEG content. Aggregate structure grows through hydrogen bond of urethane group in hard segment. Also, it was clarified that aggregate structure was affected by soft segment and its outgrowth was inhibited.

SECTION-II: SYNTHESIS OF POLYURETHANE RESIN

(I) Synthesis of BCF-TDI based polyurethane (Scheme-I) and preparation of its film

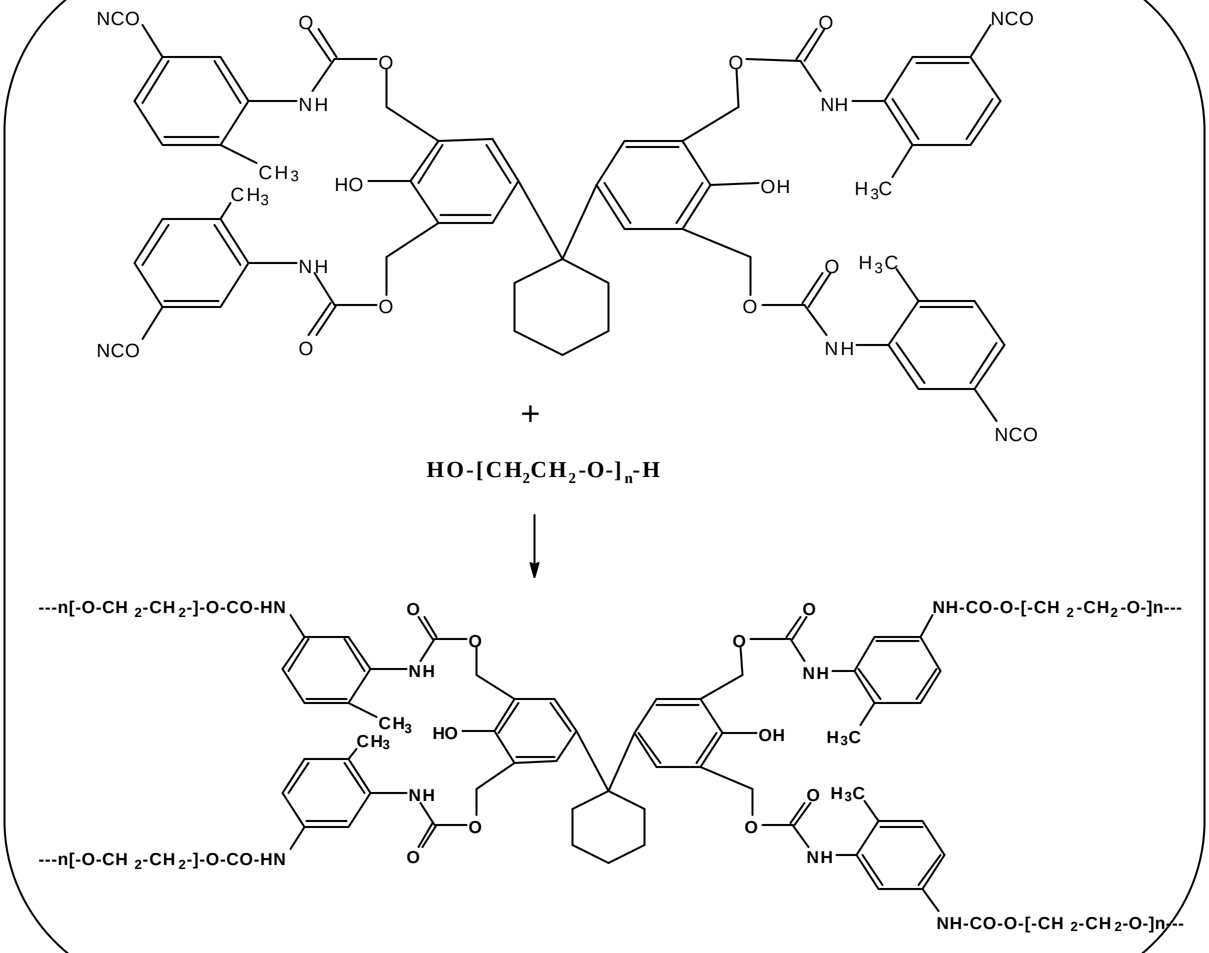
Into a 250ml beaker, 0.002mol (0.776g) BCF was dissolved in 15ml methyl ethyl ketone (MEK) at room temperature. To this solution 0.004 mol (0.696g) TDI in 5ml MEK was added and the resultant solution was stirred manually for 15 min and poured into a leveled 15cm x 15cm glass mold. The solution was allowed to dry with a controlled evaporation of MEK at room temperature. After 24 h, the film was found brittle and hard. In order to improve its elasticity, an attempt has been made by copolymerizing it with PEG-200.



Polyurethane of BCF (Scheme - I)

(II) Synthesis of BCF-TDI-PEG-200 copolyurethanes and preparation of their films

Into a 250 ml beaker, 0.002mol (0.776g) BCF was dissolved in 15ml MEK at room temperature. To this solution 0.005mol (0.870g) TDI in 5ml MEK was added and the resultant solution was stirred manually for 15 min and to this pre polyurethane, 0.001/0.002 mol PEG-200 in 5ml MEK was added drop wise with stirring. After completion of the PEG-2OO addition, the mixture was stirred for 10 min and poured into a leveled 15cm x 15cm glass mold. The solution was allowed to dry with controlled evaporation of MEK at room temperature. After 24 h, the film was removed from the mold. When PEG-200 content in co polyurethane exceeds 0.002mol, the film itself breaks into pieces. The films are hereafter designated as BPT-1 and BPT-2, respectively for 0.001mol and 0.002 mol PEG-200 in the films.



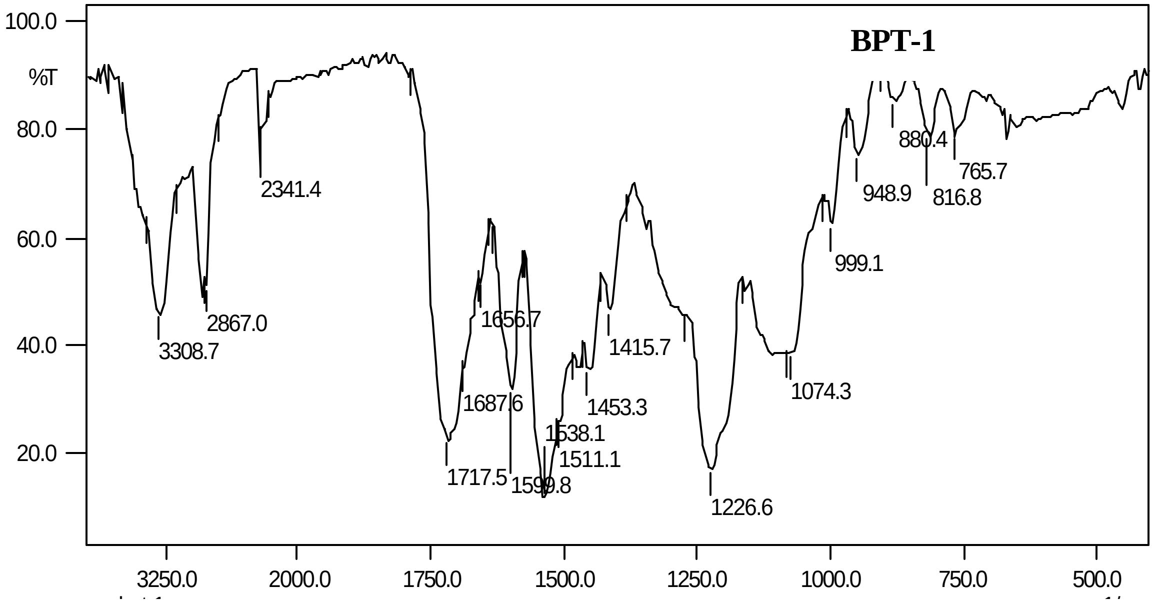
Co polyurethane (Scheme-II)

SECTION–III: SPECTRAL CHARACTERIZATION OF POLY URETHANE RESINS

This section of the chapter includes IR spectral data of the polyurethane resins.

Information about the structure of a molecule could frequently be obtained from its absorption spectrum. The masses of the atoms and the forces holding them together are of such magnitudes that usual vibrations of the organic molecules interact with electromagnetic radiations to absorb and radiate in the IR region.

IR (KBr pellet) of BPT-1 and BPT-2 were scanned on a Shimadzu FTIR-8400 spectrometer over the frequency range from 4000-400 cm^{-1}. The IR spectra of the polyurethane resins are shown in Fig.4.1. The characteristic absorption bands of polyurethanes (BPT-1 and BPT-2) besides the normal modes of alkane, alicyclic and aromatic groups are reported in Table 4.2. From Fig 4.1, it is clear that the absorption peak due to urethane stretching has increased with PEG-200 content in the co polymer indicating conversion of more number of OH groups into urethane groups.



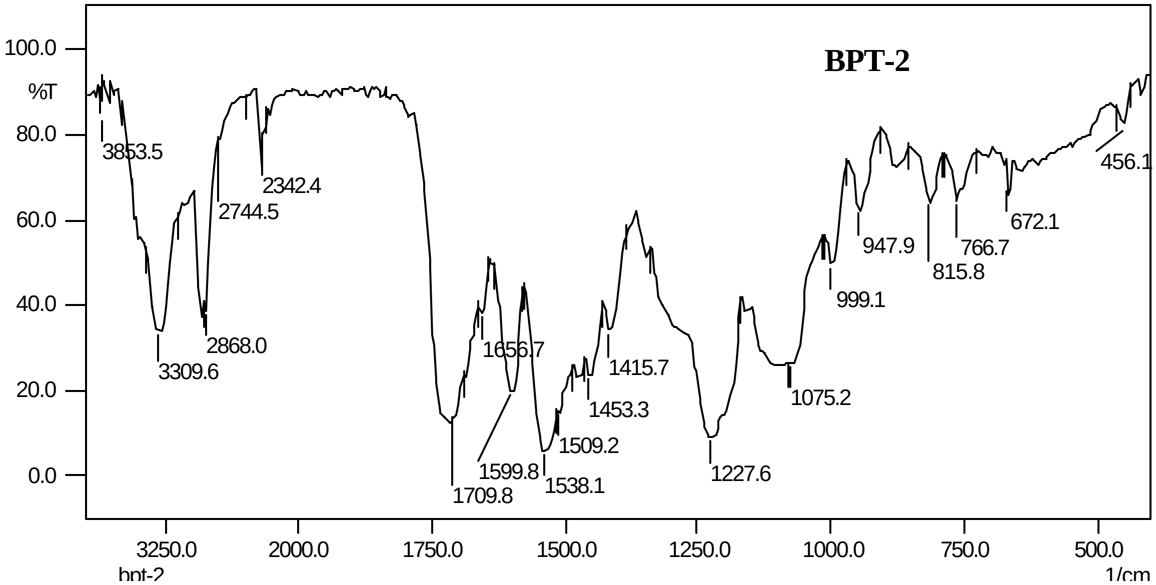
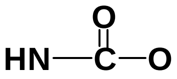
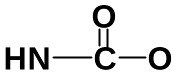


Figure 4.1 IR (KBr pellet) spectra of BPT-1 and BPT-2

Table-4.2: The characteristic IR absorption frequencies of polyurethane resins

Resin	Absorption frequency, cm^{-1}	Type
BPT-1	3308.7	-NH and -OH str.
	1717.5	 $HN-\overset{\overset{O}{\|}}{C}-O$ **str.**
	1226.6	C = O str.
BPT-2	3309.6	-NH and -OH str.
	1709.8	 $HN-\overset{\overset{O}{\|}}{C}-O$ **str.**
	1227.0	C = O str.

SECTION - IV: DENSITY MEASUREMENTS OF POLYURETHANE FILMS

A vast majority of polymers are constituted from small number of different atoms and it is possible to calculate the intrinsic volumes of polymer repeat units from the atomic radii and bond lengths. The density, specific volume and molecular mass are useful in evaluation of various thermodynamic properties of the simple as well as polymeric materials [36-38]. These data are most useful for the average distance between macromolecular chains and the extent of crystallinity in polymers.

THEORETICAL CALCULATION OF THE DENSITY

The density of the polymer can be calculated from the knowledge of the structural aspects. According to Slonimskii et al. [39] the density of the polymer may be expressed as:

$$? = \mathbf{K.M} \Big/ \mathbf{N_A S ? V} \qquad \ldots 4.1$$

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

$$\mathbf{K} = \mathbf{K_{int}} \Big/ \mathbf{K_{true}} = \frac{\mathbf{N_A S ? V_i}}{\left(\mathbf{M} / \mathbf{?} \right)} \qquad \ldots 4.2$$

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36. H. F. Mark, N. C. Gaylord and N. F. Bikales, "Encyclopedia of Polymer Science and Technology", Vol 12, Willey Inter science, New York, 1970.
37. C. Tanford, "Physical Chemistry of Macromolecules", John Willey and Sons, Inc. New York, 1961.
38. V. R. Govarikar, N. V. Vishvanathan and J. Sreedhar, "Polymer Science", Willey Eastern Ltd., 1986.
39. G. L. Slonimskii, A. A. Askadskii and A. I. Kitaigorodkii, Polym. Sci. USSR, A-**12**(**3**), 556, 1970.

Determination of density by floatation method

The densities of BPT-1 and BPT-2 films were determined by a floatation method by using CCl_4-n-hexane system at room temperature. In six different wide mouth stoppered test tubes, a small piece of film and about 5ml CCl_4 were placed and n-hexane was added drop wise with shaking till the film remained suspended throughout and allowed to equilibrate at room temperature for 24 h. The densities of the resultant mixtures were determined by usual method. The average of six measurements and standard deviation from mean value were determined for both the films. Generally physical properties of the polyurethanes largely depend on chain length and content of soft and hard segments [40].

The observed densities of BPT-1 and BPT-2 are 1.2069 ± 0.0034 and 1.1539 ± 0.0002 g/cm^3, respectively. From the observed density values, it is clear that the density has decreased with increase in PEG-200 (increasing amount of soft segment) composition in the copolyurethane film. This is mainly due to increase in intrinsic volume of the copolyurethane. Homo polyurethane has a compact network structure, while copolyurethanes have comparatively less compact structure because of incorporation of PEG-200, which decreases the packing density of the copolymer chains.

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40. S. Ghosh and N. Krishnamurti, “Preparation and characterization of UV-curable polyurethane methacrylate cationomers and their use as adhesives”, Polym. Plast. Technol. Eng., **40**, 539-547, 2001.

SECTION – V: THERMO-MECHANICAL AND ELECTRICAL PROPERTIES OF POLYURETHANE FILMS

Thermal data of materials provide wealth of informations on physico-chemical changes occurring in the system during heating. Polyurethane films are analyzed by TGA/DSC at the heating rate of 10^{o}C / min in an N_2 atmosphere. The glass transition temperature, thermal stability and kinetic parameters of the polyurethane films were determined and discussed. The tensile strength, electric strength and volume resistivity of polymer films were determined according to standard test methods and interpreted in terms of PEG-200 concentration, degree of resin cure, etc.

Mechanical and electrical properties of polyurethanes

Material properties associated with elastic and inelastic reactions to an applied force that is called mechanical properties. The mechanical properties of polymers are the foremost requirement for a designer. Mechanical and electrical properties are very useful for end use applications. Tensile data of polymers are useful for purpose of engineering design and understanding the characteristics of the materials. Electrical properties of materials are useful in predicting the relative insulation quality characteristic of material selection for specific properties in combination, to evaluate the effect of material composition and environment.

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

Most applications of polymers need load-bearing capacity. The geometrical responses to loading lead to a wide range of mechanical properties grouped under stress-strain properties, visco-elasticity and failure properties. These properties are in turn largely determined by the polymer structure (molecular weight, cross-linking, branching, segmental structure and morphology) and the nature of extent of compounding when characterizing the mechanical behavior of a polymeric system, external conditions like temperature, loading rate and environment must be considered [41, 42].

The mechanical behavior of a polymer is divided into three main groups (I) elastic (II) plastic and (III) brittle. The same sample can behave as brittle, tough or rubber-like above or below the glass transition temperature. Slow rates of testing will stimulate stiffer molecules and hardener properties. The mechanical tests are classified as impact, tensile, flexural, hardness, etc. on the basis of applied deforming stress. Among the mechanical properties tensile strength, thermal expansion, chemical resistance, conductivity, which determine the suitability of a plastic for mechanical application.

