Patel, Viren A., 2008, *“Physico-chemical Studies on some Hybrid Composites”,* thesis PhD, Saurashtra University

PHYSICO-CHEMICAL STUDIES ON SOME HYBRID COMPOSITES

A THESIS SUBMITTED TO THE
SAURASHTRA UNIVERSITY

IN THE FACULTY OF SCIENCE
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN
CHEMISTRY

By

VIREN A. PATEL

UNDER THE GUIDANCE OF
PROF. P. H. PARSANIA

DEPARTMENT OF CHEMISTRY
(DST-FIST Funded & UGC-SAP Sponsored)
SAURASHTRA UNIVERSITY
RAJKOT- 360 005
GUJARAT (INDIA)

MAY-2008

Gram: UNIVERSITY
Fax: 0281-2577633

Phone: (R) 2581097
(O) 2578512

SAURASHTRA UNIVERSITY
Rajkot - 360 005.

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

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

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

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

Date :May , 2008
Place : Rajkot.

(Mr. Viren A. Patel)

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

Date : May , 2008
Place : Rajkot.

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

TO MY BELOVED
SISTER

ACKNOWLEDGEMENTS

First and foremost, I would like to pay my homage to THE ALMIGHTY GOD, "MY PARENTS" of this lovely world, whom blessings have made this venture successful.

It is a matter of great pleasure to express my deepest gratitude to my adored research guide Dr. P. H. Parsania - Professor and Head, Department of Chemistry - Saurashtra University, Rajkot. His profound knowledge, enormous enthusiasm, academic style and wit have driven me into new heights of view in Polymer Science. He was always there to "solve" whatever "problem" I may have inadvertently created. I consider myself lucky to work under his generous guidance.

I wish to express my sincere thanks to all faculty members: Dr. A. K. Shah, Dr. V. H. Shah, Dr. H. S. Joshi, Dr. Shipra Baluja, Dr. M. K. Shah, Dr. Y. T. Naliapara, Dr. R. C. Khunt, Dr. F. D. Karia and administrative staff for their encouragement during my research work.

I am heartily thankful to my seniors and juniors Dr. Ragin Amrutia, Dr. Bhavesh Gangani, Dr. Niral Mehta, Dr. Sunil Mavani, Dr. Nimisha Joshi, Dr. Paresh Vasoya, Vrajesh Aghera, Bharat Bhuva, Pankaj Mer, Jignesh Patel, Sandip Mataria, Punit Rasadia, Urvish Pathak Suresh Koradiya, Dinesh, Renish, Purvesh and Rupa for their incredible help and constructive suggestions.

Many thanks go to my friends-colleagues: Dr. Nikhil Venkariya, Dr. Atul Manvar, Dr. Rupesh Khunt, Jalpa, Dhaval, Ravi Chaniyara, Bhavin, Bharat, Sachin, Manisha, Janak, Hitesh, Samir, Manish, Gaurang, Amit, Pankaj, Jignesh, Manoj, Satish, Kaushik, Vijay, Nilesh, Anchal, Samrat, Jagdish, Ravi Gajera, Rahul, Mehul, Nayan, Chirag, Akshay, Jyoti, and Shavan for creating a pleasant working atmosphere and for all the help I have received during the research. How can I forget to thank my intimate friends Jiger, Vaibhav and Ashok for their valuable support and motivation.

I would also like to acknowledge the help of Mr. M. J. Meghpara for tracing of the figures and Dr. M. N. Jivani for his valuable help in computations.

My sincere thanks are extended to Vijyamasi, Jignesh and Maulik for their kind co-operation during my research programmed.

I am also greatly thankful to The Directors, ERDA-Vadodara, SICART-V.V. Nagar and Polylink Indu.-Dhodka for testing facilities.

The never ending process of unsurpassable devotion, love and affection which was showered upon me by my beloved parents Mr. Amritlal Patel and Mrs. Jayshreeben Patel, my brother Parag, bhabhi Jigna, sister Jigna and brother-in-law Mukesh Rola who ever enlightened my path and boosting me to go ahead to reach the goal. At last, I would like to express my heartiest feelings towards my loving nephews-Om, Soham, and Shivam. However I assured them to be worthy, of whatever they have done for me.

-- Viren A. Patel

CONTENTS

SYNOPSIS

PHYSICO-CHEMICAL STUDIES ON SOME HYBRID COMPOSITES

Mr. Viren A. Patel

DEPARTMENT OF CHEMISTRY

SAURASHTRA UNIVERSITY

RAJKOT- 360 005

Jan. 24, 2008

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

FACULTY : **SCIENCE**
SUBJECT : **CHEMISTRY**
TITLE OF THE THESIS : **PHYSICO-CHEMICAL STUDIES ON SOME HYBRID COMPOSITES**

NAME OF THE CANDIDATE : **VIREN AMRITLAL PATEL**

REGISTRATION NO. : **3305**
DATE OF REGISTRATION : **20th Sep. 2005**
NAME OF THE GUIDE : **Dr. P. H. PARSANIA**
PROF. & HEAD
DEPARTMENT OF CHEMISTRY
SAURASHTRA UNIVERSITY
RAJKOT – 360 005
SUBMMITED TO : **SAURASHTRA UNIVERSITY**

PLACE OF THE WORK

DEPARTMENT OF CHEMISTRY
SAURASHTRA UNIVERSITY
RAJKOT-360 005
GUJRAT-INDIA

GENERAL INTRODUCTION

The term hybrid composite is used to describe composite containing more than one type of fibers. Hybrid composites are attractive structural materials because they provide designers freedom of tailoring composites and achieving properties that cannot be realized in binary system containing one type of fiber dispersed in a matrix and more cost-effective utilization of expensive fibers such as carbon and boron can be obtained by replacing them partially with less expensive fibers such as glass and aramid. Further hybrid composites provide the potential of achieving a balanced pursuit of stiffness, strength and ductility, as well as bending and membrane related mechanical properties. Hybrid composites have also demonstrated weight savings, reduced notch sensitivity, improved fracture toughness, longer fatigue life and excellent impact resistance [1].

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 [2].

Natural fiber reinforced polymer composites are superior over synthetic composites in certain properties like enhanced biodegradability, combustibility, light-weight, ease of recyclables, etc. These advantages place the natural fiber composites amongst high performance composites having economical and environmental advantages with good physical properties [3, 4].

---

1. T. W. Chou, “Hybrid composites”, Microstructural Design of Fiber Composites, 1992, p. 231.
2. M. M. Thwe and K. Liao, Plastic, “Tensile behavior of modified bamboo-glass fiber reinforced hybrid composites”, Plastics, Rubber and Compos. **31**, 422-431, 2002.
3. 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**, 295-309, 2000.
4. A. K. Bledzki and J. Gassan, “Composites reinforced with cellulose based fibres”, Prog. Polym. Sci., 24, 221-249, 1999.

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 is also 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 resins modified by inorganic materials are thermosetting resins, with excellent performance such as thermal stability, mechanical strength, and electric properties. Some reports have been appeared on synthesis and application of boron containing phenol -

---

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 -1224, 2001.
8. H. Shen and S. Nutt "Mechanical characteristics of sort fiber reinforced phenolic foams", Composite Part A: Appl. Sci. and Manuf., **34**, 899-906, 2003.
9. Hardwood, Plywood and Veneer Association. 1995, ANSI / HPVA HP. 1 1994.
10. Patent Co-operation Treaty (PCT). WO 053012 (2004) A.

formaldehyde resin [11, 12] and phosphorus containing phenol formaldehyde resin [13,14].

In order to obtain composites with good thermo-mechanical performance, it is necessary to have an adequate combination of thermally stable matrix-resin with tape or fabric type reinforcements, which act as the principal load-carrying component. In addition, the matrix must keep the reinforcement in a desired orientation, avoiding abrasion among the fibers, protecting them against environmental degradation before, during, and after composite processing, and allowing them to act as a load transfer. Thus, in a composite, both reinforcement and matrix must retain their chemical and physical identities and yet result in many properties that cannot be achieved with either of the constituents acting alone [15,16].

The literature survey on epoxy, phenolic and inorganic materials 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:

---

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**, 207-210, 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. Stab., **77**, 495-501, 2002.
13. C. S. Cho, S J. Chang, W. J. Teng and J. J. Chen, “Photosensitive phosphorylated phenol formaldehyde resin and method for preparing the same”, U S Patent -6566483, 2003.
14. C. H. Lin and C. S. Wang, “Novel phosphorus-containing epoxy resins Part I. Synthesis and properties”, Polymer, **42**, 1869-1878, 2001.
15. J. Jang, H. Chung, M. Kim and Y. Kim, “Improvement of flame retardancy in phenolic and paper-sludge-phenolic composites”, J. Appl. Polym. Sci. **69**, 2043-2050, 1998.
16. P. K. Mallick, “Fiber-Reinforced Composites: Materials, Manufacturing and Design”, 1st. Ed., Marcel Dekker Inc.: New York, 1988.

CHAPTER 1: Literature survey on cardo bisphenols, their epoxy and phenolic resins and hybrid composites

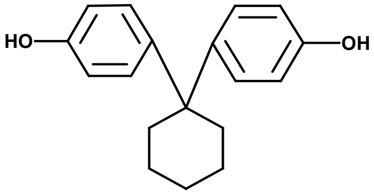
This chapter of the thesis describes up to date literature survey on syntheses and characterization of epoxy and phenolic resins, properties and applicability of natural and synthetic fibers and applications of composites in different fields of science and in routine life.

CHAPTER 2: Syntheses of cardo bisphenols based resins and their physico-chemical characterization

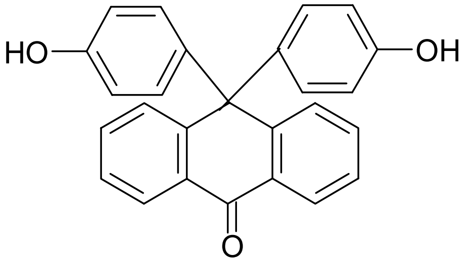
This chapter is further subdivided into ten sections

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^{0}C for 4h and was repeatedly recrystallized from methanol-water system prior to its use.



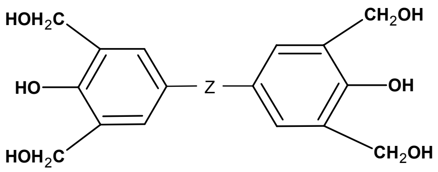
Section- II: Synthesis of 9, 9’-bis (4-hydroxy phenyl) anthrone-10 (BAN)

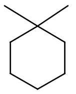


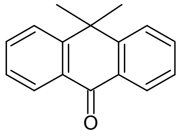
BAN was synthesized by condensing anthraquinone with phenol at 120^{0}C for 6h in the presence of stannic chloride (molar ratio 1:7:1.5, respectively) and was isolated from hot acetic acid. BAN was recrystallized repeatedly from dioxane-water system prior to its use.

Section-III: Syntheses of bisphenol-formaldehyde resins (BCF/ BANF)

BCF/BANF was synthesized by condensing Bisphenol-C/BAN and formaldehyde by using alkali as a catalyst at 70^{o}C for 1h/2.5h, respectively. Creamish solid products were repeatedly purified from methanol-water system prior to their use.

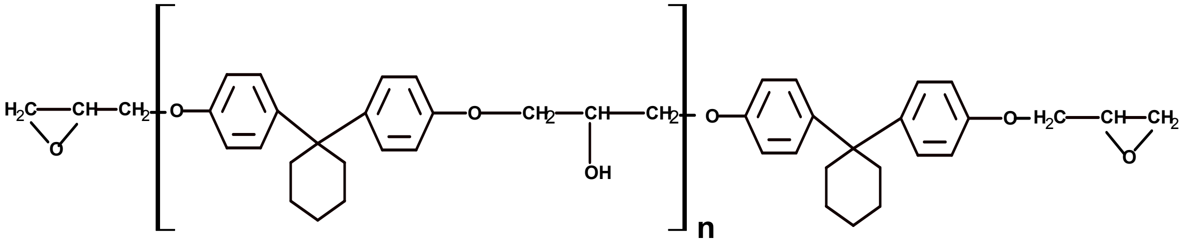


Where, BCF: Z =  ,

BANF: Z = 

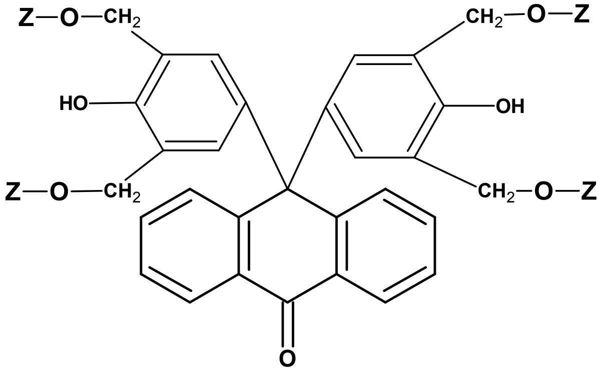
Section-IV: Synthesis of epoxy resin

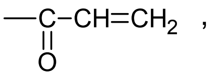
Epoxy resin of bisphenol-C (EBC) was synthesized by condensing bisphenol-C with epichlorohydrine by using isopropanol as a solvent and alkali as a catalyst at reflux temperature for 4.5 h. The resin was extracted from chloroform.



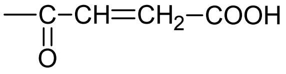
Section-V: Syntheses of BAN-formaldehyde-acrylate / maleate resins

BAN-formaldehyde-acrylate/maleate resins were synthesized by condensing BANF and acrylic acid/maleic anhydride by using 1, 4-dioxan as a solvent and phenothiazine as a catalyst at 80°C for 6 h. The solid creamish products were purified repeatedly from MEK-water system prior to their use.



Where, BANFA: Z = 

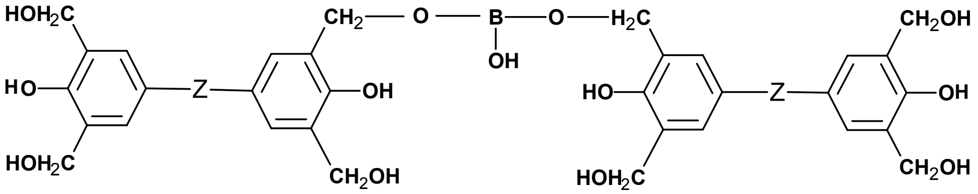
$-\underset{\underset{O}{\|}}{C}-CH=CH_2$,

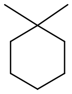
BANFM: Z = 

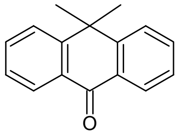
$-\underset{\underset{O}{\|}}{C}-CH=CH_2-COOH$

Section-VI: Syntheses of boron containing phenolic resins (BBCF/ BBANF)

BBCF/BBANF were synthesized by condensing BC/BAN, formaldehyde and boric acid using alkali as a catalyst at 70^{0}C for 1 h. Creamish solid products were repeatedly purified from methanol-water system prior to their use.

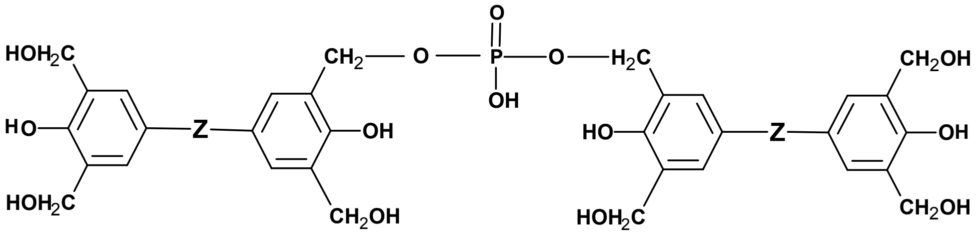


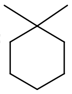
Where, BBCF: Z =  ,

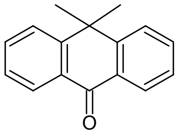
BBANF: Z = 

Section-VII: Syntheses of phosphorus containing phenolic resins (PBCF/ PBANF)

PBCF/PBANF was synthesized by condensing BCF/BANF and phosphorus oxychloride using methanol as a solvent and refluxing for 2h. PBCF and PBANF were repeatedly purified from methanol-water system prior to their use.



Where, PBCF: Z =  ,

PBANF: Z = 

Section-VIII: IR spectral characterization of resins

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

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

Section-X: 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. Physico-chemical properties of cured resins depend upon the degree of curing.

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 materials under investigation. Thermal stability and kinetic parameters such as n, A, E_a and ΔS^* of the resins have been evaluated and interpreted in this section.

CHAPTER 3 : Fabrication of composites based on mixed matrix materials of epoxy and phenolic resins and their physico-chemical characterization

This chapter is further subdivided into three sections.

Section-I: Fabrication of composites

Hybrid composites of jute, glass, carbon and sisal fibers are prepared by hand lay up compression molding under 7.6 MPa pressure at 150^0C for 2h and at room temperature for 12h. Physical properties of jute and sisal fibers are modified by alkali treatment and acrylation.

Section-II: Mechanical and electrical properties of composites

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: Water uptake study

The composites of the 5 cm x 5 cm dimensions were prepared and the edges of composites were sealed with mixed matrix materials. Water uptake study in different environment was carried out at room temperature as well as in boiling water. The data are interpreted in light of environment effect, nature of fibers, matrix materials, interfacial bonding, etc.

CHAPTER 4 : Syntheses of polyurethanes and their physico-chemical characterization

This chapter is further subdivided into seven sections.

Section – I: Introduction

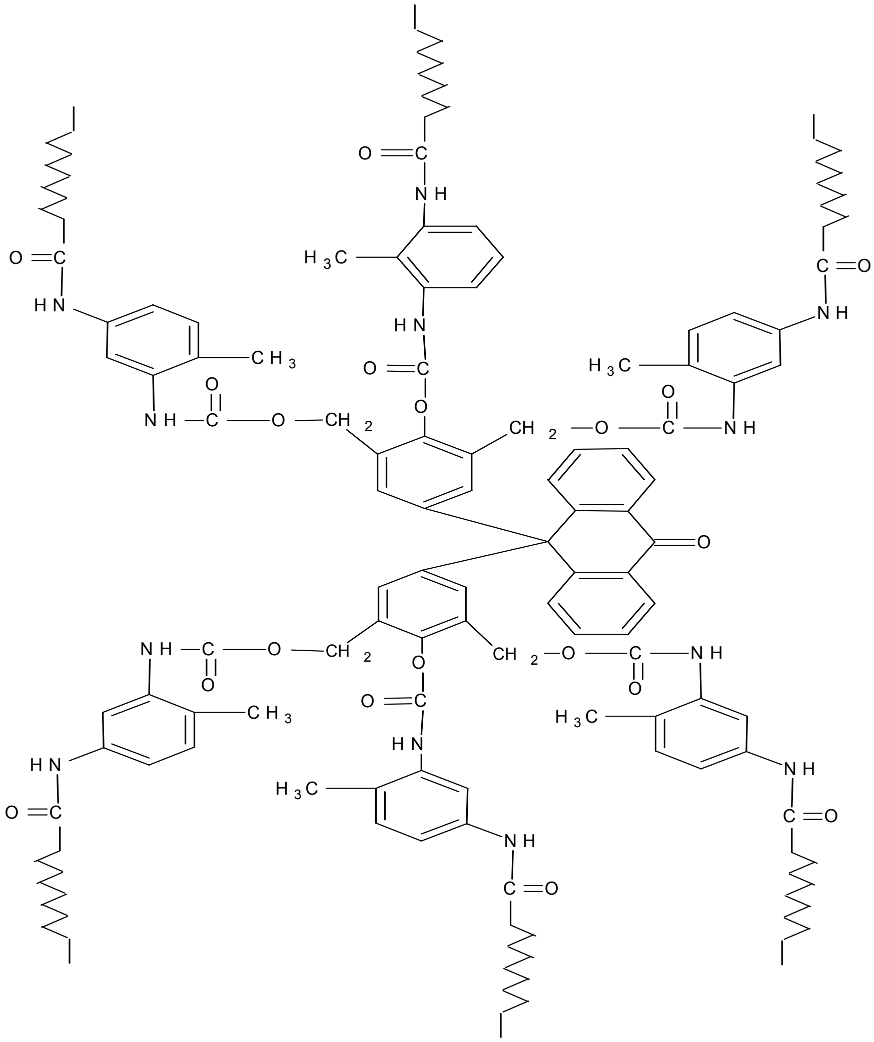
Modern technology can not be satisfied with single structured materials to fulfill economical needs of mankind. To make economic production of desired articles with desired combination of properties, it is often necessary to use complex structured materials.

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].

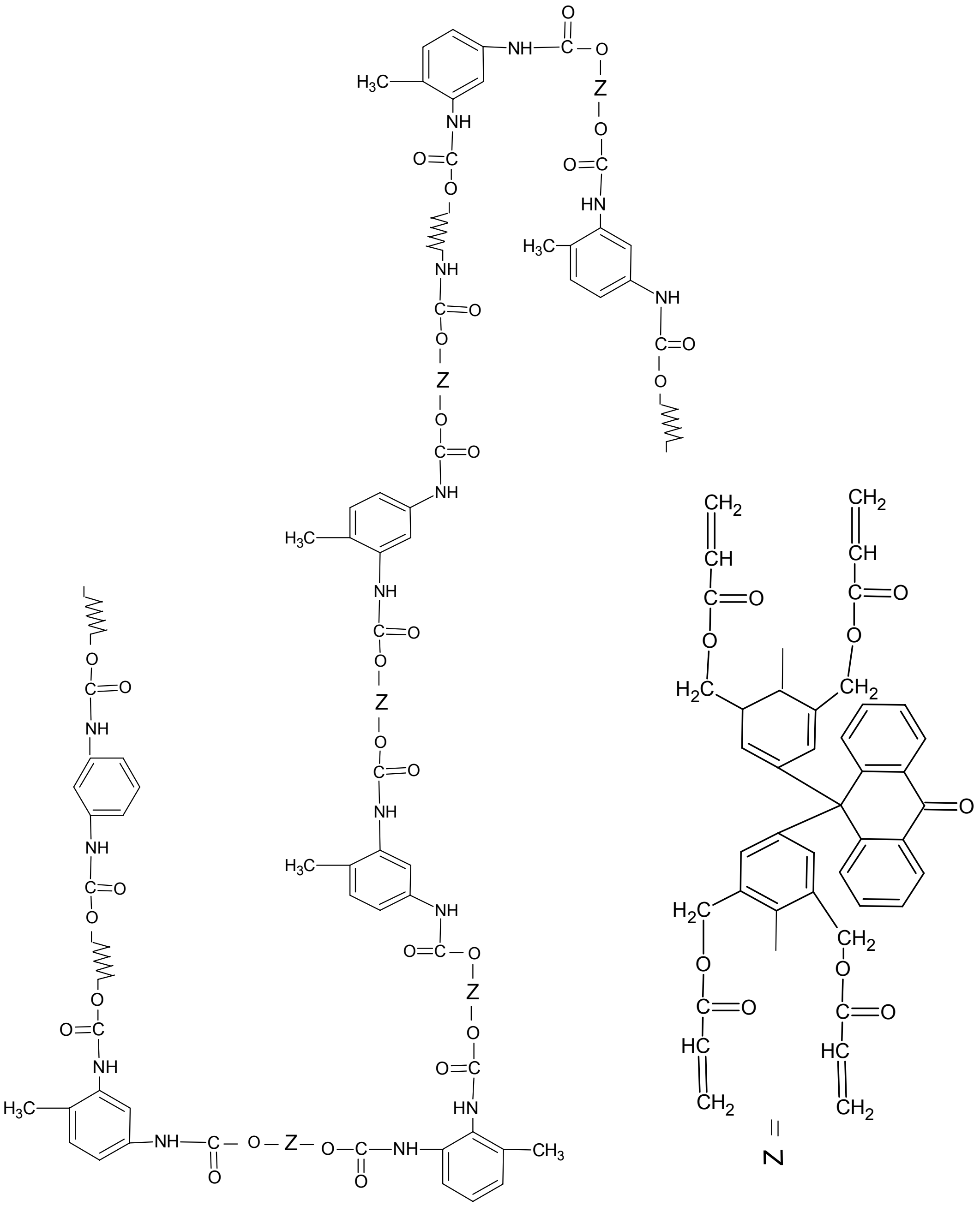
Section - II: Syntheses of polyurethane resins

(1) Synthesis and preparation of copolyurethane films

Copolyurethanes of varying compositions and their films were prepared by reacting BANF/BANFA, TDI and PEG-400/600 at room temperature for 15 min using MEK as a solvent. Hereafter films were designated as BTP and BATP for BANFand BANFA resins, respectively.



BTP



BATP

Section – III: IR characterization of copolyurethanes

Formation of polyurethane linkages in the cross-linkes copolyurethanes is supported by IR spectral data.

Section – IV: Density measurements of copolyurethane films

The densities of copolyurethane films are determined by floatation method using CCl_4-n-hexane system at room temperature and discussed in light of increasing chain length of PEG.

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

Copolyurethane films were analyzed by TGA and DSC at the heating rate of 10^0 and 20^0C min^{-1}, respectively in an N_2 atmosphere. The glass transition temperature, thermal stability and kinetic parameters of the copolyurethane films were determined and discussed. The tensile strength, electric strength and volume resistivity of copolyurethane films were determined according to ASTM methods and interpreted in terms of increasing chain length of PEG, degree of resin cure, etc.

Section – VI: Water uptake study in copolyurethane films

Water uptake sturdy in copolyurethane films was carried out in different environments at room temperature by change in mass method at the interval of 24 h.

Section – VII: Surface coating and chemical resistance study

This section describes the surface coating application of polyurethane resins on different substrates such as copper, aluminium and mild steel. The chemical resistance of coated samples is tested against water, 10% each of aqueous solutions of HCl and NaCl at room temperature for varying time interval and interpreted in light of nature of substrate.

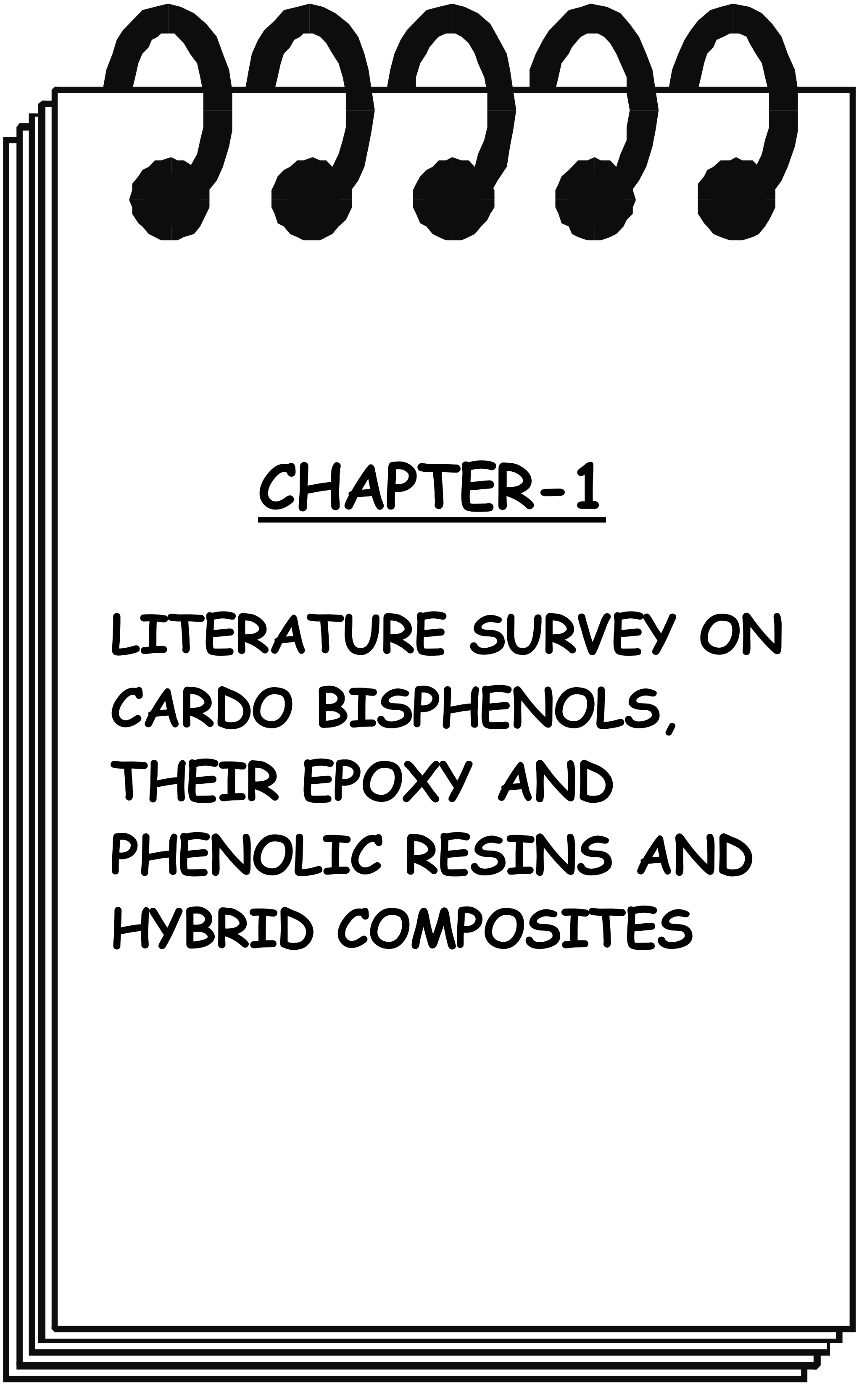
CHAPTER 5 : A brief review of the work done

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

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

(Dr. P. H. Parsania) **(Mr. Viren A. Patel)**

Prof. & Head,
Dept. of Chemistry,
Saurashtra University,
Rajkot – 360 005
Date: Jan. 24, 2008



CHAPTER-1

LITERATURE SURVEY ON CARDO BISPHENOLS, THEIR EPOXY AND PHENOLIC RESINS AND HYBRID COMPOSITES

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 man was employing a range of materials such as stones, woods, ceramics, glasses, skins, horne and fibers. Until the 19th century man's inanimate possessions, his home, his tools, his furniture, etc. were made from varieties of these classes of materials.

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

The most ancient polymeric material, mentioned in the book of 'Genesis' (Chapter-11) described that the builders in the "Babylonia" had a brick of stone and slime they had for mortar".

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

[A] LITERATURE SURVEY ON CARDO BISPHENOLS

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

Bisphenols find their applications as anti-oxidants for rubbers, oil, fat, soap and carotene; and stabilizer for polyolefin and against UV radiation, and for increasing the flex life of rubbery material. They are also used as fog inhibitors in electro photography, electroplating solvent and as wash fastening agents; they are also useful in manufacturing thermally stable polymers, epoxy resins, polyester and polyurethane resins.

Farbenind [1, 2] has reported the condensation of phenols and ketones in the presence of acetic acid, hydrochloric acid at 50^0C and also reported the melting points of 1,1’-bis(4-hydroxy phenyl)cyclohexane (186^0C), 1,1’-bis (4-hydroxy phenyl)-4-methyl cyclohexane (179^0C). The products are useful as intermediates for dyes and drugs.

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

(1) The addition of phenol to ketone

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

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

---

1. I. G. Farbenind, Fr. Patent 647, 454 1928; *C.A.* **23**, 2540, 1929.
2. I. G. Farbenind, Ger. Patent 467, 728 1927; *C.A*. **23**, 1729, 1929.
3. M. E. McGreal, V. Niederl and J. B. Niederl, J. Am. Chem. Soc., **61**, 345-348, 1939; C.A. **33**, 2130,1939.

Johnson and Musell [4,5] have reported synthesis of 1, 1’-bis(4-hydroxy phenyl)cyclohexane (I) using 5 moles of phenol, 1 mole of a cyclohexanone, H_2S or BuSH below 40^0C with 0.1- 0.3 mole dry HCl gave (I) m.p. 186-87^0C; 2Me-I, 236-240^0C; 4-Me-I 178^0C;

1, 1’-Bis(4-hydroxy-3-methyl phenyl)cyclohexane m.p. 187^0C and 1,1’-bis(4-hydroxy-3-isopropyl phenyl)cyclohexane, m.p. 109-111.5^0C. Mash containing small quantities of bisphenol (I) protect chickens from coccidiosis better than does a sulfaguanidine. They have also reported that coccidial infection in poultry may be suppressed by feeding a bisphenol (p-$HO(C_6H_4)_2$-CRR’ in which R’ is a phenyl or alkyl, R is H or alkyl).

Bender et al. [6] have reported preparation of various bisphenols by reacting phenol, NaOH and acetone. The mixture was refluxed for 16 h and acidified to pH 2-3 with 6N HCl. The yield was 47.5%. Similarly they have also synthesized 1,1’-bis(4-hydroxyphenyl)cyclohexane (m.p.187^0C); 1,1’-bis(3-methyl-4-hydroxyphenyl)cyclohexane (m.p. 186-189^0C) and 1,1’-bis(3-chloro-4-hydroxyphenyl)cyclohexane (m.p. 134-141^0C).

Bender et al. [7] have reported the preparation of bisphenols by irradiating a mixture of ketone and phenol at 20-100^0C with β- rays or ultra violet in the presence of 37% aqueous HCl or 70% aqueous H_2SO_4 as condensing agent and stirring at 30-37^0C. 1,1’-Bis(4-hydroxy phenyl)cyclohexane (m.p. 186-9^0C) was obtained in 93% yield from 1 mole cyclohexanone and 4 moles phenol.

Farbenfabriken [8] has reported the preparation of 4,4’-dihydroxy diphenyl cyclohexane (m.p.186^0C) using cyclohexanone (78 kg) and excess phenol (400 kg) in the presence of 38% HCl (80 kg) as a catalyst at room temperature for 6 days.

---

4. J. E. Johnson and D. R. Musell, “Bis(hydroxyl phenyl)cyclohexane compositions”, U.S. Patent, 2538725, 1951; C.A. **45**, 4412, 1951.
5. J. E. Johnson and D. R. Musell, “Diphenol compound composition of coccidiosic control”, U.S. Patent 2535014, 1950; C.A. **45**, 2635, 1951.
6. H. L. Bender, L. B. Conte and F. N. Apel, “Bisphenols”, U.S. Patent 2858342, 1958; C.A. **53**, 6165, 1958.
7. H. L. Bender, F. N. Apel and L. B. Conte, “Bisphenols”, U.S. Patent 2936272, 1960; C.A. **54**, 19,604, 1960.
8. Farbenfabriken, Ger. Patent 1031788, 1958; C.A. **54**, 19,603, 1960.

Tumerman et al. [9] have reported condensation of o-cresol with aliphatic, aromatic and cyclic ketones in the presence of HCl and BF_3 as catalysts. The highest reaction rate was observed in the case of Me_2CO and cyclohexanone. The condensation of o-cresol with pinacolone yielded 10-12% after 450 h of condensation.

Farbenfabriken [10] has reported chlorination of bisphenols by chlorine gas with stirring for 1h at 15^0C in nitrogen atmosphere and steam distillation of 1,1'-bis(4,4'-dihydroxydiphenyl)cyclohexane gave 1,1'-bis(3,3',5,5'-tetrachloro-4,4'-dihydroxy phenyl)cyclohexane (m.p. 148.5 - 9.5^0C).

Bilik et al. [11] have reported the preparation of bis(3-chloro-4-hydroxy phenyl)alkanes by the reaction of bis(4-hydroxy phenyl)alkanes with $SOCl_2$ and a catalyst containing or generating a SH group in chloroform or carbon tetrachloride. A mixture of 1,1'-bis(4-hydroxy phenyl)cyclohexane (7.4 g), $SOCl_2$ (40 ml) and Na_2S (0.28 g) in CCl_4 (40 ml) was heated with stirring for 3 h at 55^0C, 1h at 70^0C yielded 63-75% 1,1'-bis(3-chloro-4-hydroxy phenyl)cyclohexane of m.p. 142.5^0C (CCl_4) 82-6% 2,2'-bis(3-chloro-4-hydroxy phenyl) propane of m.p. 89-91^0C (30% aq. AcH) and 100% 3,3'-bis-(3-chloro-4-hydroxy phenyl)pentane. The title compounds are used in the preparation of incombustible polycarbonate, nonflammable epoxy resins and herbicides.

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

---

9. B. M. Tumerman, E. S. Gervits and I. V. Vesela, "Condensation of o-cresol with ketones in the presence of hydrogen chloride and boron fluoride compounds", Neffepererabotkai, Naftekhim, Nauchn-Tekhum, **8**, 46, 1965; C.A. **64**, 4977, 1966.
10. Farbenfabriken, Ger. Patent 1,073,504, 1960; C.A. **55**, 16,491, 1961.
11. I. M. Bilik, N. M. Bondarets, A. M. Serebryanyi, L. S. Rybkina and T. M. Cheryavskaya, "Bis(3-chloro-4-hydroxy phenyl)alkanes", Brit. Patent 1,047,058, 1966; C.A. **66**, 10,737, 1967.
12. S. Maeda, J. Yurimoto, S. Samukawa and Y. Kojima, "Stabilized polyurethane", Japan 14, 752(66), 1963; C.A. **66**, 86,263, 1967.

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

Farnham et al. [14] have reported condensation of ketone with a methyl group in α-position to the CO group such as acetone, PhCOMe or cyclohexanone with an excess of phenol like phenol, o-cresol and o-chlorophenol (ratio 1.3-2.0) with a free para position at 40-100^{0}C in the presence of an insoluble anhydrous sulfonated cation exchange resin.

Freudewald et al. [15] have reported the condensation of phenol (94 g) with cyclohexanone (98 g) in the presence of 2.0 g EtSH and anhydrous HCl (4.7 g) and heating at 70^{0}C in closed system for 3h to give 97% 1,1'-bis(4-hydroxy phenyl) cyclohexane.

Popova et al. [16] have reported the synthesis of monomers by condensing phenol and o-cresol with cyclohexanone to give 1,1'-bis(4-hydroxy phenyl)cyclohexane and 1,1'-bis(3-methyl-4-hydroxy phenyl)cyclohexane, respectively. These bisphenols are treated with HNO_3 in AcOH at 0^{0}C to give 1,1'-bis(3-nitro-4-hydroxy phenyl)cyclohexane and 1,1'-bis(5-nitro-3-methyl-4-hydroxy phenyl)cyclohexane, respectively, and were reduced with $SnCl_2$ in HCl and with Raney Ni to give 1,1'-bis(3-amino-4-hydroxy phenyl) cyclohexane, respectively. These monomers are useful for coordination polycondensation.

Serebryanyi et al. [17] have reported the preparation of 1,1'-bis(3-chloro-4-hydroxyphenyl)cyclohexane (0.056mole) in CCl_4 (90 ml) and $SOCl_2$ (0.13 mole) using fused Na_2S (0.005 mole) as a catalyst with stirring for 3h at 55^{0}C and 1 h at 70^{0}C gave 70% yield.

---

13. Y. Masai and M. Nakanishi, Japan 13, 248(67), 1964; C.A. **68**, 3,557, 1968.
14. A. G. Farnham, F. N. Apel and H. L. Bender, "Bisphenols", Ger. Patent 1,242,237, 1967; C.A. **68**, 59,282, 1968.
15. Freudewald, E. Joachim, Konrad and M. Frederic, "p-Phenylphenol", Fr. Patent 1,537,574, 1968; C.A. **71**, 21,868, 1969.
16. T. K. Popova and G. P. Nedonoskova, "New monomers for coordination polycondesation", Zh. Khim, 5Zh338, 1970; C.A. **75**, 6,391, 1971.
17. A. M. Serebryanyi, I. M. Bilik and N. M. "1,1,-Bis(3-chloro-4-hydroxyphenyl)cyclohexane", Mironova, Metody Poluch Khim., Reaktive Prep., U.S.S.R., **20**, 35, 1969; C.A. **76**, 85,493, 1972.

Kozlov et al. [18] have reported the condensation of o-cresol with Me_2CO in the presence of polyphosphoric acid with a catalyst-o-cresol-Me_2CO ratio of 6:3:0.53 at 40^0C gave 94% $Me_2C\text{-}(C_6H_3(OH)Me\text{-}4,3)_2$. Similar results were obtained with o-cresol and MeCOEt, Et_2CO, MeCOPr, MeCOBu, $MeCO(CH_2)_4\text{-}Me$ and $MeCO(CH_2)_5\text{-}Me$, condensation of cyclohexanone with o-cresol gave 90% 1,1'-bis(2-methyl- 4-hydroxyphenyl)cyclohexane.

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

Kozlov et al. [20] have reported the condensation of o-cresol with cyclohexanone in the presence of polyphosphoric acid. The optimum conditions for this condensation were $40\text{-}45^0C$, 70-100 wt % H_3PO_4 (72% P_2O_5), o-cresol to cyclohexanone molar ratio (3:1) for 3h; 94% 1, 1'-bis (4-hydroxy-3-methylphenyl) cyclohexane was obtained with small quantities of other isomers.

Alexandru [21] has reported the preparation of bisphenols by reaction of a ketone (cyclohexanone) with phenol, BuSH, $ClCH_2CH_2Cl$ and Me_3SiCl. The mixture was stirred and heated to $50\text{-}55^0C$ and finally at 65^0C to give bisphenol-Z.

Nagata et al. [22] have reported condensation of 4-hydroxy cyclohexanone with PhOH in 36% HCl at 60^0C for 4h to give 77% biphenyl cyclohexanol derivative. The decomposition and dehydrogenation of which in a mixture of NaOH, PhCMe: CH_2, H_2O and 5% Pd/C under N_2 at 250^0C for 4h gave 83% 4, 4'-bisphenol.

---

18. N. S. Kozlov, A. G. Klein and V. P. Sukhodolova, “Condensation of cresols with ketones in the presence of polyphosphoric acid”, Khim. Tekhnol, Obl. Tekh. Konf, 1973; C.A. **82**, 97,778, 1975.
19. O. V. Smirnova and E. Ya Robas, “Acidity constants of chlorine containing bisphenols”, Zh. Prikl Khim, **48**(3), 578, 1975; C.A. **82**, 139,099, 1975.
20. N. S. Kozlov, A. G. Klein and V. P. Sukhodolova, Vesti Akad Navuk B. SSR, Ser. Khim Navuk, **4**, 109, 1976; C.A. **85**, 176, 992, 1976.
21. B. S. Alexandru, U.S. Patent 4,766,255, 1988; C.A. **110**, 38,737, 1989.
22. Nagata, Teruyuki, Miura and Toru, Eur. Patent 2,51,614, 1988; C.A. **110**, 75,037, 1989.

Subramaniam et al. [23] have reported the synthesis of 4,4'-isopropylidene bisphenyl dicinnamate, 4,4'-cyclohexylidene bisphenyl dicinnamate, 4,4'-isopropylidene bisphenyl disalicylate, 4,4'-cyclohexylidene bisphenyl disalicylate, dioxyacetic acid and dimethyl ether of bisphenol-A and bisphenol-C. They have tested the compounds for their activity against a fungi Fusarium oxysporum by filter paper disc method and reported that dimethyl ether and the dioxyacetic acid are inactive even at the highest concentration level used, whereas both the esters are active even at the minimum concentration level used.

Islam et al. [24] have reported the synthesis of tetra halogenated 4,4'-dihydroxydiphenylalkanes. The condensation of PhOH with MeCOMe, cyclohexanone, cyclopentanone and AcPh gave respective bisphenols in 66-80% yields. The condensation of o and m-cresol with ketones gave 70, 68 and 60% yields of respective bisphenols. They have also reported bromination of bisphenols by Br-AcOH in 61-70% yields. Chlorination of bisphenols by HCl in presence of H_2O_2 gave the respective tetrachlorobisphenol derivatives in 67-87% yields. The condensation of bisphenols with $ClCH_2COOH$ in aqueous NaOH gave dioxyacetic acid derivatives of bisphenols in 61-75% yields.

Dietzler [25] has reported bromination of bisphenol in methanol-water system. Thus bisphenol was treated with bromine at 42^0C with stirring (4h). The mixture was kept for 2h at 40^0C yielded 94.4% 4, 4'-isopropylidene-bis (2, 6-dibromophenol) (181-182^0C), 4, 4'-cyclohexylidene bis(2,6-dibromo-phenol) (m.p. 190^0C).

Rao et al. [26] have reported a convenient method for the preparation of bisphenols. Cyclohexanone was treated with phenol at 40^0C and with o-cresol at

---

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

24. A. M. Islam, E. A. Hassan, M. E. Rashad, and M. M. Wassel, "Tetrahalogenated 4,4'-dihydroxydiphenylalkanes, their synthesis and some of their reactions", Egypt. J. Chem., **20**(5), 483-490, 1980.

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

26. M. V. Rao, A. J. Rojivadiya, P. H. Parsania and H. H. Parekh, "A convenient method for the preparation of bisphenols", J. Indian Chem. Soc., **64**, 758-759, 1987.

room temperature in the presence of hydrochloric acid and acetic acid to give 1, 1’-bis(4-hydroxy phenyl)cyclohexane and 1,1’-bis(3-methyl-4-hydroxy phenyl) cyclohexane, respectively.

Garchar et al. [27, 28] have studied optimization reaction conditions for the synthesis of 1,1’-bis(R,R’-4-hydroxy phenyl)cyclohexane by condensing cyclohexanone (0.05 mole) and phenol, o-cresol and 2,6-dimethylphenol (0.1 mole) in the presence of varying mixture of hydrochloric acid and acetic acid (2:1 v/v) at four different temperatures: 40^0, 50^0, 60^0 and 70^0C. They have reported optimum catalyst concentration (10-15 ml), time (30-90 min) and temperature (55-70^0C) for obtaining yields greater than 80%. They have also synthesized chloro, bromo and nitro derivatives and screened for their potential antimicrobial and antifungal activities against microbes. Some of these compounds are significantly found active against B. subtilis, S. pyogens and A. niger. The nitro compounds are found to be the most active as antifungal agents.

[B] LITERATURE SURVEY ON EPOXY AND PHENOLIC RESINS, AND HYBRID COMPOSITES

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

The broad interest in epoxy resins originates from the extremely wide variety of chemical reactions that can be used for the curing that result many different

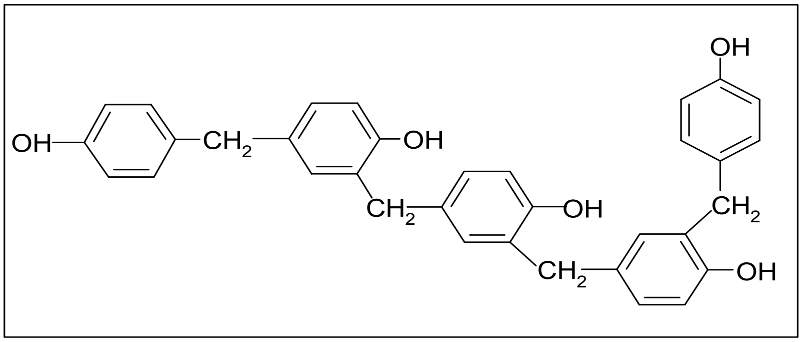
---

27. H. H. Garchar and P. H. Parsania, “Optimization reaction conditions for synthesis of 1,1’-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane”, Asian J. Chemistry, **6**, 135-137, 1994.
28. H. H. Garchar, S. H. Kalola and P. H. Parsania, “Synthesis and evaluation of bisphenol-C and its derivatives as potential antimicrobial and antifungal agents”, Asian J. Chemistry, **5**(2), 340-347, 1993.

properties. The chemistry is unique among the thermosetting resins. In contrast to the formaldehyde resins, no volatiles are given off during cure. Both epoxy and phenolics are individually superior in their respective fields. Epoxy is best for laminates in combination with glass fiber to achieve excellent electrical insulators, while phenolics are best with wood based cheap composites due to excellent adhesion with cellulosic materials.

The ability of formaldehyde to form resinous substance had been observed by chemists in the second half of the 19th century. In 1859 Butlerov described formaldehyde polymers, while in 1872 Adolf Bayer reported that phenol and aldehyde react to give resinous substances.

In 1899 Arthur Smith took out British patent 16274, on phenol–aldehyde reaction. In due course Leo Hendrik Baekeland discovered techniques of controlling and modifying the reaction that useful products could be made. The first of his 119 patents on phenol–formaldehyde plastics was taken out in 1907 and in 1910; the general Bakelite Company was formed in United States. Within a very few years the material had been established in many fields, particular for electrical insulation. The initial phenol-formaldehyde products may be of two types, novolacs and resoles. Phenolic resin chemistry has been discussed in detail elsewhere [29-33].



(I)

---

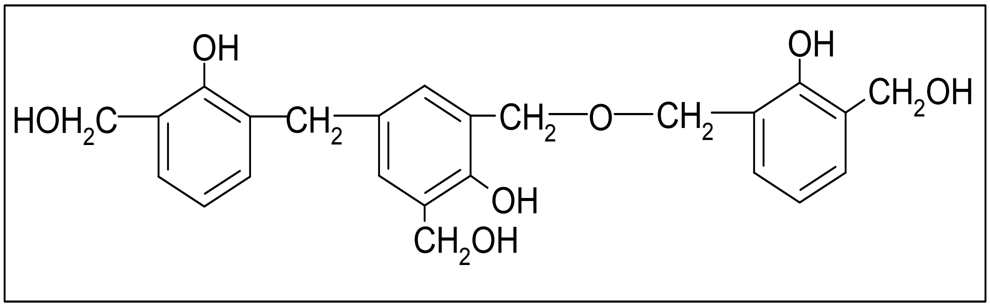
29. A. A. K. Whitehouse, E. G. K. Pritchett and G. Barnett,“Phenolic Resins”, Iiffe, London, 1967.
30. P. Robitschek and A. Lewin, “Phenolic-Resins” Iiffe. London, 1950.
31. R. W. Martin, “The Chemistry of Phenolic Resins”, John Wiley, New York, 1956.
32. N. J. L. Megson, “Phenolic Resin Chemistry”,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

Novolacs

The novolacs are prepared by reacting phenol with formaldehyde in a molar ratio of approximately 1:0.8 under acidic conditions. Under these conditions there is a slow reaction of the two reactants to form the o- and p-hydroxymethyl phenols. These materials will then slowly react with further formaldehyde to form their own methylol derivatives, which in turn rapidly react with further phenol to produce higher polynuclear phenols. The novolacs are sometime referred as two stage resins as it is necessary to add some curing agents that will enable additional methylene bridge to be formed.

Resoles

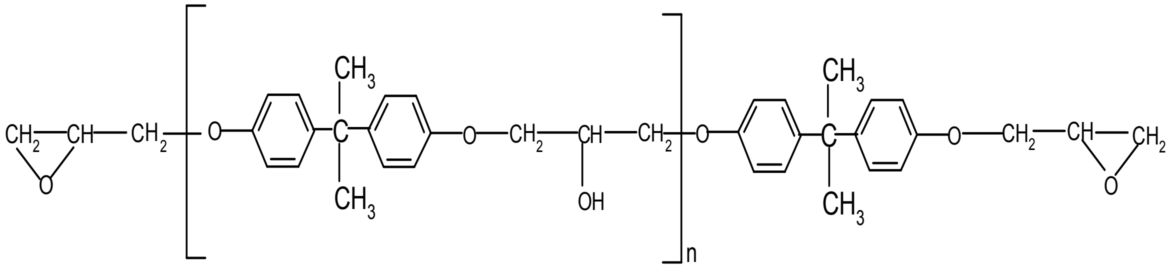
A resole is produced by reaction of phenol with an excess of formaldehyde under basic conditions. In this case, the formation of phenol-alcohols is rapid but their subsequent condensation is slow. Thus, there is a tendency for polyalcohols, as well as mono alcohols, to be formed. The resulting polynuclear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



(II)

Cast phenolic resins are important plastic material. Self extinguishing phenolic resin foams are developed recently but are more expensive than well expanded polystyrene. Other commercially practiced phenol formaldehyde resins are ‘fiber-resin performs moldings’, which provides characteristics of molded powder and laminates. Such perform moldings are particularly useful in carrying containers, protective covers, television receiver backs, molded suitcases and in computer parts. Phenolic resins are useful in surface coating materials and in adhesive preparation. They are also applied to impregnate wood and metal coil to give a rigid, heat and water resistance structure.

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



(III)

Various types of epoxy resins have been produced: glycidyl ethers, glycidylamines, linear aliphatics and cycloaliphatics. However, epoxy resin, which is a reaction product of epichlorohydrin and bisphenol-A, is most commonly used epoxy resin today, known as diglycidyl ether of bisphenol-A (DGEBA) (III).

The resin can be obtained with different degrees of polymerization ranging from low viscosity liquids to high melting solids [34] as shown in Table 1.1. In order to prepare high molecular weight resin and to avoid contamination the epoxy resin can be prepared by two-stage process. This involves first the preparation of lower molecular weight polymers with a degree of polymerization of about three and then reacted with bisphenols-A in the presence of a suitable polymerization catalyst such that the reaction takes place without evolution of by product [35].

---

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

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

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

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

Epoxy resins are widely used for land, marine and space transportation, automobile and electrical components, rehabilitations products and pollution control equipments. The characteristic properties of epoxy resins make them suitable for an increasing number of engineering applications, such as high strength and stiffness, good dielectric behavior, resistance to chemicals, low shrinkage during cure, etc. Despite of excellent properties their brittle behavior with low elongation restricts their use for high performance applications [36].

Greenlee [37] has prepared the rapid drying composition from diphenols and epichlorohydrin and esterified this product with Tall–oil.

Chemie Produkte [38] has reported the sealing composition for pipe joints and building materials. A typical composition consists of a mixture of an epoxy resin, a hardener and tar, which polymerized rapidly.

---

36. A. F. Yee, and R. A. Pearson, “Toughening mechanisms in elastomer modified epoxies: Part-1 mechanical studies”, J. Mater. Sci., **21**, 2462-2474, 1986.
37. S. O. Greenlee, “Tall-oil esters”, U.S. 2,493,486, 1949; C.A. **44**, 2770, 1950.
38. Chemie Produkte, “Epoxy resins containing sealing compositions”, Ger. 1,020,140, 1957; C.A. **54**, 179704, 1957.

Table – 1.1: Effect of reactant ratios on molecular weight

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

Petri et al. [39] have prepared epoxy resin foams from aqueous dispersions. Epoxy resin based on bisphenol-A, benzsulfohydrazide, dipropylene triamine were dispersed in water by 2,3-dibromopropyl phosphate as a dispersing medium. Rigid foam was obtained by this composition, which is suitable for architectural uses.

CIBA Ltd. [40] has reported coating composition for floors, roofs, walks and walls based on bisphenol–A epoxy resin. The composition was room temperature hardenable having quartz sand, epoxy resin, dibutyl phthalate together with triethylene tetramine. This composition has consistency of mortar and a pot life of 2.0 – 2.5h. It is spread on a concrete floor to a depth of 4mm. Hardening required 24-48h. The composition shows excellent adhesion in non-cracking and is highly resistance to chemical.

Union Carbide Co. [41] has reported curing of polyepoxides with liquid glycol diamines ($H_2N(CH_2)_3O(C_nH_{2n}O)_x(CH_2)_3NH_2$)(I), where n is 2-5 and x is 1-11. The cured compounds have excellent impact strength and flexibility and are stable as protective coatings. Thus, 100g of diglycidyl ether of 2,2'-bis(p-hydroxy-phenyl) propane was mixed with 29.4g stoichiometric amount of $H_2N\ (CH_2)_3O\ (CH_2CH_2O)_2(CH_2)_3NH_2$ for 5 min. The mixture was applied on cold-rolled steel and was cured by storing 7 days at room temperature.

Minnesta Mining and Manufacturing Co. [42] have synthesized flexible adhesive film having honeycomb structure. Thus an epoxy resin mixture (I) was prepared by heating 100 parts of glycidyl ether of bisphenol – A to 121^0C, adding 2-parts fine SiO_2 and stirring at 149^0C for 10-20 min. A mixture of 145 parts isophthaloyl dihydrazide, 10 parts MgO and 1 part dimethyl diocta decyl ammonium bentonite was added to epoxy mixture at 104^0C and the resulting mixture was milled at 77^0C to complete dispersion.

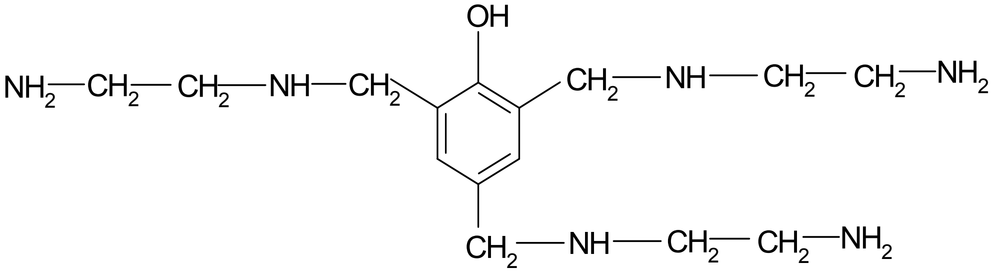
---

39. R. Petri, H. Reinhard and L. Keller, "Epoxy resin foams from aqueous dispersions" Ger. **1**,080,774, 1960; C.A. 2003, **55**, 14982, 1961.
40. CIBA Ltd., "Epoxy resin containing coatings", Brit. 8,83,521, 1961 C.A. **56** 11746, 1962.
41. Union Carbide Co. (by Norman H. Reinking.), "Liquid glycol diamine curing agent for polyepoxides", Brit. 9,04,403, 1962; C.A. **58**, 1643, 1963.
42. Minnesta Mining and Manufacturing Co. "Flexible adhesive film", Ger. 1,100,213, 1961; C.A. **58**, 11551, 1963.

Bremmer [43] has synthesized flame-retardant epoxy resin. In a typical composition tetra bromo bisphenol-A was added to bisphenol-A-diglycidyl ether (epoxide equivalent 186) at 70^0 under an N_2 atmosphere with stirring. The composition was cured by triethyl amine.

Karl [44] has reported phenol-HCHO resins for building materials. A typical material composed of phenol-HCHO resin pre condensate, acid hardener, an ethylene glycol, BuOH or terpineol ester, mineral filler [such as CaO, $Ca(OH)_2$, $CaSO_4$ or $Ca(CO_3)$ and an additive such as sand were suitable for use as building material.

Kogyo [45] has formulated epoxy resin composition hardened by phenol-block-phenol-polyamine-aldehyde reaction products at low temperature i.e. $10\text{-}15^0C$.



(IV)

On heating 200g (I) and 50g nonyl phenol for 1h at 66^0C gives the blocked curing agent. A mixture of this compound bisphenol-A-epichlorohydrin copolymer (epoxy equivalent ~190) and 2, 2-bis (o-hydroxy phenyl) propane-propylene oxide copolymer epoxide equivalent ~ 345) were cooked together. The composition has self-life of about 4 h and 70 min at 0^0C.

---

43. B. J. Bremmer (Dow Chemicals Co.), “Flame retardant epoxy resin”, U.S. 3, 294,742, 1966; C.A. **66,** 38487, 1967.
44. A. Karl, “Phenol-HCHO resins for building materials” Ger. 1,544,609, 1965; C.A. **73**, 4516, 1970.
45. A. D. Kogyo. “Hardenable epoxy resin composition”, Japan 2,126,179, 1972; C.A. **78**, 137, 425, 1973.

Galia et al. [46] have investigated flame retardant modified novolac resins with benzoxazine rings cured with isobutyl bis(glycidylpropylether) phosphine oxide as a crosslinking agent. Their curing behavior was carried out using different epoxy/phenol molar ratios with or without triphenylphosphine as a catalyst.

Bair et al. [47] were used high compositions of epoxies crosslinked with phenolic novolac are in microelectronics and packaging applications.

Saint-Globain Company [48] has reported binders based on epoxy-phenol system. In typical composition, one mol. PhOH was mixed with 2.3 moles 36% aq. HCHO and heated at 45^0C for 30 min. A 47% aq. NaOH solution was added gradually, the temperature raised to 70^0C during 15 min and maintained until the concentration of free HCHO was 8% and 0.25 mol epichlorohydrin was added. The mixture kept for few minutes and neutralized with 25% H_2SO_4. The products have good tensile strength and heat, ageing and alkali resistance.

Okhitinsk Chemical combine [49] has synthesized epoxy-phenolic resin consisting reaction product of bisphenol-A with HCHO in the presence of an alkali in the ratio 1:2:1 at room temperature, and was further reacted with 10 moles epichlorohydrin. The resulting resin has increased thermal resistance.

Hairston et al. [50] have prepared solid epoxy-novolac resin. A typical composition consists PhOH-HCHO novolac (functionally 2.13-2.31, -OH equivalent ~ 100) was combined with 2.2-2.5 times its weight of epoxy-novolac of the same functionally and epoxy equivalent ~ 164 to provide powder coating resins. Thus, 454 g novolac of 2.13 functionally was heated at 110-60^0C with 1 kg PhOH-HCHO

---

46. M. Galia, M. A. Espinosa and V. Cadiz, “Novel phosphorilated flame retardant thermosets: epoxy-benzoxazine-novolac systems”, Polymer, **45**, 6103-6109, 2004.
47. H. E. Bair, D. J. Boyle, J. T. Ryan, C. R. Taylor, S. C. Tighe and D. L. Crouthamel, “Thermomechanical properties of 1C molding compounds”, Polym. Eng. Sci., **30**, 609-617, 1990.
48. Saint-Globain Company, Epoxy-phenol resin, Fr. 1467840, 1966; CA **67**, 109261, 1967.
49. Okhtinsk Chemical combine, “Epoxy resins”, U.S.S.R. 195, 99 1966; C.A. **68**, 69721, 1968.

novolac-epoxy derivative of functionally 2.15 in the presence of tetra butyl phosphonium acetate-HOAc, resulting in a 206^0C exotherms. The product was heated at 170^0C for 3h to provide solid resin, which was incorporated into coating formulations.

Sanariya et al. [51] have reported a convenient method for the preparation of epoxy resins based on bisphenols-C. The epoxy resins of bisphenols-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mol in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was ~ 75-80 %.

Kagathara et al. [52] have reported a convenient method for the preparation of epoxy resins based on halogenated bisphenols-C. The epoxy resins of bisphenol-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mole in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was ~ 75-80 %.

Liu et al. [53] have reported combination of epoxy and novolac resins. In a typical study, a novel phosphorus- containing Ar-alkyl novolac (Ar-DoPo-N) was prepared. The Ar-DoPo-N blended with novolac and used as a curing agent for o-cresol formaldehyde novolac epoxy, resulting in cured epoxy resins with various phosphorus contents. The epoxy resins exhibited high glass-transition temperatures ($159-217^0$C), good thermal stability ($>320^0$C).

---

50. T. J. Hairston and P. P. Gestling (Dow Chemical Co.), “Solid epoxy-novolac resin”, Ger. 2,434,797, C. A. **82**,172718, 1975.
51. M. R. Sanariya, D. R. Godhani, S. Baluja and P. H. Parsania, “Synthesis and characterization of epoxy resins based on 1,1’-bis(4-hydroxyphenyl) cyclohexane and 1,1’-bis(3-methyl-4-hydroxyphenyl) cyclohexane”, J. Polym. Mater., **15**, 45-49, 1998.

Thermosetting acrylic acid resins are in general based on the monomers methacrylic ester, acrylic ester and styrene. Other monomers are incorporated to provide the reactive groups. The natural and relative amount of monomers controls the flexibility and other properties. Acrylate is used for maximum durability. Acrylate resin used for the finishing of furniture is suited to curing by UV radiation. This form of cure has proved to be successful coating application.

UV-cured acrylate resin systems have numerous applications, dental composites and dental resins, vinyl flooring, artificial nail preparations, adhesives, and glues as well as in some textiles. In the printing industry, acrylate are used in the production of photopolymer printing plates. Certain acrylate compounds are useful because they can be made to polymerize instantaneously by exposure to UV light, therefore they are used in quick-drying and in the rapid production of printing plates from photographic negatives.

Acrylic resins have been developed as an alternative to the phenolic resin solutions and other thermoset binders frequently used for binding fiber mats. Acrylic resin has good storage stability and crosslink upon heating to 180-220^{0}C. The resin is particularly suitable for binding wood fibers and other natural fibers, flax, hemp, jute or sisal [54]. The heat-curable acrylic resin can easily be applied by spraying, pouring or roller-coating the substrates for binding. Fiber composites made with the novel acrylic resin have high stiffness and good strength and fulfill the ecological requirements of the automotive industry.

---

52. V. M. Kagathara, M. R. Sanariya and P. H. Parsania, “Selected Topics in Polymer Science”, S. K. Dolui Edi., Prof. Sukumar Maiti, Polymer Award Foundation, Kolkata, PP 1-8, 2001.
53. Y. L. Liu, C. S. Wu and K. Y. Hsu, “Flame retardant epoxy resins from o-cresol novolac epoxy cured with a phosphorus containing aralkyl novolac”, J. Polym. Sci. Part A, **40**, 2329-2339, 2002.
54. R. Bernd and T. Johannes, “Thermally curable aqueous acrylic resins – a new class of duroplastic binders for wood and natural fibers” Die. Angew. Makro. Chem., **5**, 272-276, 1999.

Liliana et al. [55] have studied the thermal degradation and fire resistance of different fiber composites. Unsaturated polyester and modified acrylate resins were used as matrix composites. The smoke emission of the materials was also analyzed, as well as the performance against the fire of the bio composites and glass reinforced composites was compared. Thermal degradation indicated that the molder matrix composites with PU matrix. From the result obtained about the thermal and fire resistance of the composites, flex fiber seems to be the most adequate to be used, due to the long time to ignition and the long period prior to reach the flashover. On the other hand, the jute fiber composites showed a short duration but a quick growing with the lowest smoke emission. The low smoke is an important advantage, which reduces one of the main hazards of fire.

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 [56].

One modification of phenolic resin by boric acid which gives 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 [57-61]. In that work boron-containing resin was synthesized by formalin method [57,58].

---

55. M. B. Liliana, S. R. Exequiel, W. P. Maria and V. Analia, “Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resin and their composites with natural fibers”, Polym. Degra. Stab., **91**, 255-261, 2006.
56. 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.
57. America Potash Chem. Corp. “Organic polyborate resins”, British patent 9,57,611, 1994.
58. W. Tu, S. Wei, Plastics Ind., **4**, 16, 1981.
59. 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.

Another modification of phenolic resins can be done by phosphoric compound. It has low toxicity, is less smoky, has better compatibility with resin and good workability, and requires lower dosage for use compare to halogenated compound. Moreover it improves the adhesion between resin and metals or other substrates. Thus, the environmental pollution problems caused by conventional halogenated flame retardant have been eliminated, and adhesion between the photosensitive resin and substrate can be improved.

Some reports have appeared on the synthesis and application of phosphorus-containing phenol-formaldehyde resin [62-65]. In that work phosphorus-containing resin was synthesized by using phosphorus oxychloride [62].

[C] HYBRID COMPOSITES

Definition: There are several types of hybrid composites characterized as: (1) interply or tow-by-tow, in which tows of the two or more constituent types of fiber are mixed in a regular or random manner; (2) Sandwich hybrids, also known as core-shell, in which one material is sandwiched between two layers of another; (3) Interply or laminated, where alternate layers of the two (or more) materials are stacked in a regular manner; (4) Intimately mixed hybrids, where the constituent fibers are made to mix as randomly as possible so that no over-concentration of any one type is present in the material; (5) Other kinds, such as those reinforced with ribs, pultruded wires, thin veils of fiber or combinations of the above.

---

60. 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. Stab., **77**, 495 - 501, 2002.
61. J. G. Gao, Y. F. Liu and F. L. Wang, Polym. Mater. Sci. Eng., **11**, 31-50, 1995.
62. C. S. Cho, S. J. Chang, W. J. Teng, J. J. Chen, “Photosensitive phosphorylated phenol-formaldehyde resin and method for preparing the same”, U. S. Patent – 6566483 B2, 2003.
63. H. Bauer, M. Diatz, O. Schacker, “Phosphorus-containig mixtures, a process for their preparation and their use”, U. S. Patent – 0225414 A1, 2007.
64. L. D. Timberlake, M. V. Hanson, E. B. Edwards, “Phosphine oxide hydroxyaryl mixtures with novolac resins for co-curing epoxy resins”, U. S. Patent – 7202311 B2, 2007.
65. S. V. Levchik, E. D. Well, “A review of recent progress in phosphorus-based flame retardants”, J. Fire Sci., **24**, 345-364, 2006.

The term hybrid composite is used to describe composite containing more than one type of fibers. Hybrid composites are attractive structural materials because they provide designers freedom of tailoring composites and achieving properties that cannot be realized in binary system containing one type of fiber dispersed in a matrix and more cost-effective utilization of expensive fibers such as carbon and boron can be obtained by replacing them partially with less expensive fibers such as glass and aramid. Further hybrid composites provide the potential of achieving a balanced pursuit of stiffness, strength and ductility, as well as bending and membrane related mechanical properties. Hybrid composites have also demonstrated weight savings, reduced notch sensitivity, improved fracture toughness, longer fatigue life and excellent impact resistance [66].

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 [67].

Hybridization provides materials designers with an added degree of freedom in tailoring composites to achieve a better balance of stiffness, strength, increased failure strain, better damage tolerances, improved ability to absorb impact energy and possibly a significant reduction in cost [68]. Hence, the behavior of fiber reinforced plastic (FRP) hybrid composites under possible service conditions is a matter of significant practical interest. The mechanical behavior of FRP composites are dominated by the interfacial adhesion at the fiber-matrix interface.

---

66. T. W. Chou, “Hybrid composites”, Microstructural Design of Fiber Composites, p. 231, 1992.
67. M. M. Thwe and K. Liao, Plastic, “Tensile behavior of modified bamboo-glass fiber reinforced hybrid composites”, Plastics, Rubber and Compos. **31**,422-431, 2002.
68. B. Z. Jang, “Advanced Polymer Composites: Principles and Applications”, ASM International, Materials Park, Ohio. p. 112, 1994.

In the year between 1870 and 1890, revolution was occurring in chemistry, first synthetic (man made) resins were developed, which could be converted from liquid to solid upon 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 is known as crosslinking, which 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 a long 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.

Some of the beneficial points for using composites over conventional ones are under [69].

- 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

---

69. U. Gayer and Th. Schuh, “Automotive applications of natural fiber composites”, First International Symposium on Ligno-cellulosic Composites – UNESP- Sao Paulo State, 1999.

- 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.

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 [70].

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 [70].

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

---

70. S. Biswas, G. Srikanth and S. Nangia "Development of natural fiber composites in India"- Composites 2001 convention and trade show, Composites Fabricators Association. Tampa-FL, U.S.A., 2001,

compared in Table1.2 [71]. 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 [55].

The comparison of mechanical properties of jute and glass fibers [71] is given in Table 1.3. Jane L. O'Dell has reported the comparative properties of lignocellulosic fibers with glass and carbon fibers [72]. The comparison of properties of different fibers is given in Table-1.4.

The attractive features of natural fibers like jute [73-75], sisal [76], coir [77, 78], and banana [79] are their low cost, light weight, high specific modulus, renewability and biodegradability. Many plant fibers have lots of applicable part as commercialized materials are concerned. One of the common and very critical environmental solutions is biodegradable nature of all these natural fibers, which increases their demand in world composite manufacture markets.

Plant fibers are composed of cellulose, hemicellulose and lignin. Other components, usually regarded as surface impurities, are pectin and wax substances (Table 1.5) [80].

---

71. S. Nangia and S. Biswas, "Jute composite: Technology and business opportunities", in News and Views, 2003.
72. 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.
73. M. K. Sridhar, G. Basavarappa, S. G. Kasturi and N. Balasubramaniam, "Mechanical properties of jute/polyester composites", Ind. J. Tech., **22**, 213-218, 1984.
74. P. Kumar "Mechanical behavior of jute fiber and their composites", Ind. J. Tech., **24**, 29-32, 1986.
75. A. N. Shah and S. C. Lakkad "Mechanical properties of jute reinforced plastics", Fiber Sci. Tech., **15**, 41-45, 1981.

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 x 10^{11} Ω cm	---	6.5-7	0.4-0.5	0.7-0.8	9-14	9-10
Micro-fibrillar angle (Degree)	8.1	11	10-22	14-18	30-49	---
Cellulose Content (%)	61	65	67	81	43	---
Lignin Content (%)	12	5	12	12	45	---
Elastic Modulus(GN/m^2)	---	8-20	9-16	34-82	4-6	85.5
Tenacity (MN/m^2)	440-553	529-754	568-640	413-1627	131-175	4585
Elongation (%)	1-1.2	1.0-3.5	3-7	0.8-1.6	15-40	5.7

Table-1.3: 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

---

76. 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.
77. 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.
78. J. Rout, M. Mishra, S. K. Nayak, S. S. Tripathy and A. K. Mohanty, “Effect of surface modification of coir fiber on physico-mechanical behavior of coir-polyester composites In: A. K. Ghosh, editor. Polymers beyond AD 2000, p. 489-491,1999.
79. L. A. Pothan, S. Thomas and N. R. Neelakantan, “Short banana fiber reinforced polyester composites: Mechanical, failure ageing characteristics”, J. Reinf. Plast. Compos., **16**, 744-751, 1997.
80. 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 20^0C) by dry fiber [81]. 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 [82].

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 [81].

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 decrease 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 [83].

---

81. 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.
82. A. K. Bledzki and J. Gassan, "Composites reinforced with cellulose based fibres", Prog. Polym. Sci., **24**, 221-249, 1999.
83. 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 [84].

The elementary unit of cellulose macromolecules 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) [85]. 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 [85].

The strength and stiffness of fibers correlates with angle between the axis and fibril of the fiber [85, 86]. The smaller this angle is, the higher are the mechanical properties (Table 1.7) [85].

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.

---

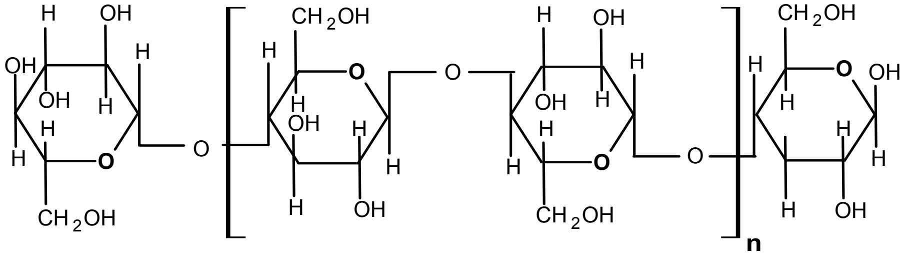
84. K. Oksman and C. Clemons, “Mechanical properties and morphology of impact modified polypropylene-wood flour composites”, J. Appl. Polym. Sci., **67**, 1503-1511, 1998.
85. A. K. Bledzki, S. Reihmane and J. Gassan, “Properties and modification methods for vegetable fibers for natural fiber composites”, J. Appl. Polym. Sci. **59**, 1329-1336, 1996.
86. S. C. O. Ugbolue, “The emission of smoke in the processing of textile fabrics”, J. Text. Inst. **70**, 412-413, 1979.

Table- 1.6: Structure parameters of vegetable fibers [85]

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

Table-1.7: Comparative values of cellulose and with conventional reinforcing fibers [86]

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



Macromolecule of cellulose [87]

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. [88, 89] 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. [90] 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 30^0C and reported that modulus of jute fibers improved by 12, 68 and 79% after 4, 6 and 8h of treatment, respectively. They have reported improvement in flexural strength with the treatment of alkalization of jute fibers.

Rana et al. [91] 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.

Dash et al. [92] have been reported the weathering and thermal behavior of jute-polyester composites by bleaching or delignification and they have reported that

---

87. J. I. Kroschwitz, “Polymers: Fibers and Textiles”, Wiley, New York, 1990.
88. 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. Technol. **62**, 911-917, 2002.
89. 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.
90. 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: Appl. Sci. Manuf., **32**, 119-127, 2001.
91. 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.

tensile modulus increased after bleaching. Overall thermal stability was found to be better than that of untreated one.

Frolini and Razera [93] 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.

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 [94].

$$\textbf{Fiber}-\textbf{OH} + \textbf{NaOH} \longrightarrow \textbf{Fiber}-\textbf{O}^{-}\,\textbf{Na}^{+} + \textbf{H}_2\textbf{O}$$

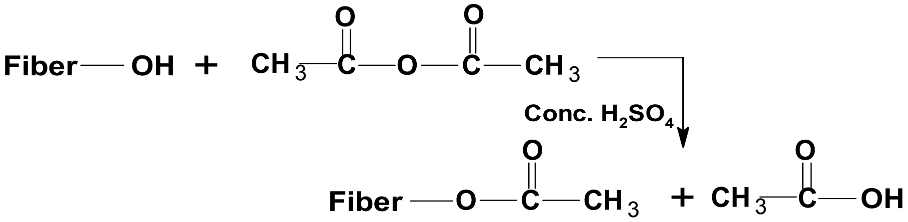
The most popular esterification method is acetylation, which has already been developed on commercial scale, first in United States [95], then in Russia [96].

---

92. 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.
93. 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.
94. R. Kozlowski, M. Wladyka and M. Helwig, “Composites based on lignocellulosic raw materials”, Mol. Cryst. Liq. Cryst., **418**, 131-151, 2004.
95. Kopper’s Acetylated wood. New Materials Technical Information No.(RDW - 400), E-106, 1961.
96. Y. Otlesnov and N. Nikitina, Latvijas Laukasaimniecibas Akademis as Raksti, 130, 50, 1977.

- **Acetylation [97]**

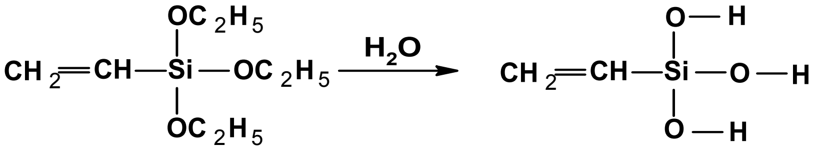
At high temperature and longer reaction time, acetic anhydride is able to swell the fiber, making reactive chemical sites more accessible too and therefore, enhancing the reaction rate. Acetylated fiber was found to be brighter and lighter in color. Acetylation at the –OH groups from cellulose and lignin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



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

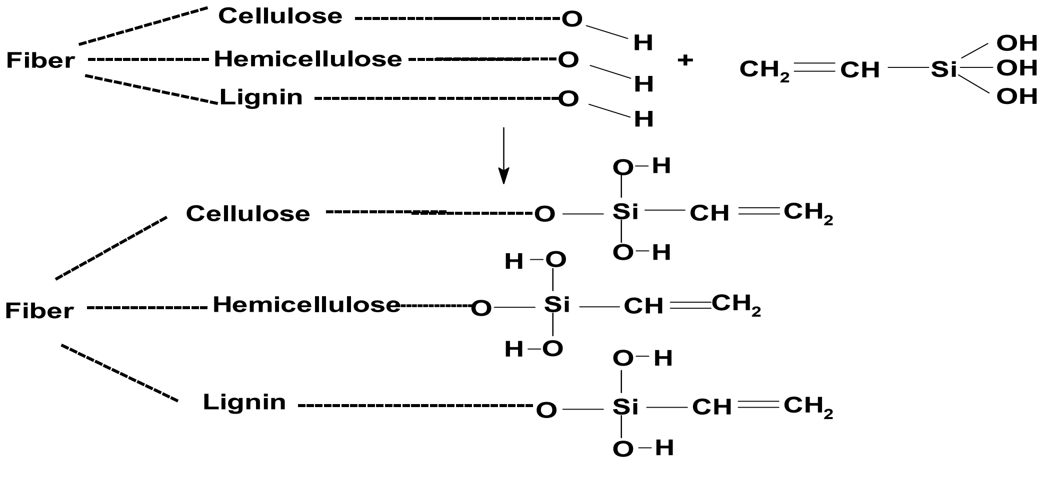
- **Silane treatment [97]**

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 the presence of moisture hydrolysable alkoxy group leads to the formation of silanols.



$$CH_2{=}CH-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{OC_2H_5}{|}}{Si}}-OC_2H_5 \xrightarrow{H_2O} CH_2{=}CH-\underset{\underset{O-H}{|}}{\overset{\overset{O-H}{|}}{Si}}-O-H$$

Hypothetical reaction of fiber and silane



---

97. 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.