Mechanical and electrical properties of polymers also depend on temperature, humidity, loading condition, rate of loading, morphology, molecular architecture, molecular weight, fillers, impurities, geometry of electrodes, electrode material, sample thickness, structure and presence of polar groups in the polymer chain, etc [43, 44].

For electrical parameters that must be studied to ascertain electrical insulation characteristics of plastic materials are volume and surface resistivity, dielectric constant, dissipation factor, dielectric strength and arc and track resistance. Today high expectations from polymers not only as insulators but even as conductors have been met with the development of electro-conductive polymers like polyaniline, polyvinyl pyridine, polypyrrole and polyacetylene.

The mechanical properties of plastics can be broadly classified as short-term, long term and surface properties. The short-term properties are measured at a constant rate of stress or strain in different modes like tension, compression,

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41. A. Krause, A. Lange and M. Erzin, “Plastics Analysis Guide, Chemical and Instrumental Methods”, Harver Pub, New York, 1983.
42. T. R. Crompton, “The Analysis of Plastics”, Pergamon Press, Oxford, 1984.
43. F. W. Billmeyer, “Textbook of Polymer Science”, 3rd Edn., John Willey and Sons. New York, 1994.
44. A. B. Mathur and I. S. Bhardvaj, “Testing and Evaluation of Plastics”, Allied Publishers Pvt. Ltd., New Delhi, 2003.

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

Choi et al. [45] have reported preparation and characterization of conductive polyurethane films. In this study, conductive polyurethane (PU) films were prepared by the condensation of poly (propylene glycol) (PPG), toluene 2,4-diisocyanate, and 3-methylthiophene (3-MT) under various preparation conditions. The effects that the reaction time and temperature have on the morphology and surface free energy were investigated by scanning electron microscopy (SEM) analysis and contact angle measurements, respectively. The mechanical properties, such as tensile strength and elongation at break, were also studied. The conductivity of the composite was as high as 42 S/cm.

Parmar et al. [46] have reported coatings based on epoxy-acrylic-graft-copolymer-modified polyurethane dispersions. The epoxy-acrylic graft copolymers were first modified with ethylene diamine to give amine-terminated blocks, which in turn reacted with isocyanate-terminated prepolymer (prepolymer mixing process) to give modified PUDs. Several experimental sets were prepared with varying compositions. The experimental sets were also prepared using conventional poly (ethylene glycol) blocks and ethylene diamine chain-extenders. The physico-chemical properties and film characteristics of the experimental sets show the dramatic improvement in important mechanical properties of PUDs due to grafting with epoxy-acrylic copolymer blocks.

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45. K. C. Choi, E. K. Lee and S. Y. Choi, "Preparation and characterization of conductive polyurethane films", J. Ind. and Eng. Chem., **11**, 66-74, 2005.
46. R. Parmar, K. Patel, J. Parmar, 'High-performance waterborne coatings based on epoxy-acrylic-graft-copolymer-modified polyurethane dispersions", Polym. Int., **54**, 488-499, 2005.

Kozakiewicz et al. [47] have studied the effect of introducing double bonds and siloxane segments to the polyurethane-urea chain on the properties of polyurethane and polyurethane-acrylic/styrene dispersions. Several properties of dispersions, coatings and films were determined, including particle size, stability, and MFFT (minimum film-forming temperatures) of dispersions, hardness, resistance to water and solvents, adhesion of coatings and mechanical properties, and the glass-transition temperature (T_g) of films. Properties of coatings and films subjected to additional curing were also investigated.

Hill et al. [48] have reported accelerated clearcoat weathering studied by dynamic mechanical analysis. Automotive basecoat/clearcoat (BC/CC) systems of the acrylic polyol/melamine formaldehyde (ACR/MF) type were analyzed by dynamic mechanical analysis (DMA) before and after exposure to QUV. Differences in weathering behavior of films prepared with three widely used poly (isocyanates) are reported. Crosslink density decreased and T_g increased during QUV exposure.

Measurements

Tensile strength (IS: 11298-Pt 2-1987), electric strength (ASTM-D149-92) and volume resistivity (ASTM-D257-92) measurements were done respectively on a Universal Tensile Testing Machine Model No. 1185 at a speed of 50mm/min., a high voltage tester (Automatic Electric- Mumbai) in air at 27^0C and Hewlett Packard high resistance meter at 500 V DC after charging for 60 sec by using 25/75 mm brass electrodes. As films of homo polyurethane of BCF and TDI were hard and brittle and therefore their mechanical and electrical properties are not determined.

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47. J. Kozakiewicz, A. Koncka-Foland, J. Skarzynski, J. W. Sobczak and M. Zielecka, “Studies on the effect of structural parameters on the properties of polysiloxaneurethane dispersions and coatings”, Surface Coat. Inter. Part B: Coatings Transactions, **89**, 31-39, 2006.
48. L. W. Hill, H. M. Korzeniowski, M. Ojunga-Andrew and R. C. Wilson, “Accelerated clearcoat weathering studied by dynamic mechanical analysis”, Prog. In Org. Coat., **24**, 147-163, 1994.

Table-4.3: Tensile, electric strength and volume resistivity of co polyurethane films

Sample	Thickness, μm	Tensile strength, MPa	Electric strength, kV/mm	Volume resistivity, Ohm cm
BPT-1	43	34	73.47	2.32×10^{14}
BPT-2	48	22	93.75	2.14×10^{16}

The tensile strength, electric strength and volume resistivity of the copolyurethanes, which contain different proportion of PEG-200, are shown in the Table4.3. From the observed results, it is clear that tensile strength has decreased marginally but electric strength and volume resistivity are improved drastically upon increasing composition of PEG-200 up to 0.002 mol.

Because of hard and brittle nature of homo polyurethane, processing is difficult but this problem can be overcome by copolymerization. In present case processing and other physical properties are improved by copolymerization. Various factors such as temperature, humidity, loading conditions, rate of loading, morphology, molecular architecture, molecular weight, molecular weight distribution, degree of cross-linking, extent of plasticization, fillers, dimensions and geometry of electrodes and electrode material, sample thickness, impurities, extent of ageing, etc affect the mechanical and electrical properties of the material. Hard and brittle nature of polyurethane is due to restricted free rotation of PU chains. Improved physical properties are mainly due to PEG-200, which imparts chain flexibility. BCF moiety imparts chain rigidity due to aromatic nature. When load is applied to the film, flexible moiety throws it away to the rigid part and consequently stress is concentrated at that point resulting in rupture at low load. Comparatively large distances among polar groups in copolyurethane restrict partial charge transfer and hence improvement in electric strength and volume resistivity.

The charge storage involves the alignment of dipoles in a material in the direction of applied electric field. The source of the dipoles is polar groups in the polymer chains, molecular asymmetry, polar additives and partial crystallinity. The charges on capacitors polarize the molecules and as a result charge increases on the surfaces. The volume resistivity mainly depends on the presence of free charges (electrons or ions) and their mobility. Thus, increasing amount of flexible moiety (PEG-200) in copolyurethane resulted in decrease in tensile strength and increase in volume resistivity and electric strength to a greater extent. The mobility of the charge is mainly restricted because of considerably long PEG segments in the copolymer chains. BPT-1 and BPT-2 possess fairly good tensile strength, excellent electric strength and volume resistivity indicating their usefulness as superior insulating materials for coating application.

Thermal analysis of polyurethane films

Most of the studies of polymers are generally carried out with dynamic thermogravimetry. Normally the sample starts losing weight at a very slow rate up to a particular temperature and there after, the rate of loss become large over a narrow range of temperature. After this temperature, the loss in weight level off. TGA curves are characteristic for a given polymer because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at the rates that are function of the polymer structure. The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evaluation of volatile products in the formation of heavier reaction products.

Pyrolysis of many polymers yields TG curves, which follows a relatively simple sigmoidal curve. In such case a weight of sample decreases slowly as reaction begins, then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction gets completed. The shape of the curves depends on the kinetic parameters: reaction order n, frequency factor A and activation energy E_a, the values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation [49, 50].

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49. D. W. Levi, L. Reich and H. T. Lee, Polym. Eng. Sci., **5**, 135, 1965.
50. H. L. Friedman, U. S. Dept. Com., Office. Tech., **24** (1959); C.A. **55**, 26. 511, 1961.

Thermally stable polymers have received extensive interest due to the increasing demands for high temperature polymers as replacements for ceramics and metals in the automotive, aerospace and microelectronics industries.

Chiang et al. [51] have studied the thermal properties of novolac type phenolic resin blended with fullerenol polyurethane and linear polyurethane. Fullerenol polyurethane (C_{60}-PU) and linear polyurethane (linear-PU) modified phenolic resins were prepared in this study. Phenolic resin/C_{60}-PU and phenolic resin/linear-PU blends show good miscibility as a result of the intermolecular hydrogen bonding existing between phenolic resin and PU modifiers. DSC and thermogravimetric analysis methods were used to study the thermal properties of phenolic resin blended with different types of PUs.

Suresh and Kishanprasad et al. [52] have reported the thermal studies of novel polyols from cardanol and developed polyurethanes. Polyols having a range of hydroxyl values (140-265 mg of KOH/g) were prepared, and structure characterization was carried out by spectroscopic techniques. Polyurethanes were formulated by reaction of these polyols with diphenyl methanediisocyanate (MDI) at an NCO/OH ratio of 1, and films were characterized for thermal stability and viscoelastic properties by thermogravimetric analysis (TGA) and dynamic rheometry, respectively. The dynamic mechanical studies show a linear increase of the T_g value with an increase in the hydroxyl value of the polyol. In TGA, when temperatures at 50% decomposition in nitrogen atmosphere are compared, polyurethanes based on diol and glycard indicate a higher thermal stability.

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51. L. Y. Chiang, C. C. M. Ma, S. C. Sung, F. Y. Wang, L. Y. Wang, C. L. Chiang, “Thermal, mechanical, and morphological properties of novolac-type phenolic resin blended with fullerenol polyurethane and linear polyurethane”, J. Polym. Sci. Part B: Polym. Phys., **39**, 2436-2444, 2001.
52. K. I. Suresh, V. S. Kishanprasad, ”Synthesis, structure, and properties of novel polyols from cardanol and developed polyurethanes”, Ind. and Eng. Chem. Res., **43**, 4504-4513, 2005.

Thermal studies of intercross-linked networks based on siliconized polyurethane-epoxy/unsaturated polyester were reported by Prabhu and Alagar [53]. Epoxy and Unsaturated polyester (UP) resins were modified with PU prepolymer and hydroxyl terminated polydimethylsiloxane (HTPDMS) using ?-aminopropyl triethoxysilane (?-APS) and vinyltriethoxysilane (VTES) as silane cross-linkers and dibutyltindilaurate (DBTL) as a catalyst. Aromatic polyamines adduct (A) and aliphatic amine (B) were used as curatives for epoxy and methyl isobutyl ketone peroxide(C) as curative for unsaturated polyester resin. The coating materials were obtained in the form of tough films. The thermal stability of the ICN coatings was studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and compared with unmodified epoxy/UP systems. The introduction of PU into unmodified epoxy/UP coating systems reduces the thermal stability due to the presence of thermally weak urethane linkages whereas, the incorporation of 10wt.% silicone into PU modified epoxy/UP systems improves their thermal stability due to the partial ionic nature, high bond energy and thermal stability of -Si-O-Si- linkage.

Lee et al. [54] have reported the effects of sulfonated polyol on the thermal properties. A polyol containing long sulfonated side chain, designated as PESS, was used to prepare aqueous polyurethane (PU) dispersions through the prepolymer mixing process in this study. The effects of this sulfonated polyol on the properties of the resultant waterborne polyurethanes (WPUs) were studied. When the content of total hydrophilic groups (i.e. sodium sulfonate group of PESS and quaternary ammonium carboxylate group of neutralized dimethylol propionic acid, DMPA) remains unchanged, the WPU dispersion with higher PESS content possesses higher average particle diameter and film decomposition temperature

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53. A. A. Prabhu and M. Alagar, “Mechanical and thermal studies of intercross-linked networks based on siliconized polyurethane-epoxy/unsaturated polyester coatings”, Prog. In Org. Coat., **49**, 236-247, 2004.
54. H. T. Lee, S. Y. Wu and R. J. Jeng, “Effects of sulfonated polyol on the properties of the resultant aqueous polyurethane dispersions”, Colloids and Surfaces A: Physico-chem. and Eng. Asp., **276**, 176-182, 2006.

due to its higher average molecular weight (MW). PESS enhances the antistatic property of the WPU films, which can be used in electronic, wrapping and coating industries. The glass transition temperature of these amorphous films is at about -45°C, irrespective of the PESS/DMPA ratio and hydrophilic group content (HGC).

Experimental

TG and DSC thermograms of BPT-1 and BPT-2 were scanned on a Universal V 2.6 D TA instrument at the heating rate of 10^0C/mm in nitrogen atmosphere over the temperature range from 35^0 to 600^0C.

Results and discussions

TGA has been proven a versatile analytical tool to assess thermal stability and kinetic parameters of polymers. Thermal methods are useful for plant engineers in designing safe and economical plants and process for manufacture of various chemicals. DSC methods are quite straight forward. The physico-chemical properties of resins are dependent upon mainly on the extent of network structure.

TG and DSC thermograms of BPT-1 and BPT-2 are presented in Fig. 4.2 to 4.5. From Fig.4.2 and 4.3, it is clear that f BPT-1and BPT-2 have followed three steps degradation kinetics. Initial decomposition temperature(T_0), temperature of 10% decomposition(T_{10}), temperature of 50% decomposition(T_{50}), decomposition range and % weight loss involved in each step are reported in Table 4.4, from which it is clear that both the polyurethanes have comparable thermal properties and followed same degradation mechanism. They are thermally stable up to about 100^oC. The observed three step degradation is due to different weak linkages in the polyurethane chains i.e. ether and urethane, which degrade selectively with the formation of free radicals. These free radicals may further undergo variety of reactions such as chain cleavage, branching, rearrangement, cross linking, etc. In case of BPT-1, the first step weight loss (2.5 %) in the temperature range 100 to 124^oC is due to moisture content The second step weight loss (54.0%) in the temperature range 181-307^oC is due to decomposition of urethane linkage leading to the formation of CO_2, alcohols, amines, aldehyde, CO, etc. and third step weight loss (19.5%) in the temperature range 307 to 436^oC is due to complete decomposition of polyurethanes. Similarly in case of BPT-2, the first step weight