- **Benzoylation [98, 99]**

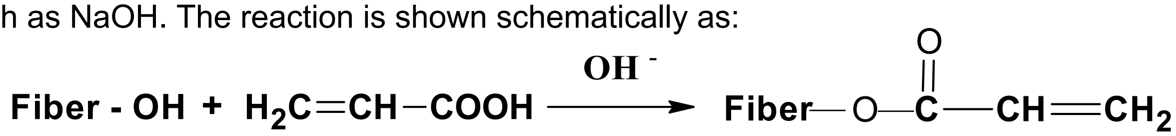
Benzoylation is an important transformation in organic synthesis. Benzoyl chloride is most often used in fiber treatment. Benzoyl chloride includes benzoyl ($C_6H_5C{=}O$) which is attributed to the decreased hydrophilic nature of the treated fiber and improved interaction with the hydrophobic PS matrix. The reaction between the cellulosic hydroxyl group of the fiber and benzoyl chloride is shown in scheme

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

Benzoylation of fiber improves fiber matrix adhesion, thereby considerably increasing the strength of composite, decreasing its water absorption and improving its thermal stability.

- **Acrylation [100,101]**

The modification occurs through the nucleophilic addition of the hydroxyl group of fibers to the acrylic acid double bond, which is catalyzed by a strong alkali, such as NaOH. The reaction is shown schematically as:

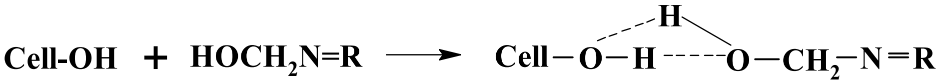


$$\text{Fiber - OH} + H_2C{=}CH{-}COOH \xrightarrow{OH^-} \text{Fiber}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}CH_2$$

---

98. S. Paul, P. Nanda, R. Gupta, “PhCOCl-Py/basic alumina as a versatile reagent for benzoylation in solvent-free conditions”, Molecules, **8**, 374-380, 2003.
99. K.C. Manikandan Nair, S. Thomas and G. Groeninckx, “Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibers”, Compos. Sci. Technol. **61**, 2519-2529, 2001.
100. M. S. Sreekala, M. G. Kumaran, S. Joseph, M. Jacob and S. Thomas, “Oil palm fibre reinforced phenol formaldehyde composites: Influence of fibre surface modifications on the mechanical performance”, Appl. Compos. Mater. **7**, 295-329, 2000.
101. M. S. Sreekala, M. G. Kumaran, S, Thomas, “Water sorption in oil palm fiber reinforced phenol formaldehyde composites”, Compos A: Appl. Sci. Manuf., **33**, 763-777, 2002.

- Treatment with compounds which contain methylol groups [102]. 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.



$$\text{Cell-OH} + HOCH_2N{=}R \longrightarrow \text{Cell}-O-H \cdots O-CH_2-N{=}R$$

The radical enhances the chemical interlocking at the surfaces.

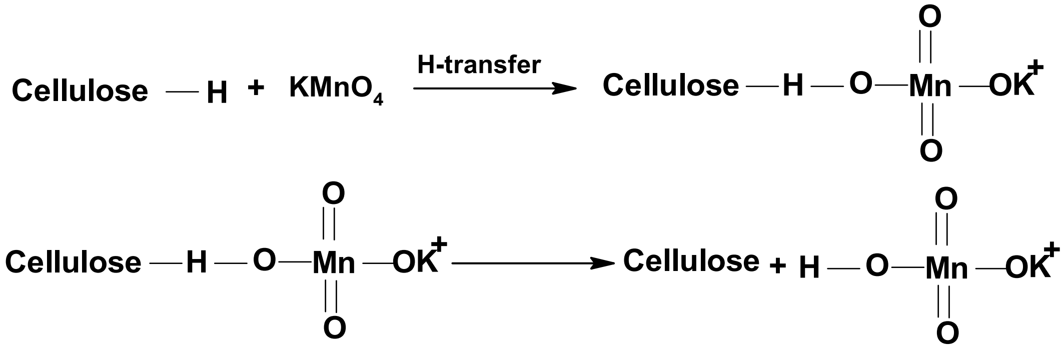
- **TDI treatment [102]**

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

$$-N{=}C{=}O + HO-\text{Fiber} \longrightarrow -N(H)-C(=O)-O-\text{Fiber}$$

- **Permanganate treatment [103]**

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



$$\text{Cellulose}-H + KMnO_4 \xrightarrow{\text{H-transfer}} \text{Cellulose}-H-O-Mn(=O)_2-OK^+$$

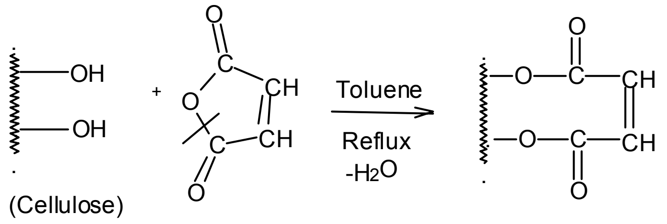
$$\text{Cellulose}-H-O-Mn(=O)_2-OK^+ \longrightarrow \text{Cellulose} + H-O-Mn(=O)_2-OK^+$$

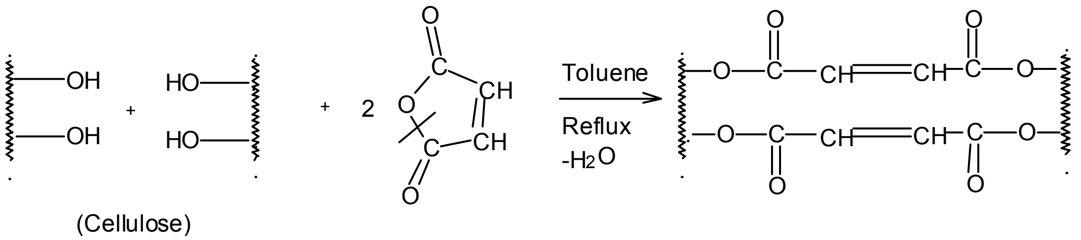
---

102. 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.
103. A. Paul, K. Joseph, S. Thomas, “Effect of surface treatments on the electrical properties of low density-polyethylene composites reinforced with short sisal fibers”, Compos. Sci. Technol., **57**, 67-79, 1997.

- **Malenization [82]**

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 neighboring cellulose molecules:





- **Peroxide Treatment [104]**

In organic chemistry, peroxide is a specific functional group or a molecule with the functional group ROOR containing the divalent ion R–O$^{\cdot}$ Organic peroxides tend to decompose easily to free radicals of the form RO$^{\cdot}$; RO$^{\cdot}$ then reacts with the hydrogen group of the matrix and cellulose fibers. For example, the peroxide initiated free radical reaction between PE matrix and cellulose fibers is shown by the following [103, 104]:

$$\mathbf{RO - RO \longrightarrow 2RO^{\cdot}}$$

$$\mathbf{RO^{\cdot} + PE - H \longrightarrow ROH + PE}$$

$$\mathbf{RO^{\cdot} + Cellulose - H \longrightarrow ROH + Cellulose^{\cdot}}$$

$$\mathbf{PE + Cellulose^{\cdot} \longrightarrow PE - Cellulose}$$

---

104. K. Joseph, S. Thomas, “Effect of chemical treatment on the tensile properties of short sisal fibre-reinforced polyethylene composites”, Polymer, **37**, 5139-5149, 1996.

Benzoyl peroxide [BP, $(C_6H_5CO)_2O$] and dicumyl peroxide [DCP, $(C_6H_5C(CH_3)_2O)_2$] are chemicals in the organic peroxide family that are used in natural fiber surface modifications.

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

Wang et al. [105] have studied the effects of pre-treated flax fibers on the performance of the fiber-reinforced composites. Lack of good interfacial adhesion and poor resistance to moisture absorption make the use of natural fiber-reinforced composites less attractive. In order to improve fiber/matrix interfacial properties, fibers were subjected to chemical treatments, namely, mercerization, silane treatment, benzoylation, and peroxide treatment. Selective removal of non-cellulosic compounds constitutes the main objective of the chemical treatments of flax fibers to improve the performance of fiber-reinforced composites. Flax fibers were derived from Saskatchewan-grown flax straws.

Hybrid composites of jute, sisal carbon and glass fibers:

Glass fiber reinforced polymer (GFRP) 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.

Carbon fiber reinforced polymer (CFRP) composites were composed primarily in the aircraft and aerospace industries because of the combination of lightweight, high stiffness, and high strength properties. Lightweight structures are preferentially needed in aerospace applications. One of the main advantages of carbon fibers is their ability to retain mechanical properties at high temperatures.

---

105. B. Wang, S. Panigrahi, L. Tabil and W. Crerar, “Pre-treatment of flax fibers for use in rotationally molded biocomposites”, J. Reinf. Plast. Compos. **26**, 447-451, 2007.

Ghosh et al. [106] 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 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.

Abdullah-Al-Kafi et al. [107] have studied that the mechanical properties were found to increase with the incorporation of dissimilar portions of glass fiber into the jute fiber-reinforced composite. Among all the resulting hybrid composites, the composite with jute to glass ratio of 1: 3 demonstrates improved mechanical properties over untreated jute composite. To further improve the properties, the surface of jute and glass fiber was irradiated under UV radiation of different intensities. UV pretreated jute and glass fibers (1: 3) at optimum intensities show the highest mechanical properties compared to untreated jute-and glass-based hybrid composites.

---

106. 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.
107. Abdullah-Al-Kafi, M. Z. Abedin, M. D. H. Beg, K. L. Pickering, and M. A. Khan, “Study on the mechanical properties of jute/glass fiber-reinforced unsaturated polyester hybrid composites: Effect of surface modification by ultraviolet radiation”, J. Reinf. Plast. Compos., **25**, 575-588, 2006.

Srivastav et al. [108] have reported the effect of different loading rates on the mechanical behavior of jute/glass reinforced epoxy hybrid composites. Surface modification was done in order to get better interfacial bonding between jute and resin. The hybrid composite showed insensitive behavior at high loading rates. The loading rate behavior of the hybrid composite was compared on the basis of different surface treatments of jute fiber. UV-treated samples have shown better yield properties at higher loading rates. Untreated samples exhibited better ILSS values at higher loading rates.

Aquino et al. [109] have evaluated the moisture absorption effect on the mechanical properties of a hybrid sandwich composite formed by orthophthalic polyester resin, reinforced by bi-directional woven fabrics of glass and jute fibers, with a central layer of polyester fabric (coremat). For the composite characterization were performed tensile and three-point-bend tests, damage mechanism analysis, and moisture absorption tests. A larger absorption was observed for the hybrid composite compared to commonly observed fiber glass composites. This behavior was related to jute fiber as well as the coremat. In the mechanical tests a strong influence of the moisture content on the mechanical properties was verified. The main characteristic of the three-point-bend test was the premature shearing fracture of the coremat under both dry and wet conditions.

John et al. [110, 111] have studied the variations of tensile strength, impact strength and compressive strength of unsaturated polyester based short sisal/glass

---

108. A. K. Srivastav, M. K. Behera, and B. C. Ray, “Loading rate sensitivity of jute/glass hybrid reinforced epoxy composites: Effect of surface modifications”, J. Reinf. Plast. Compos., **26**, 851-860, 2007.
109. E. M. F. Aquino, L. P. S. Sarmento, W. Oliveira, and R. V. Silva, “Moisture effect on degradation of jute/glass hybrid composites”, J. Reinf. Plast. Compos., **26**, 219-233, 2007.
110. K. John and S. V. Naidu, “Sisal fiber /glass fiber hybrid composites: The impact and compressive properties”, J. Reinf. Plast. Compos., **23**, 1253-1258, 2004.
111. K. John and S. V. Naidu, “Tensile properties of unsaturated polyester-based sisal fiber–glass fiber hybrid composites”, J. Reinf. Plast. Compos., **23**, 1815-1818, 2004.

hybrid composites as a function of fiber content. They observed that the impact strength and compresssive strength has been improved with increased glass fiber content and the total fiber content in the hybrid composite. The effects of alkali and silane treatments of fibers on the impact and compressive properties have also been studied and found that these treatments showed no significant effect on the impact strength of the hybrid composites. However, there was a marginal enhancement in the compressive strength over that of the untreated fiber reinforced composites.

Khanam et al. [112] have studied the variation of tensile, flexural, and compressive strengths of unsaturated polyester based sisal/silk hybrid composites as a function of fiber length. They observed that 2 cm fiber length hybrid composites have higher tensile, flexural, and compressive strength than 1 and 3 cm. The effect of alkali on the tensile, flexural and compressive properties have been studied and also found that treated hybrid composites showed higher strength than untreated composites.

John et al. [113] have performed chemical resistance tests of unsaturated polyester resin based sisal/glass hybrid composites in order to probe whether these composites can be used for making articles that are resistant to chemicals. The hybrid samples and the matrix have been tested for various acids, alkalis and solvents. It is observed from the results that the developed hybrid composites are resistant to all the tested chemicals except carbon tetrachloride.

Shan et al. [114] have reported unidirectional glass fiber reinforced and glass-carbon fiber reinforced epoxy matrix composite samples (% glass to carbon fiber volume ratio 90: 10 and 75: 25) were subject to two-point bend rupture test in

---

112. P. N. Khanam, M. M. Reddy, K. Raghu, K. John and S. V. Naidu, “Tensile, flexural and compressive properties of sisal/silk hybrid composites”, J. Reinf. Plast. Compos., **26**, 1065-1070, 2007.
113. K. John and S. V. Naidu, “Chemical resistance of sisal/glass reinforced unsaturated polyester hybrid composites, J. Reinf. Plast. Compos., **26**, 373-376, 2007.
114. Y. Shan, K. F. Lai, K. T. Wan, and K. Liao, “Static and dynamic fatigue of glass–carbon hybrid composites in fluid environment”, J. Compos. Mater., **36**, 159-172, 2002.

distilled water at 75^0C and tension-tension cyclic test in both air and distilled water at 25^0C. In the rupture test, glass–carbon hybrid samples showed prolonged rupture time in comparison to all-glass samples when loaded at 10% maximum deflection. When compared to samples tests in air, cyclic loading in water resulted in shorter fatigue lives for both all-glass and hybrid composite samples. However, hybrid samples showed better environmental fatigue resistance in water than all-glass samples, to 10^7 cycles. By incorporating appropriate amount of carbon fibers in glass fiber composite, long-term performance of glass–carbon hybrid composites under static and dynamic fatigue was substantially enhanced.

Patel et al. [115] have fabricated carbon fiber reinforced epoxy composites from the matrix resins diglycidyl ether of bisphenol-A (DGEBA) and tetraglycidyl bis(aminotolyl)cyclohexane (TGBATC) using 4,4'-diaminodiphenyl methane (DDM) as a curing agent. The composites were evaluated for their physical and mechanical properties. A significant improvement in the properties was observed on addition of 20 phr of an epoxy fortifier.

Tewari et al. [116] have characterized the solid particle erosion behavior of unidirectional carbon and glass fibre reinforced epoxy composites. The erosive wear of these composites have been evaluated at different impingement angles ($15\text{-}90^0$) and at three different fiber orientations (0^0, 45^0, and 90^0). The particles used for the erosion measurements were steel balls with diameter of 300-500 mm and impact velocity of 45 m/s. The unidirectional carbon and glass fiber reinforced epoxy composites showed semi ductile erosion behavior, with maximum erosion rate at 60^0 impingement angle. The fiber orientations had a significant influence on erosion. The morphology of eroded surfaces was examined by using scanning electron microscopy (SEM).

---

115. S. R. Patel and R. G. Patel, "Physico-mechanical roperties of carbon fiber reinforced epoxy composites", Polym. Plast. Technol. Eng., **31**, 705-712 1992.
116. U. S. Tewari, A. P. Harsha, A. M. Hager and K. Friedrich, "Solid particle erosion of carbon fiber and glass fiber-epoxy composites", Compos. Sci. Technol., **63**, 549-557, 2003.

Onal et al. [117] have studied the effect of stacking sequence on mechanical properties of stitched composites for low velocity impact damages. Tests were performed for the same volume fraction (V_f) with different hybrid sequence and ply angle. The incorporation of glass fibers in carbon reinforced structures improved impact properties and increased the strain to failure. The addition of carbon fibers to the surface of glass-reinforced composites increased the flexural modulus for undamaged samples. Tensile failure mechanism of damaged plies seems to be affected by the interaction of reinforcement property, hybrid order and ply angle.

Vanaja et al. [118] have studied the effects of fiber fraction on thermal degradation of composites containing glass, carbon and glass/carbon hybrid reinforcements in a bifunctional epoxy resin system were studied. Thermogravimetric technique was used to monitor the weight loss with the temperature. The degradation patterns so obtained were correlated with the fiber fraction of the composites.

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.

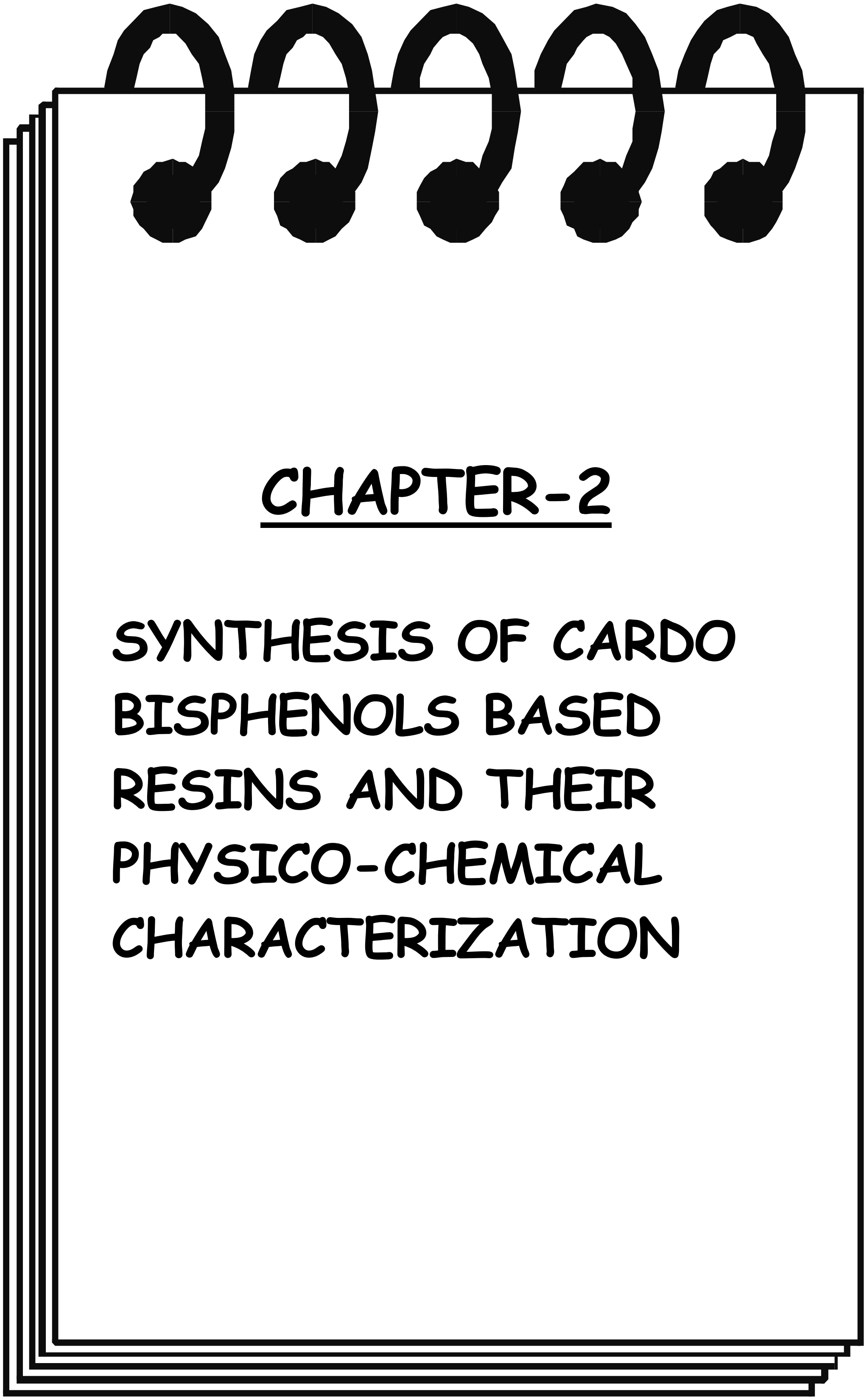
Following are the aims and objectives of the present work:

I. To evaluate thermal, mechanical and electrical properties of the polymers and resins.

---

117. L. Onal and S. Adanur, “Effect of stacking sequence on the mechanical properties of glass–carbon hybrid composites before and after impact”, J. Indust. Text., **31**, 255-271, 2002.
118. A. Vanaja and R. M. V. G. K. Rao, “Fibre fraction effects on thermal degradation behaviour of GFRP, CFRP and hybrid composites”, J. Reinf. Plast. Compos., **21**, 1389-1398, 2002.

II. To fabricate jute, sisal, carbon and glass fibers based sandwich and hybrid composites.
III. To evaluate mechanical and electrical properties of the composites.
IV. To study water absorption behavior of the composites in various environments.
V. To study coating and chemical resistance of copolyurethane resins.



CHAPTER-2

SYNTHESIS OF CARDO BISPHENOLS BASED RESINS AND THEIR PHYSICO-CHEMICAL CHARACTERIZATION

This chapter is further subdivided into ten sections

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

SECTION-II: SYNTHESIS OF 9, 9'-BIS(4-HYDROXY PHENYL)ANTHRONE-10 (BAN)

SECTION-III: SYNTHESES OF BISPHENOL-FORMALDEHYDE RESINS (BCF/ BANF)

SECTION-IV: SYNTHESIS OF EPOXY RESIN OF BISPHENOL-C

SECTION-V: SYNTHESES OF BAN-FORMALDEHYDE-ACRYLATE/ MALEATE RESINS

SECTION-VI: SYNTHESES OF BORON CONTAINING PHENOLIC RESINS (BBCF/ BBANF)

SECTION-VII: SYNTHESES OF PHOSPHORUS CONTAINING PHENOLIC RESINS (PBCF/ PBANF)

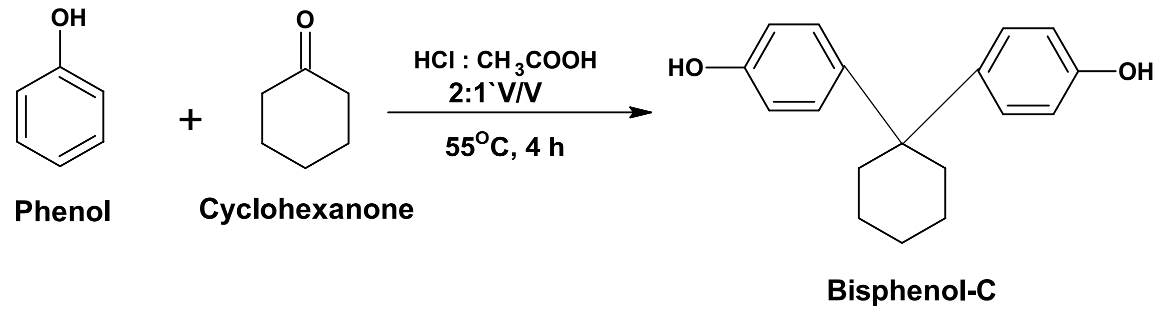
SECTION-VIII: IR SPECTRAL CHARACTERIZATION OF RESINS

SECTION-IX: DETERMINATION OF EPOXY EQUIVELENT OF THE EPOXY RESIN

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



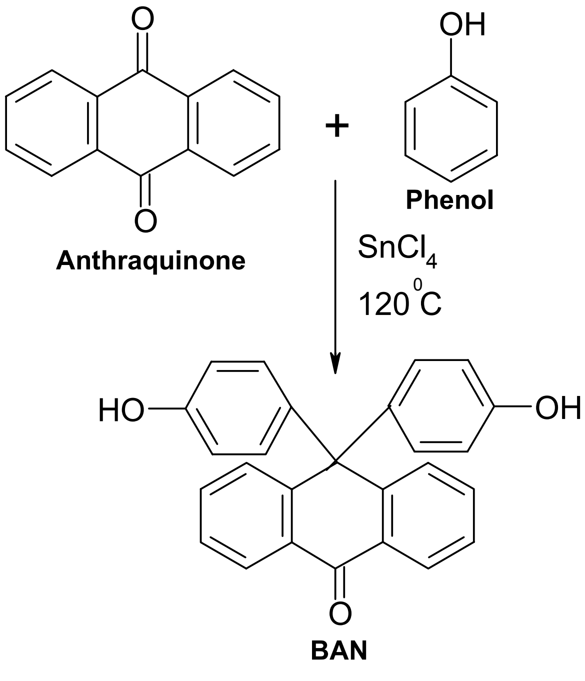
I

---

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**, 758-759, 1987.
2. H. H. Garchar, H. N. Shukla and P. H. Parsania, "Kinetics of formation of 1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane", Indian Acad. Sci. (Chem. Sci.), **103**, 149-153, 1991.

SECTION-II: SYNTHESIS OF 9,9'-BIS(4-HYDROXY PHENYL) ANTHRONE-10 (BAN)

9,9'-Bis(4-hydroxy phenyl)anthrone-10 (BAN) (III) was synthesized according to the reported method [3]. Thus, anthraquinone (0.1 mol, 20.8 g) was condensed with phenol (0.7 mol, 65.8 g) at 120ºC in presence of stannic chloride (0.15 mol, 17.5 g) for 6h. Excess phenol was removed by steam distillation and product was boiled in an acetic acid to remove resinous material. The dark brown colored product was filtered, washed well with boiling water and dried at 50ºC. Crude BAN (light gray) was dissolved in 2N NaOH solution and filtered through cotton plug. The yellowish solution so obtained was acidified with dilute HCl, filtered, washed well with water and dried. BAN was further recrystallized repeatedly from dioxan-water system to get pure, white shining crystals of yield ~ 80 % and m.p. was 324 º C.



II

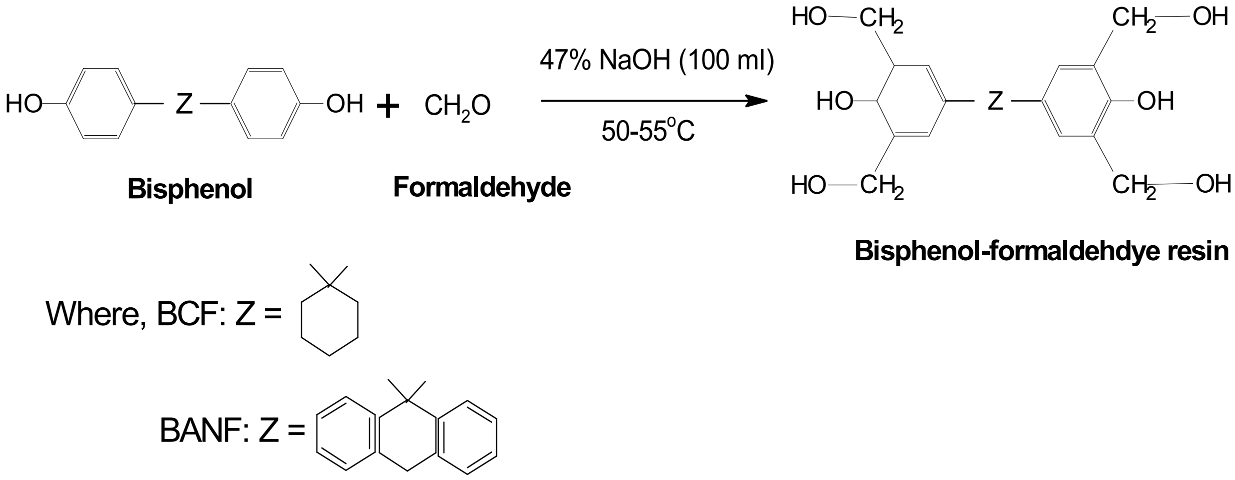
---

3. S. V. Vinogradova, S. N. Salazkin, L. A. Beridge, A. I. Mzhel'skii, A. A. Askadski, G. L. Slonimskii, and V. V. Korshak, "Polyarylates from 9,9'-bis-(4-hydroxy phenyl) anthrone-10", Polym. Sci . USSR; **11** (1-3), 27-36, 1969.

SECTION-III: SYNTHESES OF BISPHENOL-FORMALDEHYDE RESINS (BCF/ BANF)

Bisphenol-formaldehyde resins (BCF/BANF) (II) were synthesized according to reported method [4].

In a 1- liter flask equipped with a condenser, BC (0.5 mol, 134 g)/ BAN (0.5 mol, 189 g) and 37% formaldehyde solution (2.1 mol, 202 ml) were charged. Reaction mixture was heated at 50-55°C for 1h/2h, respectively. 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/BANF is soluble in acetone, 1, 4-dioxane, DMF and DMSO.



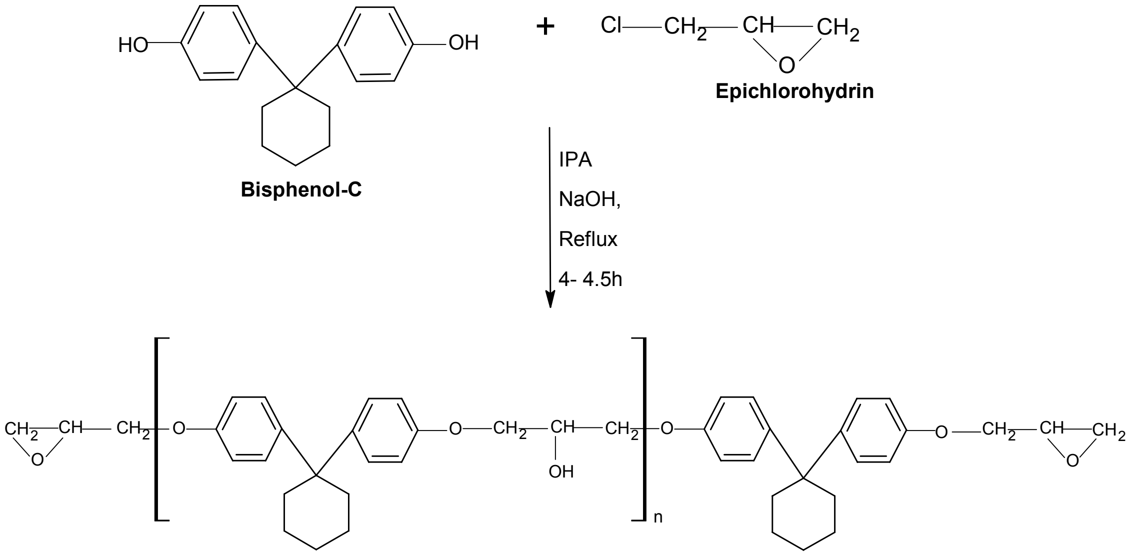
III

---

4. 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-IV: SYNTHESIS OF EPOXY RESIN OF BISPHENOL-C

Epoxy resin of BC of general structure (IV), here after designated as EBC, was synthesized according to the reported method [5]. Thus, BC (0.5 mol, 134 g), epichlorohydrin (1.1 mol; 138.8 g) and isopropanol (250 ml) were placed in a round bottomed flask equipped with a condenser. The mixture was brought to reflux with stirring and 1.25 mol NaOH in 50 ml water was slowly added to the solution and the refluxed for 4.5 h. The separated solid resin was isolated by filteration and liquid resin by distillation of excess of isopropanol. The solid and liquid resins were washed well with water and extracted in chloroform and evaporated to dryness. Highly transparent yellowish color resin was formed which is soluble in $CHCl_3$, acetone, 1, 4-dioxan, DMF, 1, 2-dichloroethane and DMSO; and partially soluble in ethanol and isopropanol.



Epoxy resin

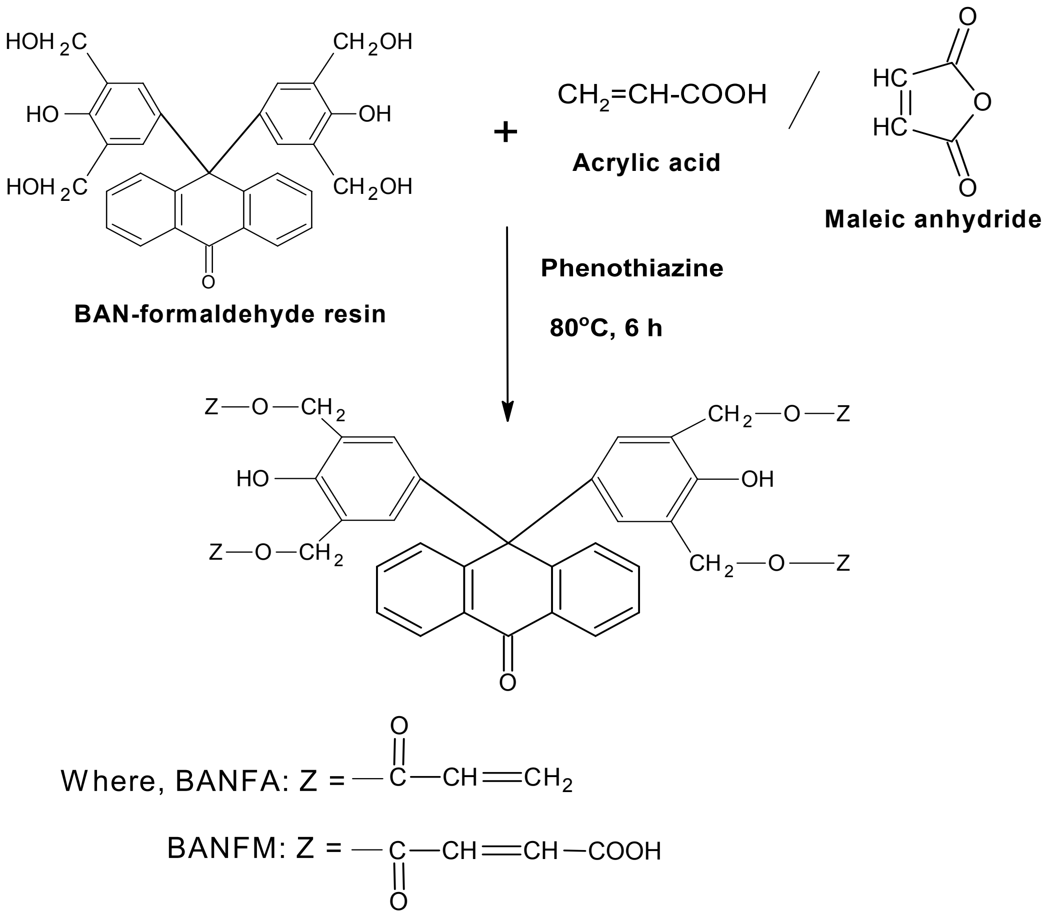
IV

---

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

SECTION-V: SYNTHESES OF BAN-FORMALDEHYDE-ACRYLATE/ MALEATE RESINS

BAN-formaldehyde-acrylate/maleate resins (V) were synthesized by condensing BANF (0.01 mol / 4.98 g) and acrylic acid (0.04 mol /2.9 ml)/maleic anhydride (0.04 mol / 3.92 g) and by using 1,4-dioxan as a solvent and phenothiazine as a catalyst at 80° C for 6h [6]. Brownish green solid product was obtained, which was purified repeatedly from MEK-water system prior to its use.



Where, BANFA: $Z = -\overset{\overset{\displaystyle O}{||}}{C}-CH{=}CH_2$

BANFM: $Z = -\underset{\underset{\displaystyle O}{||}}{C}-CH{=}CH-COOH$

V

---

6. P. J. Vasoya, N. M. Mehta and P. H. Parsania, “Mechanical, electrical and water absorption study of jute/glass/jute-bamboo/glass-bamboo-bisphenol-C-formaldehyde-acrylate a value added composites”, Polym. Plast. Techol. Eng., **46**, 621-628, 2007.

SECTION-VI: SYNTHESES OF BORON CONTAINING PHENOLIC RESINS (BBCF/ BBANF) [7-9]

To a 250 ml three neck flask equipped with a mechanical stirrer, a thermometer and a condenser in a thermostat, were placed 0.1 mol BC/BAN, 0.4 mol formaldehyde (37%) and 20 ml NaOH (47%) and stirred at 70^0C for 1 h. A 0.1 mol boric acid was added to this system and stirred at 110^0C for 45 min and poured in water (Scheme-VI). Separated creamish solid was filtered, washed well with distilled water and dried at 50^0C. Similarly other samples were prepared by changing boric acid composition. The reaction yield was 88-90 %. Herewith resins are designated as BBCF-1 to BBCF-3 and BBANF-1 to BBANF-3. The numerical figures indicate feed mole composition of boric acid in the resin formation. The resins were purified repeatedly from methanol-water system. The resins are soluble in common solvents such as acetone, ethyl acetate, 1, 4-dioxan, methyl ethyl ketone, etc.

Resinification can be divided into two steps [7]. In the first step bisphenols react with formaldehyde to form tetramethylol bisphenols and the second step involves reaction with boric acid (Scheme-VI). The reactivity of methylol group with boric acid is higher than that of phenolic hydroxyl group and hence second step reaction proceeds with the reaction between methylol and phenolic hydroxyl groups to form borate linkages.

Borate content of the resin is determined gravimetrically. The known weight of resin is ignited in crucible until all the carbon is eliminated and achieved weight to the nearest 0.1 mg of known weight. Each test of the all resins have carried out in triplicate and average value is reported in Table 2.1. Obtained residue which is in the form of boron oxide can be calculated as:

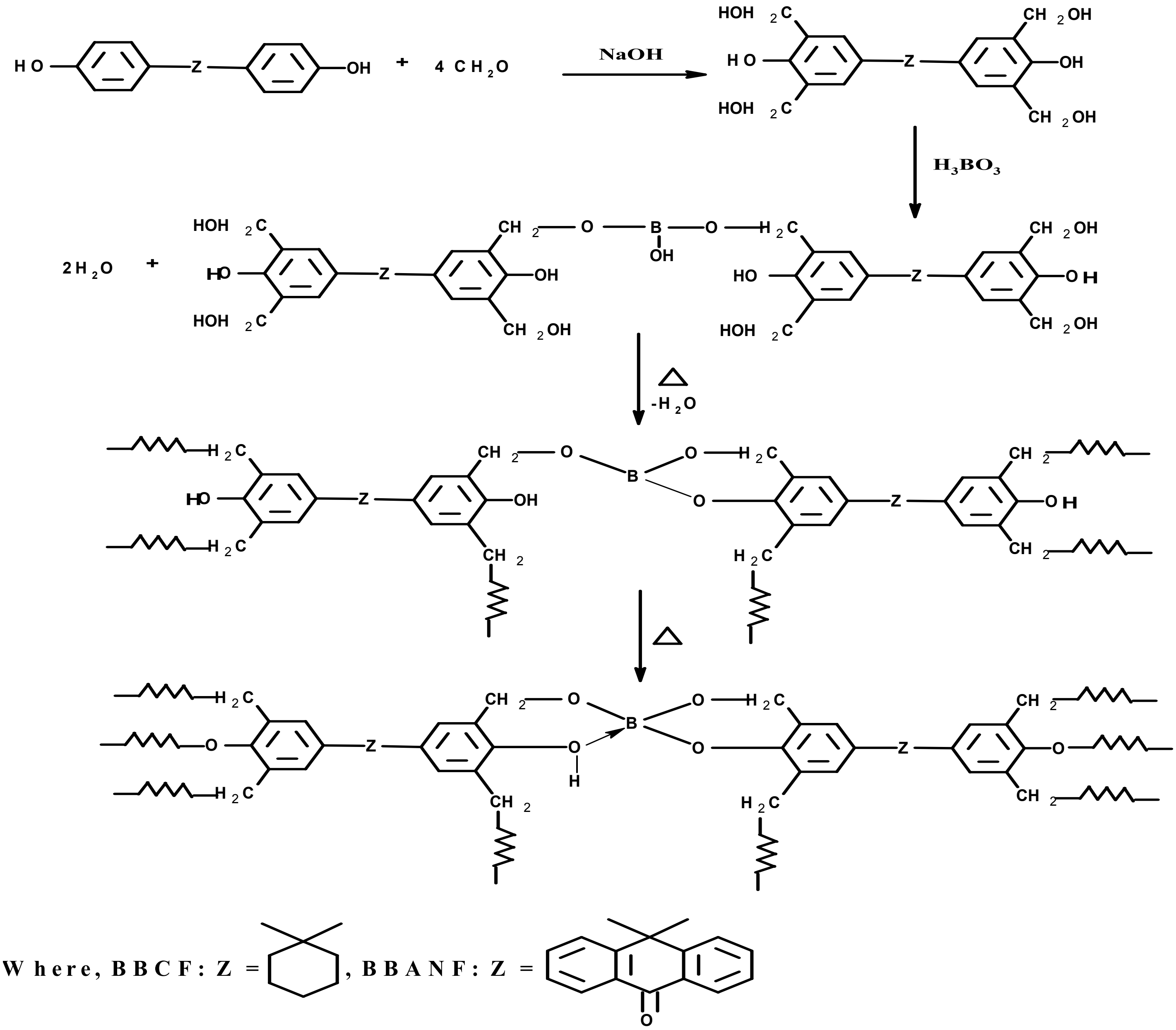
% Boron content = $(W_1/W_2) \times 100$

Where, W_1 is the weight of residue and W_2 is the known weight of resin

From Table 2.1 it is observed that practically no change in boron content is observed even with increasing boric acid feed composition.