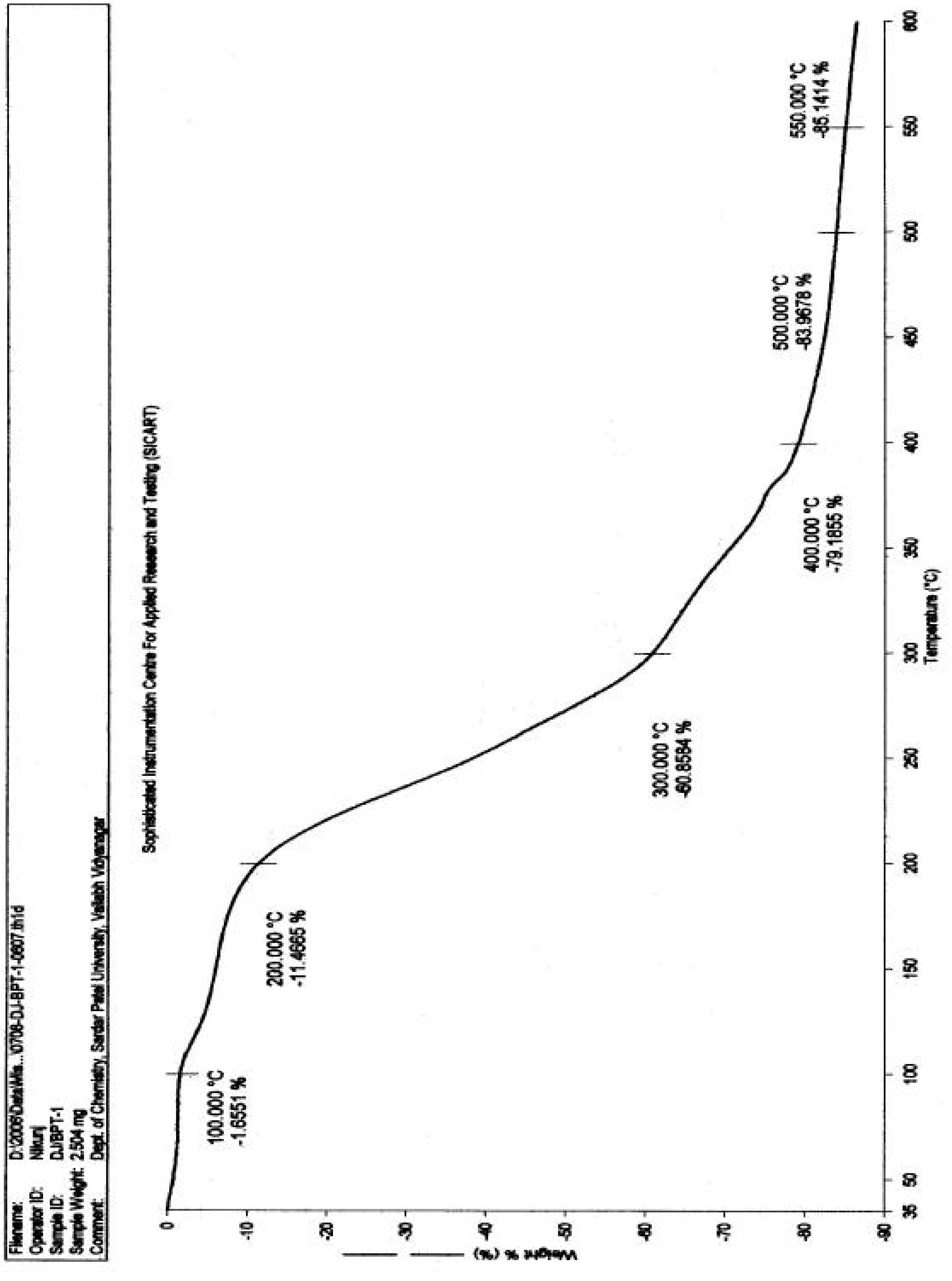

Fig. 4.2 TG thermogram of BPT-1 at the heating rate of 10^{o}C/min in an N$_2$ atmosphere

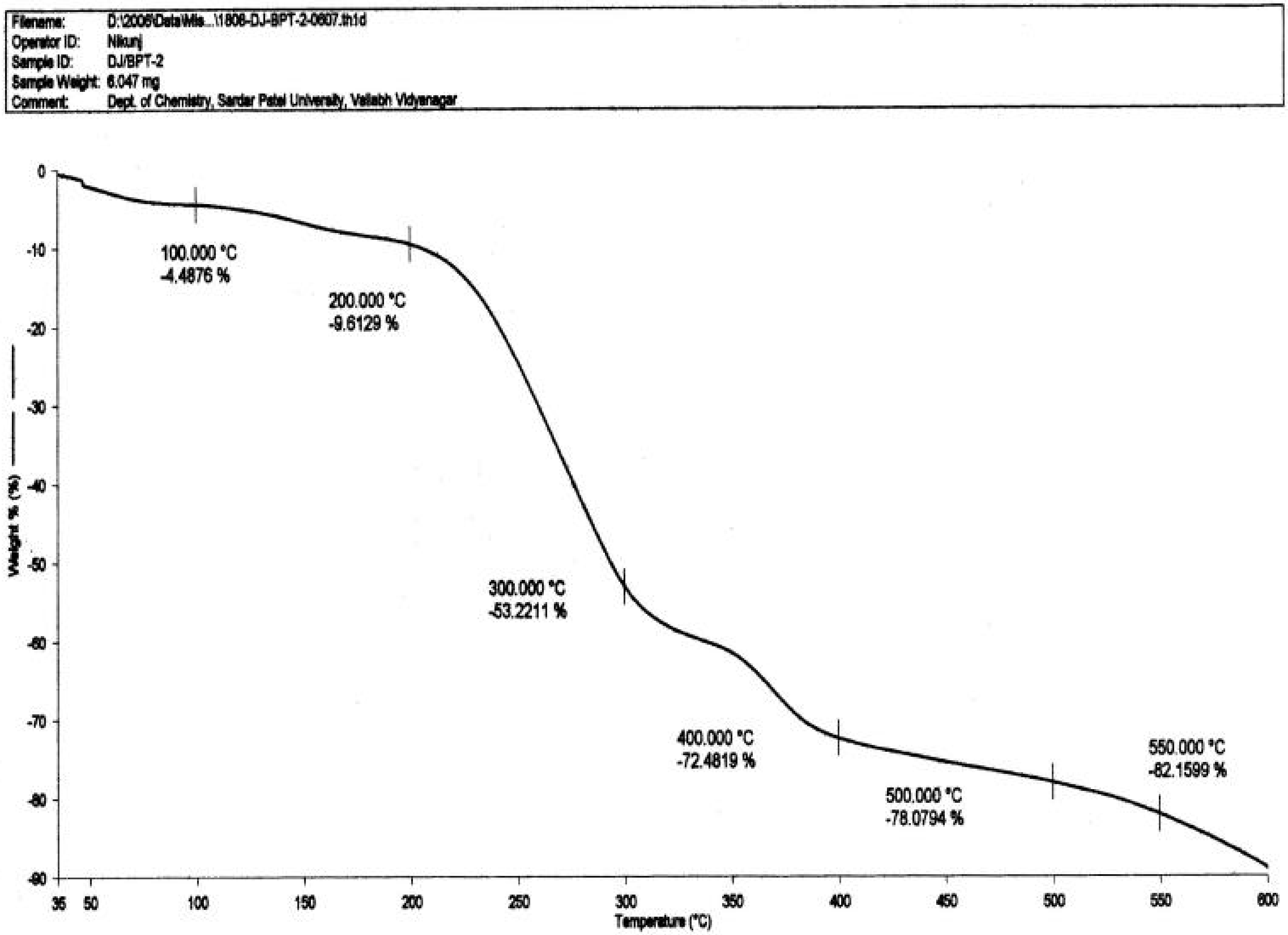

Fig. 4.3 TG thermogram of BPT-2 at the heating rate of 10°C/min in an N_2 atmosphere

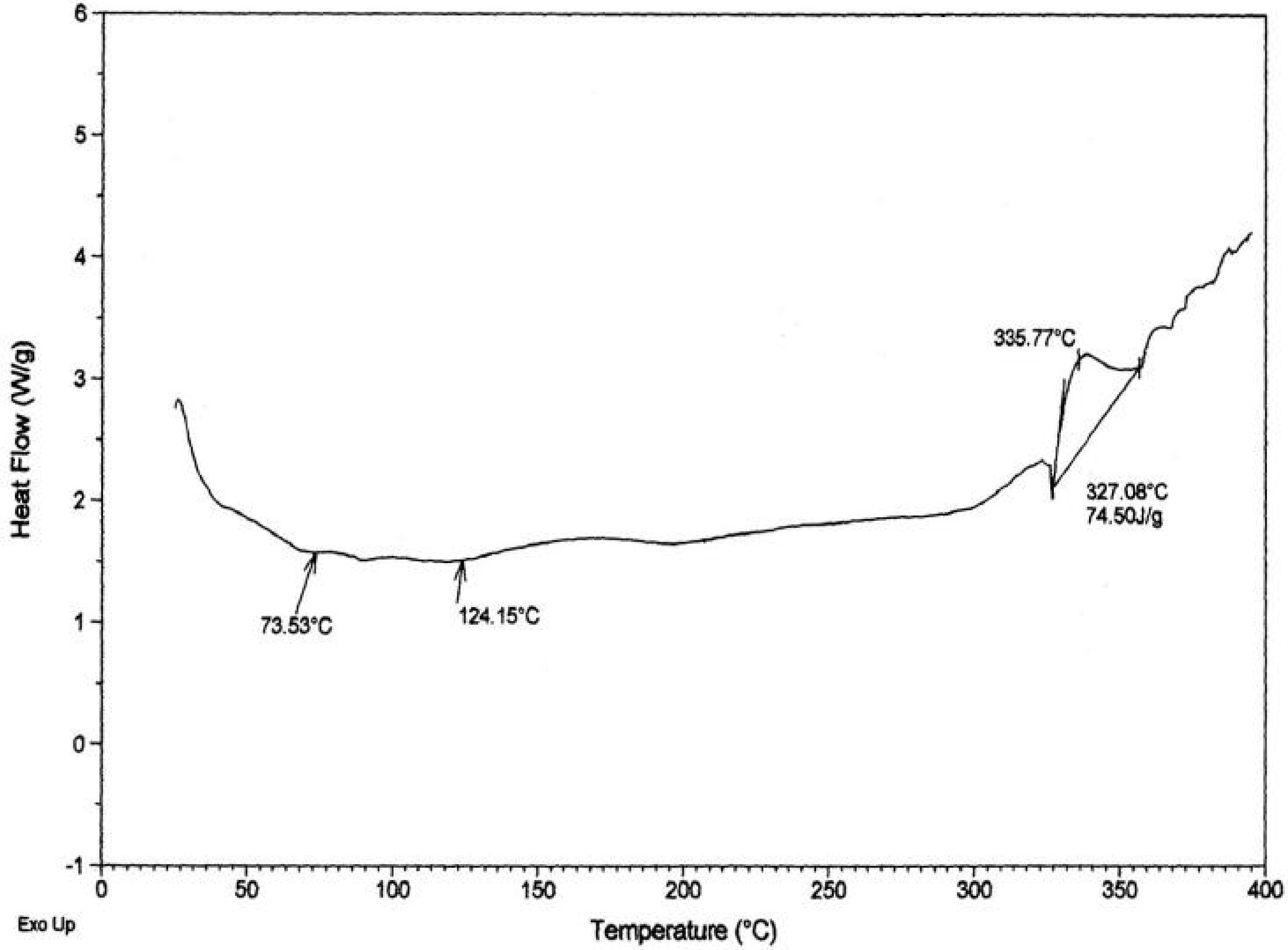

Fig. 4.4 DSC thermogram of BPT-1 at the heating rate of 10^{o}C/min in an N_2 atmosphere

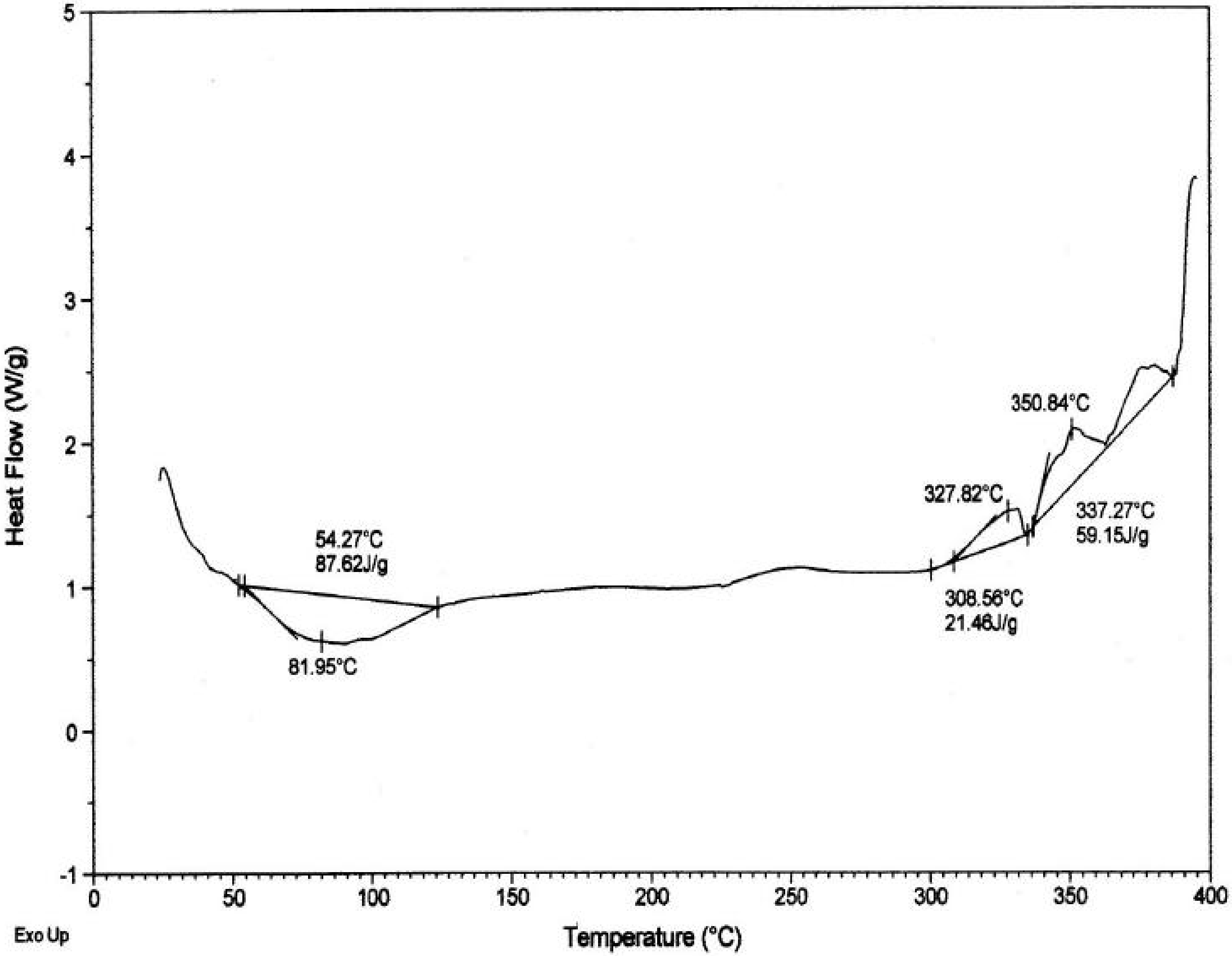

Fig. 4.5 DSC thermogram of BPT-2 at the heating rate of 10^{o}C/min in an N_2 atmosphere

loss (3.7%) in the temperature range 100 to 200°C is due to moisture content, the second step weight loss (47.3%) in the temperature range 200 to 313°C is due to decomposition of urethane linkage leading to the formation of CO_2, alcohols, amines aldehyde, CO, etc. and third step weight loss (10.9%) in the temperature range 350 to 400°C is due to complete decomposition of polyurethane.

DSC transitions of BPT-1 and BPT-2 are reported in Table 4.5. For BPT-1, the endothermic transition at 73.53°C is due to some physical change and the endothermic and exothermic transitions at 124.15 and 335.77°C, respectively are due to the decomposition and are further confirmed by TGA over those temperature ranges. For BPT-2, the endothermic and exothermic transitions at 81.95 and 327.82°C, respectively are due to some physical changes and those of exothermic transitions at 350.84 and 384.5°C, respectively are because of decomposition and confirmed by TGA over those temperature ranges. Thus, both BPT-1 and BPT-2 are useful up to about 180-200°C in nitrogen atmosphere. From the observed facts, it is observed that there is no effect of PEG content on thermal stability is observed but for T_{10} and T_{50}, shifted towards higher temperature with increasing PEG content in BPT film.

TABLE-4.4: TGA Data of BPT-1 and BPT-2 at the heating rate of 10^{0}C/min in nitrogen atmosphere

Sample	T_0	T_{10}	T_{50}	Decomposition range, ^{0}C	% weight loss
BPT-1	100	193	273	100-124 181-307 307-436	2.5 54.0 19.5
BPT-2	100	204	293	100-200 200-313 350-400	3.7 47.3 10.9

TABLE-4.5: DSC Data of BPT-1 and BPT-2

Sample	DSC transitions	Peak Temp., ^{o}C
BPT-1	Endo	73.53(P)
	Endo	124.15(D)
	Exo	335.77(D)
BPT-2	Endo	81.95(P)
	Exo	327.82(P)
	Exo	350.84(D)
	Exo	384.5(P)

SECTION-VI: CHEMICAL RESISTANCE STUDY OF POLYURETHANE FILMS

Polymeric materials absorb moisture in humid atmosphere and when immersed in water. The extent of water absorption mainly depends on the presence of hydrophilic polar groups, void volume, additives, humidity and temperature. Hydrolytic stability of polymeric materials depends on the nature and molecular structure of polymers. The tendency of water absorption by polar groups present in polymers increases the dissociation and hydrolysis and hence introduces ionic impurities, which affect electrical and mechanical properties to a greater extent.