---

7. J. Gao, L. Xia, Y. Liu, “Structure of a boron-containing bisphenol-F- formaldehyde resin and kinetics of its thermal degradation”, Polym. Deg. Stab., **83**, 71-81, 2004.
8. Y. Liu, J. Gao, R. Zhang, “Thermal properties and stability of boron-containing phenol-formaldehyde resin formed from paraformaldehyde”, Polym. Deg. Stab., **77**, 495-501, 2002.
9. J. Gao, Y. Liu, F. Wang, “Structure and properties of boron-containing bisphenol-A formaldehyde resin”, Eur. Polym. J., **37**, 207-210, 2001.



(VI)

BBCF-1: BC: Formaldehyde: Boric acid (1:4:1)

BBCF-2: BC: Formaldehyde: Boric acid (1:4:2)

BBCF-3: BC: Formaldehyde: Boric acid (1:4:3)

BBANF-1: BAN: Formaldehyde: Boric acid (1:4:1)

BBANF-2: BAN: Formaldehyde: Boric acid (1:4:2)

BBANF-3: BAN: Formaldehyde: Boric acid (1:4:3)

SECTION-VII: SYNTHESES OF PHOSPHORUS CONTAINING PHENOLIC RESINS (PBCF/ PBANF)

Phosphorus containing phenolic resins were synthesized according to reported method [10]. Into a tree neck flask equipped with a stirrer, thermometer and a condenser were placed 0.1 mol BCF/BANF and 50 mi methanol. The solution was cooled to 0-5^{0}C and 0.1 mol phosphorus oxychloride was added drop wise over a period of 30 min. The reaction mass was refluxed 2h and the product was isolated from chilled waster, filtered, washed and dry at 50^{0}C and were repeatedly purified from methanol-water system. Similarly other samples were prepared by changing phosphorus oxychloride composition. The reaction yield was 80-82 %. Herewith resins are designated as PBCF-1 to PBCF-3 and PBANF-1 to PBANF-3. The numerical figures indicate feed mole composition of phosphorus oxychloride in the resin formation. The resins were purified repeatedly from methanol-water system. The resins are soluble in common solvents such as acetone, ethyl acetate, 1, 4-dioxan, methyl ethyl ketone, etc.

The reactivity of methylol group with phosphorus oxychloride is higher than that of phenolic hydroxyl group and hence reaction between methylol and phenolic hydroxyl groups to form phosphate linkages.

Phosphate content of the resin is determined gravimetrically. The known weight of resin is ignited in crucible until all the carbon is eliminated and achieved weight to the nearest 0.1 mg of known weight. Each test of the all resin has carried out in triplicate and average value is reported in Table 2.1. Obtained residue which is in form of phosphorus oxide can be calculated as:

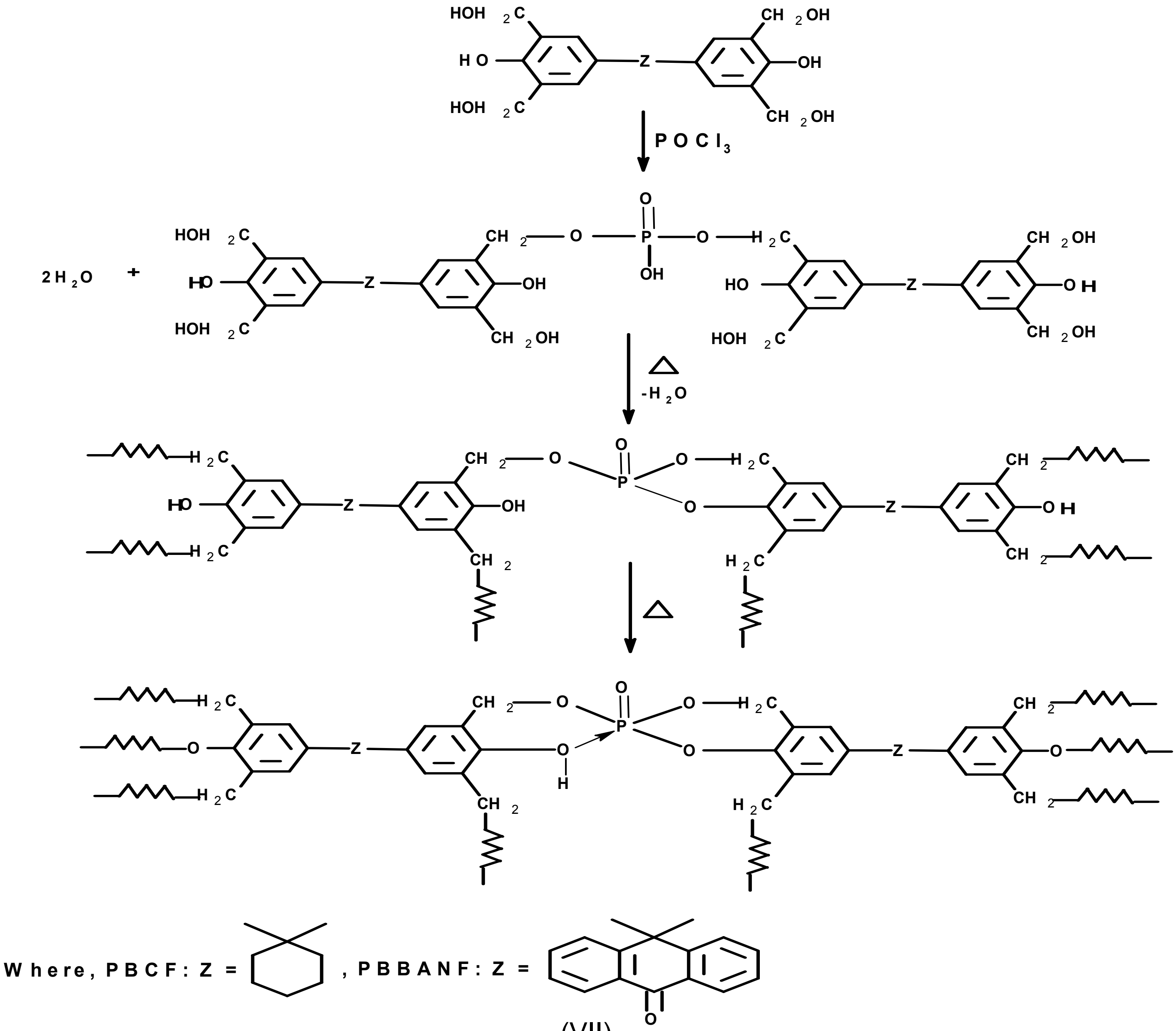
% Phosphorus content = $(W_1/W_2) \times 100$

Where, W_1 is the weight of residue and W_2 is the known weight of resin

From Table 2.2 it is observed that practically no change in phosphate content is observed even with increasing phosphorus oxychloride feed composition.

---

10. C. S. Cho, S. J. Chang, W. J. Teng, J. J. Chen, “Photosensitive phosphorylated phenol-formaldehyde resin and method for preparing the same”, U. S. Patent – 6566483 B2, 2003.



(VII)

PBCF-1: BCF: Phosphorus oxychloride (1:1)
PBCF-2: BCF: Phosphorus oxychloride (1:2)
PBCF-3: BCF: Phosphorus oxychloride (1:3)

PBANF-1: BANF: Phosphorus oxychloride (1:1)
PBANF-2: BANF: Phosphorus oxychloride (1:2)
PBANF-3: BANF: Phosphorus oxychloride (1:3)

Table 2.1: Boron content in the phenolic resins determined by gravimetry

Resin	% B_2O_3	Resin	% B_2O_3
BBCF-1	4.12	BBANF-1	4.23
BBCF-2	4.18	BBANF-2	4.30
BBCF-3	4.24	BBANF-3	4.34

Table 2.2: Phosphorus content in the phenolic resins determined by gravimetry

Resin	% P_2O_5	Resin	% P_2O_5
PBCF-1	3.71	PBANF-1	*3.69*
PBCF-2	3.80	PBANF-2	*3.79*
PBCF-3	*3.90*	PBANF-3	*3.88*

SECTION-VIII: 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 wave number or wavelength of the radiation transmitted. At 100% transmission, all the energy of radiation passes through the molecule. At lower values of % transmission, some of the energy is being absorbed by the compound. Each spike in the infrared (IR) spectrum represents absorption of energy. These spikes are called absorption bands.

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

The intensity of an absorption band depends on the size of dipole moment change associated with the vibration. In other words, depends on polarity of the vibrating bond. Intensity of the absorption 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 BCF, BANF, BANFA, BANFM, BBCF-1, BBANF-1, PBCF-1 and PBANF-1 resins were scanned on a 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 2.8. The characteristic absorption bands (cm^{-1}) for each system are reported in Tables 2.3 and 2.4.

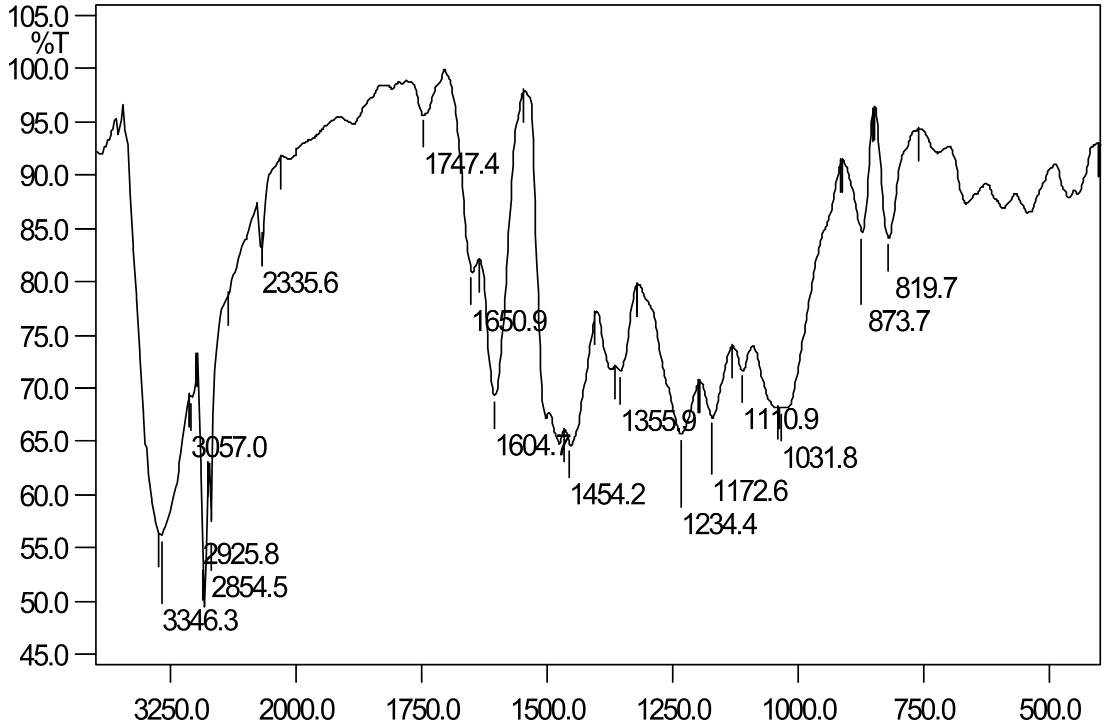


Fig. 2.1: IR (KBr) spectrum of BCF

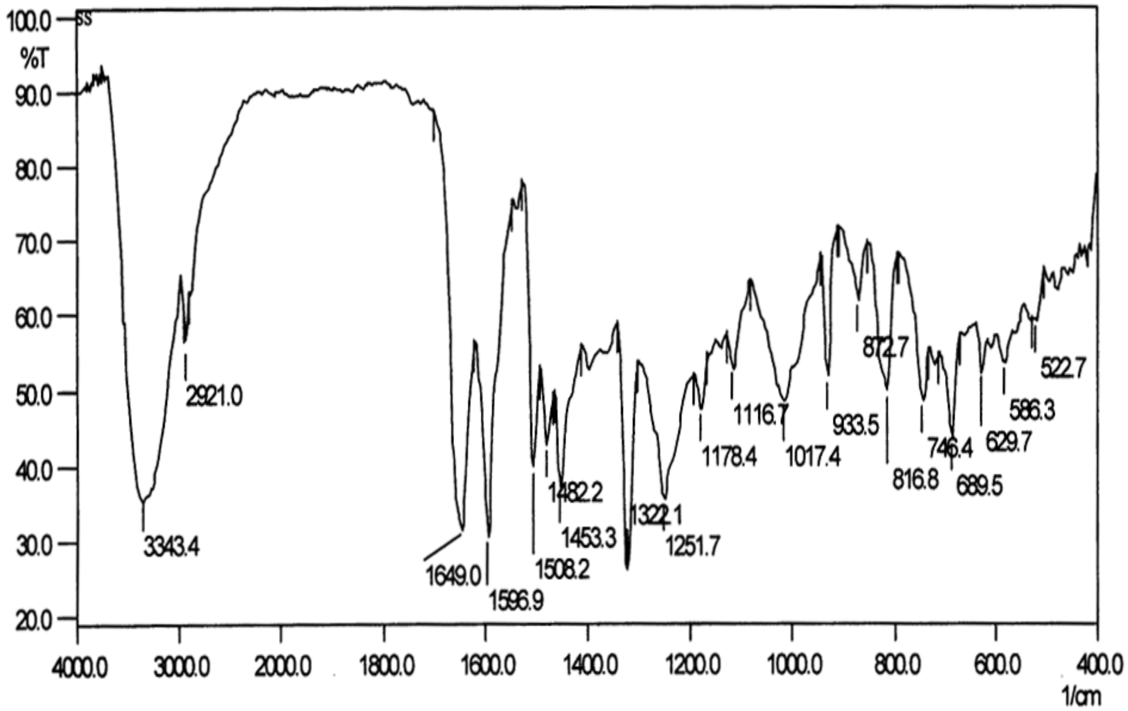


Fig. 2.2: IR (KBr) spectrum of BANF

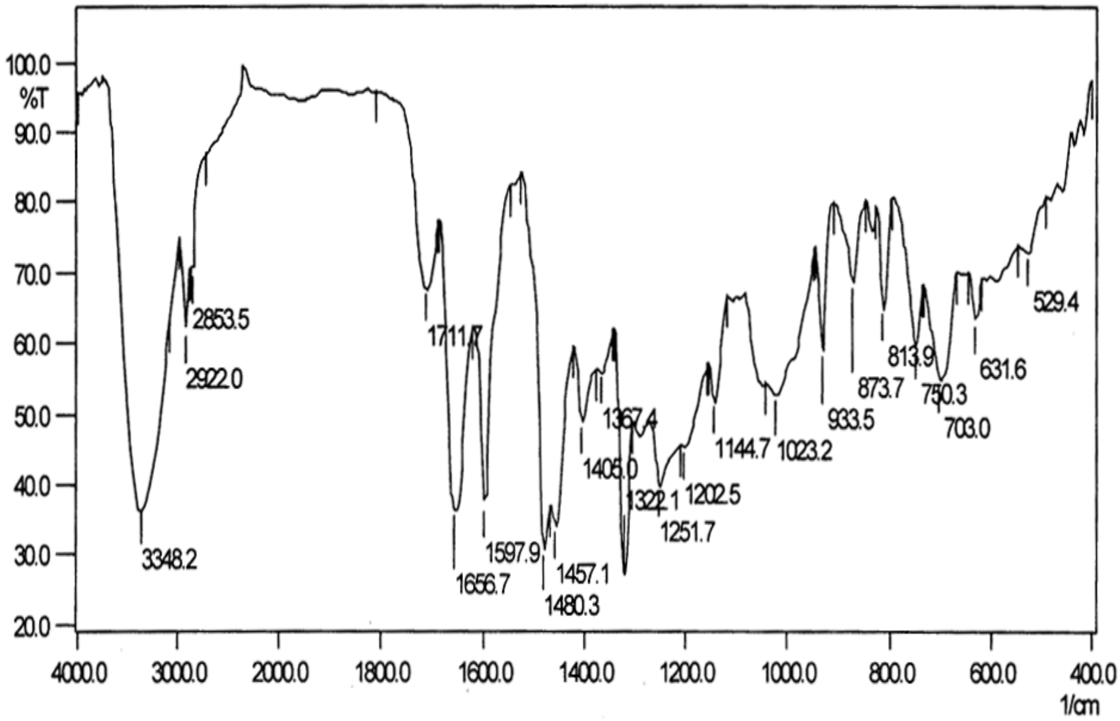


Fig. 2.3: IR (KBr) spectrum of BANFA

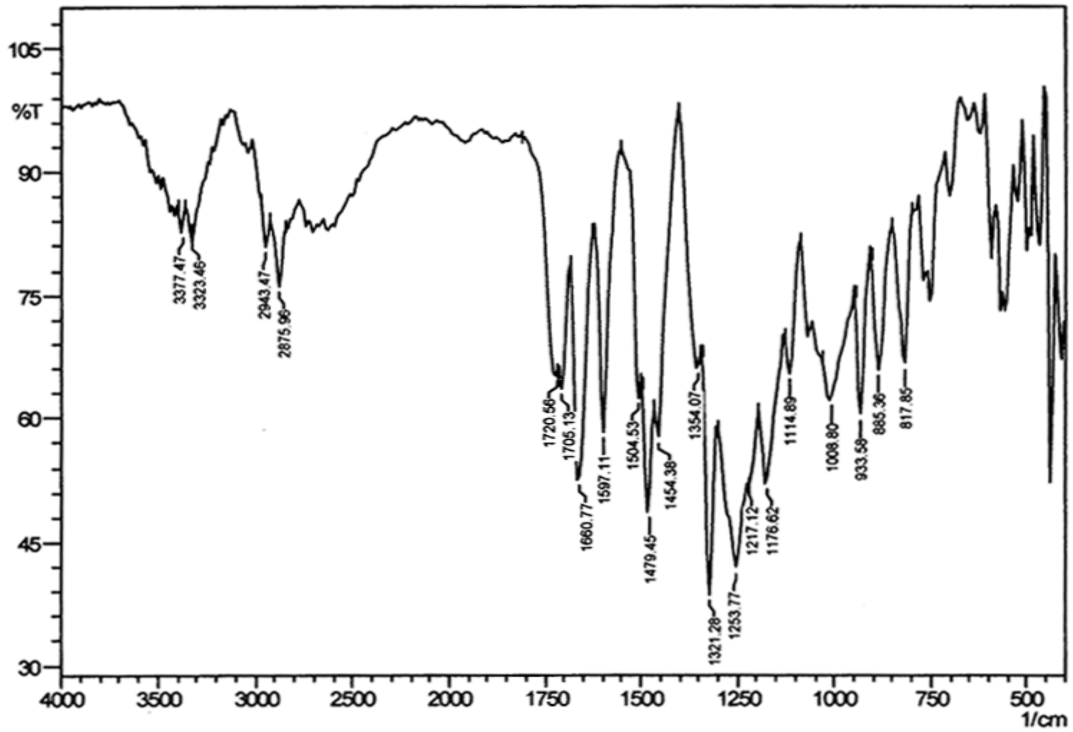


Fig. 2.4: IR (KBr) spectrum of BANFM

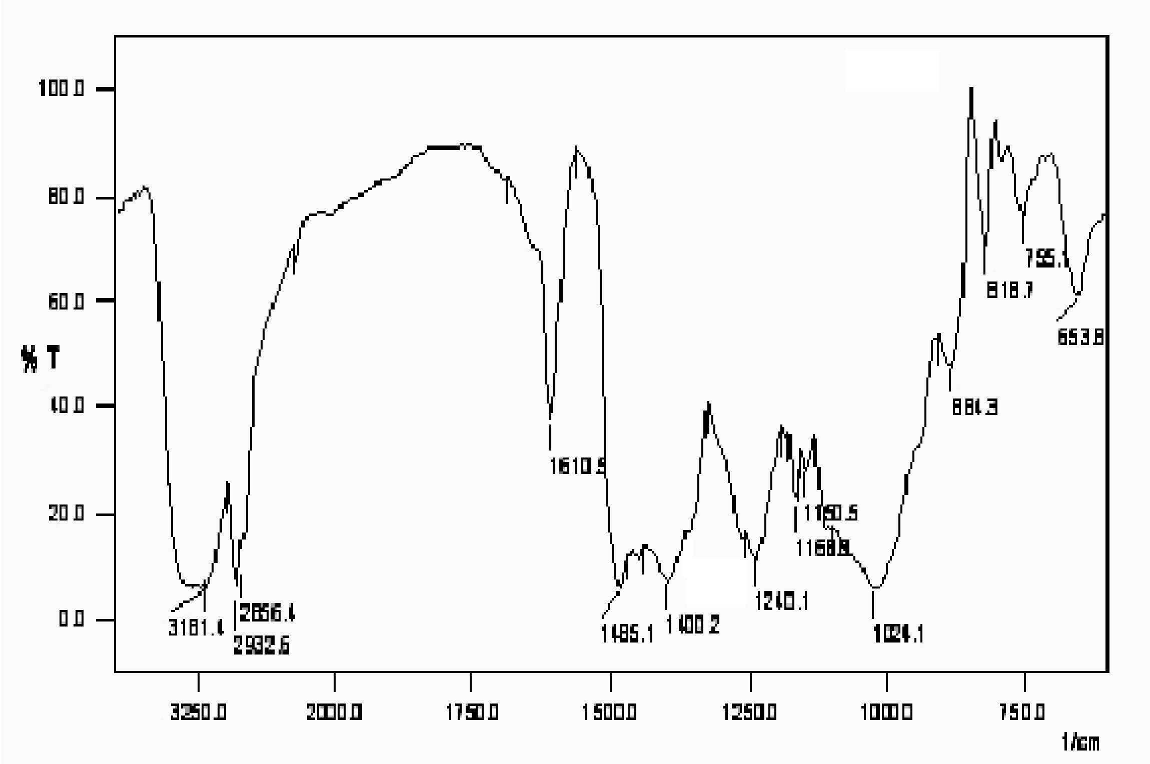


Fig. 2.5: IR (KBr) spectrum of BBCF-1

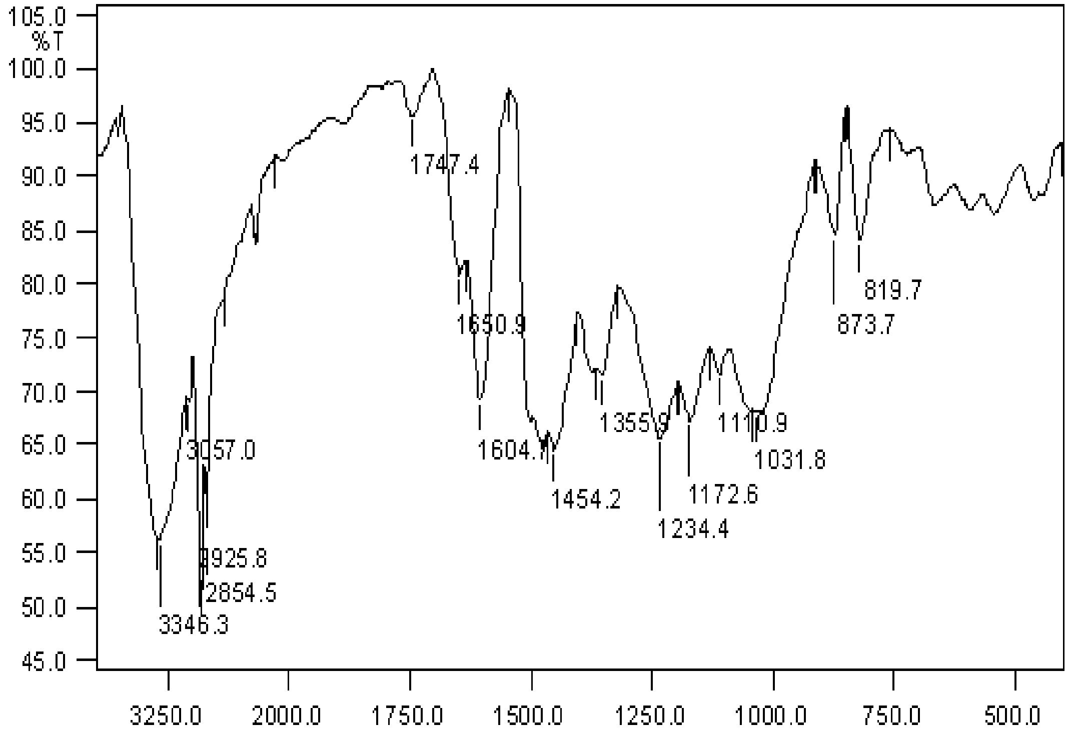


Fig. 2.6: IR (KBr) spectrum of BBNAF-1

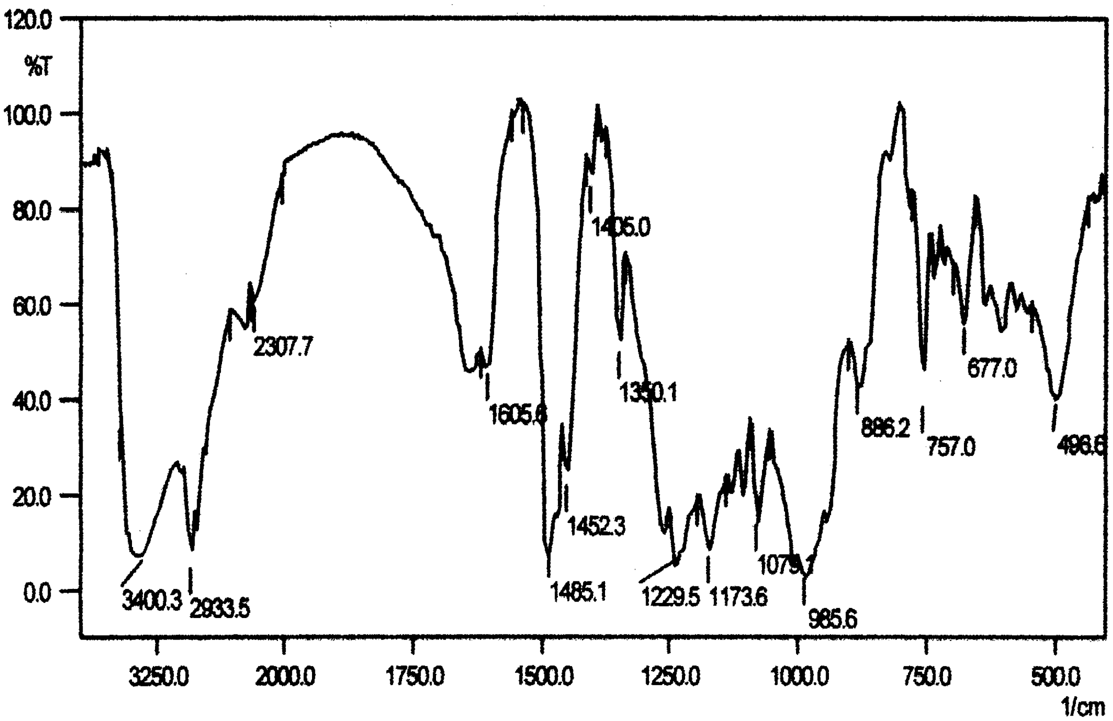


Fig. 2.7: IR (KBr) spectrum of PBCF-1

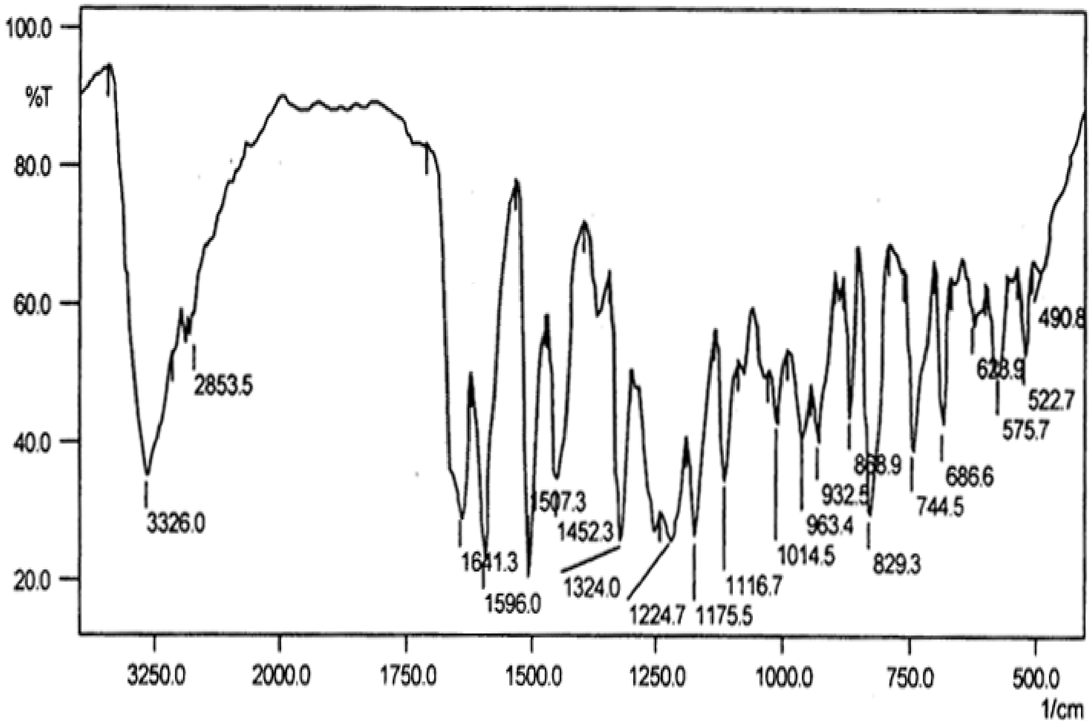


Fig. 2.8: IR (KBr) spectrum of PBNAF-1

Table 2.3: The characteristic absorption frequencies of BCF, BANF, BANFA and BANFM

Types	Group vibration mode	Observed IR frequencies, (cm^{-1})				Expected frequencies, (cm^{-1})
		BCF	BANF	BANFA	BANFM	
Alkane -CH$_3$ and -CH$_2$-	C-H (υas)	2925.8	2921.0	2922.0	2943.4	2975-2950
	C-H (υs)	2854.5	-	2853.5	2875.9	2880-2860
	C-H def, -CH$_3$	1454.2	1453.3	1457.1	1454.3	1470-1435
	C-H def, -CH$_2$-	1496.4	1482.2	1480.3	1479.4	1485-1445
	Twistiing & Wagging	1234.4	1251.7	1251.7	1253.7	~1250
	Skeletal CH$_2$ 4 or >	-	746.4	750.3	750.0	750-720
Ar-OH	O-H (str.)	3346.3	3343.4	3348.2	3377.4	3600-3200
	C-O (str.)	1172.6	1178.4	1144.7	1176.6	1230-1140
Arom-atic	C-H (i.p.d.)	1110.9	1116.7	1144.7	1114.8	1258±11, 1175±6, 1117±7, 1073±5 (1,4 sub.)
	C-H (o.o.p.d.)	873.7	872.7	873.7	885.3	900-860, 860-800 (1,2,4 sub.)
	C=C (str.)	1604.7	1596.9	1597.9	1597.1	1600±6, 1579±6
Ester	C=O (str.)	1747.4	-	1711.7	1720.5	1780-1710
	C-O(str.)	1234.4	1251.7	1251.7	1253.7	1300-1250
Ketone	C=O (str.)	-	1649.0	1656.7	1660.7	1700-1640

Table 2.4: The characteristic absorption frequencies of BBCF-1, BBANF-1, PBCF-1 and PBANF-1 resins

Types	Group vibration mode	Observed IR frequencies, (cm^{-1})				Expected frequencies, (cm^{-1})
		BBCF-1	BBANF-1	PBCF-1	PBANF-1	
Alkane -CH$_3$ and -CH$_2$-	C-H (υas)	2932.6	2925.8	2933.5	2935.7	2975-2950
	C-H (υs)	2856.4	2854.5	2856.6	2853.5	2880-2860
	C-H def, -CH$_3$	1453.4	1454.2	1452.3	1452.3	1470-1435
	C-H def, -CH$_2$-	1485.1	1485.4	1485.1	1452.3	1485-1445
	Twistiing & Wagging	1240.1	1234.4	1254.3	1250.1	~1250
	Skeletal CH$_2$ 4 or >	755.1	-	757.0	744.5	750-720
Ar-OH	O-H (str.)	3181.4	3346.3	3400.3	3326.0	3600-3200
	C-O (str.)	1224.7	1229.5		1168.8	1230-1140
Arom-atic	C-H (i.p.d.)	1175.5	1173.5 1110.9	1172.6 1118.6	1150.5 1116.7	1258±11, 1175±6, 1117±7, 1073±5 (1,4 sub.)
	C-H (o.o.p.d.)	884.3 818.7	873.7 819.7	886.2	888.9 826.3	900-860, 860-800 (1,2,4 sub.)
	C=C (str.)	1610.5	1604.1	1605.6	1596.0	1600±6, 1579±6
Borate	B-O (str.)	1400.2	1355.9	-	-	1400-1350
Phos-phate	P=O (str.)	-	-	1258.3	1258.6	1300-1240
	P-O-C (str.)	-	-	985.6 1075.1	932.5 963.4 1014.5	1088-920
Ketone	C=O (str.)	-	1650.9	1643.3	1641.3	1700-1640

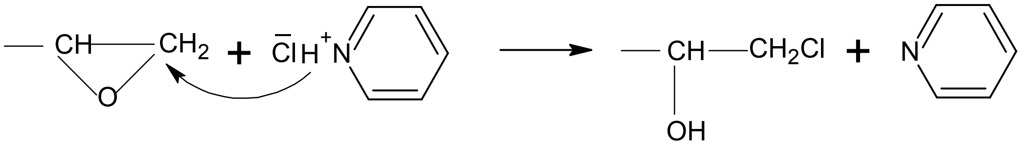
SECTION-IX: DETERMINATION OF EPOXY EQUIVELENT OF THE EPOXY RESIN

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

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

Epoxide equivalent may be determined by infrared analysis. The characteristic absorption band for the epoxy group is from 877.2 to 806.5 cm^{-1} for terminal epoxy groups; from 847.5 to 775.2 cm^{-1} for internal epoxy groups; and from 769.2 to 751.8 cm^{-1} for triply substituted epoxy group [11].

The epoxide equivalent may be determined from changes in intensity as related to change in molecular weight using the absorption band of the epoxy group at 912.4 or 862.1 cm^{-1} in comparison to aromatic band at 1610.3 cm^{-1}.



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

Greenlee [12] has described the method for epoxy equivalent. The epoxide content of the complex epoxide resins were determined by heating a 1 g sample of the epoxide composition with an excess of pyridine containing pyridine hydrochloride at the boiling point for 20 min and back titrating the excess pyridine hydrochloride

---

11. J. Bomstein, “Infrared spectra of oxirane compounds”, Anal. Chem. **30**, 544-546, 1958.

with 0.1 N sodium hydroxide by using phenolphthalein as an indicator and considering that 1 HCl is equal to 1 epoxide group [12].

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

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

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

---

12. S. O. Greenlee; (Devoe & Raynolds Co. New York) “Phenol aldehyde and epoxide resin compositions”, U. S. Pat. 2,502,145 (1949); C.A. **44**, 5614, 1950.
13. J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss “Organic Analysis (J. Mitchell Jr., ed.)”, 1, 127, Interscience, New York, 1953.

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

The number 0.016 is the mili equivalent weight of oxygen in grams. The epoxide equivalent of the resin used was found to be 576.

SECTION-X: 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 [15] 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

---

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

15. R. T. Conley, “Thermal stability of polymers”, Marcell Dekker, New York, 1973.

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 [16].

The thermal studies throw light on molecular architecture of polymers such as degree of polymerization, orientation, crystal perfection, percentage crystallinity, the extent of chain branching, strength of various bonds holding together polymer molecules, on the kinetic of depolymerization, on the 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 polymers and resins.

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

---

16. H. C. Anderson, “Thermal degradation of epoxy polymers”, J. Appl. Polym. Sci., **6**, 484-488, 1962.
17. Q. Wang and W. Shi, “Kinetic study of thermal decomposition of epoxy resins containing flame retardant components”, Polym. Deg. Stabi., **91**, 1747-1754, 2006.

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.

Laza et al. [18] have studied the dynamic-mechanical properties of different mixtures formed by an epoxy resin (DGEBA type) and a phenolic resin (resole type) cured by triethylene tetramine and/or p-toluene sulphonic acid at different concentrations have been studied by means of dynamic mechanical thermal analysis (DMTA). All samples were cured by pressing at 90^0C during 6h. The mechanical studies were performed between -100 to 300^0C 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. [19]. 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. [20] have reported the cure study of addition-cure-type and condensation-addition-type phenolic resins by the incorporation of propargyl and methylol groups on to novolac backbone, a series of addition-curable phenolic resins and condensation-addition dual-cure type phenolic resins (novolac modified by propargyl groups referred as PN, and novolac modified by propargyl and methylol groups simultaneously referred as MPN) were synthesized.

---

18. J. M. Laza, J. L. Vilas, M. T. Garay, M. Rodríguez and L. M. León, “Dynamic mechanical properties of epoxy-phenolic mixtures”, J. Polym. Sci., Part B: Polym. Phy., **43**, 1548-1557, 2005.
19. F. Barontini, K. Marsanich, L. Petarca and V. Cozzani, “Thermal degradation and decomposition products of electronic boards containing BFRs”, Ind. and Eng. Chem. Res., **44**, 4186-4193, 2005.

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 detail. 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 60^0C. These novel resins have a bright prospect of application as matrix for thermal-structural composite materials.

Thermal degradation of cross linked resins in controlled atmospheres have studied by Bouajila et al. [21]. 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. [22]. They have studied the thermal degradation behavior of a range of commercially available phenolic, epoxy and polyester resins by simultaneous DTA-TGA under a flowing air atmosphere. Thermal analytical

---

20. M. Wang, L. Wei and T. Zhao, “Cure study of addition-cure-type and condensation-addition type phenolic resins”, Eur. Polym. J., **41**, 903-917, 2005.
21. 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.-Polym. Compos., **11**, 345-357, 2003.

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 fiber, 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. [23] 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 cross linked via ethynyl phenyl azo groups were the most thermally stable systems. Propargylated novolac and phenyl ethynyl functional phenolics showed intermediate thermal stability. The maximum char yield was also given by ethynyl phenyl azo system. Non-isothermal kinetic analysis of the degradation reaction implied that all the polymers undergo 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 volatilization process in the kinetics of degradation. The usefulness of DSC and TGA in various fields of chemistry is described in Table 2.5.

---

22. B. K. Kandola, A. R. Horrocks, P. Myler and D. Blair, “Thermal characterization of thermoset matrix resins”, ACS Symposium Series, **797**, 344-351, 2001.
23. C. P. Reghunadhan Nair, R. L. Bindu and K. N. Ninan, “Thermal characteristics of addition-cure phenolic resins”, Polym. Deg. Stab., **73**, 251-263, 2001.

Table 2.5: 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 [24, 25].

---

24. D. W. Levi, L. Reich and H. T. Lee, "Degradation of polymers by thermal gravimetric techniques", Polymer Eng. Sci., **5**, 135-141, 1965.
25. H. L. Friedman, "The mechanism of poly(tetrafluoroethylene) pyrolysis", U. S. Dept. Com., Office. Tech., 24 PP (1959), C. A. **55**, 26511, 1961.

Reich and Levi [26] 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:

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

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

$$k = Ae^{E_a/RT} \qquad \text{...2.2}$$

C is defined as the conversion with respect to initial material

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

---

[26] 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

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

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

$$f(C) = (1 - C)^n \qquad \text{...2.5}$$

where, n = order of the reaction.

Upon substituting Eqns. 2.2 and 2.5 into Eqn. 2.1

$$\frac{dC}{dt} = Ae^{-E_a/RT}(1 - C)^n \quad \text{or} \quad \frac{dC}{dT} = \left(\frac{A}{\beta}\right)\left(e^{-E_a/RT}\right)(1 - C)^n \qquad \text{... 2.6}$$

where β = Rate of heating.

Methods of single heating rate

1. Freeman – Carroll [27] and Anderson-Freeman [28] method

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

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

---

27. E. S. Freeman and B. Carroll, “The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate”, J. Phys. Chem., **62**, 394-397, 1958.
28. D. A. Anderson and E. S. Freeman, “Kinetics of the thermal degradation of polystyrene and polyethylene”, J. Polym. Sci., **54**, 253-260, 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 $-E_a/R$ and the intercept equal to n.

Using Eqn. 2.7, Anderson-Freeman derived Eqn. 2.8:

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

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

2. Sharp-Wentworth method [29]

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

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

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

3. Chatterjee method [30]

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

---

29. J. H. Sharp and S. A. Wentworth, “Kinetic analysis of thermo- gravimetric data”, Anal. Chem., **41**, 2060-2062, 1969.

30. P. K. Chatterjee, “Application of thermogravimetric techniq- ues to reaction kinetics”, J. Polym. Sci., **3**, 4253-4262, 1965.

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

Where, W_1 and W_2 are the sample weight.

4. Horowitz and Metzger method [31]

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

$$\ln\left[\ln(1-C)^{-1}\right] = \frac{E_a}{RTs^2}\theta \qquad \text{...2.11}$$

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

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

$$\ln E_a - \ln\left(RTs^2\right) = \ln A - \ln\beta - \frac{E_a}{RTs} \qquad \text{...2.12}$$

$$A = \frac{k_b T}{h} e^{\Delta S^*/R} \qquad \text{...2.13}$$

where k_b is the Boltzmann constant

Use of multiple heating rates

(1) Anderson [32] method

Anderson [32] and Friedman [33] 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.

---

31. H. H. Horowitz and G. Metzger, Ana. Chem., **35**, 1464, 1963.
32. H. C. Anderson, “Thermogravimetry of polymer pyrolysis kinetics”, J. Polym. Sci., **6**, 175-182, 1964.

The relation is $$\ln R_t = \ln A + n\ln(1 - C) - \frac{E_a}{RT} \qquad \text{...2.14}$$

where $R_t = \beta C / dT$

The plot of $\ln R_t$ against 1/T at various fixed degree of conversion would be a straight line with slope equal to $-E_a/R$ at a fixed degree of conversion. In order to evaluate the values of n and A, Eqn. 2.15 can be employed by considering 1/T = $1/T_0$ when $\ln R_t = 0$

$$\frac{E_a}{RT_0} = \ln A + n\ln(1 - C) \qquad \text{...2.15}$$

According to Eqn. 2.15, the plot of E_a/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 [33]

Friedman [17] has developed following Eqn. 2.16:

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

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 $-E_a/R$ and

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

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 [34]

Ozawa has developed the following Eqn. 2.18:

$$\log\int_0^C \frac{dC}{(1-C)^n} \approx \log\frac{AE_a}{RT} - \log\beta - 2.315 - 0.4567\left(\frac{E_a}{RT}\right) \qquad \text{...2.18}$$

---

33. H. L. Friedman, "Kinetics of thermal degradation of char-forming plastics from thermogravimetry-application to a phenolic resin", J. Polym. Sci., **C6**, 183-195, 1964.
34. T. Ozawa, "A new method of analyzing thermogravimetric data", Bull. Chem. Soc. Jap., **38**, 1881-1886, 1965.

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

Thermal data of materials provide wealth of informations on physico-chemical changes occurring in the system during heating. DSC and TG thermograms of the resins under investigation were scanned on a Universal V-3.0G TA and Perkin Elmer TGA model No. Pyris-I at the heating rate of 10^0C and 20^0C min^{-1} in an N_2 atmosphere, respectively.

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 [35]. Thermal methods are based upon the relationship between temperature and some properties of a system such as mass, heat of reaction or volume, etc [36,37].

DSC (Figs. 2.9-2.15) and TG (Figs. 2.16-2.22) thermograms of BANF, BANFA, BANFM, BBCF-1, BBANF-1, PBCF-1 and PBANF-1 were scanned without thermal treatment. DSC transition temperatures, initial decomposition temperature (T_0), temperature of 10 % weight loss (T_{10}), temperature of maximum weight loss (T_{max}), temperature of final decomposition (T_f), decomposition range, % weight loss and % residual weight at the end of the reaction are reported in Table 2.6. From Figs. 2.16-2.22, it is observed that no T_g is detected clearly. Transitions at 80.9^0C (Endo) for BANF, 109.3^0C (Exo) for BANFA, 81.2^0C (Endo) for BANFM, 90.9^0C (Endo) for BBCF-1, 75.2^0C (Endo) for PBCF-1 and 112.5^0C (Endo) for PBANF-1 are due to some physical change and it is further confirmed no weight loss over that temperature in corresponding TG thermogram (Figs. 2.16-2.22). Other exothermic

---

35. Jovan Mijovic, “Cure kinetics of neat vs reinforced epoxies”, J. Appl. Polym. Sci., **31**, 1177-1187, 2003.
36. 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.
37. R. C. Machenizie, “Differential thermal analysis”, Vol 1 and 2, Academic Press, New York, 1970.

transitions at 279.3^{0}C for BANF, 276.3^{0}C for BANFA, 292.9^{0}C for BANFM, 237.1^{0}C for BBCF-1, 285.7^0, 317.9^0 and 353.6^{0}C for BBANF-1, 241.4^0 and 312.6^{0}C for PBCF-1 and 297.3^{0}C for PBANF-1 are due to degradation of resin. At low temperature (100^0-200^{0}C), in some of the resin, weight loss is observed, which is due to self curing of methylol groups with evolution of water and formaldehyde. The resultant cured resins degrade at high temperature (>300^{0}C) forming cross linked structure leaving high amount of residue. BCF-1 and PBCF-1 have followed two step degradation reactions. First step involved chemical transition, i.e. self curing of methylol groups and second step involved decomposition of new product formed leaving 37.2 % and 32.1 % residue at 600^{0}C, respectively indicating formation of highly thermally stable polymer. BBANF-1 is thermally stable up to about 125^{0}C and followed single step decomposition leaving 40.7 % residue at 600^{0}C. High residue above 600^{0}C indicated formation of cyclic structure, which ultimately converted into low molecular mass volatile hydrocarbons and boron oxide and phosphate oxide. Thus, pyrolysis is a complex reaction leading to a variety of reactions.

The resins under investigation are thermosetting type and possess self curing property upon they undergo self curing with release of formaldehyde and water with formation of thermally stable resins, which degrade at elevated temperature. Degradation reaction is a complex reaction involving a variety of reactions namely cleavage, branching, rearrangement, cross-linking, etc. Selective degradation occurs from weak linkages and free radicals may be formed, which may further undergo recombination to form new compounds, which may degrade at higher temperature and ultimately converted into low molecular mass substances. In case of boron and phosphorus containing resins corresponding oxides will be left. High amount of residual weights confirmed formation of cross-linked polymers.

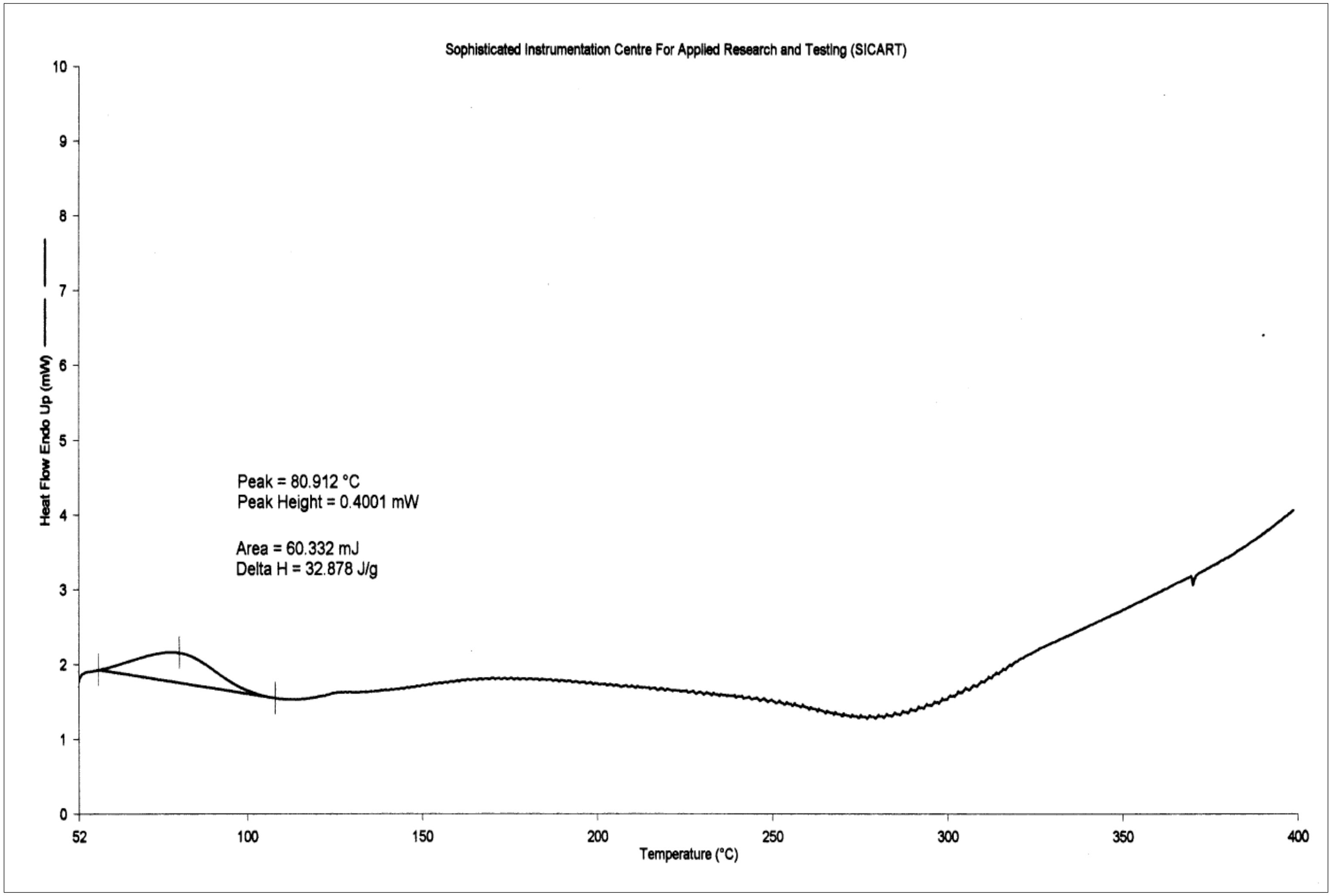


Fig. 2.9: DSC thermogram of BANF at the heating rate of 20^0C/min in an N_2 atmosphere

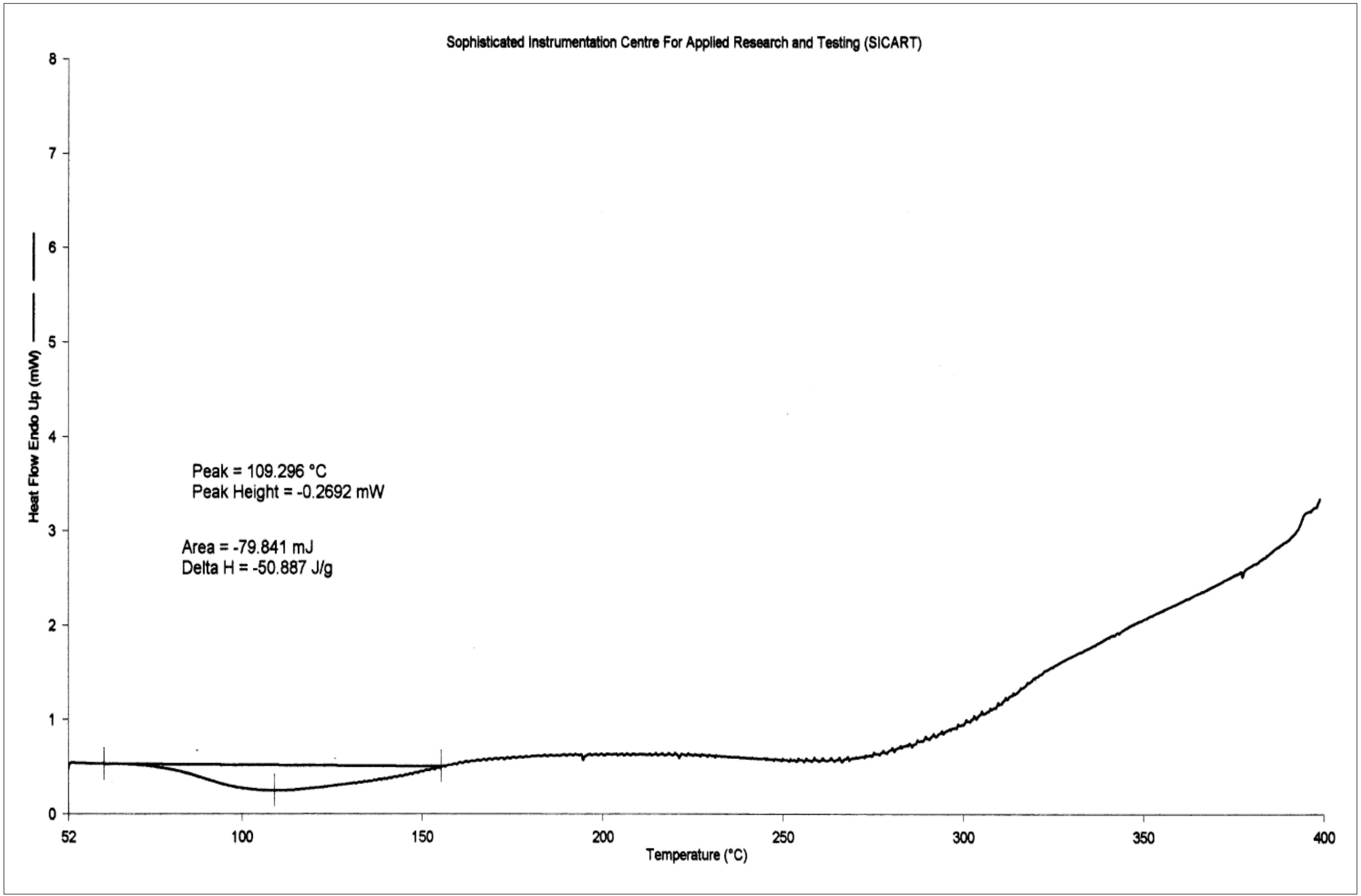


Fig. 2.10: DSC thermogram of BANFA at the heating rate of 20^0C/min in an N_2 atmosphere

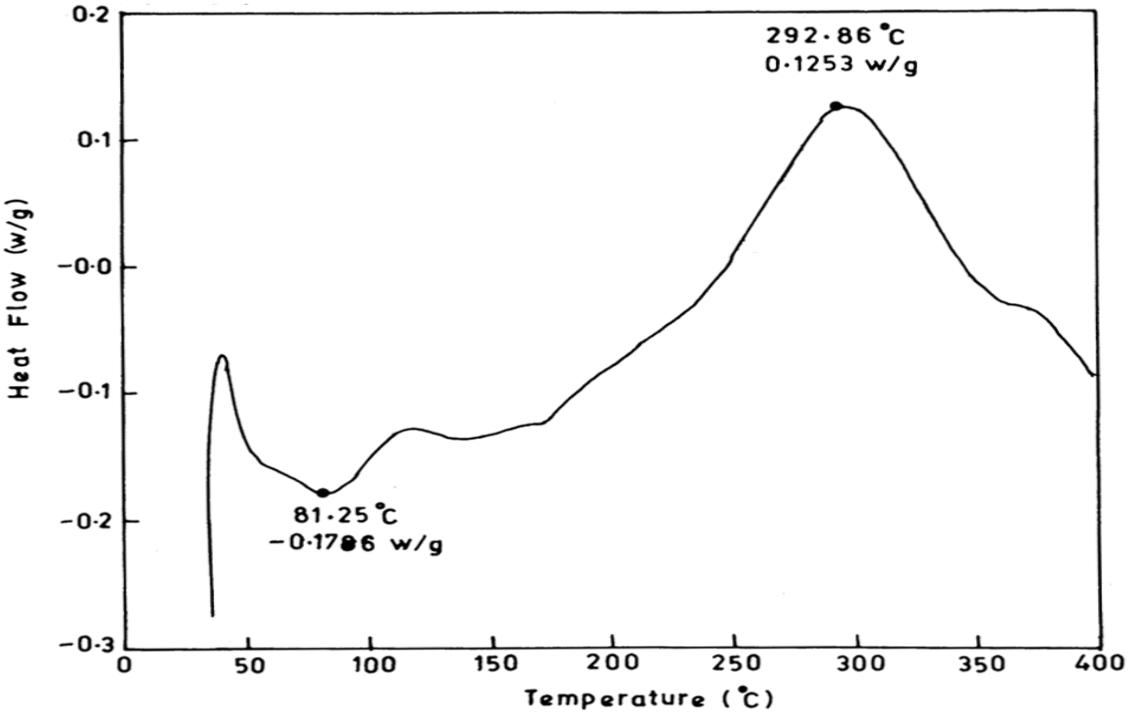


Fig. 2.11. DSC thermogram of BANFM at the heating rate of 20^{0}C/min in an N_2 atmosphere

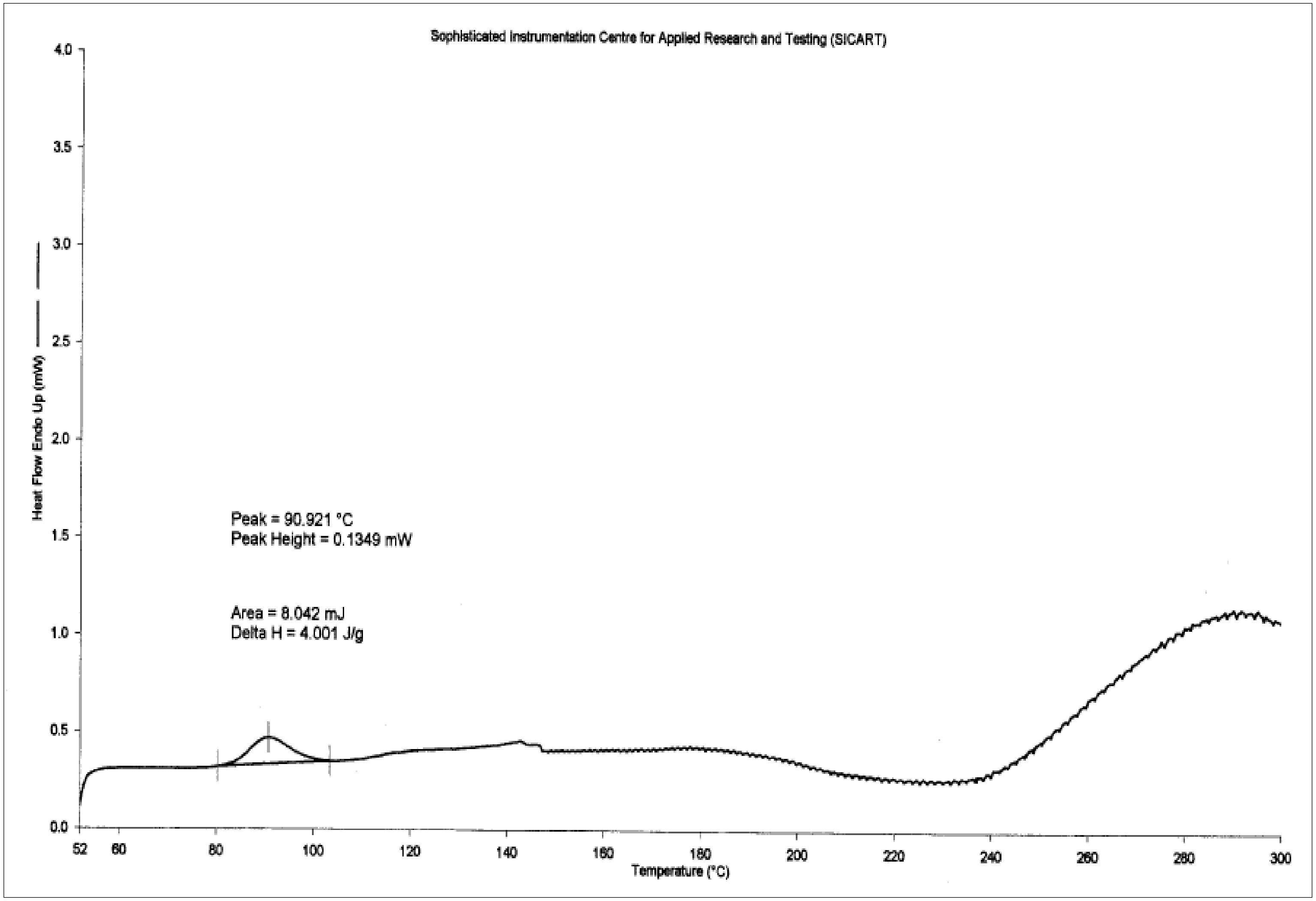


Fig. 2.12: DSC thermogram of BBCF-1 at the heating rate of 20^0C/min in an N_2 atmosphere

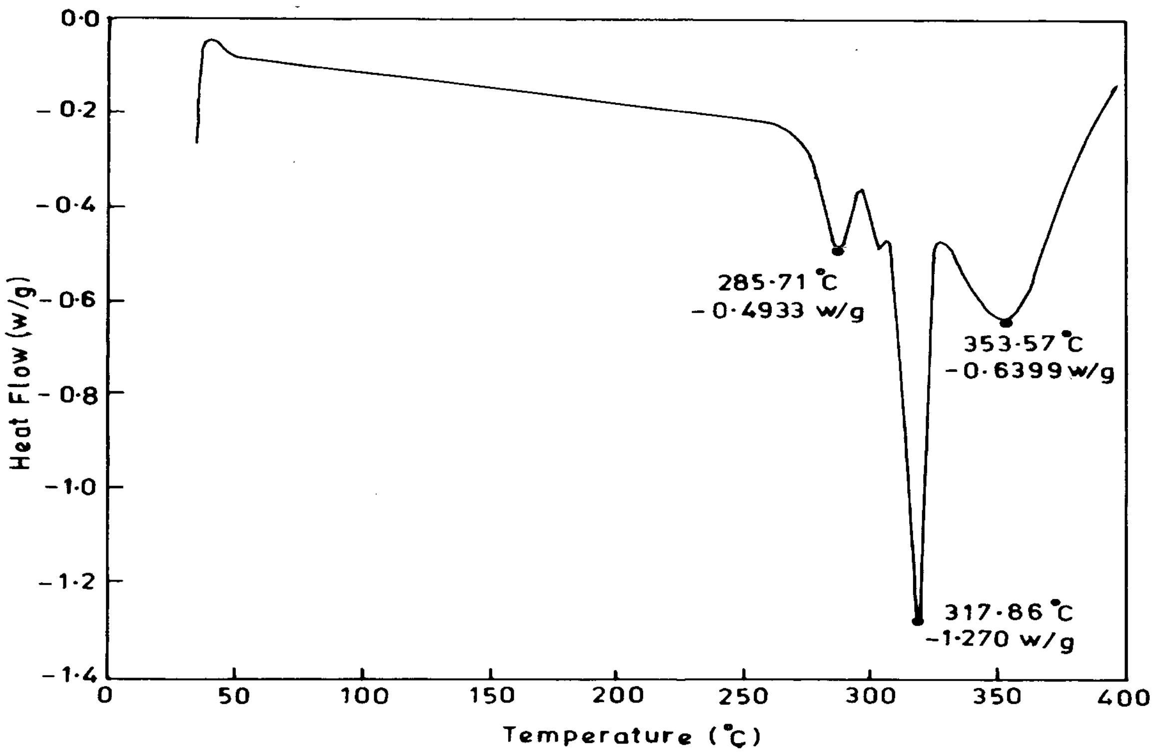


Fig. 2.13: DSC thermogram of BBANF-1 at the heating rate of 20^{0}C/min in an N_2 atmospheres

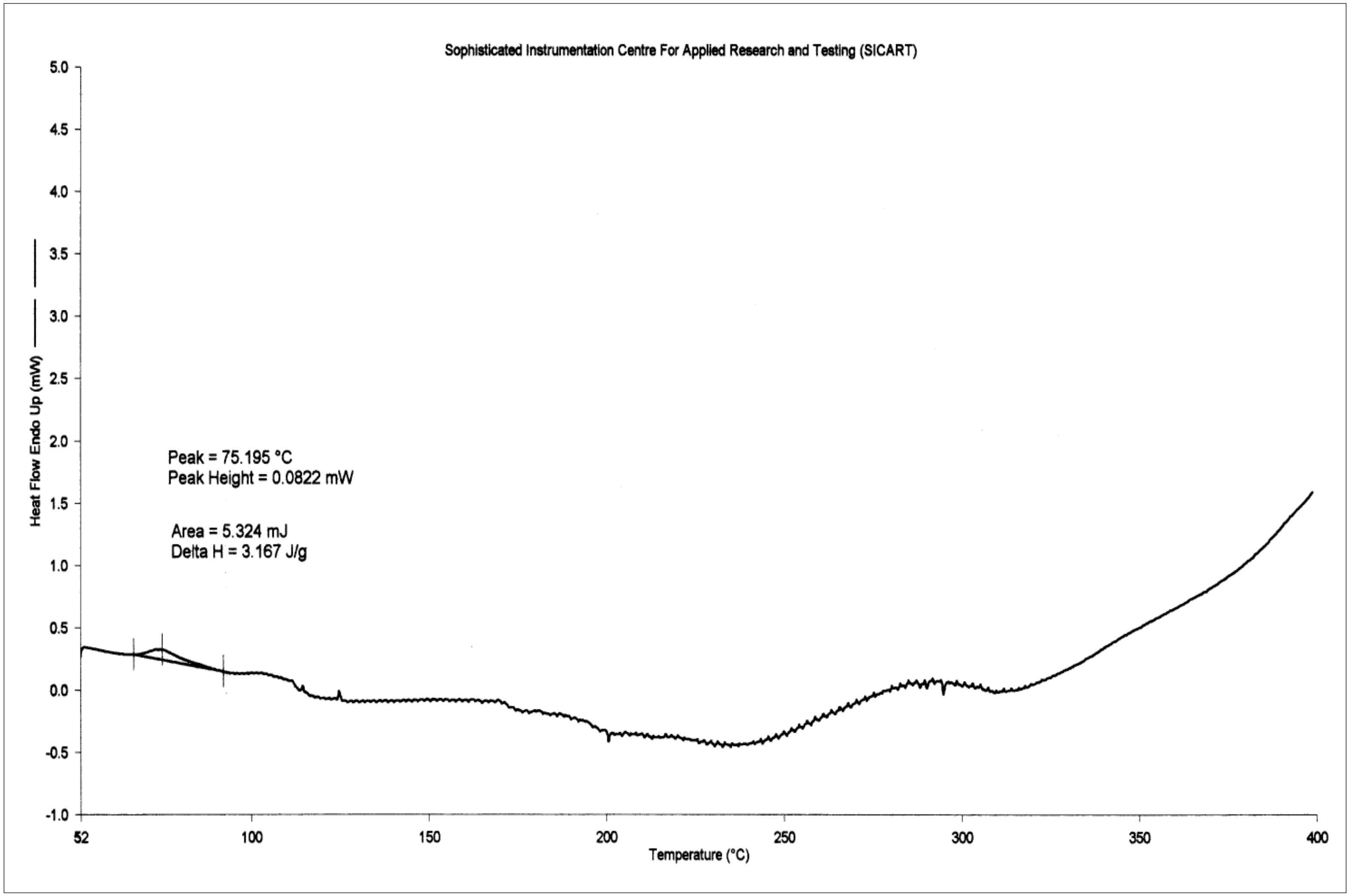


Fig. 2.14: DSC thermogram of PBCF-1 at the heating rate of 20^0C/min in an N_2 atmosphere

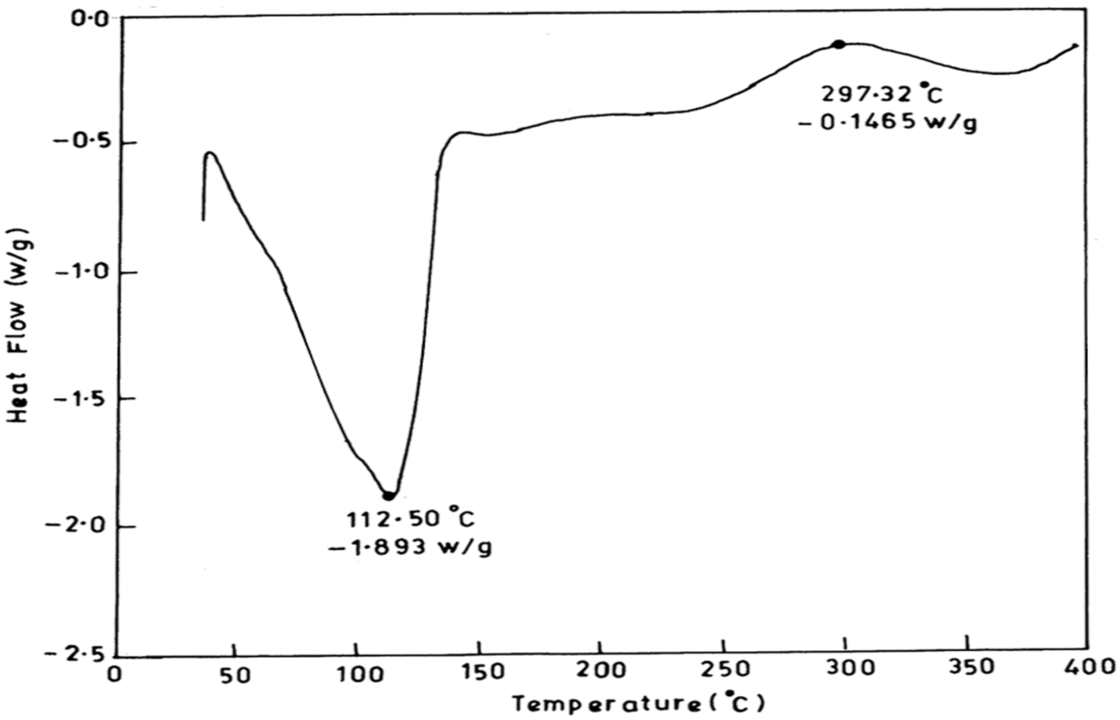


Fig. 2.15: DSC thermogram of PBANF-1 at the heating rate of 20^{0}C/min in an N$_2$ atmospheres

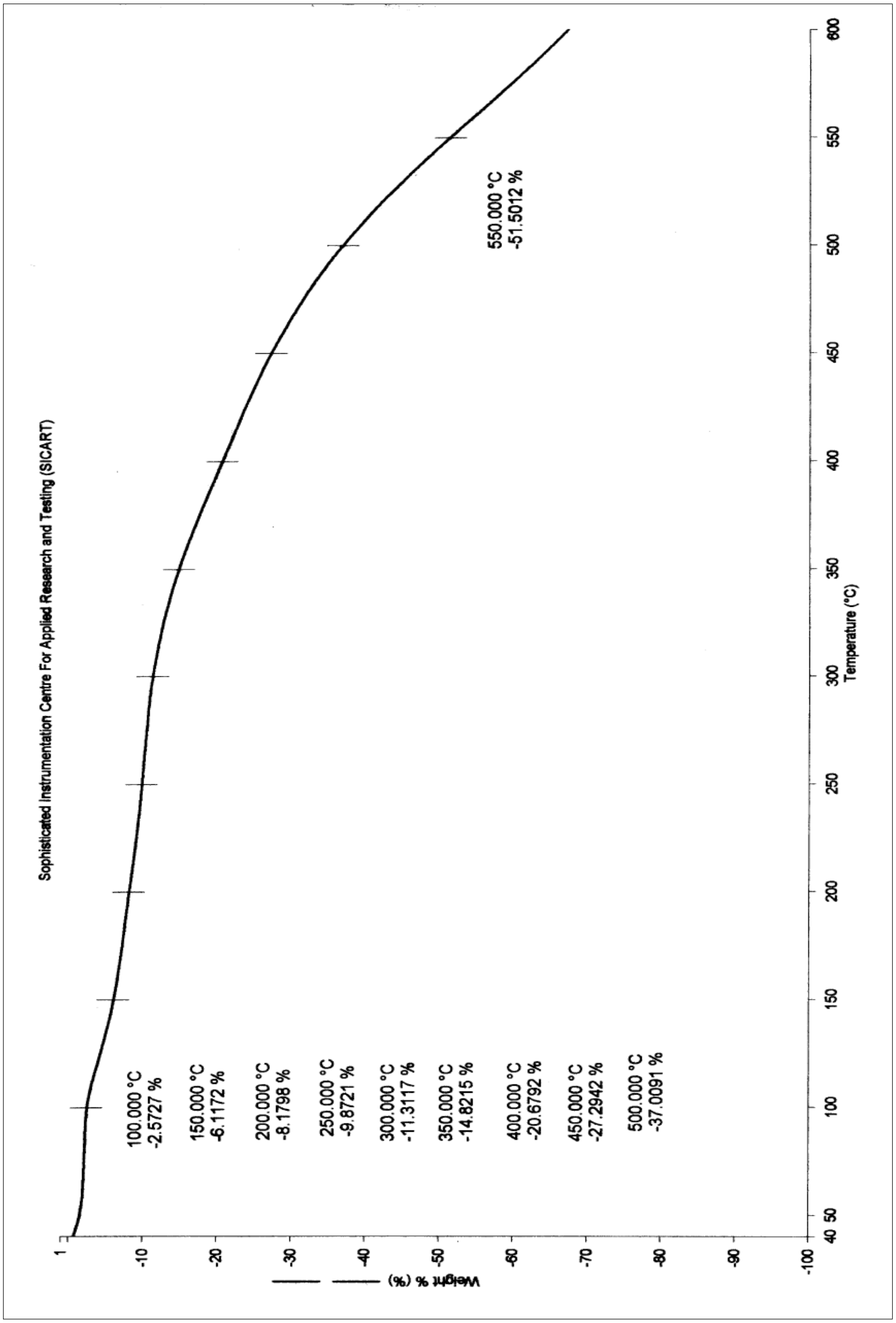


Fig. 2.16: TG thermogram of BANF at the heating rate of 10^0C/min in an N_2 atmosphere

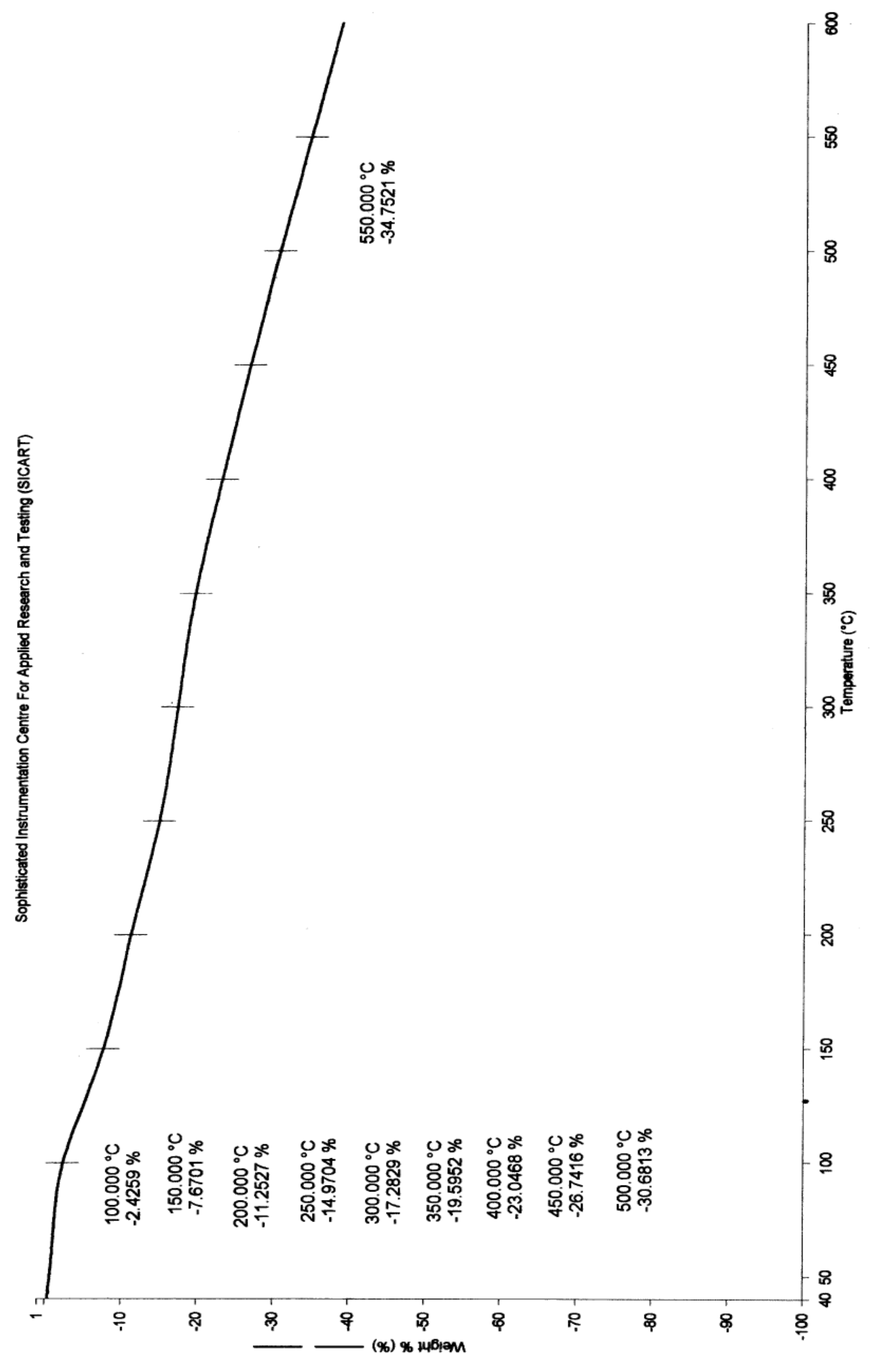


Fig. 2.17: TG thermogram of BANFA at the heating rate of 10^{0}C/min in an N_2 atmosphere