Penetration of water in polymeric films may be transported through micro cracks. Absorbed water may induce irreversible changes like chemical degradation, cracking and debonding. Cracking and blistering cause high water absorption, while leaching of small molecules results in decrease in weight [55]. The chemical resistance of the films against water and 10% each of acids, alkalis and salt was carried out by change in weight method. The chemical resistance of the material is determined by averaging the change in mass of several specimens.

Chemical resistance of BPT-1 and BPT-2 films against various reagents at room temperature was determined according to change in weight method:

$$\%?\,\mathbf{M} = \left[{(\mathbf{M}_2 - \mathbf{M}_1)}\big/{\mathbf{M}_1} \right] \mathbf{X100} \qquad \ldots 4.3$$

where ?M is the change in weight, M_1 is the initial weight and M_2 is the weight after chemical treatment with time.

Chemical resistance of BPT-1 and BPT-2 films against pure water, aqueous 10% each of HCl, H_2SO_4, HNO_3, NaOH, KOH and NaCl was determined at the interval of 24h. The weight gain or loss observed with passage of time is shown in Table- 4.4 from which it is observed that in case of BPT-1, equilibrium water

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55. R. Bao and A. F. Yee, “Effect of temperature on moisture absorption in bismaleimides resin and its carbon fiber composites”, **43**, 3987-3996, 2002.

absorption in pure water (25.64%), NaCl (29.78%) and KOH (19.37%) solutions established within 24 h but in NaOH solution it increased up to 168 h and reached equilibrium value (26.06 %). In acid environments water absorption increased with the passage of time up to about 168-192 h and reached equilibrium values. The equilibrium water uptake in HCl, H_2SO_4 and HNO_3 solutions is 39.16, 28.57 and 23.92%, respectively.

BPT-1 has greater tendency to absorb water in pure water, saline, alkaline, and acidic environments. In case of BPT-2, it remained unaffected in pure water and saline environments. In NaOH solution equilibrium water uptake (0.9 %) reached within 24 h but in KOH solution it increased with time and equilibrium (8.57%) reached after one week. In HCl and H_2SO_4 solutions, BPT-2 remained unaffected up to about 48-72 h and then % water absorption increased with time and reached equilibrium value (1.79 % for HCl and 4.43 % for H_2SO_4). The equilibrium span for HCl solution is 144 h while for H_2SO_4 solution it is 240 h. In HNO_3 solution weight gain increased up to about 48 h and reached equilibrium (1.22%). Thus, BPT-2 has tendency to absorb water in acidic and alkaline environments. Water absorption is greater in KOH environments. The chemical resistance of copolyurethane is improved to a great extent by increasing amount of hydrophobic alkyl residue (PEG-200) in the copolyurethane chains.

Table-4.4: Chemical resistance data of BPT-1 and BPT-2 films at room temperature

Film sample	Time (h)	H_2O	NaCl	NaOH	KOH	HCl	H_2SO_4	HNO_3
BPT-1	24	25.64	29.78	23.93	19.37	23.77	16.42	10.42
	48	25.64	29.78	23.93	19.37	24.47	17.85	12.88
	72	25.64	29.78	23.93	19.37	26.57	19.28	14.11
	96	25.64	29.78	23.93	19.37	29.37	21.42	15.95
	120	25.64	29.78	23.93	19.37	32.16	24.28	18.40
	144	25.64	29.78	23.93	19.37	36.36	25.71	20.85
	168	25.64	29.78	23.93	19.37	39.16	27.85	23.92
	192	25.64	29.78	25.53	19.37	39.16	28.57	23.92
	216	25.64	29.78	26.06	19.37	39.16	28.57	23.92
	240	25.64	29.78	26.06	19.37	39.16	28.57	24.53
	264	25.64	29.78	26.06	19.37	39.16	29.28	24.53
	288	25.64	29.78	26.06	19.37	39.16	29.28	24.53
	312	25.64	29.78	26.06	19.37	39.16	29.28	25.02
BPT-2	24	0.0	0.0	0.9	0.009	0.0	0.0	0.61
	48	0.0	0.0	0.9	1.90	0.0	0.0	1.20
	72	0.0	0.0	0.9	2.85	0.0	0.63	1.22
	96	0.0	0.0	0.9	4.76	0.57	1.26	1.22
	120	0.0	0.0	0.9	4.76	0.57	2.53	1.22
	144	0.0	0.0	0.9	6.6	1.70	3.16	1.22
	168	0.0	0.0	0.9	7.6	1.70	3.79	1.22
	192	0.0	0.0	0.9	7.6	1.70	3.79	1.22
	216	0.0	0.0	0.9	7.6	1.70	3.79	1.22
	240	0.0	0.0	0.9	8.57	1.70	4.43	1.22
	264	0.0	0.0	0.9	8.57	1.70	4.43	1.22
	288	0.0	0.0	0.9	8.57	1.70	4.43	1.22
	312	0.0	0.0	0.9	8.57	1.70	4.43	1.22

The water absorption tendency of BPT-1 and BPT-2 films in different environments is probably due to micro cracks and voids [56, 57], and partly due to surface solvolysis of polar groups by different electrolytic ions. The strong electrolytes may change water structure and hence transportation of water through cracks and blistering. The absorbed water induces irreversible changes such as chemical degradation and cracking. Hydrophilic groups cause blistering. Cracking and blistering cause high water absorption. Urethane linkages are polar groups and contain lone pairs of electrons, which form H- bonds with solvated molecules and hence increase in water uptake. The stability of urethane linkages in harsh saline, acidic and alkaline environments indicates that BPT-2 can be used as a coating material in harsh conditions especially humid and marine environments.

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56. Q. Lin, X. Zhou and G. Dai, “Effect of hydrothermal environment on moisture absorption and mechanical properties of wood flour-filled polypropylene composites”, J. Appl. Polym. Sci. **85**, 2824-2833, 2002.
57. A. Espert, F. Vilaplana and S. Karisson, “Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties”, Compos. Part-A, **35**, 1267-1275, 2004.

SECTION-VII: SURFACE COATING AND ITS CHEMICAL RESISTANCE

This section of the chapter describes the surface coating application of polyurethane resin on different substrates such as copper, tin, mild steel and glass. The chemical resistance of coated samples is tested against water, acid and alkali at room temperature for varying time interval and interpreted in light of nature of substrate. A coating is a covering that is applied to an object to protect it or change 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 minium for 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 endavour to a scientifically regulated industry. For many years natual 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 pigments and oils. The properties of the finished products 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 coatings that control absorption or emission for temperature control, aircraft coatings that withstand the effect of UV radiation, absorption and the impact of air and dirt [58].

There are generally four components of paints and coatings: binders, diluents, fillers, and additives. However, only the binder is absolutely required. The binder is the part, which eventually solidifies to form the dried paint film. The diluent serves to adjust the viscosity of the paint. It is volatile and does not become part of the paint film. Anything else is an additive.

Key developments in coating industries

- Early chemists relied on natural products for varnishes based on fossilized resins and natural oils.
- The attempts have been made to modify the natural resins to produce synthetic natural products.
- Another key development of rubber and then phenolic resin followed by alkyd, urea and melamine formaldehyde resins.
- Other ‘Leap frog’ achievements came in around 1944-silicone based paints and in 1947-epoxy resins.
- There after the coating industry was revolutionized by development of PVA and acrylic lacquers, powder coatings, water-borne paints, UV-cure coatings, cationic electro coatings and clear-over color top coats.

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 help to form 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.

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58. J.H. Boatwright; Organic Coating; “Their Origin and Development” R.B.Seymour and H.F. Mark, Elsevier, p-9, New York (1990).

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.

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 [59].

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

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

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

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59. R. D. Deanin, "Polymer Structure, Properties and Applications", Cabners books, division of Cabners publishing company, Inc., 1972.

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

- Automotive industry: OEM, on line repair, refinishes.
- General industry: protective 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.

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.

The automotive industry is the largest user of polyurethane coatings, using 30% of total volume. The breakdown markets for polyurethane coatings in Western Europe are shown in the Table-4.5.

Polyurethane coatings are available in both one and two pack forms. A two component coatings will be simplified with the polyols, 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 in known as the pot life and is normally expressed either as the time taken for coating to dwell or time taken for a specific viscosity increase. The pot life can vary enormously between one and eight hours [60]. The pot life can be affected by type of polyol and polyisocyanate, NCO/OH ratio, temperature, solvent, level of catalyst, etc.

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60. M. Drukenbrod, Technically speaking: "Polyurethane coatings for the present and the future", Oct.-1993.

Table-4.5: 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

Table-4.6 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 lacquers	Physical drying

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 use 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.

In the present study, the isocyanate used for polyurethane synthesis is TDI (Toluene diisocyanate), accounts for the biggest volume of aromatic isocyanate used in surface coatings. TDI exists in tow isomeric forms, 2,4- and 2,6-TDI, and is usually supplied commercially as a 80/20 blend of the two [61].

Under the ASTM D16 norm, the American Society for Testing and Materials has classified the polyurethane coatings into six categories as described in the Table 4.6.

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61. H. Ulrich, “Chemistry and Technology of Isocyanate”, John Willey and Sons, 1996.

EXPERIMENTAL

Into a 250 ml beaker, 0.002mol (0.776g) BCF was dissolved in 15ml MEK at room temperature. To this solution 0.005mol (0.870g) TDI in 5ml MEK was added and the resultant solution was stirred manually for 15 min and to this prepolyurethane, 0.001/0.002 mol PEG-200 in 5ml MEK was added drop wise with stirring. After completion of the PEG-200 addition, the mixture was stirred for 10 min. The resins hereafter designated as BPT-1 and BPT-2. The resultant solution was applied on each of 5cm x 1cm glass, aluminium, copper and steel plates by means of a smooth brush. All the plates were allowed to dry at room temperature for 24 hour. A very fine coating was observed on plates with good adhesion to the substrates.

Chemical resistance of coatings

All the coated plates were subjected to chemical resistance by immersing in each of distilled water, 10% aqueous NaCl and HCl solutions. These immersed plates were observed after every 24 hour. The observed change in weight with the passage of time is shown in Tables-4.7 and 4.8 for BPT-1 and BPT-2, respectively.

From Table- 4.7, it is observed that in case of BPT-1, water absorption in pure water is the minimum in copper plate (0.29%) and maximum in steel plate (2.36%), while 1.56% in aluminium after 24 h. Then it increased upto 1.10, 2.50 and 3.93% for copper, aluminium and steel plates, respectively. Equilibrium uptake time is 144h for copper plate and 168h for steel and aluminium plates.

In NaCl solution, water absorption is the minimum in copper plate (1.34%) and maximum in steel plate (4.21%), while 2.51% in aluminium after 24 h. Then it increased up to 2.53, 6.75 and 5.31% for copper, aluminium and steel plates, respectively. Equilibrium uptake time is 192h for copper, steel and aluminium plates. In HCl solution, water absorption is the minimum in aluminium plate (3.11%) and maximum in copper plate (4.54%), while 4.36% in steel plate after 24 h. Then it increased up to 7.04, 6.18 and 6.32% for copper, aluminium and steel plates, respectively.

Table-4.7: Chemical resistance study of BPT-1 on different substrates

Medium	Time, h	BPT-1		
		% Wt. change		
		Copper	Steel	Aluminium
Water	24	0.29	2.36	1.56
	48	0.36	2.41	1.64
	72	0.49	2.59	1.79
	96	0.89	2.89	1.98
	120	1.9	3.23	2.35
	144	1.10	3.91	2.49
	168	1.11	3.93	2.50
	192	1.11	3.93	2.51
	216	1.11	3.93	2.51
NaCl	24	1.34	4.21	2.71
	48	1.72	4.33	2.95
	72	1.97	4.57	3.29
	96	2.26	4.91	3.66
	120	2.39	5.60	4.07
	144	2.44	6.71	4.93
	168	2.49	6.73	5.26
	192	2.53	6.75	5.31
	216	2.54	6.75	5.31
	240	2.54	6.75	5.31

Contd. …

Medium	**Time, h**	**BPT-1**		
		% Wt. change		
		Copper	**Steel**	**Aluminium**
HCl	24	4.54	4.36	3.11
	48	5.69	4.71	3.54
	72	6.87	5.13	4.37
	96	6.92	5.76	4.96
	120	6.98	6.03	5.64
	144	7.03	6.26	5.83
	168	7.04	6.31	6.17
	192	7.04	6.32	6.18
	216	7.04	6.32	6.18

Table-4.8: Chemical resistance study of BPT-2 on different substrates

Medium	Time, h	BPT-2		
		% Wt. change		
		Copper	Steel	Aluminium
Water	24	0.11	1.49	1.89
	48	0.19	1.66	2.11
	72	0.28	1.81	2.46
	96	0.39	1.97	2.53
	120	0.52	2.25	2.56
	144	0.71	2.54	2.61
	168	0.93	2.67	2.63
	192	0.93	2.69	2.63
	216	0.94	2.69	2.63
NaCl	24	0.63	2.53	2.71
	48	0.71	2.69	2.95
	72	0.87	3.28	3.29
	96	1.08	3.93	3.66
	120	1.28	4.85	4.07
	144	1.35	5.11	4.93
	168	1.39	5.16	5.26
	192	1.42	5.19	5.31
	216	1.44	5.19	5.31
	240	1.44	5.19	5.31

Contd. …

Medium	Time, h	BPT-2		
		% Wt. change		
		Copper	Steel	Aluminium
HCl	24	4.01	3.91	2.81
	48	4.89	3.99	2.87
	72	5.94	4.36	2.96
	96	6.15	4.81	3.37
	120	6.23	5.67	3.98
	144	6.31	5.84	4.67
	168	6.40	6.08	4.68
	192	640	6.09	4.69
	216	6.40	6.09	4.69

Equilibrium uptake time is 168 h for copper and 192 h for aluminium and steel plates. In case of BPT-2, water absorption in pure water is the minimum in copper plate (0.11%) and maximum in aluminium plate (1.89%), while 1.49% in steel plate after 24 h. Then it increased up to 0.93, 2.63 and 2.69% for copper, aluminium and steel plates, respectively. Equilibrium uptake time is 168h for copper and aluminium plates, while 192 h for steel plate. In NaCl solution, water absorption is the minimum in copper plate (0.63%) and maximum in aluminium plate (2.71%), while 2.53% in steel plate after 24 h. Then it increased up to 1.44, 5.31 and 5.19% for copper, aluminium and steel plates, respectively. Equilibrium uptake time is 192 h for copper, aluminium and steel plates.

In HCl solution, water absorption is the minimum in aluminium plate (2.81%) and maximum in copper plate (4.01%), while 3.91% in steel plate after 24 h. Then it increased up to 6.40, 4.68 and 6.09% for copper, aluminium and steel plates, respectively. Equilibrium uptake time is 168 h for copper, aluminium and steel plates.

BPT-2 shows the better moisture resistance in water, saline and acidic environments than BPT-1. The chemical resistance of copolyurethane is improved to a great extent by increasing amount of hydrophobic alkyl residue (PEG-200) in the copolyurethane chains.

Hydrophilic groups cause blistering. Cracking and blistering cause high water absorption. Urethane linkages are polar groups and contain lone pairs of electrons, which form H-bonds with solvated molecules and hence increase in water uptake. The stability of urethane linkages in harsh saline and acidic environments indicates that BPT-2 can be used as a coating material in harsh conditions especially humid and marine environments.

This chapter describes the density, viscosity and ultrasonic velocity measurements of BCFA resin solutions in different solvents at 30°, 35° and 40°C are determined. Various acoustical parameters of this resin are also discussed in this chapter.

INTRODUCTION

Ultrasonic is the study of high frequency sound waves, usually in excess of 20 KHz (20,000 Cycles per sec). Around 1880 [1-3] Curies discovered the piezoelectric effect, which established the basis of ultrasound for the present day generation. Most modern ultrasonic devices rely on transducers (energy converters), which are composed of piezoelectrical material. Ultrasonic technology is now a days employed in a wide range of applications in medicine, biology, industry, material science, agriculture, oceanography, dentistry, consumer industry, sonochemistry research, etc. due to its non-destructive nature [4-9] .