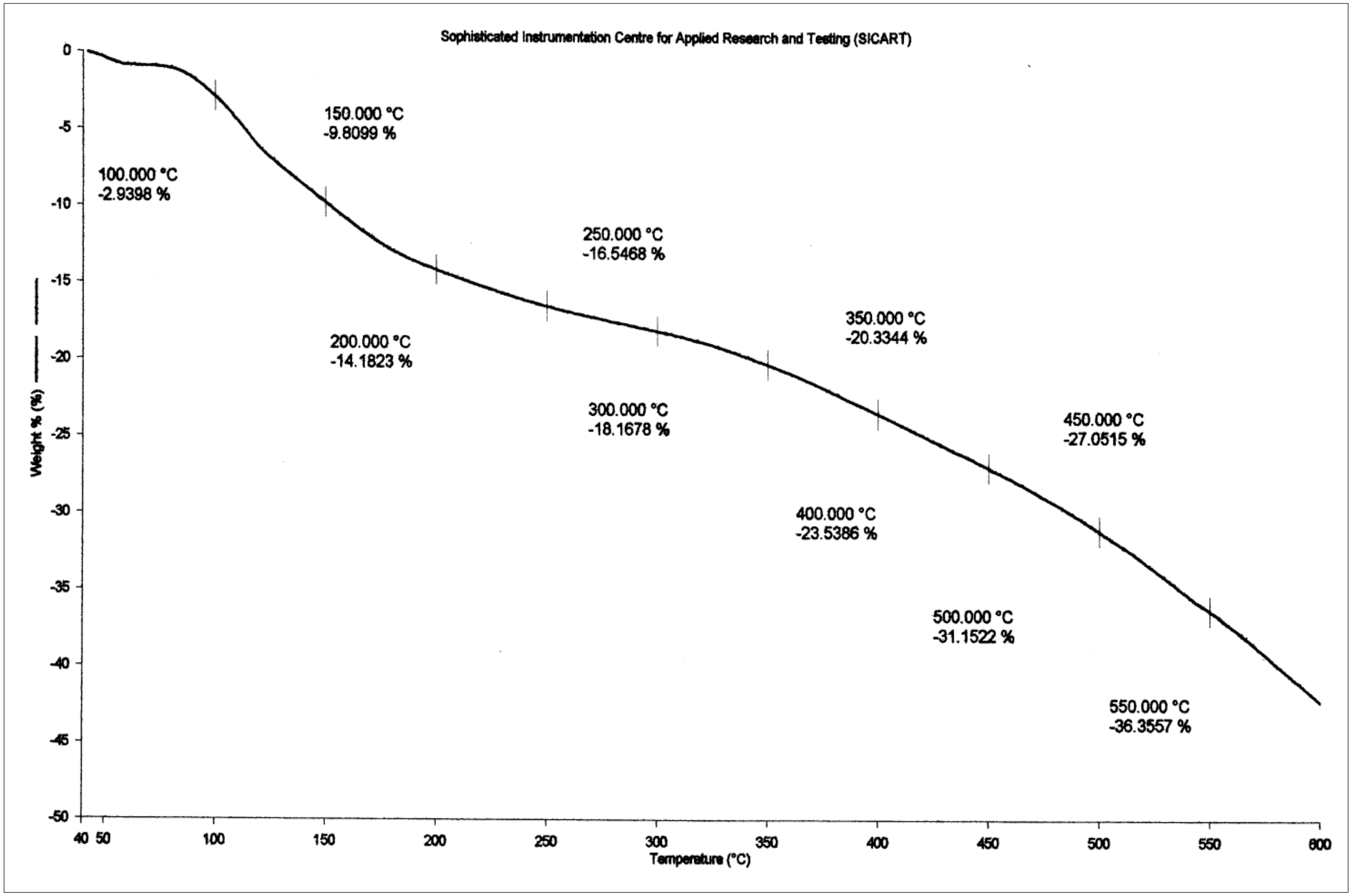


Fig. 2.18: TG thermogram of BANFM at the heating rate of 10^0C/min in an N_2 atmosphere

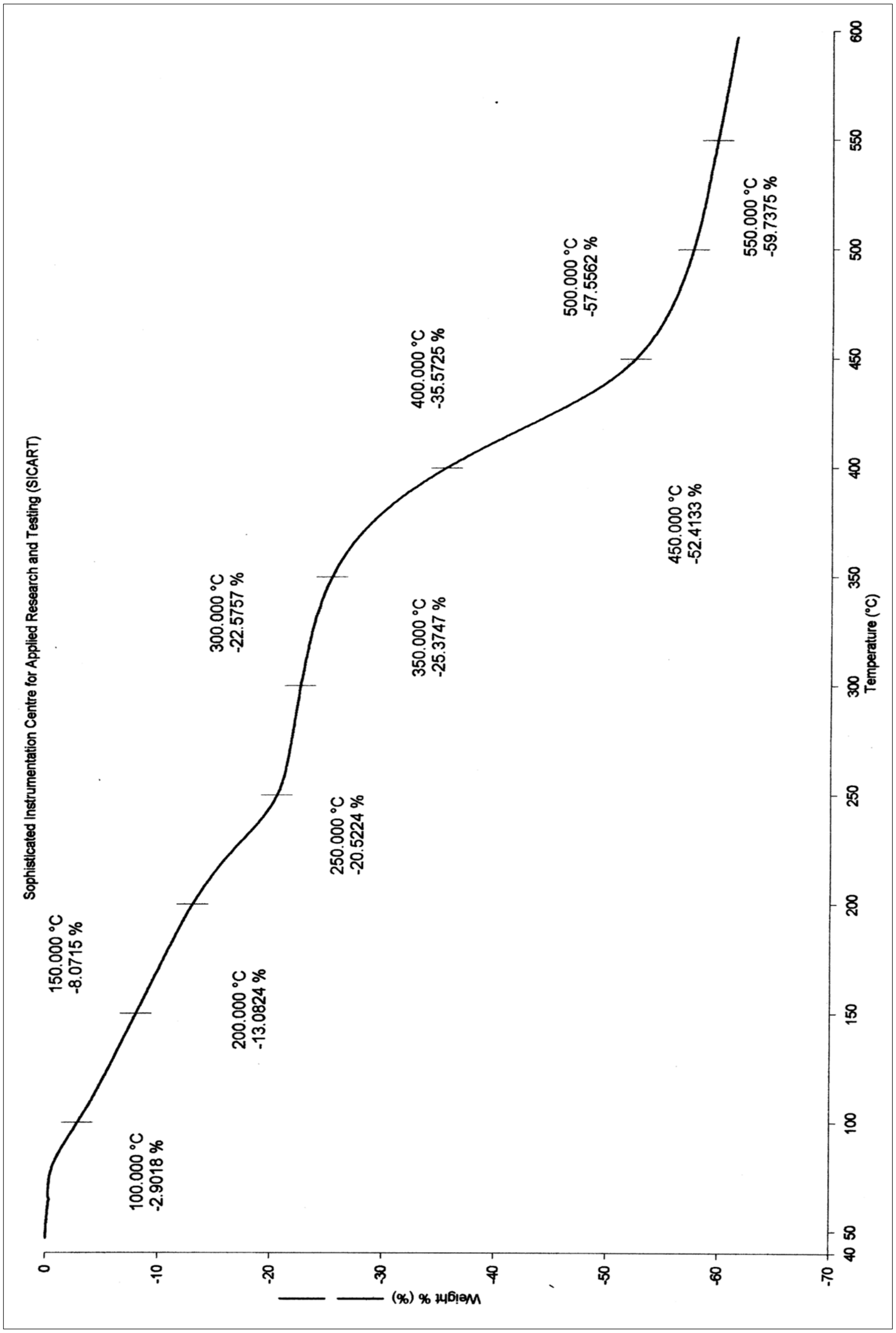


Fig. 2.19: TG thermogram of BBCF-1 at the heating rate of 10^0C/min in an N_2 atmosphere

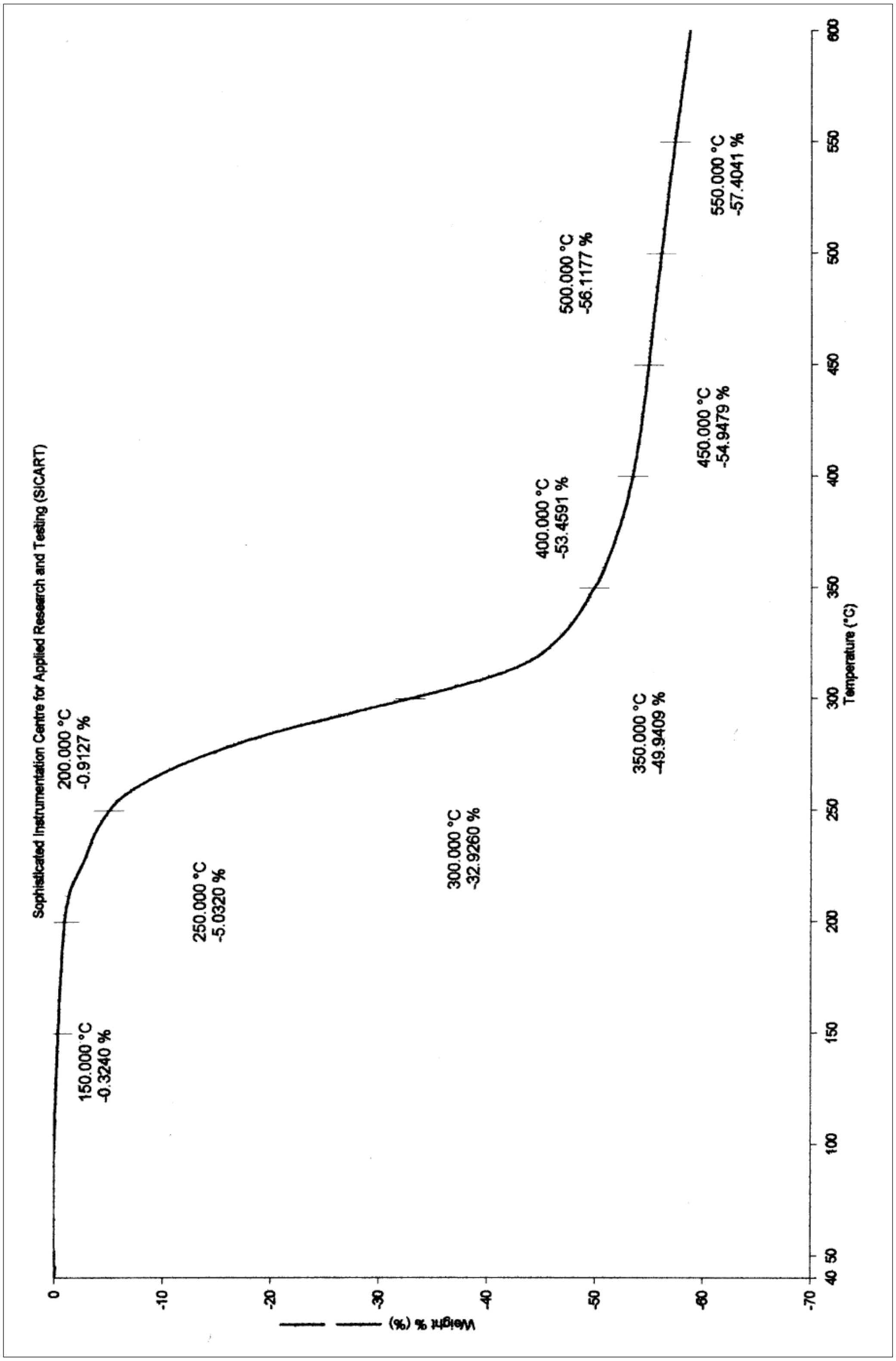


Fig. 2.20: TG thermogram of BBANF-1 at the heating rate of 10^0C/min in an N_2 atmosphere

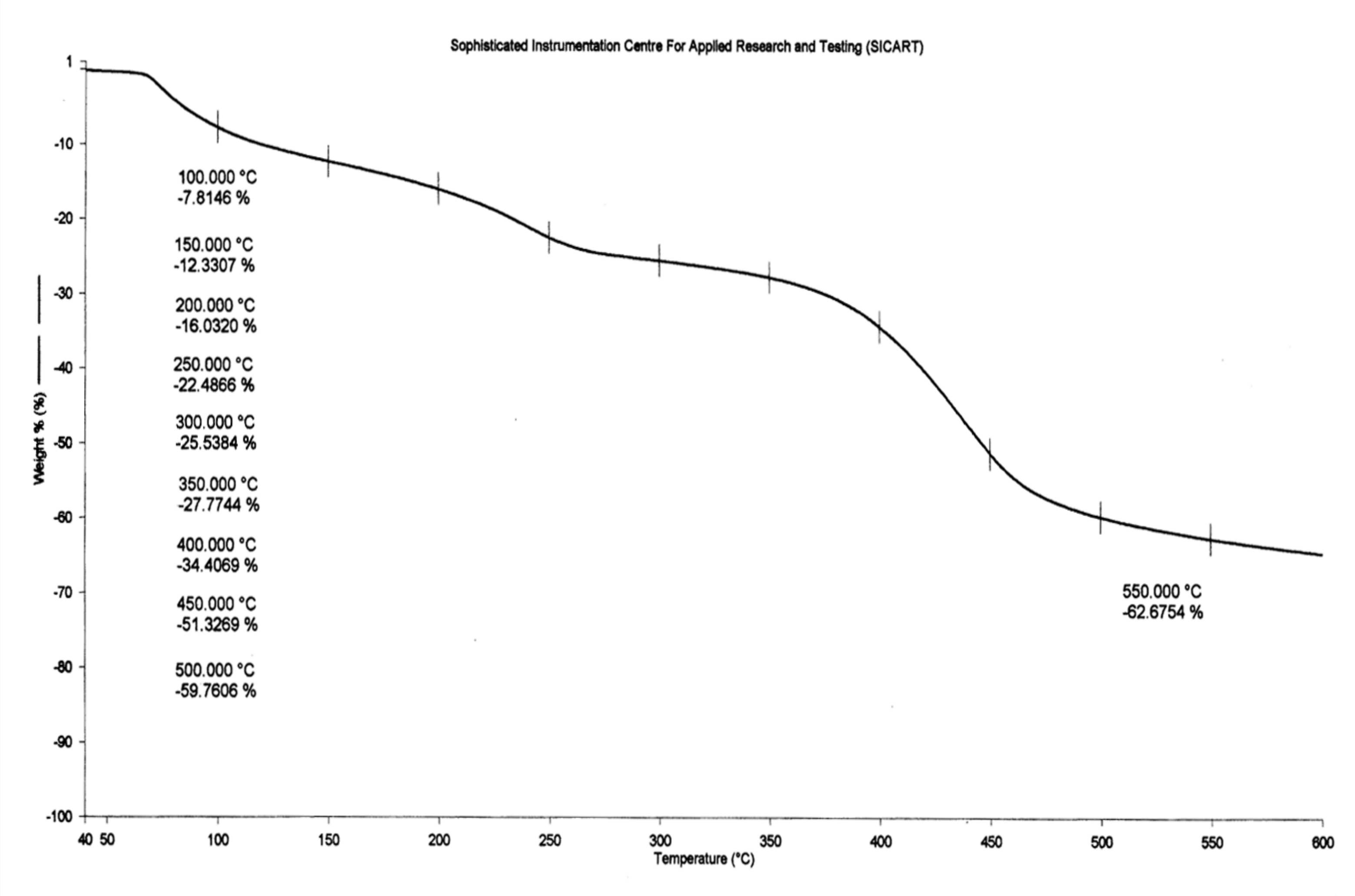


Fig. 2.21: TG thermogram of PBCF-1 at the heating rate of 10^0C/min in an N_2 atmosphere

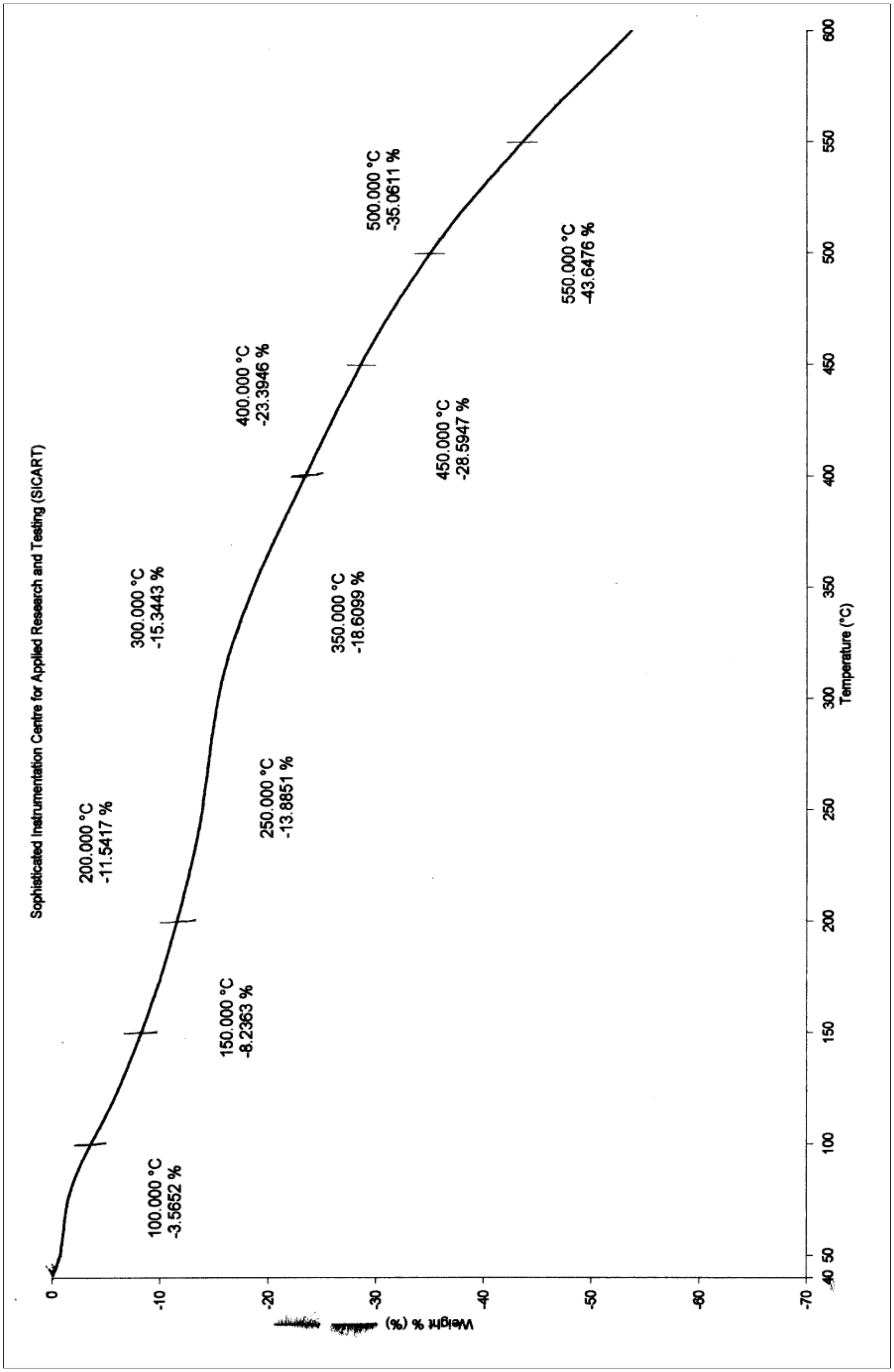


Fig. 2.22: TG thermogram of PBANF-1 at the heating rate of 10^0C/min in an N_2 atmosphere

Table-2.6: DSC and TGA data of resins

Resin	DSC Transition Temp., ^{0}C	T_0, ^{0}C	T_{10}, ^{0}C	T_f, ^{0}C	T_{max}, ^{0}C	Decompn. range, ^{0}C	%Wt. loss	% Resi-due
BANF	80.9 (Endo) 279.3 (Exo)	307.5	243.6	-	-	-	-	30.7
BANFA	109.3 (Exo) 276.3 (Exo)	-	160.8	-	-	-	-	59.2
BANFM	81.2 (Endo) 292.9 (Exo)	71.3 307.5	150.0	254.2 -	-	72-255 -	-	58.3
BBCF-1	90.9 (Endo) 237.1 (Exo)	71.7 319.5	167.5	267.0 543.4	417.4	72-267 320-543	42.5	37.2
BBANF-1	285.7 (Exo) 317.9 (Exo) 353.6 (Exo)	125.6	267.1	425.6	289.4	125.6-425.6	23.7	40.7
PBCF-1	75.2 (Endo) 241.4 (Exo) 312.6 (Exo)	62.8 169.2 339.4	112.8	121.3 287.8 534.1	426.15	62-122 169-288 339-535	43.9	32.1
PBANF-1	112.5 (Endo) 297.3 (Exo)	73.4 287.2	173.4	241.5 -	-	73-242 -	-	44.7

Kinetic parameters such as energy of activation (E_a), frequency factor (A), order of reaction (n) and entropy change (ΔS^*) are determined according to Anderson-Freeman method [28].

$$\Delta \ln dW/dt = n \, \Delta \ln W - (E_a/R) \, \Delta (1/T) \qquad .....2.19$$

$$A = E\beta / RT^{2} \; e^{E_a/RT} \qquad .....2.20$$

$$\Delta S^* = R \ln (Ah/kT) \qquad .....2.21$$

Where βthe rate of heating, R is is the gas constant, h is the Planck's constant, T is the temperature and k is the Boltzmann constant. Other symbols have their own usual meaning. Detail calculations are shown in Tables 2.7-2.9 and the plots of Δlndw/dt against ΔlnW are presented in Figs. 2.23-2.25 for BBCF-1, BBANF-1 and PCBF-1, respectively. Kinetic parameters of other resins were not determined because of small weight loss besides absence of T_f. This might be due to formation of highly thermally stable compounds as confirmed high amount of residues at elevated temperatures. The least square values of above mentioned parameters along with regression coefficients (R^2) are reported in Table 2.10 from which it is clear that BBCF-1, BBANF-1 and PBCF-1 resins followed fractional order degradation kinetics. The activation energy is found to be higher for BBCF-1 as compared to BBANF-1 and PBCF-1. Different magnitudes of kinetic parameters suggested different degradation mechanism. In accordance with theory higher is the value of E_a higher is the value of A. The ΔS^* values of BBCF-1, BBANF-1 and PBCF-1 are determined at their respective T_{max} according to equation 2.21 and is also reported in Table 2.10. Thus, the large and negative magnitude of ΔS^* confirmed highly ordered transition states.

Table: 2.7: The calculation scheme for BBCF-1 by Anderson-Freeman method

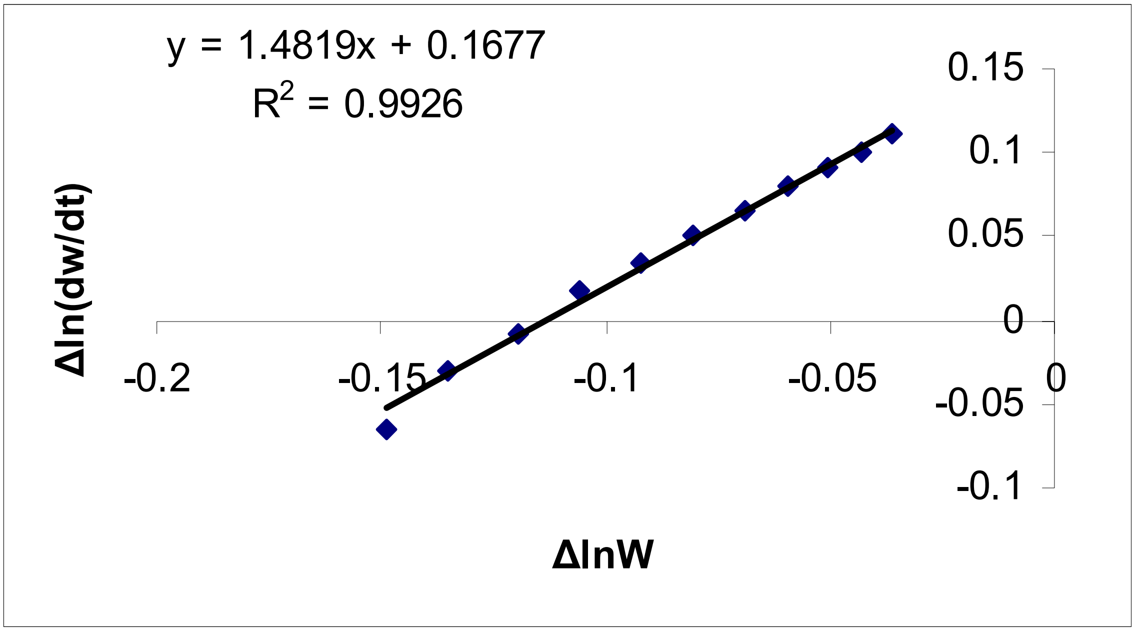
$10^3/T$	% Wt. loss	W	lnW	dw\dt	lndw/dt	ΔlnW	Δlndw/dt
1.41	47.97	11.08	2.405	3.47	1.244	-0.148	-0.064
1.42	46.19	12.86	2.554	3.70	1.308	-0.135	-0.029
1.43	44.33	14.72	2.689	3.81	1.337	-0.119	-0.007
1.44	42.46	16.59	2.808	3.84	1.345	-0.105	0.018
1.45	40.61	18.44	2.914	3.77	1.327	-0.092	0.035
1.46	38.83	20.22	3.006	3.64	1.291	-0.080	0.050
1.47	37.14	21.91	3.086	3.46	1.241	-0.069	0.065
1.48	35.57	23.48	3.156	3.24	1.175	-0.059	0.080
1.49	34.13	24.92	3.215	2.99	1.095	-0.050	0.090
1.50	32.83	26.22	3.266	2.73	1.004	-0.042	0.100
1.51	31.68	27.37	3.309	2.47	0.904	-0.036	0.111

Table: 2.8: The calculation scheme for BBANF-1 by Anderson-Freeman method

$10^3/T$	% Wt. loss	W	lnW	dw\dt	lndw/dt	ΔlnW	Δlndw/dt
1.71	42.22	12.54	2.528	5.2	1.648	-0.152	-0.109
1.72	40.15	14.61	2.681	5.8	1.757	-0.141	-0.098
1.73	37.93	16.83	2.823	6.4	1.856	-0.128	-0.075
1.74	35.62	19.14	2.951	6.9	1.931	-0.117	-0.056
1.75	33.23	21.53	3.069	7.3	1.987	-0.106	-0.040
1.76	30.80	23.96	3.176	7.6	2.028	-0.096	-0.025
1.77	28.37	26.39	3.272	7.8	2.054	-0.087	-0.012
1.78	25.97	28.79	3.360	7.9	2.066	-0.078	0
1.79	23.61	31.15	3.438	7.9	2.066	-0.070	0.025
1.80	21.32	33.44	3.509	7.7	2.041	-0.063	0.039
1.81	19.13	35.63	3.573	7.4	2.00	-0.056	0.055

Table: 2.9: The calculation scheme for PBCF-1 by Anderson-Freeman method

$10^3/T$	% Wt. loss	W	lnW	dw\dt	lndw/dt	ΔlnW	Δlndw/dt
1.37	56.81	5.89	1.773	2.70	0.993	-0.229	-0.125
1.38	55.29	7.41	2.002	3.06	1.118	-0.202	-0.096
1.39	53.63	9.07	2.204	3.37	1.214	-0.177	-0.068
1.40	51.87	10.83	2.382	3.61	1.283	-0.156	-0.048
1.41	50.03	12.67	2.539	3.79	1.332	-0.139	-0.023
1.42	48.14	14.56	2.678	3.88	1.355	-0.123	-0.002
1.43	46.23	16.47	2.801	3.89	1.358	-0.108	0.018
1.44	44.34	18.36	2.910	3.82	1.340	-0.095	0.040
1.45	42.50	20.20	3.005	3.67	1.300	-0.082	0.064
1.46	40.76	21.94	3.088	3.44	1.235	-0.070	0.084



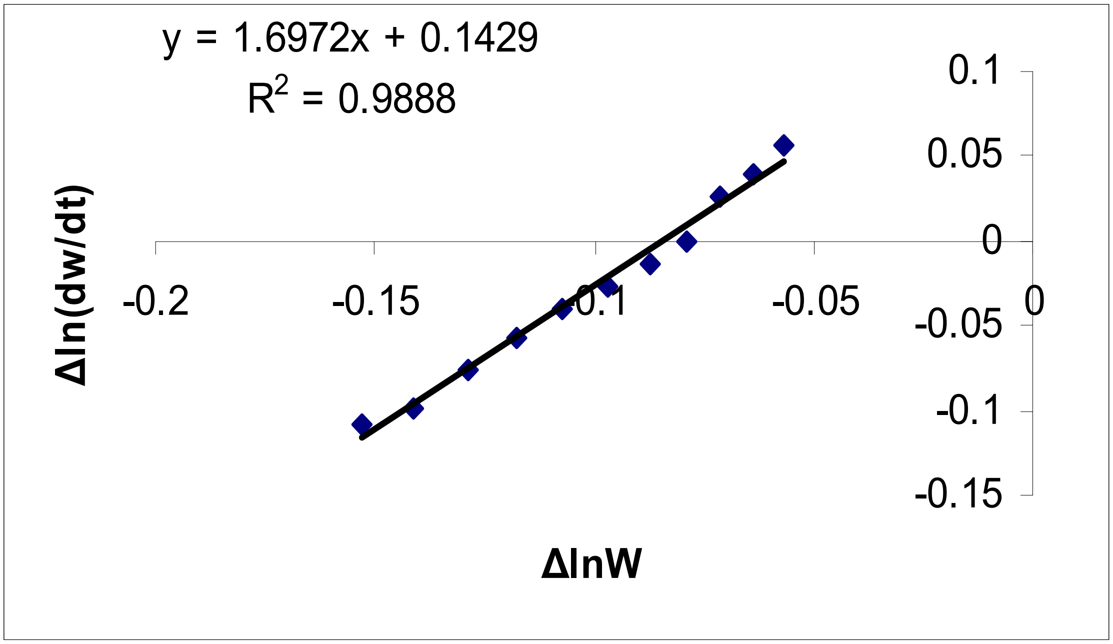


Fig. 2.24. The Anderson-Freeman plots for BBCF-1 and BBANF-1

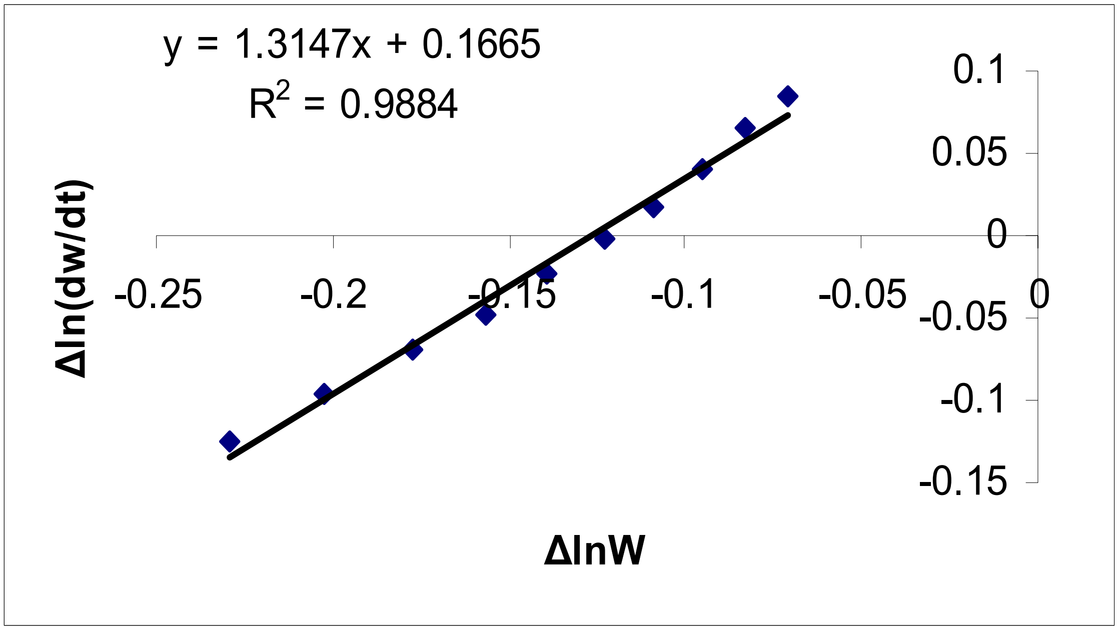


Fig. 2.25. The Anderson-Freeman plots for PBCF-1

Table 2.10: Kinetic parameters of BBCF-1, BBANF-1 and PBCF-1

Resin	n	E_a, kJ	A, S^{-1}	ΔS*, J deg^{-1}	Regression coefficient, R^2
BBCF-1	1.48	168	3.6×10^{10}	-49.8	0.993
BBANF-1	1.70	122	1.64×10^{9}	-73.8	0.989
PBCF-1	1.32	51	1.23×10^{2}	-231.1	0.988

CHAPTER-3

FABRICATION OF COMPOSITES BASED ON MIXRD MATRIX MATERIAL OF EPOXY AND PHENOLIC RESINS AND THEIR PHYSICO-CHEMICAL CHARACTERIZATION

This chapter of the thesis describes the up to date literature survey on the composites based on jute, sisal, carbon and glass fibers. The fabrication process, mechanical and electrical properties, water uptake study of mixed matrix material of epoxy and phenolic resins 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 COMPOSIT ES

SECTION-III: WATER UPTAKE STUDY OF COMPOSITES

GENERAL INTRODUCTION

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

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

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

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

Reinforcing fibers

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

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

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

- Low cost
- Light weight, Low density
- Easy availability
- Enhanced energy recovery and biodegradability
- High strength to weight ratio

- High specific strength
- Reduced tool wear and safer handling
- Reduced dermal and respiratory irritation
- Easy surface modification

SECTION-I: FABRICATION OF COMPOSITES

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

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

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

In literature many researchers have reported the fabrication of composites by hand lay-up technique since 1978 onwards [1-7].

---

1. Carignani and Giancarlo, “GRP expanded plastic composites”, Kunstat. Ger. Plast., **68**, 8-17, 1978.
2. P. K. Pal, “Jute reinforced plastics: A low cost composite material”, Plast. and Rubber Proc. and Appl., **4**, 215-222, 1984.
3. Mc Cormack and E. William, “Fabrication and joining of polymer-matrix composites: Flight-vehicle materials, structures, and dynamics–assessment and future directions”, J. Appl. Polym. Sci., **1**, 348-356, 1994.
4. M. A. Hayat and S. M. A. Suliman, “Mechanical and structural properties of glass reinforced phenolic laminates”, Polym. Test., **17**, 79-85, 1998.
5. J. Sinke, “Manufacturing of GLARE parts and structures”, App. Compos. Mater., **10**, 293-305, 2003.

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) and sisal fibers (Agave veracruz) used in present study were collected from the local market. Bisphenol-C-formaldehyde (BCF) [8] and bisphenol-C based epoxy (EBC) [9] resins were synthesized and purified according to previous publications.

Alkali treatment and acrylation of jute and sisal fibers

Fiber can be modified by various ways such as mercerization, bleaching or grafting with polymeric materials and surface coating with various interfacial agent

---

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. Seetharamu and Kishore, “Influence of moisture absorption on electrical characteristics of glass-epoxy polymer composite system”, Proceedings of the International Symposium on Electrical Insulating Materials, **3**, 605, 2005.
8. M. R. Sanariya, D. R. Godhani, S. Baluja and P. H. Parsania, “Synthesis and characterization of epoxy resins based on 1,1’-bis(4-hydroxyphenyl) cyclohexane and 1,1’-bis(3-methyl-4-hydroxy phenyl) cyclohexane”, J. Polym. Mater., **15**, 45-49, 1998.
9. 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.

[10,11,12]. Woven jute matrices (15cm x 15cm and 5cm x 5cm) and chopped sisal fibers (5-6mm) were soaked in a 5% NaOH solution at 30^0C 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 100^0C for 4h. Alkali treatment can remove natural and artificial impurities and produce a rough surface topography. This increases the effective surface area available for wetting by the matrix resin.

In order to improve surface modification of jute fibers especially to reduce water sorption, alkali treated jute fibers were reacted with aqueous 10 wt. % acrylic acid at reflux temperature to convert hydrophilic hydroxyl groups into hydrophobic vinyl ester groups [13, 14].

Fabrication of jute composites

Mixed matrix material (EBC and BCF 10-50 wt. %) used for the composite preparation were 50 wt. % of jute fabric of 15 cm x 15 cm (10 sheets) and 5 cm x 5 cm (10 sheets). BCF used was 10-50 wt. % of EBC. BCF possesses self curing property as well as a hardener for EBC. The purpose of using BCF as a hardener was to lower the curing temperature (>150^0C) of EBC. Required matrix material was

---

10. A. K. Bledzki, H. P. Fink and K. Speacht, “Unidirectional hemp and flax EP and PP-composites: Influence of defined fiber treatments”, J. Appl. Polym. Sci”, **93**, 2150-2156, 2004.
11. H. K. Mishra, B. N. Dash, S. S. Tripathy and B. N. Padhi, “A study on mechanical performance of jute-epoxy compostes”, Polym. Plast. Technol. Eng. **39**,187-198, 2000.
12. X. Li, L. G. Tabil and S. Panigrahi, “Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review”, J. Polym. Environ., **15**, 25–33, 2007.
13. P. Ganan, I. Mondragon, “Fique fiber-reinforced polyester composites: Effects of fiber surface treatments on mechanical behavior”, J. Mater. Sci., **39**, 3121-3128, 2004.
14. M. S. Sreekala, M. G. Kumaran, S. Thomas, “water sorption in oil palm fiber reinforced phenol formaldehyde composites”, Composite Part A: Appl. Sci. Manuf., **33**, 763-777, 2002.

dissolved in 100/10 ml acetone and the solution was applied to jute sheets with a smooth brush. The prepregs were dried in sunlight for 15 min, staked one over other and pressed between two preheated stainless steel plates under 7.6 MPa pressure at 150^0C for 2 h and at room temperature for 12 h. Silicone spray was used as a mold releasing agent. For water uptake study, the edges of 5 cm x 5 cm composites were sealed using same matrix materials. Hereafter composites are designated as JEBCF-10 to JEBCF-50 for untreated and TJEBCF-50 for treated jute fibers, respectively. Numerical numbers indicate BCF content in the mixed matrix material. Fibers and resin contents in the composites are reported in Table 3.1.

Fabrication process of alternate glass- jute hybrid composites

Mixed matrix material [EBC and BCF of 50 wt. % of glass -jute fibers for 15 cm x 15 cm/5 cm x 5 cm sheets] used for the composite preparation were 50 wt. % of glass-jute (treated and untreated) fabrics. Required matrix materials were dissolved in 100/10 ml acetone and the solution was applied to glass-jute sheets (15 cm x 15 cm / 5 cm x 5 cm) with a smooth brush. Nine such prepregs were dried in sunlight for 15 min, staked alternatively one over other and pressed between two preheated stainless steel plates under 7.6 MPa pressure at 150^0C for 2 h and at room temperature for 12 h. Silicone spray was used as a mold releasing agent. For water uptake study, the edges of 5cm x 5cm composites were sealed using same matrix materials. Hereafter composites are designated as UJG-50 and TJG-50 for untreated and treated jute-glass fibers, respectively. Numerical figures indicate 50 wt. % of each of EBC and BCF content in the mixed matrix material. Fibers and resin contents in the composites are reported in Table 3.2.