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1. A. P. Cracknell; "Ultrasonics", Wykenham Publishers, Chapter 6, 92, 1980.
2. J. Curie and P. Curie, Compt. Rend., **91**, 294, 1880.
3. J. Curie and P. Curie; Compt. Rend., **93**, 1137, 1881.
4. G. L. Gooberman, "Ultrasonics, Theory and Applications". The English Universities Press Ltd., London, EC4 1968.
5. Y. Gefen, M. Rosen and A. Rosen, Mater. Sci. Eng., **8**, 246, 1971.
6. W. Well and R. A. Pethrik, "Ultrasonic investigations of linear and star shaped polybutadiene polymers in solutions of cyclohexane, hexane and ethylbenzene", Polymer. **23**, 369-378, 1982.
7. V. A. Tabhne, O. P. Chimankar, S. Agrawal and S. N. Rao, J. Acoust. Soc. Ind., XXVI, 110, 1998.
8. G. Chandrasekhar, P. Venkatesu and M. V. P. Rao, "Excess molar volumes and speed of sound of ethyl acetate and butyl acetate with 2-alkoxyethanols at 308.15 K", J. Chem. Eng. Data, **45**, 590-597, 2000.
9. T. J. Mason, Editor., Sonochemistry: "The uses of ultrasounds in Chemistry", Royal Soc. of Chem., 1990.

It is most useful in investigating various organic liquids, polymers and aqueous and nonaqueous electrolyte solutions. It provides a wealth of information about molecular interactions, the nature and strength of interactions. It offers a rapid nondestructive method for characterizing materials. The extensive uses of polymers in technology have promoted ultrasonic studies to understand the structures of polymers and furnish knowledge on solvophilic or solvophobic nature of polymers [10-13]. Applications in materials science include the determination of some properties of solids such as compressibility, specific heat ratios, elasticity [14], etc. Ultrasound has also proved to be very useful for both soldering and welding. It is reported to improve the quality of homogenized milk. With the tracking of submarines, oceanographic applications include mapping the counters of the sea bottom, discovering sunken ships and searching for schools of fish. Ultrasonic testing and evaluation techniques are widely used for obtaining information about micro structural and mechanical properties of metals and found wide applications in medical and biological fields [15-17].

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10. R. A. Pethrick, J. Macromol. Chem., C **9**, 91-99, 1973.
11. C. V. Suryanarayana and J. Kuppusami, J. Acous. Soc. Ind., **4**, 75-82, 1976.
12. J. F. Rajasekaran, R. Balakrishnan and V. Arumugam, “Internal pressure-free volume relationship for rubber solutions”, J. Pure Appl. Ultrason., **19**, 76-85, 1997.
13. G. Ravichandran and T. K. Nambinarayanan, “Acoustical studies in aqueous solutions of dihydrogen phosphates of sodium and potassium”, Acous. Lett. **19**, 245-257, 1996.
14. K. S. Suslick and G. J. Price, Ann. Rev. Mater. Sci., **29**, 295, 1999.
15. J. A. Szpunar and D. C. Himz, J. Mater. Sci., **24**, 1233, 1990.
16. J. J. Gilman, B. J. Cunningham and A. C. Holt, “Method for monitoring the mechanical state of a material”, Mater. Sci. and Engg., **39** A, 125-133, 1990.
17. J. Jaykumar, P. Palanichamy and R. Baldev, J. Nuc. Mater., **243**, 225, 1998.

Further, cleaning is the most common type of applications of ultrasonic, which includes the removal of grease, dirt, rust and paint from metal, ceramic glass and crystal surfaces. Another area where ultrasonic is now-a-days being used, is to obtain the information about microstructures [18, 19]. It is reported that these ultrasonic waves provide valuable information about the structure of solids [20, 21].

By ultrasonic velocity measurements, the molecular interactions in pure liquids [22-25], aqueous solutions [26] and liquid mixtures [27,28] can also be studied. It is a powerful, effective and reliable tool to investigate properties of polymers [29-32].

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18. B. B. Nath and S. P. Bhattacharya, J. Ind.Chem.Soc., **68**, 483, 1991.
19. J. D. Panday, Y. Akhtar and A. K. Sharma, Ind. J. Chem. Soc., **37**,1094, 1998.
20. S. P. Yawale, S. V. Pakade and C. S. Adagonkar, Proc. Sol. State. Sym. (BARC), 30c, 66c, 1987.
21 S. Mukherjee, C. Basu and U. S. Ghosh, “Ultrasonic properties of vanadium pentoxide-phosphorus pentoxide amorphous materials at different temperatures”, J. Non-Cryst. Solids, **144**, 159-168, 1992.
22. S. S. Yadav, Y. P. Singh and J. Ragkumar, J. Ind. Coun. Chem.,**16**, 20, 1999.
23. S. C. Bhatt, H. Semwal, V. Lingwal, K. Singh and B. S. Semwal, J. Acous. Soc. India, **28**, 293, 2000.
24. R. P. Varma and S. Kumar, “Ultrasonic velocity and density measurements of ammonium soaps in 2-propanol”, Ind. J. Pure and Apply. Phy., **38**, 96-107, 2000.
25. M. Kalidoss and S. Ravi, Statistical Mechanics and its application, **312**, 59, 2002.

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

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

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26. S. Kamila, S. Jena and V. Chakravarthy, "Studies on acoustic behavior, viscosity, and density of some commercial extractants and their molecular interaction with diluent, modifier and extractant", J. Solution Chem., **365**, 33-46, 2004.
27. A. Dhanalakshmi and S. Sekar, "Internal pressure and thermodynamic property studies in inulin", J. Pure Appl. Ultrason., **21**, 97-105, 1999.
28. G. L. N. Sastry, J. Acous. Soc.- India, **14**, Da-1 to Da-8, 1986.
29. M. Mohamed and K. Koga, J. Thermal. Anal., **34**, 685, 1994.
30. M. V. Kok, J. Thermal. Anal., **24**, 899, 2002.
31. K. Ramanathan and S. Ravichandran, "Ultrasonic study of mixed salt solutions of ammonium sulphate and ammonium chloride", J. Pure Appl. Ultrason., **26**, 12-18, 2004.
32. J. S. Oh, J. G. Jang and Y. C. Bae, "Physical properties of polymer blends and their theoretical consideration", Polym., **38**, 3761-3769, 1997.

Sound velocity measurements on condensation polymers in protic or aprotic solvents are carried out by Parsania et al. [33-50] and investigated the influence of solvent, concentration, temperature and the nature of the substituents on the structure of polymers and molecular interactions in the solutions under investigations.

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33. S. H. Kalola and P. H. Parsania, "Evaluation of density and acoustical parameters of poly (2-methoxy) cyanurate of 1,1'-bis(3-methyl-4-hydroxyphenyl) cyclohexane", Proc. Ind. Acad. Sci. (Chem. Sci.), **107**, 73-77, 1995.
34. J. A. Desai and P. H. Parsania, "Acoustical studies of cardo polysulfonates of 1, 1'-bis (4-hydroxy-phenyl) cyclohexane with 1,3-benzene disulfonyl chloride in different solvents at 30^{o}C", J.Polym. Mater., **13**, 79-83 ,1996.
35. M. M. Kamani and P. H. Parsania, "Ultrasonic velocity studies of chloroform and dichloroethane solutions of cardo polysulfone of 1,1'-bis (3-methyl-4-hydroxyphenyl)-cyclohexane and 4,4'-difluoro diphenyl sulphone" J. Pure and Appl. Ultrason.,**18**, 46-54, 1996.
36. M. M. Kamani and P. H. Parsania, "Ultrasonic studies of chloroform-dioxane binary solutions of polysulfonate of 1,1'-bis(3-methyl-4-hydroxyphenyl) cyclohexane with toluene-2,4-disulfonyl chloride", J. Polym. Mater., **13**, 191-194, 1996.
37. A. R. Shah and P. H. Parsania, "Ultrasonic velocity studies on poly (4, 4'cyclohexylidene-2, 2'-dimethyl diphenylene/diphenylene-3, 3'-benzophenone disulfonates) in chlorinated and aprotic solvents at 30^{o}C", J. Polym. Mater., **14**, 33-41 1997.
38. K. M. Rajkotia and P. H. Parsania, "Studies on acoustical properties of poly (4,4'-cyclopentylidene diphenylene-2,4-disulfonate) in different solvents at 30^{o}C",Eur. Polym. J., **33**, 1005-1010, 1997.
39. A. R. Shah and P. H. Parsania, "Acoustic properties of poly (4,4'-cyclohexylidene-R,R'- diphenylene-3, 3'-benzophenonedisulfonates) at 30^{o}C", Eur. Polym. J., **33**(**8**), 1245-1250, 1997.
40. M. M. Kamani and P. H. Parsania "Ultrasonic studies of solutions of polysulfonate of 1,1'-bis (3-methyl-4-hydroxyphenyl) cyclohexane and toluene-2,4-disulfonyl chloride", J. Pure and Appl. Ultrason.,**19**, 89-93, 1997.

41. M. R. Sanariya and P. H. Parsania, "Studies on sound velocity and acoustical parameters of epoxy resins based on bisphenol-C", J. Pure and Appl. Ultrason., **22**, 54-59, 2000.
42. V. M. Kagathara, M. R. Sanariya and P. H. Parsania, "Sound velocity and molecular interaction studies on chloro epoxy resins solutions at 30^{o}C" Eur. Polym. J., **36**, 2371-2374, 2000.
43. F. Karia and P. H. Parsania, "Ultrasonic velocity studies and allied parameter of poly (4, 4'-cyclohexylidene-R, R'-diphenylene diphenyl methane-4,4'-disulfonate)solutions at 30^{o}C", Eur. Polym. J., **36**, 519-524, 2000.
44. D. R. Godhani, Y. V. Patel and P. H. Parsania, "Ultrasonic velocity and acoustical parameters of poly (4,4'-diphenyl phthalide diphenyl methane-4, 4'-disulfonate)-DMF solutions at 30^{0}, 35^{0} and 40^{0} C" J. Pure and Appl. Ultrason., **23**, 58-62, 2001.
45. D. R. Godhani and P. H. Parsania, "Studies on acoustical properties of poly (4, 4'-diphenylphthalide-diphenyl-4, 4'disulfonate) at 30^{o}", J. Ind. Chem. Soc., **79**, 620-623, 2002.
46. Y. V. Patel, D. R. Bhadja and P. H. Parsania "Ultrasonic study of poly (R, R', 4, 4'–cyclohexylidene diphenylene phosphorochloridate)-DMF solutions at different temperatures", J. Pure and Appl. Ultrason., **24**, 47-53, 2002.
47. D. R. Godhani, V. M. Kagathara and P. H. Parsania, "Investigation of molecular interactions in polysulfonates of phenolphthalein with 4, 4'-diphenylether/3,3'-benzophenone sulfonyl chloride solutions at different temperatures", J. Polym. Mater., **19**, 343-348, 2002.
48. Y. V. Patel and P. H. Parsania, "Ultrasonic velocity study of poly(R,R',4,4'-cyclohexylidene diphenylene diphenyl ether-4,4'-disulfonate solutions at 30^{o}, 35^{o}and 40^{o}C", Eur. Polym. J., **38**(**10**), 1971-1977, 2002.
49 V. M. Kagathara and P. H. Parsania, "Studies on ultrasonic velocity and acoustical parameters of bromo epoxy resins of bisphenol-C solutions at different temperatures ", Europ. Polym. J., **38**(**3**), 607-610, 2002.
50. B. G. Manwar, S. H. Kavthia and P. H. Parsania, "Ultrasonic velocity study of poly (R, R', 4, 4'-cyclohexylidene diphenylene toluene-2, 4-disulfonates) solutions at 30, 35 and 40^{o}C", J. Pure and Appl. Ultrason., **26**, 49-57, 2004.

EXPERIMENTAL

Materials

The solvents and chemicals used in the present investi- gation were purified according to reported methods [51]. Bisphenol-C-formaldehyde-acrylate resin (BCFA) was synthe- sized in our laboratory; synthesis was reported in section-IV of Chapter-2.

Measurements

Ultrasonic velocity, density and velocity measurements on pure solvents: Ethanol (EtOH), methyl ethyl ketone (MEK) and N, N'-dimethyl formamide (DMF) and BCFA solutions (0.5 to 4.0 wt %) were made at three different temperatures: 30, 35, 40 $\pm$ 0.1^{o}C, respectively by using F 81 Ultrasonic Interferometer (2 MHz) (Mittal Enterprises, New Delhi), specific gravity bottle and Ubbelohde viscometer. Ultrasonic velocity (U), density (?) and viscosity (?) measurements were accurate to $\pm$ 0.2%, $\pm$0.0001 gcm^{-3} and $\pm$0.1%, respectively.

(1) Density measurements

The densities of pure solvents and solutions were measured by means of specific gravity bottle at three different temperatures: 30^{o}, 35^{o} and 40^{o}C by determining the weights of distilled water, solvents and solutions. The density (ρ) was calculated according to Eqn. 5.1 with an accuracy of $\pm$ 0.0001 g/cm^{3}.

$$\rho\ (g / cc) = \frac{\mathrm{Wt. of solvent/solution}}{\mathrm{Wt. of water}} \qquad \ldots\ 5.1$$

(2) Viscosity measurements

The method for determining the dynamic viscosity or coefficient of viscosity of liquids relies on Stoke's law. In present investigation, suspended level viscometer developed by Ubbelohde was used. The viscometer was

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51. E. S. Proskaur and A. Weisberger, "Techniques of Organic Solvents", New York, (1995).

washed with chromic acid, distilled water, acetone and then dried at 50°C in an oven. Viscometer was suspended in a thermostat at 30 ± 0.1°C and measured quantity of the distilled water / solvent / solution was placed into the viscometer reservoir by means of a pipette and thermally equilibrated for about 10 min. The efflux time of liquid between two marks was measured by means of digital stopwatch with an accuracy of ± 0.01 sec. Three replicate measurements on each liquid were made and the arithmetic mean was considered for the purpose of calculations.

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

$$\frac{?_1}{?_2} = \frac{t_1 ?_1}{t_2 ?_2} \qquad \ldots 5.2$$

Where η_1, ρ_1, t_1 and η_2, ρ_2, t_2 are the viscosities, densities and flow times of standard and unknown samples, respectively.

(3) Sound velocity measurements

Ultrasonic interferometer (F-81) (Mittal Enterprises, New Delhi) was used in the present investigation. The working of interferometer was tested by measuring the sound velocity of pure solvents: Ethanol (EtOH), methyl ethyl ketone (MEK) and N, N'-dimethylformamide (DMF) and comparing the results with literature data. The advantage of this instrument is that the quantity of sample needed for measurement is small (15-20 ml).

The measuring cell (2 MHz) with quartz crystal was filled with the solvent/solution and then micrometer with reflector plate was fixed. The circulation of water from the thermostat (at 30°, 35° and 40°C) was started and the experimental liquid in the cell is allowed to thermally equilibrate. The high frequency generator was switched on and the micrometer was rotated very slowly so as to obtain a maximum or minimum of the anode current. A number of maximum readings of anode current (n) were counted. The total distance (d) traveled by the micrometer for n=20 were read. The wave length (λ) was determined according to Eqn. 5. 3:

$$l = \frac{2d}{n} \qquad \text{…5.3}$$

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

$$U = l \,.\, F \qquad \text{…5.4}$$

The density (ρ), viscosity (η) and velocity (U) data of BCFA solution at three different temperatures are reported in Tables 5.1 - 5. 3.

It is observed graphically that ρ, η and U increased with concentration (C) and decreased with temperature (T) except MEK system at 35^{o}C, where ρ varied nonlinearly. ρ, η and U data are correlated with concentration at all the three different temperatures.

1. Specific acoustical impedance:

$$Z = U? \qquad \text{…5.5}$$

2. Isentropic compressibility:

$$?_s = \frac{1}{U^2?} \qquad \text{…5.6}$$

3. Rao's molar sound function [52]:

$$R = \frac{M}{?} U^{1/3} \qquad \text{…5.7}$$

Where M is the apparent molecular weight of the solution and can be calculated according to Eqn. 5.8:

$$M = M_1 W_1 + M_2 W_2 \qquad \text{…5.8}$$

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[52] S. Bagchi, S. K. Nema and R. P. Singh, "Ultrasonic and viscometric investigation of ISRO polyol in various solvents and its compatibility with polypropylene glycol", Eur. Polym., J., **22**(**10**), 851-860, 1989.

Where W_1 and W_2 are weight fractions of solvent, and polymer repeat unit, respectively. M_1 and M_2 are molecular weights of solvent and polymer repeat unit, respectively.

4. Van der Waals constant [53]:

$$b = \frac{M}{?}\left[1-\left[\frac{RT}{MU^2}\right]\left[\sqrt{1+\frac{MU^2}{3RT}}-1\right]\right] \qquad ...5.9$$

5. Internal pressure [54]:

$$p = bRT\left(\frac{K?}{U}\right)^{1/2}\frac{?^{2/3}}{M^{7/6}} \qquad ...5.10$$

Where R (8.314 $JK^{-1}mol^{-1}$) is the gas constant and b is the packing factor and K (4.28×10^9) is a constant. The π depends on temperature, density, sound velocity and specific heat at constant pressure.

6. Free volume [11]:

$$V_f = \left[\frac{MU}{K?}\right]^{3/2} \qquad ...5.11$$

7. Intermolecular free path length [55]:

$$L_f = K(?_s)^{1/2} \qquad ...5.12$$

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

8. Classical absorption coefficient [56]:

$$\left(a/f^2\right)_{cl} = \frac{8p^2?}{3U^3?} \qquad ...5.13$$

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53. P. Vigoureux, "Ultrasonic", Chapmann and Hall, London (1952).
54. C. V. Suryanarayana, J. J. Kuppuswamy, Acoust. Soc., **9**(**1**), 4, 1954.
55. B. Jacobson, Nature, 173, 772, 1954.
56. T. V. S. Subrahmanyam, A. Viswanadhasharma and K. Subbarao, J. Acoust. Soc., **7**(**1**), 1, 1979.

Table-5.1: The density (?), viscosity (?), sound velocity (U) and pooled precision standard deviation (Sp) data of BCFA solutions in EtOH at three different temperatures: 30^{o}, 35^{o} and 40^{o}C.

Conc., %	Density ?, kg / m^{-3}	Viscosity ?, m Pas	Ave. Dist. d.10^{3},m	Wave length ?.10^{3},m	U ms^{-1} (F=2MHz)	Std. devi. mm
BCFA+ EtOH at 30^{o} C						
0	772.4	0.695	5.677	0.5677	1135.4	±0.0025
0.5	776.2	0.727	5.687	0.5687	1137.4	0.0022
1.0	778.8	0.777	5.700	0.5700	1140	0.0024
1.5	779.2	0.821	5.685	0.5685	1137	0.0023
2	780.6	0.867	5.708	0.5708	1141.6	0.0047
3	782.7	0.917	5.724	0.5724	1144.8	0.0029
4	783.9	0.947	5.749	0.5749	1149.8	0.0028
BCFA+ EtOH at 35^{o} C						
0	771.6	0.658	5.668	0.5668	1133.2	±0.0019
0.5	774	0.699	5.686	0.5686	1137.2	0.0037
1.0	776.6	0.718	5.692	0.5692	1138.4	0.0018
1.5	777.9	0.796	5.706	0.5706	1141.2	0.0021
2	779.5	0.827	5.716	0.5716	1143.2	0.0043
3	781.3	0.858	5.724	0.5724	1144.8	0.0022
4	782.4	0.898	5.738	0.5738	1147.6	0.0022
BCFA+ EtOH at 40^{o} C						
0	771.2	0.000617	5.567	0.5567	1130.8	±0.0029
0.5	772.7	0.000635	5.554	0.5554	1132	0.0034
1.0	775.4	0.000685	5.488	0.5488	1133.8	0.0069
1.5	776.9	0.000759	5.534	0.5534	1134.8	0.0022
2	778.3	0.000796	5.563	0.5563	1136.6	0.0020
3	779.8	0.000824	5.583	0.5583	1138.2	0.0020
4	781.1	0.000871	5.594	0.5594	1139.8	0.0034

Table-5.2: The density (?), viscosity (?), sound velocity (U) and pooled precision standard deviation (Sp) data of BCFA solutions in MEK at three different temperatures: 30°, 35° and 40°C.

Conc., %	Density ?, kg / m^{-3}	Viscosity ?, m Pas	Ave. Dist. d.10^3,m	Wave length ?.10^3,m	U ms^{-1} (F=2MHz)	Std. devi. mm
BCFA+ MEK at 30° C						
0	802.5	0.352	5.843	0.5843	1168.6	±0.0019
0.5	807.1	0.388	5.854	0.5854	1170.8	0.0017
1.0	808.8	0.403	5.869	0.5869	1173.8	0.0014
1.5	810.7	0.427	5.873	0.5873	1174.6	0.0014
2	812.6	0.461	5.877	0.5877	1175.4	0.0038
3	814.8	0.489	5.885	0.5885	1177	0.0032
4	817.7	0.509	5.935	0.5935	1187	0.0028
BCFA+ MEK at 35° C						
0	800.1	0.334	5.786	0.5786	1157.2	±0.0021
0.5	802.5	0.354	6.093	0.6093	1159.8	0.0021
1.0	807.1	0.377	5.790	0.5790	1162.4	0.0018
1.5	815.2	0.403	5.754	0.5754	1164.2	0.0021
2	815.8	0.434	5.807	0.5807	1166	0.0032
3	817	0.463	5.829	0.5829	1168.4	0.0024
4	818.4	0.48	5.863	0.5863	1170.6	0.0024
BCFA+ MEK at 40° C						
0	800.3	0.315	5.652	0.5652	1130.4	±0.0027
0.5	805.9	0.337	5.558	0.5558	1132.2	0.0026
1.0	807.1	0.354	5.676	0.5676	1135	0.0029
1.5	809.1	0.387	5.697	0.5697	1139.4	0.0014
2	810.9	0.412	5.714	0.5714	1142.8	0.0035
3	813.1	0.446	5.734	0.5734	1146.8	0.0033
4	815.9	0.471	5.750	0.5750	1150	0.0036

Table-5.3: The density (?), viscosity (?), sound velocity (U) and pooled precision standard deviation (Sp) data of BCFA solutions in DMF at three different temperatures: 30^{o}, 35^{o} and 40^{o}C.

Conc., %	Density ?, kg / m^{-3}	Viscosity ?, m Pas	Ave. Dist. d.10^{3},m	Wave length ?.10^{3},m	U ms^{-1} (F=2MHz)	Std. devi. mm
BCFA+ DMF at 30^{o} C						
0	927.2	0.715	7.023	0.7023	1404.6	±0.0036
0.5	928.4	0.758	7.167	0.7167	1433.4	0.0036
1.0	930.1	0.776	7.179	0.7179	1435.8	0.0028
1.5	931.7	0.795	7.194	0.7194	1438.8	0.0025
2	934.1	0.826	7.216	0.7216	1443.2	0.0029
3	935.9	0.854	7.265	0.7265	1453	0.0039
4	938.2	0.878	7.348	0.7348	1469.6	0.0059
BCFA+ DMF at 35^{o} C						
0	919.7	0.693	7.004	0.7004	1400.8	±0.0043
0.5	926.8	0.721	7.167	0.7167	1433.4	0.0022
1.0	928.9	0.754	7.177	0.7177	1435.4	0.0015
1.5	930.3	0.779	7.187	0.7187	1437.4	0.0014
2	931.9	0.803	7.193	0.7193	1438.6	0.0021
3	934.1	0.829	7.324	0.7324	1464.8	0.0027
4	936.6	0.85	7.424	0.7424	1484.8	0.0023
BCFA+ DMF at 40^{o} C						
0	916.4	0. 677	7.104	0.7104	1420.8	±0.0021
0.5	924.9	0.703	7.115	0.7115	1423	0.0026
1.0	927.1	0.739	7.134	0.7134	1426.8	0.0022
1.5	929.4	0.752	7.145	0.7145	1429	0.0028
2	930.1	0.791	7.159	0.7159	1431.8	0.0026
3	932.4	0.81	7.166	0.7166	1433.2	0.0027
4	934.8	0.832	7.185	0.7185	1437	0.0026

9. Solvation number [10]:

$$S_n = \frac{M_2}{M_1\left(1-{?_s}\big/{?_{s_1}}\right)\left(\frac{100-X}{X}\right)} \qquad \ldots 5.14$$

Where X is the number of grams of solute in 100g of the solution

The degree of linearity was judged on the basis of correlation coefficient (g). A fairly good to excellent correlation between a given parameter and concentration is observed in the studied solvent system at three different temperatures. The observed correlation between ρ and C, η and C, and U and C is g =0.960-0.996, 0.954-0.989 and 0.928-0.986, respectively. The obtained g values supported a fairly good to excellent linear dependence of ρ, η and U with C and T.

From Tables- 5.1 to 5.3, it is clear that the change in ρ and U with C and T are not as appreciable as η because molecular motion is much more affected by polymer-solvent and polymer-polymer interactions in solutions [57-60]. The increase of ρ, η and U with C supported increase in cohesive forces due to powerful molecular interactions, while decrease of these parameters with T indicated decrease in cohesive forces. The increasing temperature has two opposite effects namely increase of molecular interactions (structure formation) and destruction of structure formed previously as a result of thermal fluctuation [61].

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57. R. K. Senthil and C. Rakkappam, Asian J. Phys., **6**, 467, 1997.
58. B. Saraf and K. Samal, Acoustica, **55**, 60, 1984.
59. S. Das, R. P. Singh and S. Maiti, “Ultrasonic velocities and rao formulism in solution of polyesterimides”, Polym-Bull., **2**, 400-409, 1980.
60. W. Bell and R. A. Pethrick, “Ultrasonic investigations of linear and star shaped polybutadiene polymers in solutions of cyclohexane, hexane and ethylbenzene”, Polym., **23**, 369-378, 1982.
61. R. A. Pethrick and B. T. Poh, “Ultrasonic attenuation and adiabatic compressibility of poly (ethylene oxide)-water mixtures”, British Polym. J., **15**, 149-157, 1983.

Thus increase of T favors increase of kinetic energy and volume expansion and hence results decrease of ρ and η, while it increases intermolecular distance (free path length). The density and viscosity of medium, pressure, temperature, etc. affect the velocity. The molecular interactions cause chain expansion and hence increase of viscosity. A polymer-solvent interaction in solutions is of great value since the extension of chain is markedly influenced by the molecular interactions, which furnish knowledge on solvophilic or solvophobic nature of the polymers under investigation. The solvated molecules affect polymer processing from solutions.

With a view to understand the effect of concentration, temperature, nature of solvents and the structure of resin on solvophilicity or solvophobicity, various acoustical parameters were determined by using the experimental data on ρ, η and U of BCFA solutions at three temperatures according to standard relations. The concentration and temperature dependence of acoustical parameters furnish wealth of information regarding strength of molecular interactions occurring in the solutions. Various acoustical parameters are fitted with concentration and least square equations along with correlation coefficients are reported in Tables- 5.4 – 5.6.

From Tables- 5.4 to 5.6, it is clear that the linear decrease of isentropic compressibility (κ_S), internal pressure (π) and free path length (L_f), with C and T in DMF system supported existence of strong molecular interactions. V_f increased nonlinearly with C and T in EtOH, while it decreased nonlinearly with C and increased with T in MEK system also supported presence of strong molecular interactions. The concentration and temperature dependent plots of κ_S,π, L_f and V_f are presented in Figs. 5.1 5.4, respectively.

Table - 5.4: The correlation equations and correlation coefficients for BCFA + EtOH solutions

Polymer	Correlation equation (correlation coefficient)		
	30^o	35^o	40^o
BCFA+EtOH	ρ=2.2118C + 775.64 (0.9726)	ρ=2.3C + 774.02 (0.9331)	ρ=2.2471C + 772.87 (0.9211)
	η=6E-05C + 0.0007 (0.9534)	η=6E-05C + 0.0007 (0.9202)	η=6E-05C + 0.0006 (0.9104)
	U=3.5059C + 1134.8 (0.8804)	U=2.9647C + 1136.1 (0.9671)	U=2.1882C + 1131.5 (0.9734)
	Z=5258.8C+ 880132 (0.975)	Z=4935.3C+ 879363 (0.9603)	Z=4264.7C + 874454 (0.948)
	κ_S=-9E-12C + 1E-09 (0.9504)	κ_S=-8E-12C + 1E-09 (0.9618)	κ_S=-0.0657C + 7.8681 (0.99)
	V_f=6E-09C + 7E-08 (0.9066)	V_f= 6E-09C + 8E-08 (0.8685)	V_f=3E-09C^2 - 9E-09C + 1E-07 (0.9112)
	r= -0.0031C + 0.497 (0.8756)	r=-0.0026C + 0.4957 (0.9259)	r=-0.0018C + 0.4995 (0.9454)
	R = 9E-05C +0.0006 (1)	R = 9E-05C + 0.0006 (1)	R=9E-05C+ 0.0006 (1)
	b=9E-06C + 6E-05 (1)	b=9E-06C + 6E-05 (1)	b=9E-06C + 6E-05 (1)
	π= -6E+07C +8E+08 (0.9991)	π= -6E+07C + 8E+08 (0.9935)	π= -6E+07C + 7E+08 (0.9941)
	L_f = -3E-13C +7E-11 (0.946)	L_f = -3E-13C + 7E-11 (0.9681)	L_f = -2E-13C + 7E-11 (0.9587)
	τ= 7E-14C + 1E-12 (0.9303)	τ= 7E-14C + 9E-13 (0.9086)	τ= 8E-14C+ 9E-13 (0.9008)
	$(\alpha/f^2)_{cl}$ =1E-15C+2E-14 (0.9163)	$(\alpha/f^2)_{cl}$= 1E-15C+2E-14 (0.9042)	(α/f^2)cl =-4E- 16C^2+ 3E-15C +1E-14 (0.9754)

Table-5.5: The correlation equations and correlation coefficients for BCFA + MEK solutions

Polymer	Correlation equation (Regression coefficient)		
	30^o	35^o	40^o
BCFA+MEK	$\rho= 2.9882C + 805.97$ (0.9907)	$\rho= -2.2131C^2 + 14.183C + 796.29$ (0.9377)	$\rho= 2.8706C + 804.59$ (0.9922)
	$\eta= 4E-05C + 0.0004$ (0.9638)	$\eta=4E-05C + 0.0003$ (0.9536)	$\eta= 4E-05C + 0.0003$ (0.9746)
	$U=3.9647C + 1168.5$ (0.8616)	$U=2.9882C + 1159.3$ (0.9727)	$U=5.1529C + 1130.7$ (0.965)
	$Z=6729.4C+ 941758$ (0.9664)	$Z=7270.6C + 932425$ (0.8261)	$Z=7347.1C + 907673$ (0.9739)
	$\kappa_S= -1E-11C + 1E-09$ (0.9686)	$\kappa_S= -8E-12C + 9E-10$ (0.9831)	$\kappa_S= -9E-12C + 9E-10$ (0.943)
	$V_f= 7E-09C^2-3E-08C +4E-07$ (0.6413)	$V_f= 1E-08C^2 - 6E-08C + 5E-07$ (0.9338)	$V_f=9E-09C^2 - 5E-08C + 5E-07$ (0.9071)
	$r=-0.0036C + 0.4668$ (0.873)	$r= -0.0027C + 0.4752$ (0.9599)	$r= -0.0047C + 0.5007$ (0.9736)
	$R= 8E-05C+ 0.0009$ (0.9999)	$R=8E-05C + 0.0009$ (0.9986)	$R=8E-05C + 0.0009$ (1)
	$b= 8E-06C + 9E-05$ (0.9996)	$b=8E-06C + 9E-05$ (1)	$b=8E-06C + 9E-05$ (1)
	$\pi= -1E+07C+ 3E+08$ (0.9818)	$\pi= -1E+07C + 3E+08$ (0.9727)	$\pi= -1E+07C + 3E+08$ (0.9756)
	$L_f= -4E-13C + 7E-11$ (0.9769)	$L_f= -3E-13C + 6E-11$ (0.8957)	$L_f= -3E-13C + 6E-11$ (0.9442)
	$\tau= 4E-14C + 5E-13$ (0.9366)	$\tau= 4E-14C+ 4E-13$ (0.9543)	$\tau= 4E-14C + 4E-13$ (0.9713)
	$(\alpha/f^2)_{cl} =-1E-16C^2+ 1E-15C+7E-15$ (0.9732)	$(\alpha/f^2)cl=-1E-16C^2+1E-5C + 7E-15$ (0.992)	$(\alpha/f^2)cl =-1E-16C^2+ 1E-15C + 7E-15$ (0.9939)