Fabrication of glass-sisal hybrid composites

Hybrid matrix material used for the composite preparation was 50 wt. % of glass-sisal fibers (25 wt. % EBC and 25 wt. % BCF). Thus, 8.35 g / 0.93 g (25 wt%) EBC and 8.35 g / 0.93 g (25 wt.%) BCF were dissolved in 100 ml/10 ml acetone and the resultant solution was applied to two 15 cm x 15 cm/ 5 cm x 5 cm glass fabric (8.4 g/ 0.9 g) with a smooth brush and remaining solution was mixed with (25 g/2.8 g) chopped sisal fibers. The glass fabrics were dried in sunlight for 15 min and sisal fibers were stuffed uniformly between two impregnated glass fabrics and pressed

Table- 3.1: Fiber and matrix material content in jute composites

Size, cm x cm	Types of composite	Wt. of Jute fibers, g	Wt. of EBC, g	Wt. of BCF, g
15x15 / 5x5	JEBCF-10	61.4/6.9	27.6/3.1	3.1/0.3
	JEBCF-20	61.2/6.7	24.5/2.7	6.1/0.7
	JEBCF-30	61.3/6.8	21.5/2.4	9.2/1.0
	JEBCF-40	61.4/6.7	18.4/2.0	12.3/1.3
	JEBCF-50	61.5/6.8	15.4/1.7	15.4/1.7
	TJEBCF-50	61.5/6.9	15.4/1.7	15.4/1.7

Table - 3.2: Fiber and matrix material contents in alternate glass-jute hybrid composites

Size, cm x cm	Types of composite	Wt. of fiber (Glass + jute), g	Wt. of EBC, g	Wt. of BCF, g
15 x 15	UJG-50	45.2 (20.8 + 24.4)	11.3	11.3
5 x 5	UJG-50	5.0 (2.3 + 2.7)	1.25	1.25
15 x 15	TJG-50	45.2 (20.8 + 24.4)	11.3	11.3
5 x 5	TJG-50	5.0 (2.3 + 2.7)	1.25	1.25

between two preheated stainless steel plates under 7.6 MPa pressure at 150^0C for 2 h and at room temperature for 12 h. Silicone spray was used as a mold releasing agent. Similarly 5 cm x 5 cm composites were fabricated for water uptake and boiling water study. Hereafter composites are designated as USG-50 and TSG-50 for untreated and treated sisal-glass fibers, respectively. Numerical figures indicate 50 wt. % of each of mixed matrix material. Fibers and resin contents in the composites are reported in Table 3.3.

Fabrication of jute/glass-carbon hybrid composites

Partially oxidized carbon fibers were collected from IPCL, Vadodara. Chopped Carbon fibers (5-6 mm) were used for preparation of hybrid composites. Varying proportions (10-50 wt. %) of hybrid matrices (EBC and BCF) [50 wt. % of jute/glass fabric and partially oxidized chopped carbon fibers (5-6mm)] were used for preparing sandwich composites. Required matrix material was dissolved in 100ml acetone and applied to two 15 cm x 15 cm jute/glass fabrics with a smooth brush and remaining solution was mixed with 25 g carbon fibers. The jute/glass fabrics were dried in sunlight for 15 min and carbon fibers were stuffed uniformly between two impregnated jute/glass fabrics and pressed between two preheated stainless steel plates under 7.6 MPa pressure at 150^0C for 2 h and at room temperature for 12 h. Silicone spray was used as a mold releasing agent. For water uptake study, the edges of 5 cm x 5 cm composites were sealed using same matrix materials. Hereafter composites are designated as JCEBCF-10 to JCEBCF-50, TJCEBCF-50 and GCEBCF-50 for jute, treated jute and glass-carbon fibers, respectively. Numerical figures indicates 50 wt. % of each of EBC and BCF content in the hybrid matrix material. Fibers and resin contents in the composites are reported in Table 3.4.

Table-3.3: Fiber and matrix material contents in glass-sisal hybrid composites

Size, cm x cm	Types of composite	Wt. of fiber (glass + sisal), g	Wt. of EBC, gm	Wt. of BCF, gm
15 x 15	USG-50	33.4 (8.4+ 25)	8.35	8.35
5 x 5	USG-50	3.7 (0.9+ 2.8)	0.93	0.93
15 x 15	TSG-50	33.4 (8.4+ 25)	8.35	8.35
5 x 5	TSG-50	3.7 (0.9+ 2.8)	0.93	0.93

Table - 3.4: Fiber and matrix material contents in jute-carbon hybrid composites

Types of composite	Size, cm x cm	Wt. of fiber (jute + carbon), g	Wt. of EBC, g	Wt. of BCF, g
JCEBCF-10	15 x 15	37.2 (12.2 + 25)	16.7	1.9
	5 x 5	4.1 (1.3 + 2.8)	1.8	0.2
JCEBCF-20	15 x 15	37.1 (12.1 + 25)	14.8	3.7
	5 x 5	4.1 (1.3 + 2.8)	1.6	0.4
JCEBCF-30	15 x 15	37.3(12.3 + 25)	13.1	5.6
	5 x 5	4.2 (1.4 + 2.8)	1.4	0.6
JCEBCF-40	15 x 15	37.2 (12.2 + 25)	11.1	7.4
	5 x 5	4.1 (1.3 + 2.8)	1.2	0.8
JCEBCF-50	15 x 15	37.3(12.3 + 25)	9.3	9.3
	5 x 5	4.1 (1.3 + 2.8)	1.0	1.0
TJCEBCF-50	15 x 15	37.4(12.4 + 25)	9.4	9.4
	5 x 5	4.3 (1.5 + 2.8)	1.1	1.1
GCEBCF-50	15 x 15	33.5(8.4 + 25)	8.4	8.4
	5 x 5	3.7 (0.9 + 2.8)	0.9	0.9

SECTION-II: MECHANICAL AND ELECTRICAL PROPERTIES OF COMPOSITES

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 materials 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 [15]. 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 types of stresses on it. Depending upon the mode of application, composite must be strong to suit the job. The geometrical response to loading leads to a wide range of mechanical properties grouped under stress-strain properties, visco-elasticity and failure properties.

Various mechanical properties of composites depend upon following factors:

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

---

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

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 Ω cm or Ω m)
- Surface resistivity (usually measured in Ω)

The electrical properties of polymeric 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.

Abdul Khalil et al. [16] have studied the mechanical and physical properties of oil palm empty fruit bunch/glass hybrid reinforced polyester composites. Hybrid laminate composites with different weight ratios (w/w) of chopped strand mat (CSM) glass fibers: oil palm empty fruit bunch fiber (EFB) 3:7, 5:5, 7:3, 9:1 were prepared. The enhancement of tensile, flexural and impact properties of the composites were observed with increasing loading of both EFB and glass fibers. The mechanical properties of EFB/glass hybrid polyester composite were found to be much higher than that EFB/polyester composite. Resistance to water absorption and thickness swelling properties of the composite were improved by the incorporation of glass

---

16. H. P. S. Abdul Khalil, S. Hanida, C. W. Kang and N. A. Nik Fuaad, “Agro-hybrid composite: The effects on mechanical and physical properties of oil palm fiber (EFB)/glass hybrid reinforced polyester composites”, J. Reinf. Plast. Compos., **26**, 203-218, 2007.

fiber while a reverse trend was observed as the EFB fiber content was increased in composites. In general the hybrid composites exhibited good properties compared to the EFB/polyester composites.

Priya and Rai et al. [17] have reported that the addition of a relatively small amount of glass fabric to the biofiber (silk fabric) reinforced epoxy matrix enhances the mechanical properties of the resulting hybrid composites. It has also been observed that the properties increased with the increasing weight fraction of reinforcement content to the maximum extent. The water uptakes of hybrid composites were observed to be less than that of unhybridized composites.

Samal et al. [18] have studied on dynamic mechanical behaviour of sisal-glass fiber reinforced PP composites (SGRP). Variation in mechanical strength and storage modulus with the addition of fibers and MAPP were investigated. Mechanical tests revealed an increase in the fiber loading from 10% to 30%. Further the SGRP composites prepared using 15 wt. % of glass and 15 wt. % sisal fibers, exhibited improved mechanical performance as compared with the virgin matrix as well as 30 % SFRP composites. The fiber matrix morphology of the interface region in the composites was examined employing SEM analysis of the tensile fracture specimens. Dynamic mechanical data showed an increase in the storage modulus of the treated composites.

Arib et al. [19] 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

---

17. S. Padma Priya and S. K. Rai, “Mechanical performance of biofiber/glass-reinforced epoxy hybrid composites”, J. Indus. Text., **35**, 217-226, 2006.
18. S. K. Samal, S. Mohanty and S. K. Nayak, “Fabrication and characterization of sisal/glass and polypropylene hybrid composites”, Advan. Mater. Res., **29-30**, 271-274, 2007.
19. R. M. N. Arib, S. M. Sapuan, M. M. H. M. Ahmad, M. T. Paridah and K. Zaman, “Mechanical properties of pineapple leaf fibre reinforced polypropylene composites”, Mater. and Designs, **27**, 391-396, 2006.

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%.

Khondker et al. [20] have studied the static and impact 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 micro structural 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.

Bosze et al. [21] 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 reported flexural strength (944 MPa), the flexural modulus (47.4 GPa) and the shear strength (55.3 MPa).

Shao-Yun Fu et al. [22] have prepared hybrid composites of polypropylene

---

20. 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.
21. 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.
22. Shao-Yun Fu, B. Lauke, E. Mader, Chee-Yun Yue, X. Hu, Yiu-Wing Mai, “Hybrid effects on tensile properties of hybrid short glass fiber and short carbon fiber reinforced polypropylene composites”, J. Mater. Sci., **36**, 1243-1251, 2001.

reinforced with short glass fibers and short carbon fibers using extrusion compounding and injection molding techniques. It was noted that the tensile strength and modulus of the hybrid composites increased while the failure strain of the hybrid composites decreased with increasing the relative carbon fiber volume fraction in the mixture. The hybrid effects for the tensile strength and modulus were studied by the rule of hybrid mixtures (RoHM) using the tensile strength and modulus of single-fiber composites, respectively. The strength shows a positive deviation from that predicted by the RoHM and hence exhibits a positive hybrid effect. However, the values of the tensile modulus are close to those predicted by the RoHM and thus the modulus shows no existence of a hybrid effect.

Wu et al. [23] have reported electrical and mechanical characterization of hybrid CFRP sheets. Six types of specimens have 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.

Hou et al. [24] 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 void 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, and 10% higher tensile and 18% higher compression strengths were obtained in composite laminates fabricated by the DVB process.

---

23. 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.
24. 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 [25].

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

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

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

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

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

The working voltage applied to an electrical insulating material must be much lower than the voltage, which causes the material rupture. Electrical discharge through a material at a minimum voltage called break down or disruptive voltage Vbr [26]. In some cases voltage lower than the break down voltage give rise to a surface discharge that not penetrate deep into the bulk of a material. The basic characteristic of an electrical insulating material is its breakdown or dielectric strength Ebr (also called electric strength), which is a minimum strength of the uniform electric field that causes dielectric breakdown. The breakdown voltage (Ubr) is proportional to the electric field strength (Ebr) 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 [27].

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.

---

25. Composites in Civil Engineering, Science Tech Entrepreneur, March-2001.
26. H. D. Rozman, Y. S. Yeo, G. S. Tay and A. Abu baker, "The mechanical and physical properties of polyurethane composites based on rice husk and polyethylene glycol", Polym. Test., **22**, 617- 628, 2003.
27. O. M. Kazarnovasky, B. M. Tareev, I. O. Forsilova and L. I. Lybimov "Testing of electrical insulating materials", Mir Publishers, Moscow, 1982.

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

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

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.

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.

The tensile strength (ASTM-D-638-91) and flexural strength (ASTM-D-790-92), measurements were carried out on a Universal Tensile Testing Machine, Model No. 1185 at a speed of 50mm/min. Electric strength (IEC:243-Pt.1-1988) and volume resistivity (ASTM-D-257-1992) a high voltage tester (Automatic Electric-Mumbai) in air at 27^0C by using 25/75mm brass electrodes and a Hewlett Packard high resistance meter at 500V DC after charging for 60 sec, respectively. Each test was carried out in triplicate and the average values were considered. Mechanical (tensile and flexural strengths) and electrical (electric strength and volume resistivity) properties of the composites are presented in Table- 3.9.

Table - 3.6: Technologies to produce advanced composite structures [28]

Elastomers matrix	Wet impregn-ation	Long fiber	Short fiber	Prepreg	Casting
Polyurethane	Yes	Possible	Yes	No	Yes
Rubber matrix	Yes	Possible	Yes	No	Yes
Foam matrix					
Polyurethane	Yes	Yes	Yes	Yes	Yes
Phenolic	Yes	Yes	Yes	Yes	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

---

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

Table - 3.7: Technologies to produce advanced composite structures with thermoset matrix [28]

Techniques	Wet impregnation	Long fiber	Short fiber (1- 50) mm	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 [28]

Thermoplastic matrix & fiber	**Wet Impregnation**	**Long fiber**	**Short fiber**	**Prepreg with thermoplastic resin**	**Sheet Transformation**
Thermoplastic injection	Yes	No	No	Yes	-
Filament winding	-	No	Yes	-	-
Pultrusion	-	No	Yes	-	-
Compression molding	Yes	No	Yes	Yes	Sheet
Vacuum forming	-	No	Yes	Yes	Sheet only
Braiding	-	No	No	Yes	-
Continuous press lamination	-	No	Yes	Yes	Yes
Extrusion	Yes	No	Yes	Yes	Sheet

Table - 3.9: Mechanical and electrical properties of the composites

Composite	Tensile strength, MPa	Flexural strength, MPa	Electric strength, kV/mm	Volume resistivity, ohm cm
JEBCF-10	28.6	37.4	1.1	>4.1 x 10^{16}
JEBCF -20	30.8	37.6	0.32	>5.2 x 10^{16}
JEBCF -30	37.6	37.8	0.30	>5.41 x 10^{16}
JEBCF -40	42.5	37.9	0.26	>5.13 x 10^{16}
JEBCF -50	44.3	56.2	0.18	>4.13 x 10^{16}
TJEBCF-50	63	65	0.72	5.1 x 10^{16}
UJG-50	87	66	2.71	1.23 x 10^{12}
TJG-50	112	89	3.89	1.77 x 10^{12}
USG-50	26.4	46.7	1.41	1.27 x 10^{12}
TSG-50	35.3	64.1	1.93	1.81 x 10^{12}
JCEBCF-10	5.13	5.06	1.82	3.16 x 10^{12}
JCEBCF-20	6.19	11.54	1.80	3.02 x 10^{12}
JCEBCF-30	7.33	16.37	1.67	8.95 x 10^{11}
JCEBCF-40	9.06	16.48	1.64	5.24 x 10^{12}
JCEBCF-50	10.0	17.0	1.60	5.90 x 10^{12}
TJCEBCF-50	14.65	19.33	2.09	6.79 x 10^{12}
GCEBCF-50	21.4	24.53	1.62	5.71 x 10^{12}

Mechanical properties of natural fiber based composites depend upon several factors such as fiber strength, fiber content, fiber orientation, fiber length, interfacial bond strength, fillers, compatibilizers and impact modifiers, degree of cross-linking, mode of testing, test conditions, etc. [29, 30]. The tensile strength (σ) of the composites was calculated by measuring the load value (W) at the point of breaking and cross sectional area (A).

$$\sigma = \frac{W}{A} \quad \text{…3.2}$$

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

$$\text{Flexural strength} = \frac{1.5FL}{wt^2} \quad \text{…3.3}$$

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.

Comparative mechanical and electrical properties of JEBCF-10 to JEBCF-50 and composites

Tensile strength, flexural strength, electrical strength and volume resistivity of JEBCF-10 to JEBCF-50 are reported in Table-3.9 from which it is clear that tensile strength has increased with BCF content in the composites, while a little change is observed in flexural strength except JEBCF-50. Increase in tensile strength indicates increase in interfacial bond strength through cross-linking and H-bonding. Good interfacial bond strength is necessary for effective stress transfer from matrix to fiber in the composites. There are two types of interfacial interactions namely covalent and H-bonding. Hydroxyl groups of jute serve as reaction sites with various

---

29. 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.
30. 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.

functional groups present in the mixed matrix material (hydroxyl, epoxide and methylol groups). Jute fibers serve as filler as well as a reactive component. BCF possesses self curing property and it can also react with epoxy and hydroxyl groups of jute fibers to form covalent and H-bonds and hence improvement in interfacial bond strength.

Electric strength and volume resistivity of JEBCF-10 to JEBCF-50 are reported in Table-3.9 from which it is clear that electric strength has decreased with increasing amount of BCF content in the composite, while volume resistivity has increased with BCF content upto 30 wt. % and then it is decreased. Decrease in electric strength with increasing BCF content in composites is probably due to brittle nature of the cross-linked matrix material, which may not sustain electrical force. Due to formation of covalent and H-bonds between mixed matrix material and between jute fibers and matrix, volume resistivity is improved considerably. Decrease in volume resistivity of the composite above 30 wt. % indicates polar nature of the composites due to more number of free phenolic and jute OH groups.

Comparative mechanical and electrical properties of JEBCF-50 and TJEBCF-50 composites

From Table-3.9 it is clear that tensile strength has increased from 44.3 MPa to 63 MPa (42.2%) and flexural strength has increased from 56.2 MPa to 64 MPa (13.9%) on alkali treatment and acrylation. Similarly electric strength has increased from 0.18 to 0.72 kV/mm (400%) and volume resistivity has increased from 4.13 x 10^{16} to 5.1 x 10^{16} Ωcm (123.5 %.). The increase in tensile strength, flexural strength, electric strength and volume resistivity after alkali treatment and acrylation are due to change in chemical composition, crystallinity, strength and surface modification of the fibers [31]. 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 [32].

---

31. P. Ganan and I. Mondragon, “Effect of fiber treatments on mechanical behavior of short fique fiber reinforced polyacetal composites”, J. Compos. Mater. **39**, 633-646, 2005
32. 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 and electrical properties of UJG-50 and TJG-50 composites

From Table-3.9 it is clear that tensile strength has increased from 87 MPa to 112 MPa (28.73%) and flexural strength has increased from 66 MPa to 89 MPa (34.84%) on alkali treatment and acrylation. Similarly electric strength has increased from 2.71 to 3.89 kV/ mm (43.54 %) and volume resistivity has increased from 1.23 x 10^{12} to 1.77 x 10^{12} Ωcm (143.90%). The increase in tensile strength, flexural strength, electric strength and volume resistivity after alkali treatment and acrylation are due to change in chemical composition, crystallinity, strength and surface modification of the fibers [31]. Addition of glass fiber to a jute-based composite usually shows a more positive hybrid effect by the significant improvement in mechanical and electrical properties than that of the unhybridized.

Comparative mechanical and electrical properties of USG-50 and TSG-50 composites

From Table-3.9 it is clear that tensile strength has increased from 26.4 to 35.3 MPa (33.7%) and flexural strength has increased from 46.7 to 64.1 MPa (37.3%) on alkali treatment and acrylation. Similarly electric strength has increased from 1.41 to 1.93 kV/ mm (36.9 %) and volume resistivity has increased from 1.27 x 10^{12} to 1.81 x 10^{12} Ωcm (42.5%). The increase in tensile strength, flexural strength, electric strength and volume resistivity after alkali treatment and acrylation are due to change in chemical composition, crystallinity, strength and surface modification of the fibers [31]. Addition of glass fiber to a sisal-based composite usually shows a more positive hybrid effect by the significant improvement in mechanical and electrical properties than that of the unhybridized. Mechanical properties of composites depend on the fiber content, fiber orientation, additives like fillers, compatibilizer and impact modifier and mode of testing [33]. Thus, fiber modification led to substantial improvement in tensile strength, flexural strength, electric strength and volume resistivity.

---

33. M. S. Sreekala, M. G. Kumaran, S. Joseph, M. Jacob, S. Thomas, “Oil palm fibre reinforced phenol formaldehyde composite: Influence of fibre surface modifications on the mechanical performance”, Appl. Compos. Mater. **7**, 295-329, 2000.

Comparative mechanical and electrical properties of JCEBCF-10 to JCEBCF-50 composites

In Table-3.9 JCEBCF-10 to JCEBCF-50 possess 5.13-10.0 MPa tensile strength, 5.06-17.0 MPa flexural strength, 1.82 to 1.60 kV/mm electric strength and 3.16 to 5.90 x 10^{12} ohm cm, resistivity. Tensile and flexural strengths of the composites have increased with increase in BCF content in the hybrid matrix material indicating increasing good interfacial bonding and toughness of the hybrid materials. These may also be due to increase of cross-link density. There are two possible interfacial interactions namely covalent and H-bonding. Hydroxyl groups of jute serve as reaction sites with hydroxyl, epoxide and methylol groups of hybrid matrix material. BCF can also undergo self curing and react with hydroxyl and epoxide group to form network structure. Decrease in electric strength with increasing BCF content in the composites indicated increase in degree of cross-linking density and brittleness which may not sustain electrical force. Decrease in volume resistivity with BCF content (upto 30 %) indicated formation of more number of polar groups as a result of reactions among polar groups of reinforcing fibers and matrices. Increase in volume resistivity above 30 % BCF content in the composites indicated increase in cross-linking due to self curing of BCF besides curing between EBC and BCF resins and hence formation of non-polar groups, which resulted in decrease in volume resistivity.

Comparative mechanical and electrical properties of JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites

From Tabel-3.9 it is clear that tensile strength, flexural strength, electric strength and volume resistivity have been increased by 46.50, 13.71, 24.40 and 15.15 %, respectively on alkali treatment and acrylation. The increase in tensile strength, flexural strength, electric strength and volume resistivity after alkali treatment and acrylation are due to change in chemical composition, crystallinity, strength and surface modification of the fibers. In comparison to JCEBCF-50 and TJCEBCF-50 mechanical properties of GCEBCF-50 are somewhat higher due to high mechanical properties of glass fibers.

SECTION-III: WATER UPTAKE STUDY OF COMPOSITES

Water uptake study in different environments

It is sometimes stated that a given material has a good environmental resistance or alternatively the material may be stated to be poor or excellent in this respect. The resistant to different environments (acid, alkali, salt and water) is determined by change in weight method. 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.

Different environmental 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 [34,35].

The water uptake 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 [36].

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 chain. 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.

---

34. R. B. Seymour, “Treatise on Analytical Chemistry”, 3, 341-391, Interscience Publication, New York.
35. O. M. Dazornovasky, B. M. Tareev, I. O. Forsilova and L. I. Lybimov, “Testing and Electrical Insulating Materials”, Mir Publishers, Moscow, 1982.
36. J. A. Brydson, “Plastics Materials”- 6th Ed. Butterworth-Heinemann Ltd. 1995.

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].

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 [37].

Water uptake study of JEBCF-10 to JEBCF-50 composites

The water uptake 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 was reached.

The % water uptake with the passage of square root of soaking time curves at room temperature for JEBCF-10 to JEBCF-50 in water, 10 % aq. HCl and 10 % aq. NaCl environments are shown in Figs. 3.1-3.5 from which it is observed that water uptake increased with passage of time and remained constant after ~ 168 h (equilibrium time). Equilibrium water content for all the five composites in different environments are reported in Table 3.10 from which it is observed that equilibrium water content has decreased (24.35-14.33 % for H_2O, 18.13-12.34 % for 10 % aq. NaCl and 26.26-17.27 % for 10 % aq. HCl) with increasing BCF content in the composite. Observed water uptake tendency of the composites in different environments is HCl > H_2O > NaCl. Decrease in water uptake tendency of the composite with increasing amount of BCF in mixed material is due to self curing of BCF and reactions of OH groups of jute with EBC and BCF resulting in hydrophobic groups (methylene and ether linkages) indicating increase in cross-linking density i.e. hydrophobicity.

---

37. 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.

For unidimensional water uptake in semi-infinite plate exposed on both sides to same environment, the amount of water uptake (M) at any time t is given by,

$$\%M = \frac{W_m - W_d}{W_d} \times 100 \quad \ldots \mathbf{3.4}$$

Where M is the moisture content, W_m is the weight of the moist sample and W_d is the weight of the dry sample.

Assuming unidimensional Fickian diffusion in composite, an attempt has been made to determine diffusivity (D_X) in different environments. Diffusivity is further assumed to depend only on temperature but independent of moisture content and stress levels in composites.

The relation between % water uptake and diffusivity is given by,

$$M = \frac{4M_m}{h}\left(\frac{t}{\pi}D_X\right)^{1/2} \quad \ldots \mathbf{3.5}$$

Where M_m is the equilibrium water content, h is the sample thickness and t is soaking time.

Diffusivity in a given environment can be determined from the initial slope of the plot of % M against $t^{1/2}$ (Figs. 3.1-3.5). Diffusivity in JEBCF-10 to JEBCF-50 in water, 10 % aq. HCl and 10 % aq. NaCl solutions is reported in Table 3.10 from which it is clear that D_x has increased (1.51-5.60 x 10^{-12} for H_2O, 2.08-5.73 x 10^{-12} for 10 % aq. NaCl and 1.27-3.87 x 10^{-12} for 10 % aq. HCl m^2/s) with increasing BCF content in the composite. Increase in D_x with BCF content in all the three environments studied is due to void formation during self curing of BCF with release of formaldehyde and water. Cracking and blistering of fibers influence diffusivity [38, 39]. Microcracks are due to brittle nature of the cross-linking products of EBC and BCF. Observed diffusivity order is NaCl > H_2O > HCl.

Boiling water study

Water uptake in the composites mainly depends on the temperature and independent of water content. Effect of temperature on water uptake in JEBCF-10 to JEBCF-50 was carried out at boiling temperature of water (Fig. 3.6). From Fig. 3.6 it is evident that equilibrium is reached after 6 h in all the composite systems. Equilibrium water content is reported in Table 3.10 from which it is clear that equilibrium water content at boiling temperature has decreased with increasing BCF content in the composite.

---

38. S. Lin-Gibson, V. Baranauskas, J. S. Riffle and U. Sorathia, "Cresol novolac–epoxy networks: Properties and processability", Polymer, **43**, 7389-7398, 2002.
39. L. R. Bao. A. F. Yee, "Effect of temperature on moisture absorption in a bismaleimide resin and its carbon fiber composites", Polymer, **43**, 3987- 3997, 2002.

Table-3.10: Water uptake and diffusivity data of JEBCF-10 to JEBCF-50 composites at room temperature

Composite	%, Equilibrium water content at room temperature			Diffusivity(D_x), 10^{-12}, m^2/s			% Eqm. water content in boiling water
	H_20	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl	
JEBCF-10	24.35	18.13	26.26	1.51	2.08	1.27	24.57
JEBCF-20	20.90	15.95	23.14	2.29	3.64	2.07	20.71
JEBCF-30	16.35	14.66	20.94	3.72	4.08	2.13	16.40
JEBCF-40	16.91	13.84	18.94	4.91	4.44	2.18	17.18
JEBCF-50	14.33	12.34	17.27	5.60	5.73	3.87	14.51

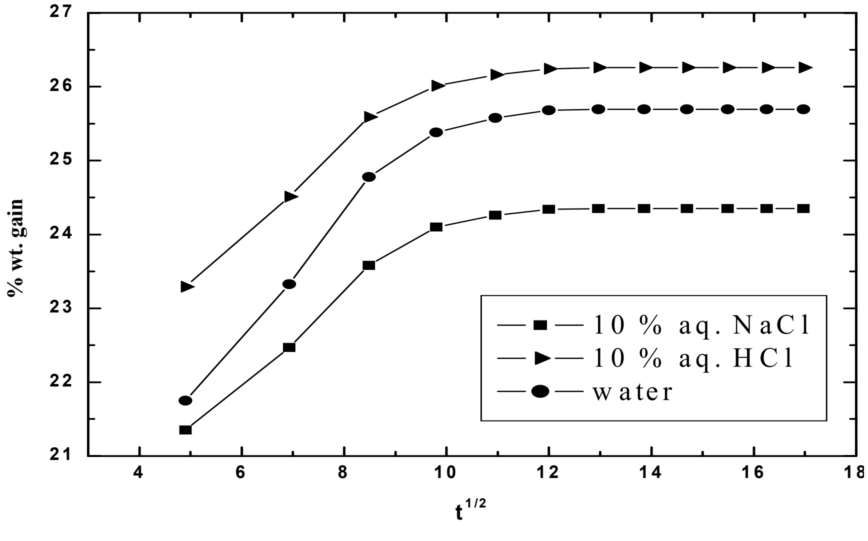


Fig. 3.1: The plots of % weight gain against $t^{1/2}$ for JEBCF-10 at room temperature.

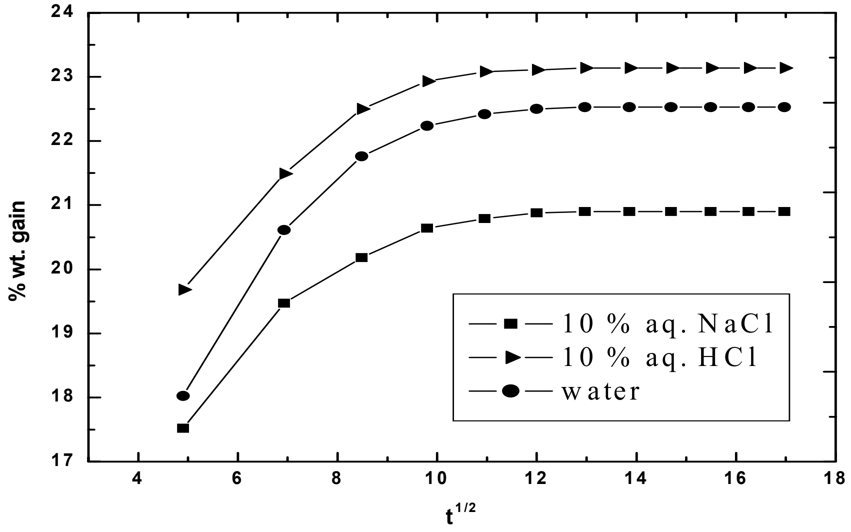


Fig. 3.2: The plots of % weight gain against $t^{1/2}$ for JEBCF-20 at room temperature.

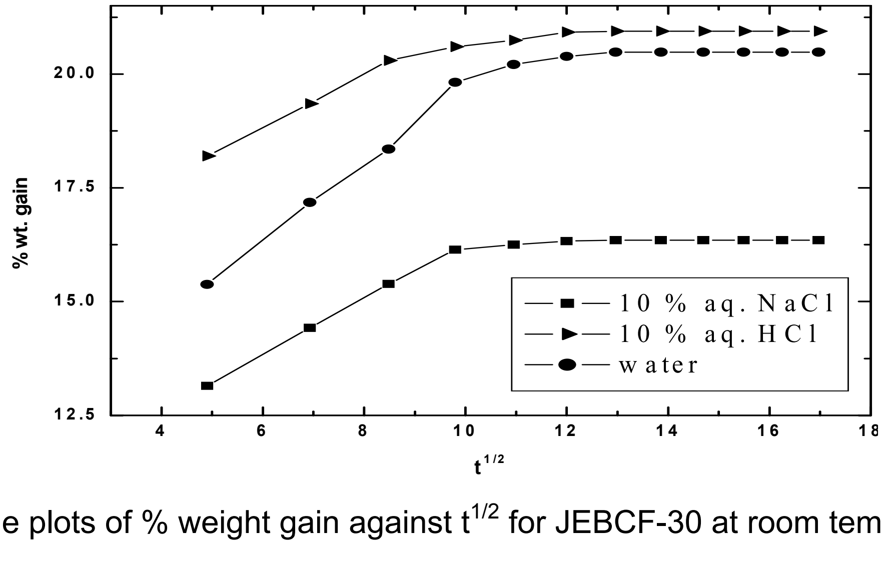


Fig. 3.3: The plots of % weight gain against $t^{1/2}$ for JEBCF-30 at room temperature.

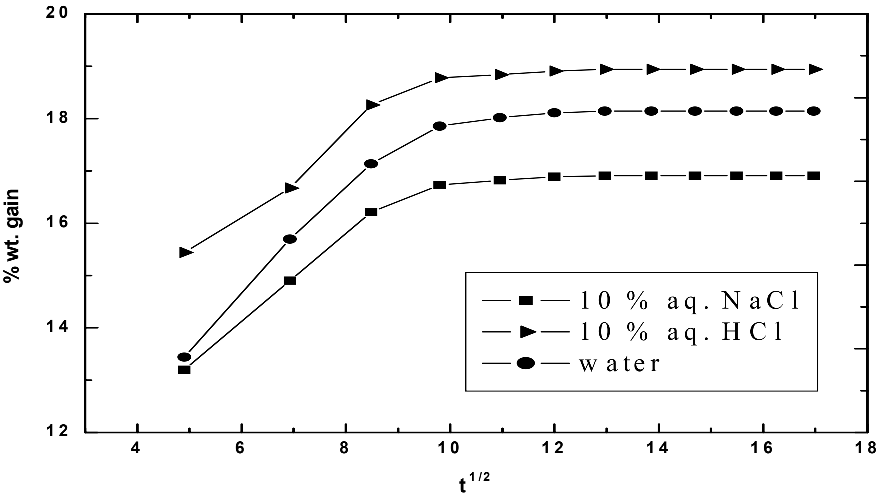


Fig. 3.4: The plots of % weight gain against $t^{1/2}$ for JEBCF-40 at room temperature.

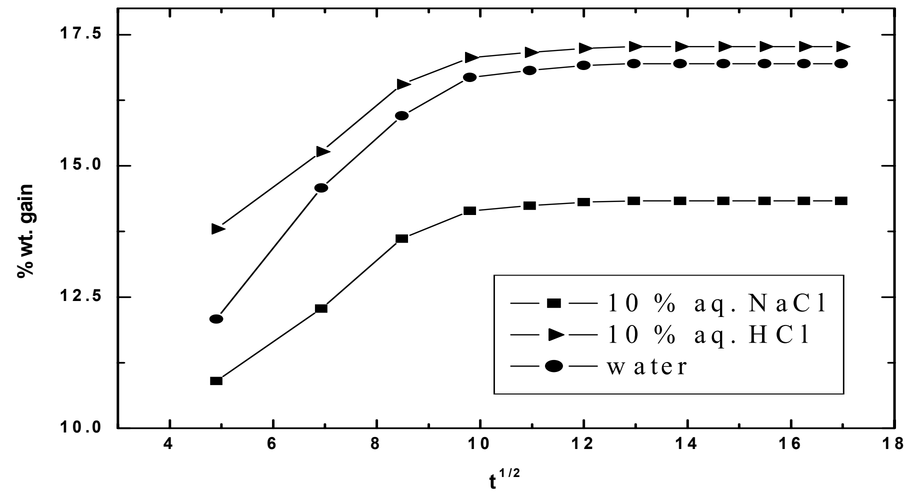


Fig. 3.5: The plots of % weight gain against $t^{1/2}$ for JEBCF-50 at room temperature.

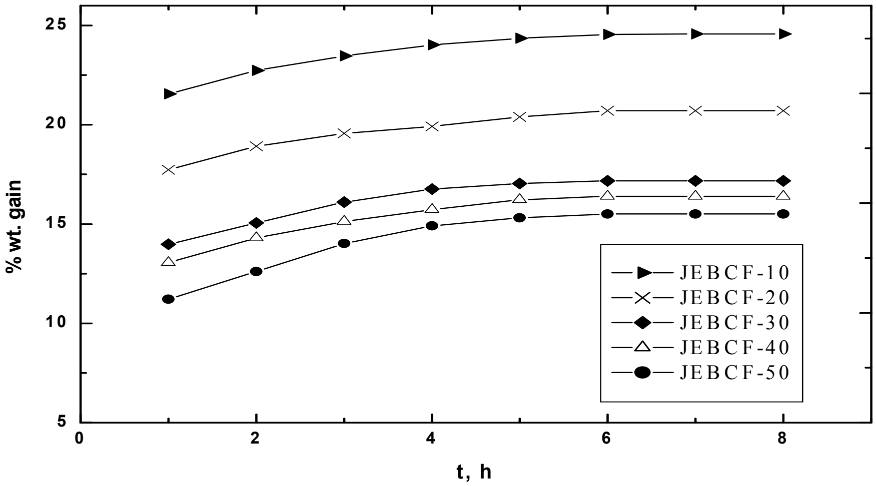


Fig. 3.6: The plots of % weight gain against time (t) for JEBCF-10 to JEBCF-50 in boiling water.

Water uptake study of JEBCF-50 and TJEBCF-50 composites

For JEBCF-50 and TJEBCF-50 composites, the percentage weight gain with the passage of time ($t^{1/2}$) is shown in Figs. 3.7-3.9 for water, 10% aq. HCl and 10% aq. NaCl, respectively. It can be seen from Figs. 3.7-3.9 that water uptake becomes nearly constant after 168 h for JEBCF-50 composites and 120 h for TJEBCF-50 composites in water, 10% aq. HCl and 10% aq. NaCl environments, respectively. The equilibrium water content and time for water, 10% aq. HCl and 10% aq. NaCl environments are recorded in Table 3.11. It is clear from Figs. 3.7-3.9 that % water uptake increased with time and remained almost constant after equilibrium was established and a considerable decrease in water uptake is observed in TJEBCF-50 composites in all the three environments. Drastic reduction in water uptake is due to replacement of hydrophilic –OH groups of jute fibers to water repellent ester groups. High equilibrium water content in acidic environment is due to surface solvolysis of the composites. The π-electrons of benzene ring and CH=CH of acrylic acid form weak H-bonding as compared to H-bonding with polar ester groups. It is observed that the percentage water uptake by TJEBCF-50 composites is relatively lower than that of JEBCF-50 due to esterification of hydrophilic –OH groups present in jute fibers. Ester groups are known to water repellency. From Table 3.11, it is clear that diffusivity has decreased considerably on esterification of fibers. In boiling water study, from Table 3.11 and Fig. 3.10, it is evident that equilibrium water uptake time is reduced in TJEBCF-50 composites as compared to JEBCF-50 composites. This is due to esterification of fibers.

Table-3.11: Water uptake and diffusivity data of JEBCF-50 to TJEBCF-50 composites at room temperature

Composite	%, Equilibrium water content at room temperature			Diffusivity(D_x), 10^{-12}, m^2/s			% Eqm. water content in boiling water
	H_20	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl	
JEBCF-50	14.3	12.3	17.3	5.6	5.7	3.9	14.5
TJEBCF-50	6.3	4.9	8.8	4.7	4.8	2.2	4.2

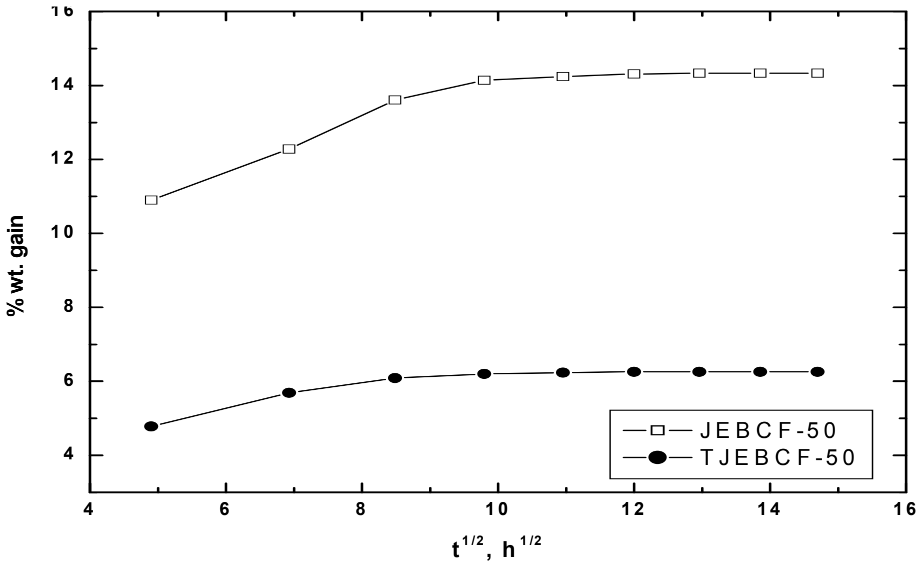


Fig. 3.7: The plots of % weight gain against $t^{1/2}$ for JEBCF-50 and TJEBCF-50 composites in water at room temperature.