Table-5.6: The correlation equations and correlation coefficients for BCFA + DMF solutions

Polymer	30^{o}C	35^{o}C	40^{o}C
BCFA+DMF	$\rho=2.7941C+927.48$ (0.9774)	$\rho=2.7118C + 926.01$ (0.9891)	$\rho=2.6882C + 924.41$ (0.9703)
	$\eta=4E-05C + 0.0007$ (0.979)	$\eta=4E-05C + 0.0007$ (0.9483)	$\eta=4E-05C + 0.0007$ (0.9363)
	$U=10.224C+1425.2$ (0.9577)	$U=15.318C + 1418.4$ (0.9056)	$U=3.6941C + 1422.7$ (0.946)
	$Z=13529C + 1E+06$ (0.9724)	$Z=18235C + 1E+06$ (0.9422)	$Z=6470.6C + 1E+06$ (0.8897)
	$\kappa_S= -9E-12C+5E-10$ (0.9827)	$\kappa_S= -1E-11C + 5E-10$ (0.9269)	$\kappa_S= -4E-12C+ 5E-10$ (0.9509)
	$V_f= 9E-09C+ 2E-07$ (0.9449)	$V_f= 1E-08C + 2E-07$ (0.845)	$V_f=8E-09C + 2E-07$ (0.8369)
	$r= -0.0116C+ 0.2066$ (0.9566)	$r= -0.0173C + 0.2143$ (0.8979)	$r= -0.0042C + 0.2094$ (0.9384)
	$R= 7E-05C + 0.0009$ (0.9999)	$R=7E-05C + 0.0009$ (0.9996)	$R=7E-05C + 0.0009$ (1)
	$b= 6E-06C + 8E-05$ (0.9999)	$b=6E-06C + 8E-05$ (0.9999)	$b=6E-06C + 8E-05$ (1)
	$\pi= -2E+07C +5E+08$ (0.9979)	$\pi=-2E+07C +5E+08$ (0.9979)	$\pi= -2E+07C + 5E+08$ (0.9948)
	$L_f= -4E-13C + 5E-11$ (0.9657)	$L_f=-6E-13C + 5E-11$ (0.932)	$L_f=-2E-13C+ 5E-11$ (0.9195)
	$\tau= 1E-14C + 5E-13$ (0.8983)	$\tau =-9E-15C^2+5E-14C + 5E-13$ (0.9689)	$\tau =2E-14C + 5E-13$ (0.9233)
	$(\alpha/f^2)_{cl} =-7E-17C^2+ 5E-16C + 7E-15$ (0.9699)	$(\alpha/f^2)_{cl}= -1E-16C^2 + 7E-16C+ 7E-15$ (0.9125)	$(\alpha/f^2)_{cl} =3E-16C+7E-15$ (0.9185)

The correlation coefficients (?) for κ_S, π, L_f and V_f are -0.963 to -0.992, -0.986 to -0.999, -0.946 to -0.988 and 0.915 to 0.972 (DMF), respectively indicated fairly good to excellent linear relationships except EtOH and MEK systems in which V_f varied with C. In EtOH it followed second order with ? = 0.955 to 0.998. While in MEK it followed higher order polynomial relationship with ? = 0.956 to 0.986.

Other acoustical parameters such as specific acoustical impendence (Z), Van der Waal's constant (b), classical absorption coefficient $(\alpha/f^2)_{cl}$ and viscous relaxation time (τ) also supported existence of strong molecular interactions. Z, b, $(\alpha/f^2)_{cl}$ and τ increased linearly with C and decreased linearly with T. The observed correlation coefficients for Z, b, $(\alpha/f^2)_{cl}$ and τ are 0.909-0.987, 1.000, 0.951-0.987 and 0.948-0.985, respectively. It is observed that practically no temperature effect is observed on b and π. Thus, a fairly good to excellent linearity is observed in the present study supporting strong molecular interactions occurring in the BCFA solutions. π, V_f and τ are three basic thermodynamic parameters for liquid systems. Internal pressure of a solution is single factor, which appears to vary with intermolecular interactions namely solvation, ion-solvent interactions, solute-solvent interaction and quantum mechanical forces of dispersion and dielectric forces, which play an important role in transport properties of solutions. Increase of π and decrease of V_f and vice-versa are measure of cohesion forces. Decrease in κ_S with C supported fully compressed solvated molecules by electrical forces present in the solute molecule. Thus, various acoustical parameters suggested solvophilic nature of BCFA in the solvent systems investigated and it is further supported by positive values of solvation number S_n (Fig. 5.5). At 30^{o}C, S_n increased up to about 2% and then decreased with C, while it increased linearly at 35^{o}C (? = 0.946) and 40^{o}C (0.985) in EtOH system. Solvation increased after 35^{o}C. In MEK system, S_n increased linearly up to 35^{o}C (? = 0.939- 0.978) and nonlinearly with C at 40^{o}C. In DMF system, S_n increased linearly with C (? = 0.976) and it increased nonlinearly up to about 3% and then it decreased at 35^o and 40^{o}C. At 35^{o}C and 40^{o}C in DMF system, S_n followed second order relationship with C. In solution both solvent-polymer and polymer-polymer interactions occur and overall value is decided by the predominant interactions and as a result nonlinear behavior is observed in many cases. The interactions depend upon the nature of solvent and solute, structure and presence of substituents, temperature, pressure, etc. From Fig. 5.4, it is clear that solvation is powerful in ethanol and minimum in DMF system. The decrease in S_n with T indicates decrease in cohesive forces, while decreases in S_n with C indicate polymer-polymer interaction. When temperature increases the tendency of molecules to move away increases and the probability of molecular interactions decreases, and as a result cohesive forces decreases [62]. $(\alpha/f^2)_{cl}$ and τ are affected by ?, ? and U. Increase of $(\alpha/f^2)_{cl}$ and τ with C can be explained in terms of the motion of macromolecular interchain forces [62]. A contribution of acoustic relaxation is accounted due to entropy fluctuation associated in solution of dynamically formed physical entity [61]. The presence of polar groups in the solute molecule enhances molecular interactions. The solvation phenomena result in the change of molar volume and hence molar compressibility.

Hydroxyl and ester groups of BCFA are polar groups, which form H-bonds with solvent molecules. The observed solvation tendency of BCFA with studied solvents is EtOH > MEK > DMF. The dipole-dipole interaction of opposite type favors structure formation; while of the same type disrupt the structure formed previously. In DMF system solvation is minimum and that might be due to steric hindrance. Thus, BCFA possesses structure forming tendency in the studied solvents.

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62. S. Kalyansundaram, A. Manuel Stephan and A. Gopalan, “Molecular interaction studies on poly (methyl methacrylate) in chloroform”, J. Polym. Mater., **12**, 323-333, 1995.

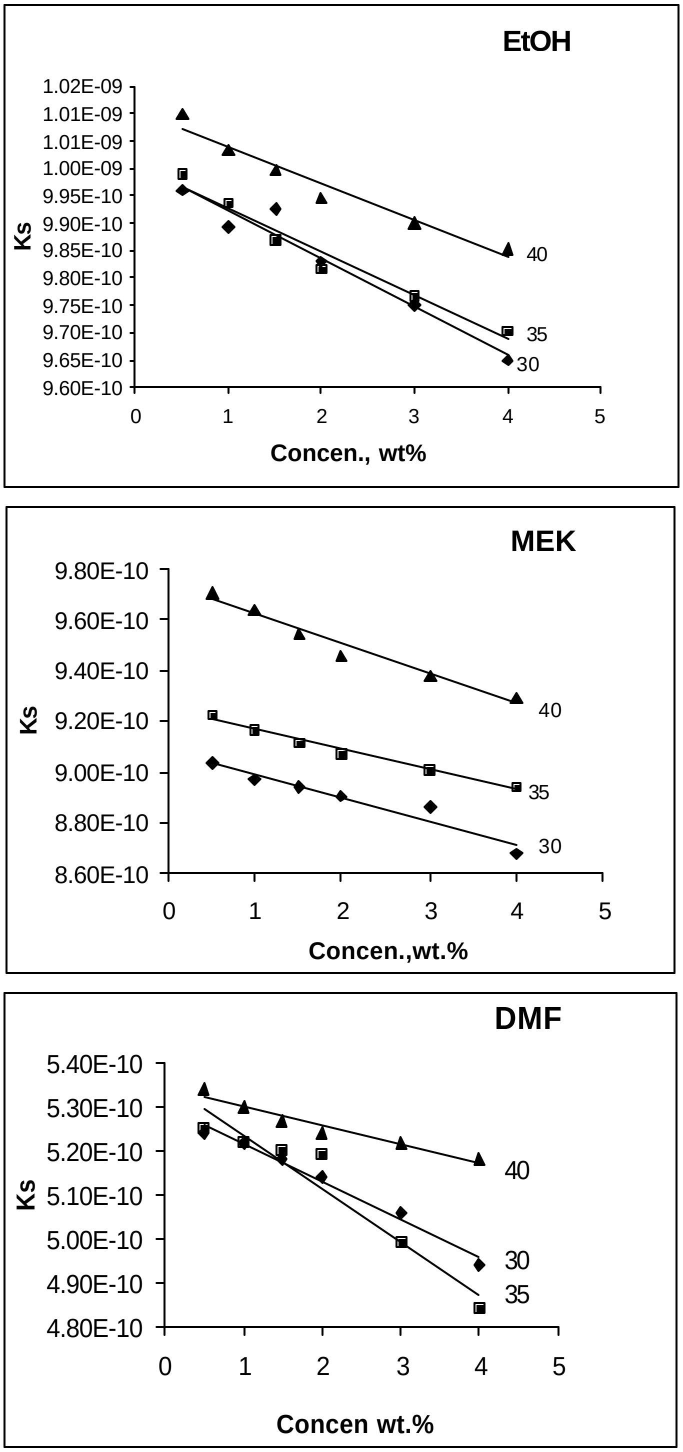
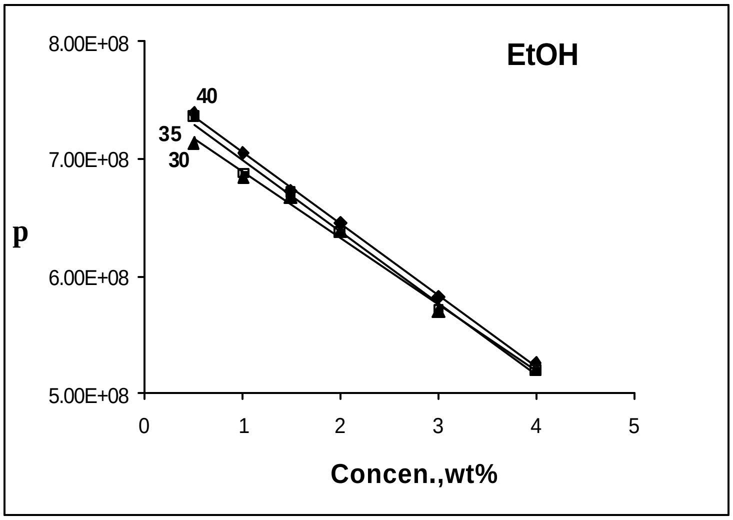
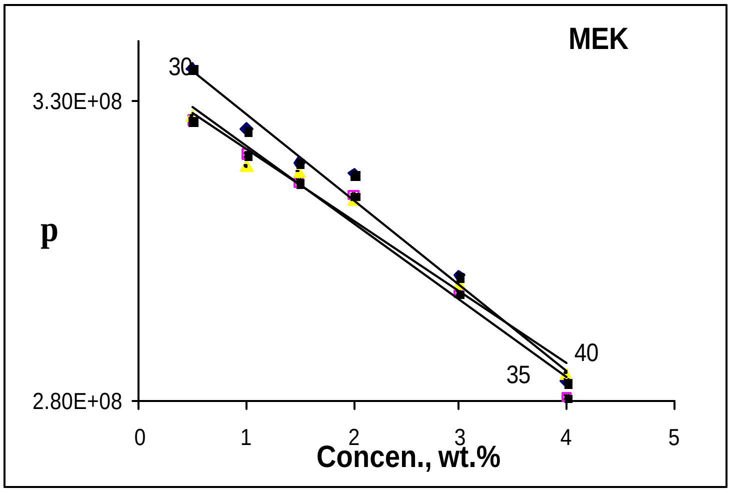


Fig 5.1: **The plots of isentropic compressibility (k_S) against concentration at 30^0, $35^0$and 40^0C for BCFA.**





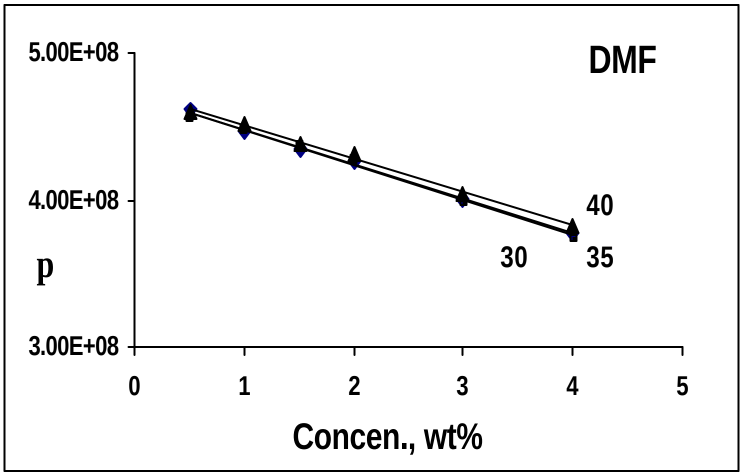


Fig 5.2: The plots of (p) internal pressure against concentration at 30^0, $35^0$and 40^0C for BCFA.

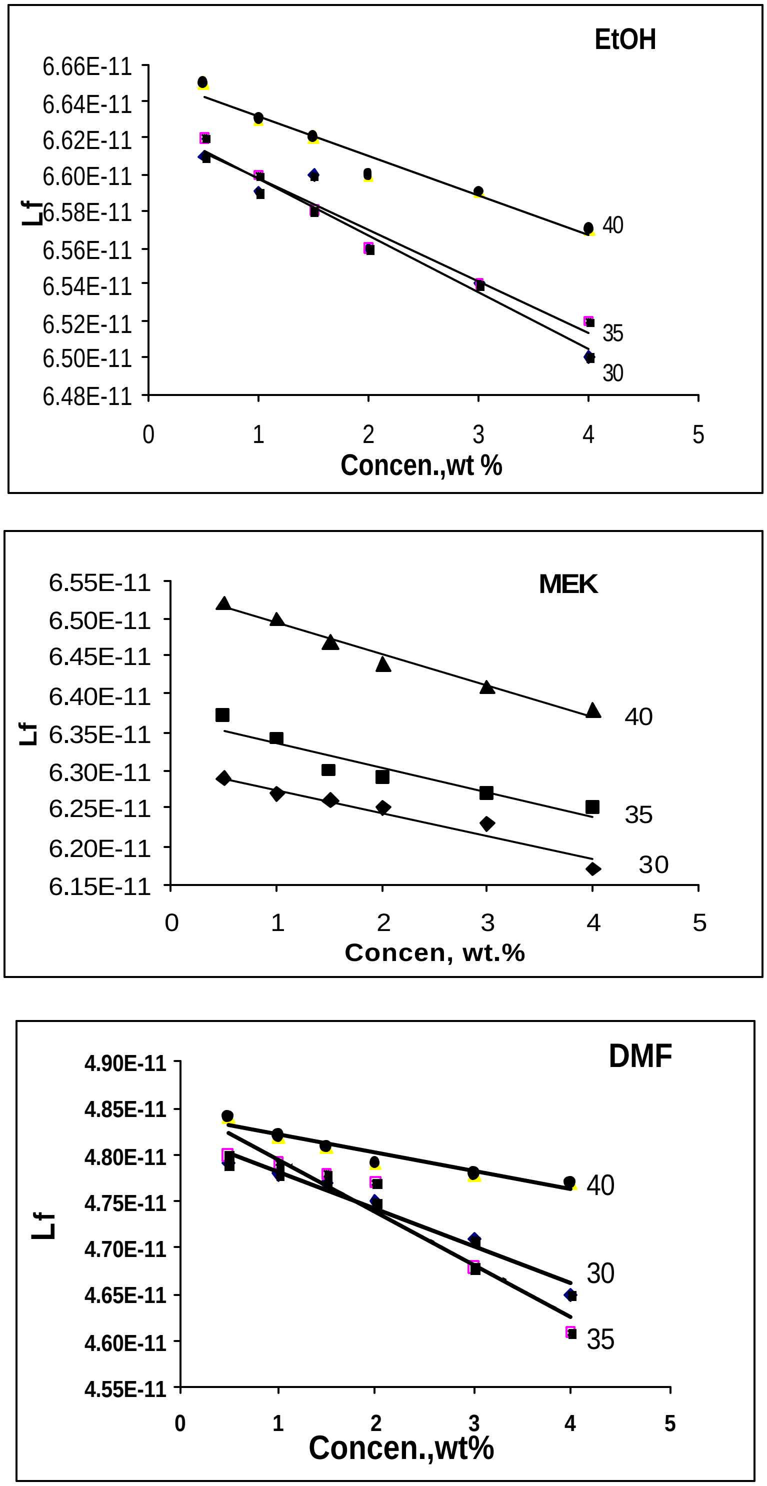
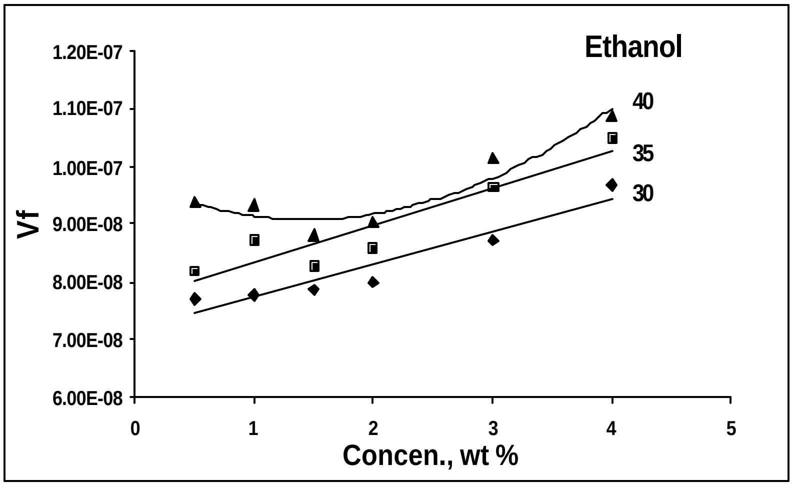
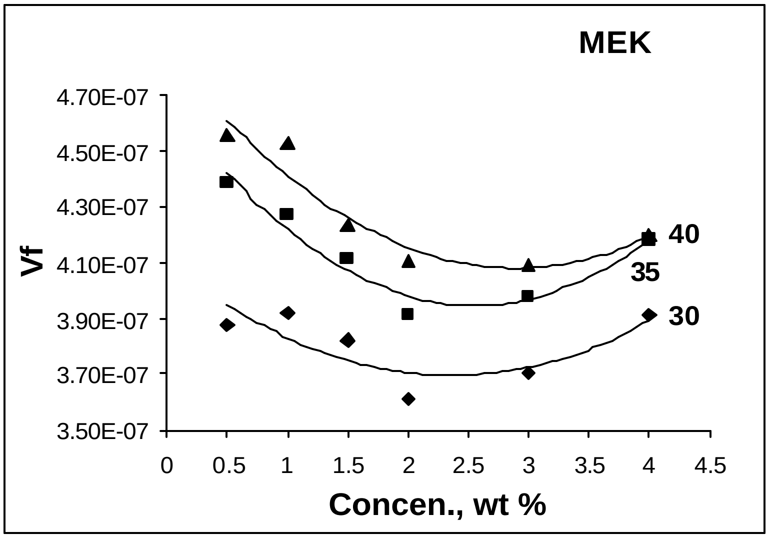


Fig 5.3: **The plots of (L_f) free path length against concentration at 30^0, $35^0$and 40^0C for BCFA.**





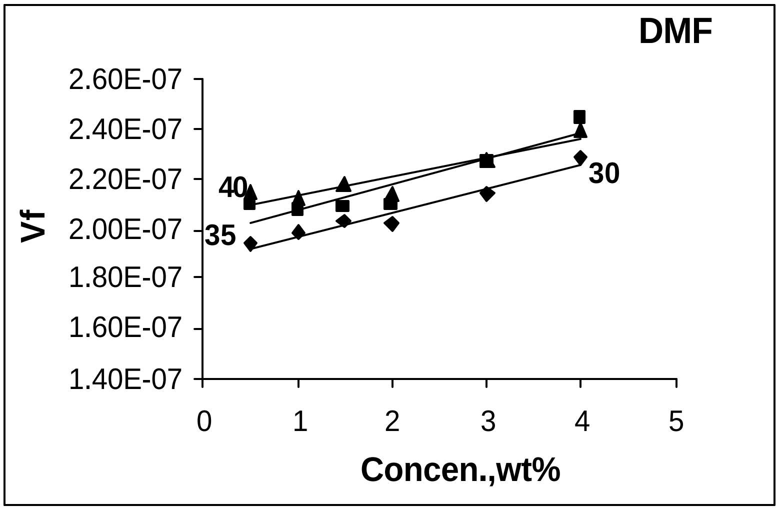
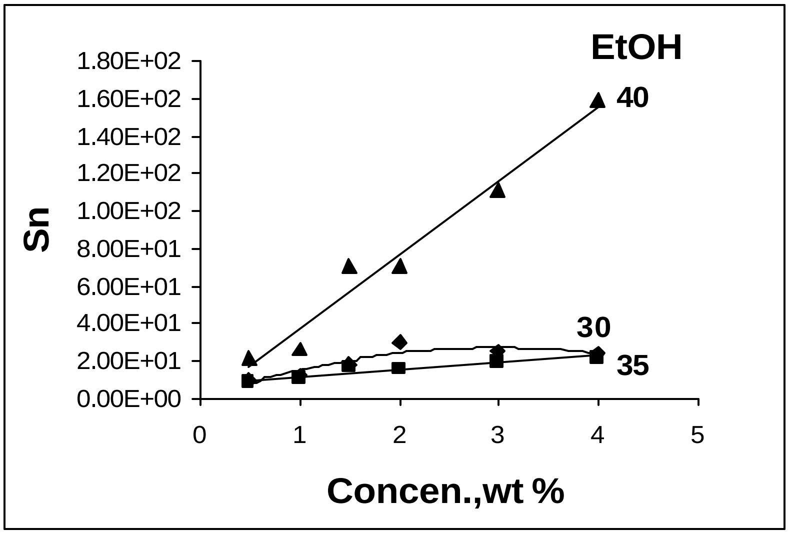
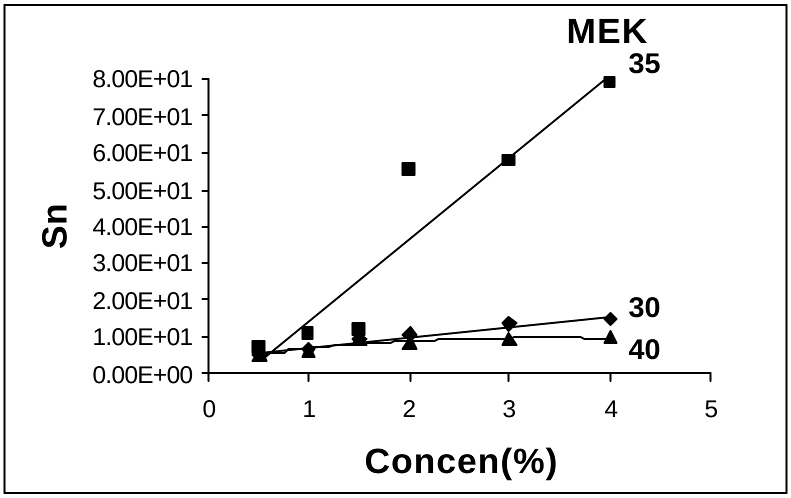


Fig 5.4: The plots of (V_f) free volume against concentration at 30^0, $35^0$and 40^0C for BCFA.





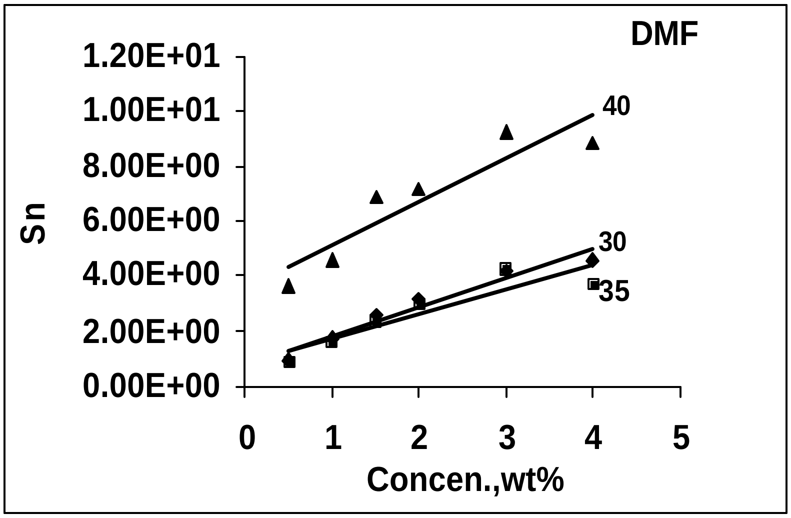


Fig 5.5: **The plots of (Sn) solvation number against concentration at 30^0, 35^{0}and 40^{0}C for BCFA.**

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

CHAPTER-1

This chapter describes the general introduction and up to date literature survey on phenolic resins, properties of natural fibers, fabrication, characterization and applications of glass, jute and sandwich composites.

CHAPTER-2

This chapter deals with the synthesis of bisphenol-C- formaldehyde based self cured resin and its modification by acrylic and boric acids. The resins are characterized by IR spectral data. Kinetic of thermal degradation of the resins have been studied by TGA/DSC.

CHAPTER-3

This chapter of the thesis elaborates the fabrication of jute, glass and sandwich composites of bisphenol-C-formaldehyde resin. The mechanical and electrical properties of the composites are determined according to standard test methods. Tensile strength of sandwich glass-jute composite has decreased, while flexural strength has improved substantially in comparison to jute and it is almost half of the glass composite indicating improvement in stiffness of the hybrid composite.

The tensile strength of hybrid composites: Jute-WH, Jute-CH, Jute-JH and Jute-RH have decreased by 53 - 72% as compared to Jute composite. Comparatively Jute-WH composite has almost two times tensile strength as compared to Jute-CH, Jute-JH and Jute-RH hybrid composites. Out of four biomass fibers selected, WH is found more effective in stress transfer as compared to remaining three husks. In glass and Glass-WH composites tensile strength of Glass-WH composite is only 12.4% than glass composite and flexural strength is 12.34% than glass composite.

The flexural strength of Jute-WH (52.6%), Jute-JH (94.5%) and Jute-CH (152.6%) has increased to a greater extent upon hybridization, while for BCF-

Jute-RH (26.3%) it is decreased. All hybrid composites except Jute-RH possess excellent flexural strength as compared to Jute composite.

Electric strength of glass-jute hybrid composite is intermediate of glass and jute composites, while volume resistivity is almost half of the pure composites indicating considerable decrease in insulating property upon hybridization.

There is no much change in dielectric breakdown strength is observed between jute composite and hybrid composites: Jute-CH, Jute-RH, Jute-WH and Jute-JH, but volume resistivity of Jute-WH and Jute-JH composites has increased respectively 437.4% and 196.7% as compared to jute composite, while for Jute-CH and Jute-RH it is decreased by 2.3 to 25.2%. In Glass-WH composite volume resistivity is decreased 31.46% and dielectric breakdown strength is decreased 64.17% than glass composite. Jute-WH and Jute-JH composites possess superior volume resistivity as compared to Jute-RH and Jute-CH composites.

Water absorption in composites is determined by change in weight method at room temperature in pure water and 10% each of aqueous solutions of HCl and NaCl at the interval of 24h. The malinization is successfully implemented for jute fibers by maleic anhydride that produces water repellency by partial replacement of hydrophilic –OH groups by ester groups. It shows excellent moisture protection to composite, even specimens fully immersed in water, acidic and saline environments. It is observed that the percentage moisture uptake by untreated jute composites is relatively higher than that of treated one.

Glass-jute hybrid composite showed high diffusivity as compared to Glass-BCF composite. %Equilibrium moisture uptake time is found to be 36h in all the three environments. It is found that all the composites possess excellent hydrolytic stability towards water, acid and saline and even in boiling water.

Mechanical, electrical and water absorption data are interpreted in light of nature of fibers and resin, fiber orientation, fiber loading, test conditions, etc. The composites may be useful for low load bearing applications and also in electrical and electronic industries as well as in marine vessels.

CHAPTER-4

This chapter of the thesis deals with the synthesis and coating applications of polyurethane resins, BCF-TDI and PEG-200 PUs were characterized by IR spectral data, thermo-mechanical and electrical properties and also for their chemical resistance in different environments at room temperature for varying time interval. Chemical resistance of PU coated glass and metal plates was carried out according to change in mass method. PU films possess good thermo-mechanical and electrical properties as well as excellent hydrolytic stability.

The density of films is determined by a floatation method and it is observed that the density has decreased upon increasing concentration of PEG-200 (BPT-1: ?= 1.2069 g/cm^3 and BPT-2: ?=1.1539 g/cm^3). BPT-1 and BPT-2 possess respectively tensile strength, electric strength and volume resistivity of 34 MPa, 73.47 kV /mm, 2.32 x 10 ^{14} ohmcm and 22 MPa, 93.75 kV /cm, 2.14x 10 ^{16} ohmcm. Thus, density and tensile strength have decreased, while electric strength and volume resistivity have increased with PEG-200 concentration. Increasing amount of PEG-200 in copolymer film resulted in drastic reduction of moisture absorption. BPT-2 film may find its excellent coating application under relatively concentrated (10%) acidic (HCl, H_2SO_4 and HNO_3), alkaline (NaOH and KOH) and saline environments.

CHAPTER-5

This chapter describes the acoustical properties of BCFA resin solutions at 30^0, 35^0 and 40^{0}C. Various acoustical parameters such as isentropic compressibility ($?_s$), specific acoustical impendance (Z), Rao's molar sound function (R), Van der wals constant (b), internal pressure (p), classical absorption coefficient $(a/f^2)_{cl}$, viscous relaxation time (t), solvation number (S_n), free volume (V_f) and intermolecular free length (L_f) were determined and discussed in light of effect of solvent, temperature, concentration and nature of the resin.

A good to excellent correlations are found and linear relations are expressed in the form of correlation equations. These parameters are very important for understanding the structure, solute-solvent and solute-solute interactions occurring in a particular system at a constant temperature.

The increase of ρ, η and U with C supported increase in cohesive forces due to powerful molecular interactions, while decrease of these parameters with T indicated decrease in cohesive forces. A linear decrease of isentropic compressibility (κ_S), internal pressure (π) and free path length (L_f), with C and T in DMF system supported existence of strong molecular interactions. V_f increased nonlinearly with C and T in EtOH, while it decreased nonlinearly with C and increased with T in MEK system also supported presence of strong molecular interactions. Z, b, $(\alpha/f^2)_{cl}$ and τ increased linearly with C and decreased linearly with T , which supported existence of strong molecular interactions.

The observed solvation tendency of BCFA with studied solvents was EtOH > MEK > DMF. In DMF system solvation was the minimum and that might be due to steric hindrance. Thus, BCFA possesses structure forming tendency in the studied solvents.