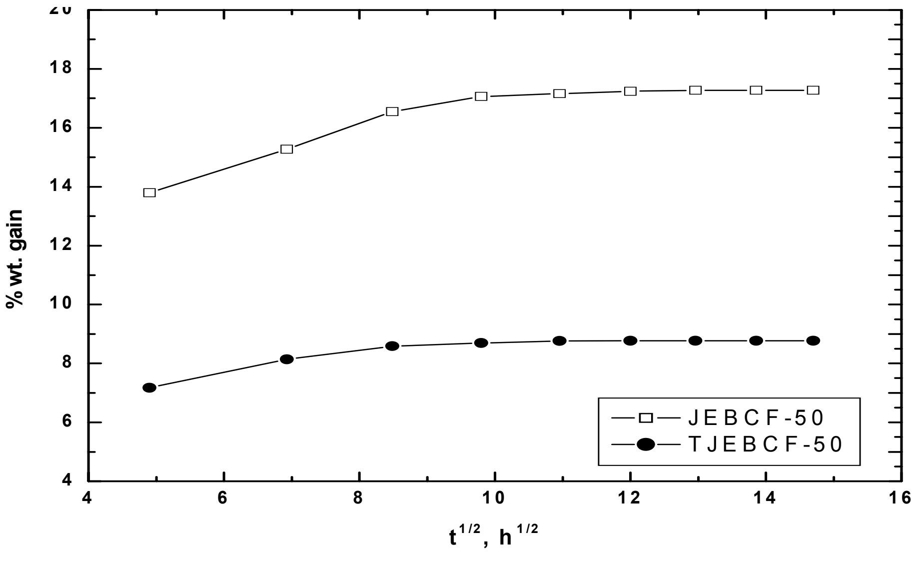


Fig. 3.8: The plots of % weight gain against $t^{1/2}$ for JEBCF-50 and TJEBCF-50 composites in 10 % aq. HCl at room temperature.

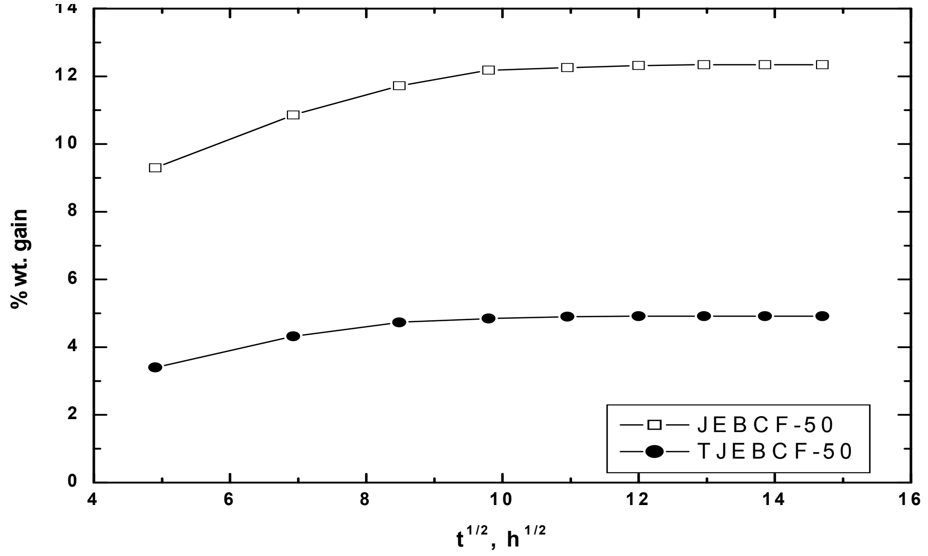


Fig. 3.9: The plots of % weight gain against $t^{1/2}$ for JEBCF-50 and TJEBCF-50 composites in 10 % aq. NaCl at room temperature.

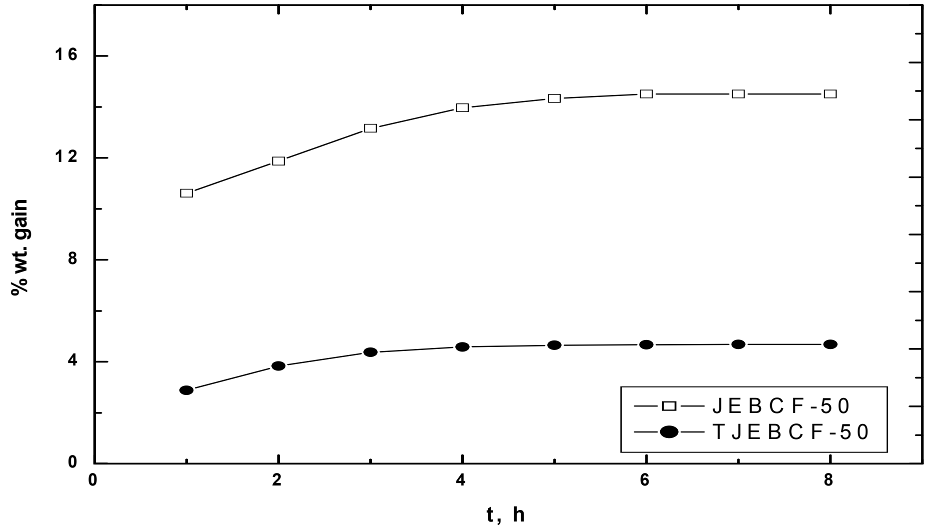


Fig. 3.10: The plots of % weight gain against time for JEBCF-50 and TJEBCF-50 composites in boiling water.

Water uptake study of UJG-50 and TJG-50 composites

For UJG-50 and TJG-50 composites, the percentage weight gain with the passage of time ($t^{1/2}$) is shown in Figs. 3.11-3.13 for water, 10 % aq. HCl and 10 % aq. NaCl, respectively. It can be seen from Figs. 3.11-3.13 that water uptake becomes nearly constant after 168, 168 and 144 h for UJG-50 composites and 120, 144 and 144 h for TJG-50 composites in water, 10 % aq. HCl and 10 % aq. NaCl environments, respectively. The equilibrium water content and time for water, 10 % aq. HCl and 10 % aq. NaCl environments are recorded in Table 3.12. It is clear from Figs. 3.11-3.13 that % water uptake increased with time and remained almost constant after equilibrium was established and a considerable decrease in water uptake is observed in TJG-50 composites in all the three environments. Drastic reduction in water uptake is due to replacement of hydrophilic –OH groups of jute fibers to water repellent ester groups. It is observed that the percentage water uptake by TJG-50 composites is relatively lower than that of UJG-50 due to esterification of hydrophilic –OH groups present in jute fibers.

From Table 3.12, it is clear that diffusivity has decreased considerably on esterification of fibers. Observed diffusivity order is NaCl > H_2O > HCl. In boiling water study, from Table 3.12 and Fig. 3.14, it is evident that equilibrium water uptake time is reduced in TJG-50 composites as compared to UJG-50 composites. This is due to esterification of fibers.

Table- 3.12: Water uptake and diffusivity data of UJG-50 to TJG-50 composites

Compo-site	%, Equilibrium water content at room temperature			Diffusivity(D_x), 10^{-11}, m^2/s			% Eqm. water content in boiling water
	H_20	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl	
UJG-50	9.18	7.69	12.07	1.41	0.99	1.99	9.19
TJG-50	4.90	3.39	6.17	0.70	0.45	0.96	4.95

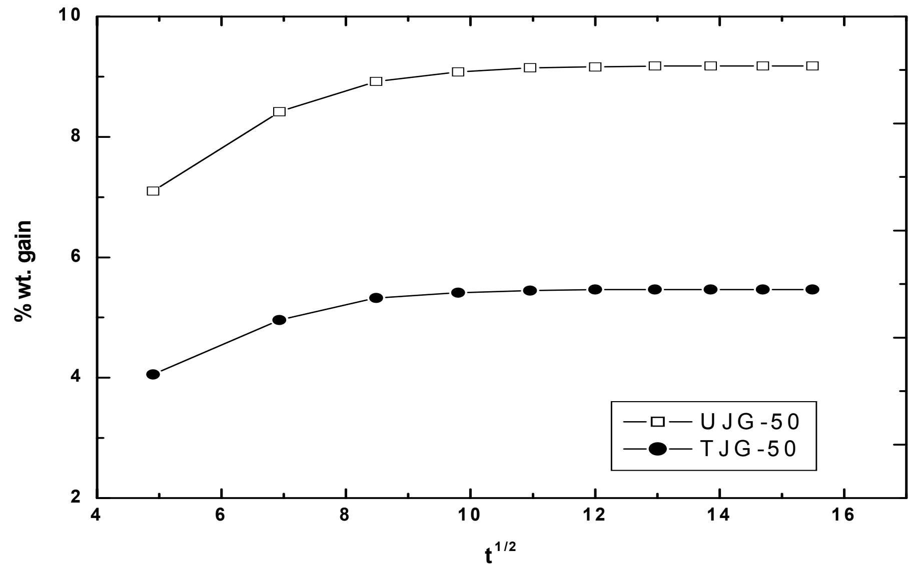


Fig. 3.11: The plots of % weight gain against $t^{1/2}$ for UJG-50 and TJG-50 composites in water at room temperature.

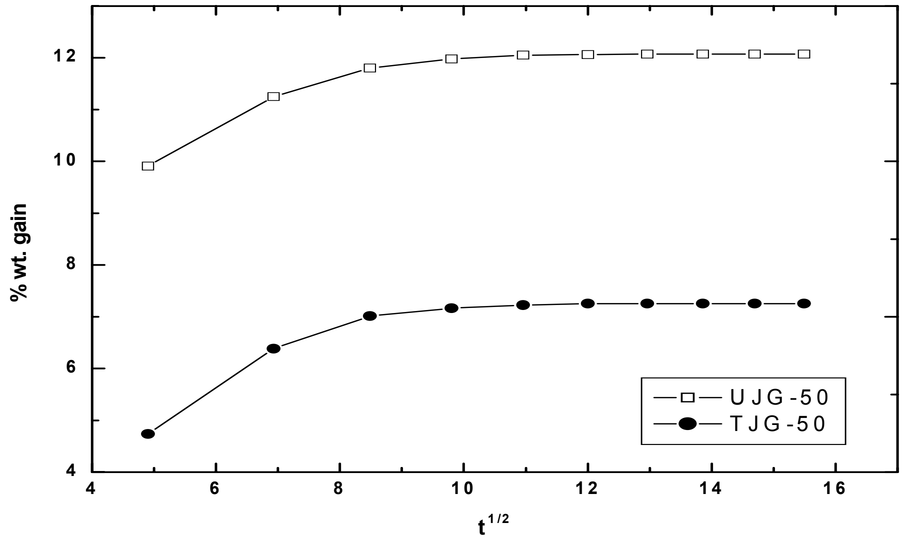


Fig. 3.12: The plots of % weight gain against $t^{1/2}$ for UJG-50 and TJG-50 composites in 10 % aq. HCl at room temperature.

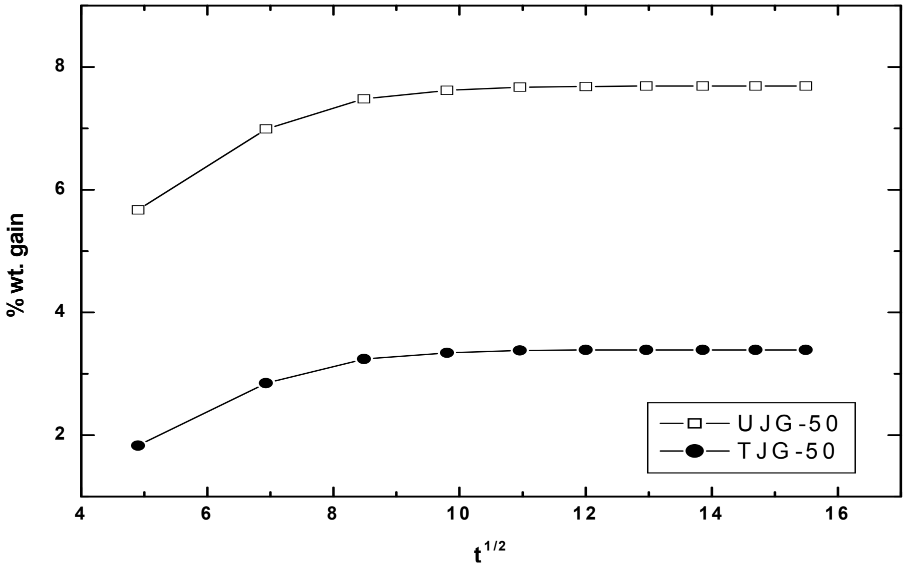


Fig. 3.13: The plots of % weight gain against $t^{1/2}$ for UJG-50 and TJG-50 composites in 10 % aq. NaCl at room temperature.

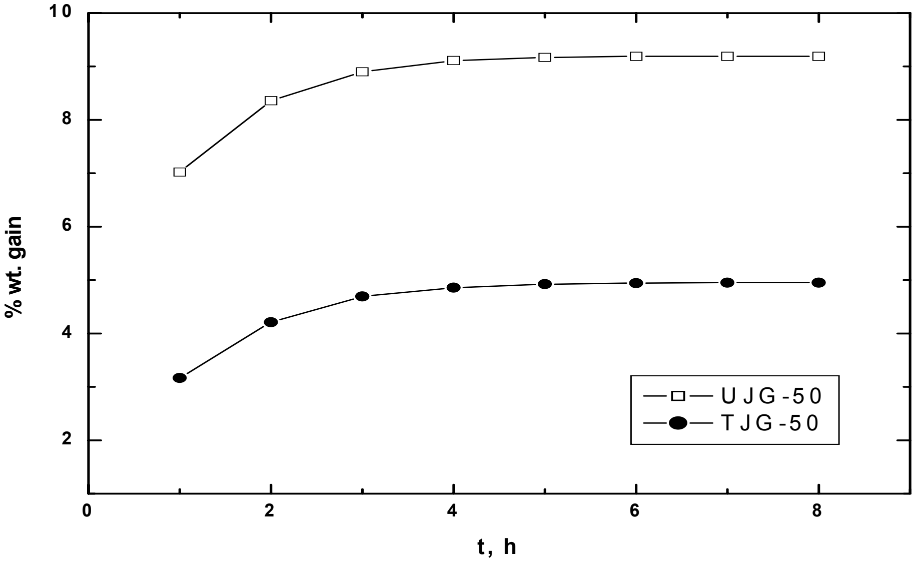


Fig. 3.14: The plots of % weight gain against time for UJG-50 and TJG-50 composites in boiling water.

Water uptake study of USG-50 and TSG-50 composites

For USG-50 and TSG-50 composites, the percentage weight gain with the passage of time ($t^{1/2}$) is shown in Figs. 3.15-3.17 for water, 10 % aq. HCl and 10 % aq. NaCl, respectively. The equilibrium water content and time for water, 10 % aq. HCl and 10 % aq. NaCl environments are recorded in Table 3.13. It is clear from Figs. 3.15-3.17 that % water uptake increased with time and remained almost constant after equilibrium was established and a considerable reduction in water uptake is observed in TSG-50 composites in all the three environments. The equilibrium water content and equilibrium time for water, 10 % aq. HCl and 10 % aq. NaCl environments are recorded in Table 3.13. A reduction in water uptake is due to replacement of hydrophilic –OH groups of sisal fibers to water repellent acrylate groups by esterification. The presence of strong electrolytes in water affected water structure and hence water sorption tendency and diffusivity. High equilibrium water content in acidic environment is probably due to surface solvolysis of the composites. Observed diffusivity order is NaCl > H_2O > HCl.

In boiling water study, from Table 3.13 and Fig. 3.18, it is evident that equilibrium water uptake time is reduced in TSG-50 composites as compared to USG-50 composite. This is due to esterification of fibers.

Table-3.13: Water uptake and diffusivity data of USG-50 and TSG-50 composites

Compo-site	%, Equilibrium water content at room temperature			Diffusivity(D_x), 10^{-11}, m^2/s			% Eqm. water content in boiling water
	H_20	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl	
USG-50	10.07	7.91	12.13	0.71	1.02	0.40	9.8
TSG-50	8.47	6.40	11.00	0.82	1.73	0.59	8.1

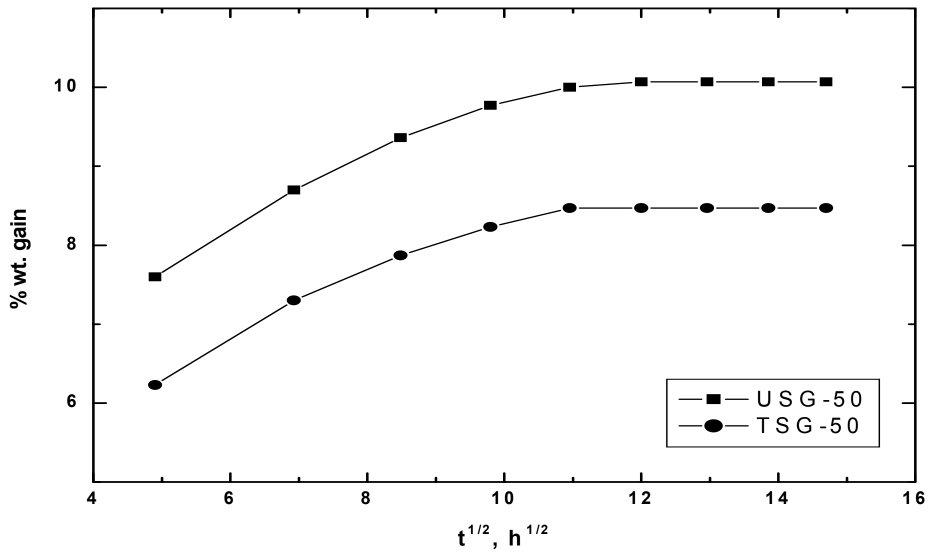


Fig. 3.15: The plots of % weight gain against $t^{1/2}$ for USG-50 and TSG-50 composites in water at room temperature.

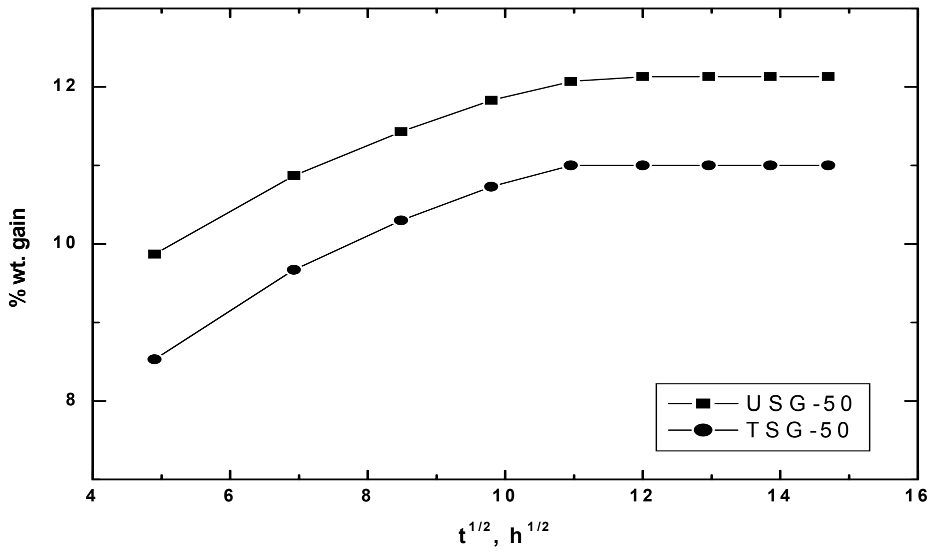


Fig. 3.16: The plots of % weight gain against $t^{1/2}$ for USG-50 and TSG-50 composites in 10 % aq. HCl at room temperature.

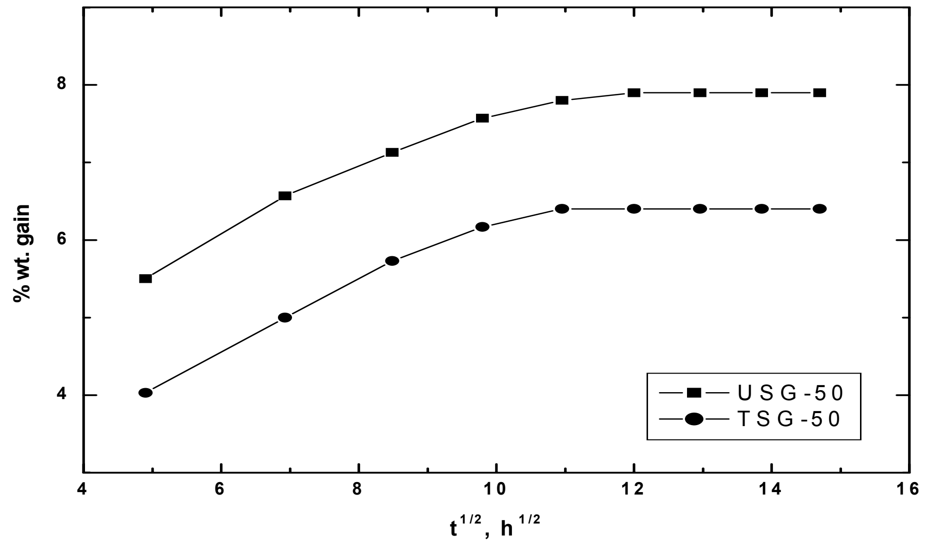


Fig. 3.17: The plots of % weight gain against $t^{1/2}$ for USG-50 and TSG-50 composites in 10 % aq. NaCl at room temperature.

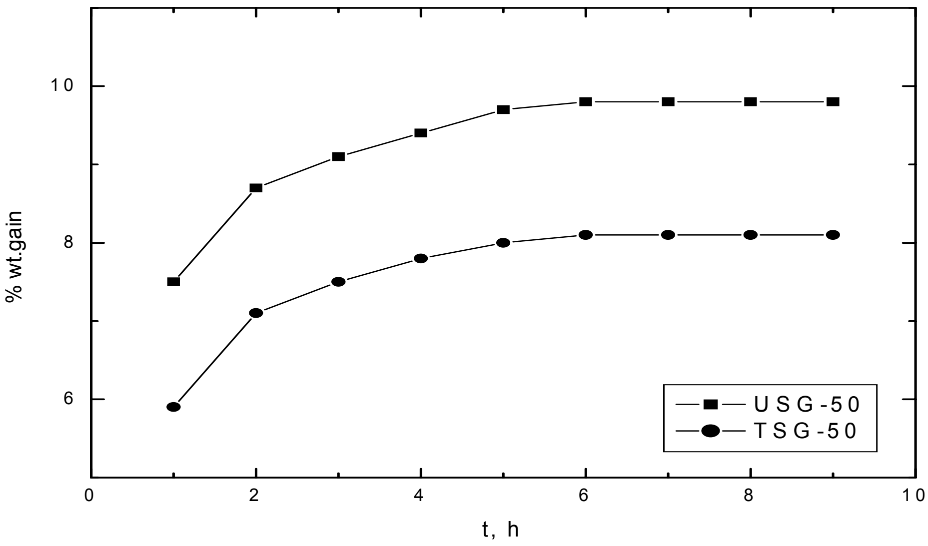


Fig. 3.18: The plots of % weight gain against time for USG-50 and TSG-50 composites in boiling water.

Water uptake study of JCEBCF-10 to JCEBCF-50 composites

For JCEBCF-10 to JCEBCF-50 composites, the % water absorbed with the passage of square root of soaking time curves at room temperature for JCEBCF-10 to JCEBCF-50 in water, 10 % aq. HCl and 10 % aq. NaCl environments are shown in Figs. 3.19-3.23 from which it is observed that water uptake increased with the passage of time upto ~ 144 h (equilibrium time) and then remained constant. Equilibrium water content for all the five composites in different environments are reported in Table 3.14 from which it is observed that equilibrium water content has decreased (8.00-5.87 % for H_2O, 5.77-4.1 % for 10 % aq. NaCl and 10.0-7.40 % for 10 % aq. HCl) with increasing BCF content in the composites. Diffusivity in JCEBCF-10 to JCEBCF-50 in water, 10 % aq. HCl and 10 % aq. NaCl solutions is reported in Table 3.14 from which it is clear that D_x has increased (1.0-1.51 x 10^{-11} m^2s^{-1} for H_2O, 2.0-2.93 x 10^{-11} m^2s^{-1} for 10 % aq. NaCl and 0.72-0.96 x 10^{-11} m^2s^{-1} for 10 % aq. HCl) with increasing BCF content in the composite. Increase in D_x with BCF content in all the three environments studied is due to void formation during self curing of BCF with release of formaldehyde and water. Observed diffusivity order in the composites is NaCl > H_2O > HCl. Effect of temperature on water uptake in JCEBCF-10 to JCEBCF-50 was carried out at boiling temperature of water (Fig. 3.24). From Fig. 3.24 it is evident that equilibrium is reached after 6 h in all the composite systems. Equilibrium water content is reported in Table 3.14 from which it is clear that equilibrium water content at boiling temperature has decreased with increasing BCF content in the composite.

Table-3.14. Water uptake and diffusivity data of JCEBCF-10 to JCEBCF-50 composites

Composite	%, Equilibrium water content at room temperature			Diffusivity(D_x), 10^{-11}, m^2/s			% Eqm. water content in boiling water
	H_20	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl	
JCEBCF-10	8.00	5.77	10.00	1.00	2.00	0.72	7.1
JCEBCF-20	7.67	5.70	9.03	1.13	2.05	0.87	6.7
JCEBCF-30	7.10	5.13	8.67	1.29	2.44	0.89	6.3
JCEBCF-40	6.27	4.33	7.53	1.36	2.60	0.92	5.9
JCEBCF-50	5.87	4.1	7.40	1.51	2.93	0.96	5.5

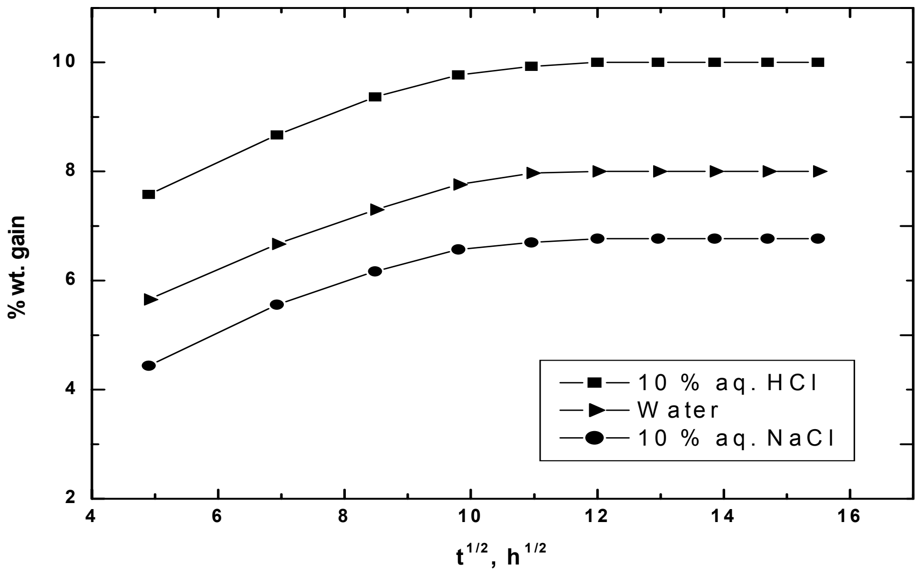


Fig. 3.19: The plots of % weight gain against t$^{1/2}$ for JCEBCF-10 at room temperature

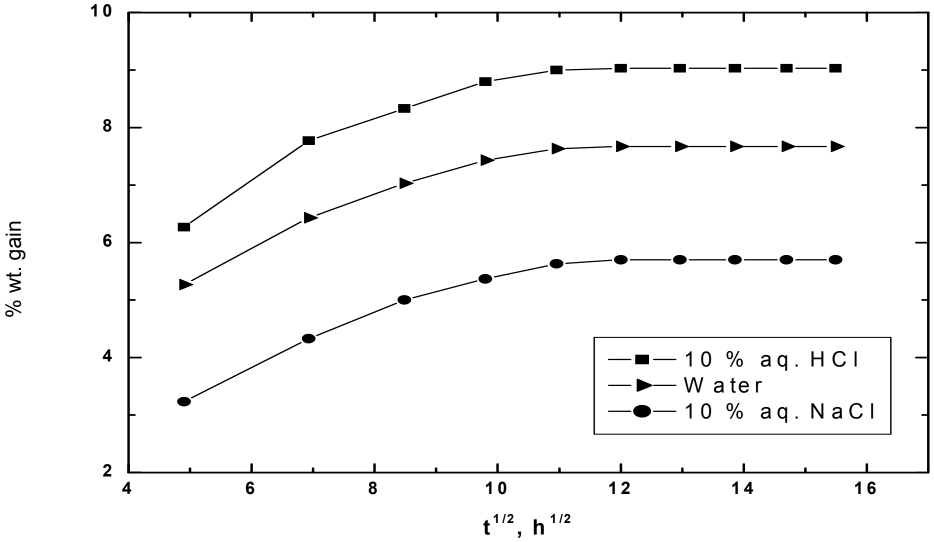


Fig. 3.20: The plots of % weight gain against t$^{1/2}$ for JCEBCF-20 at room temperature

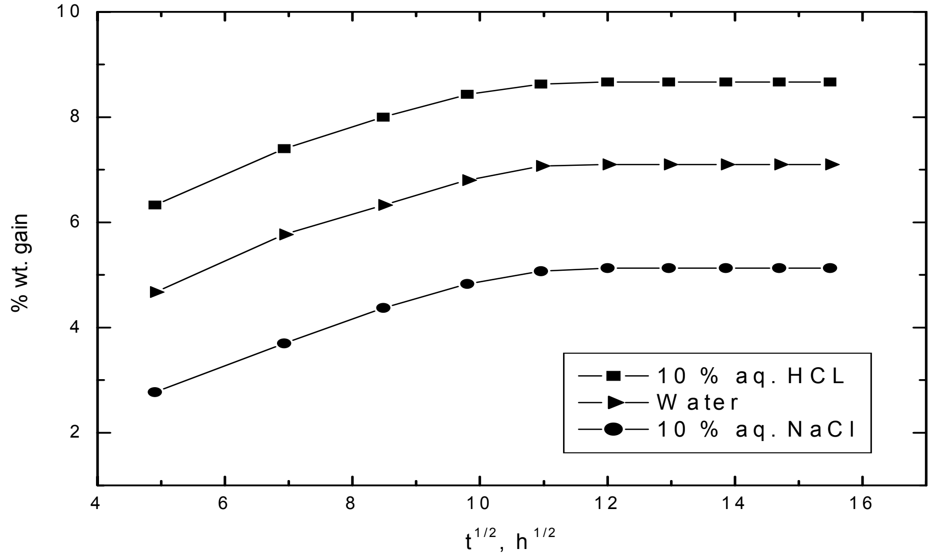


Fig. 3.21: The plots of % weight gain against $t^{1/2}$ for JCEBCF-30 at room temperature

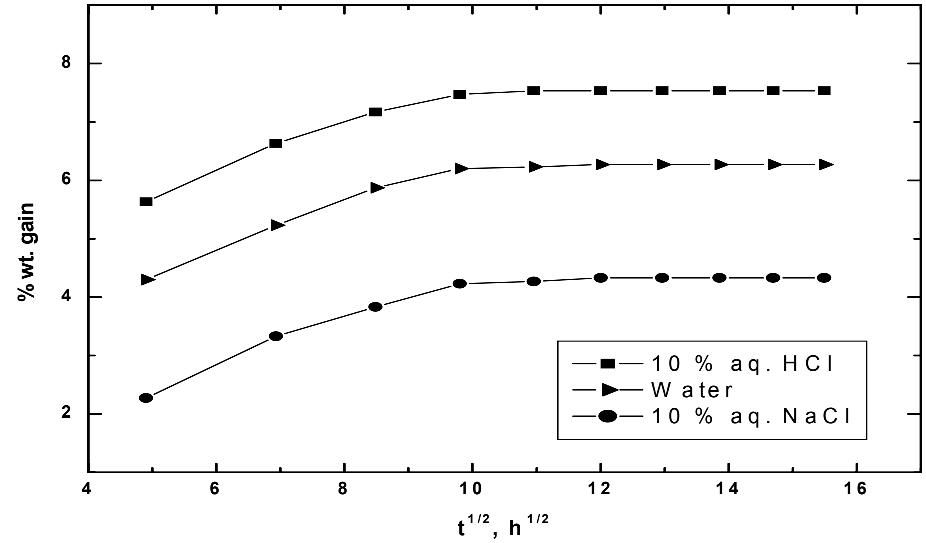


Fig. 3.22: The plots of % weight gain against $t^{1/2}$ for JCEBCF-40 at room temperature.

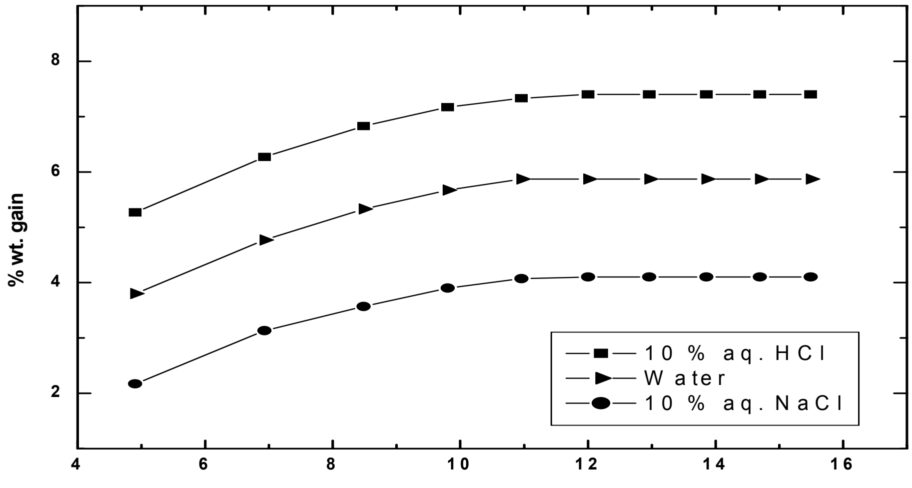


Fig.3.23: The plots of % weight gain against $t^{1/2}$ for JCEBCF-50 at room temperature.

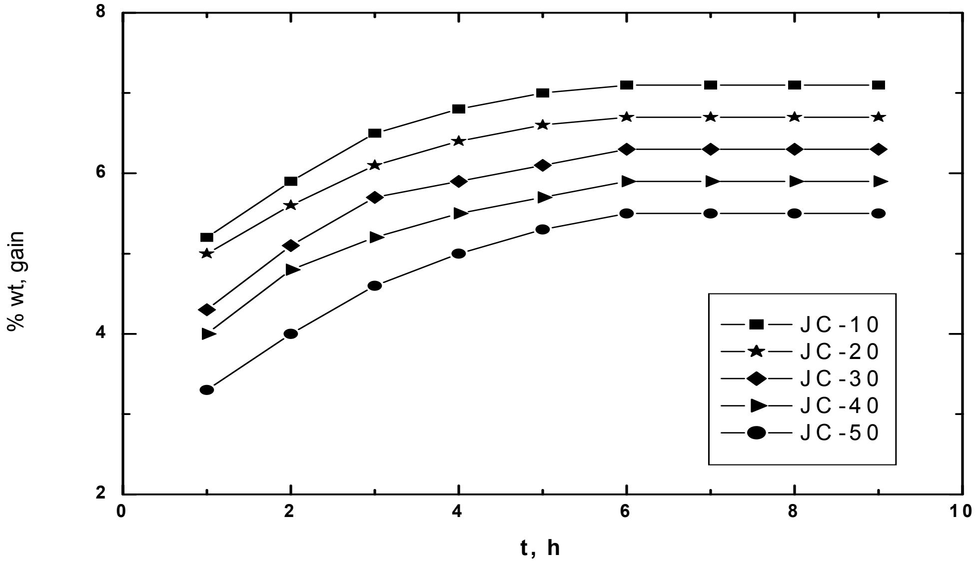


Fig. 3.24: The plots of % weight gain against time (t) for JCEBCF-10 to JCEBCF-50 in boiling water.

Water uptake study of JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites

For JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites, The percentage weight gain with the passage of time ($t^{1/2}$) is shown in Figs. 3.25-3.27 for water, 10 % aq. HCl and 10 % aq. NaCl, respectively. It can be seen from Figs. 3.25-3.27 that water uptake becomes nearly constant after 120 h for JCEBCF-50, 120 h for TJCEBCF-50 and 96 h for GCEBCF-50 composites in water, 10 % aq. HCl and 10 % aq. NaCl environments, respectively. The equilibrium water content and time for water, 10 % aq. HCl and 10 % aq. NaCl environments are recorded in Table 3.15. It is clear from Figs. 3.25-3.27 that % water absorption increased with time and remained almost constant after equilibrium was established and a considerable decrease in water absorption is observed in TJCEBCF-50 composite in all the three environments as compared to JCEBCF-50 composite. Drastic reduction in water absorption is due to replacement of hydrophilic –OH groups of jute fibers to water repellent ester groups. It is observed that the percentage water absorption by TJCEBCF-50composites is relatively lower than that of JCEBCF-50 due to esterification of hydrophilic –OH groups present in jute fibers. Ester groups are known to water repellency. Water uptake in GCEBCF-50 is found lower because natural fibers possess more moisture gain tendency as compared to synthetic fibers. From Table 3.15, it is clear that diffusivity has increased considerably on esterification of fibers. Observed diffusivity order is NaCl > H_2O > HCl. In boiling water study, from Fig. 3.28, it is evident that the water absorption in JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites is the maximum after 6h and remained almost constant.

The presence of strong electrolytes have affected water structure and hence water diffusivity in the composites. Diffusivity in composites was affected on the size of the hydrated ions. On the basis of experimental findings we may state that diffusivity is higher in saline environment due to small hydrated ions. Moreover all types of composites possess excellent hydrolytic stability even in boiling water and in highly acidic and saline environments indicating their usefulness in marine appliances besides low load bearing applications in construction and building industries as well as in electric and electrical fields.

Table-3.15. Water uptake and diffusivity data of JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites

Composite	**%, Equilibrium water content at room temperature**			**Diffusivity(D_x), 10^{-11}, m^2/s**			**% Eqm. water content in boiling water**
	H_20	10 % aq. NaCl	10 % aq. HCl	H_2O	10 % aq. NaCl	10 % aq. HCl	
JCEBCF-50	5.87	4.10	7.40	1.51	2.93	0.96	5.5
TJCEBCF-50	4.77	3.73	5.90	1.86	3.02	1.33	4.4
GCEBCF-50	2.73	1.90	3.83	1.51	2.89	0.93	2.6

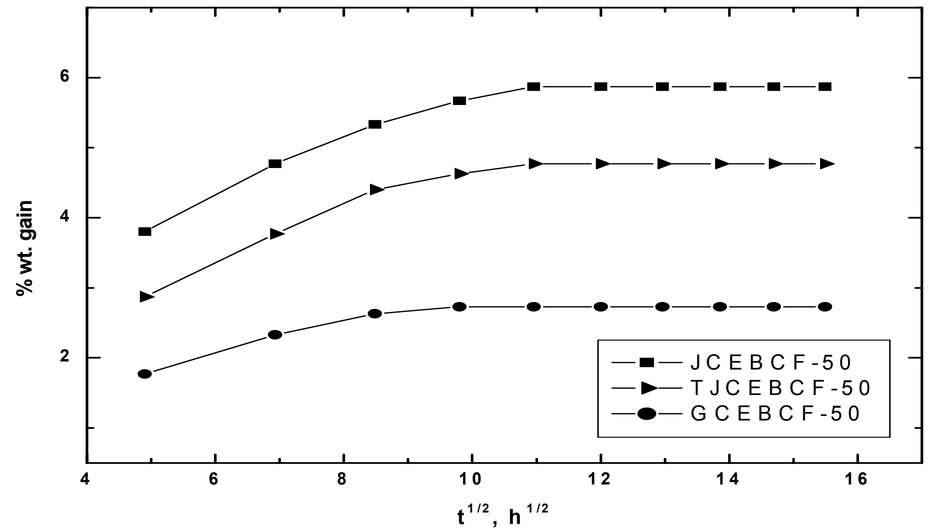


Fig. 3.25: The plots of % weight gain against $t^{1/2}$ for JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites in water at room temperature.

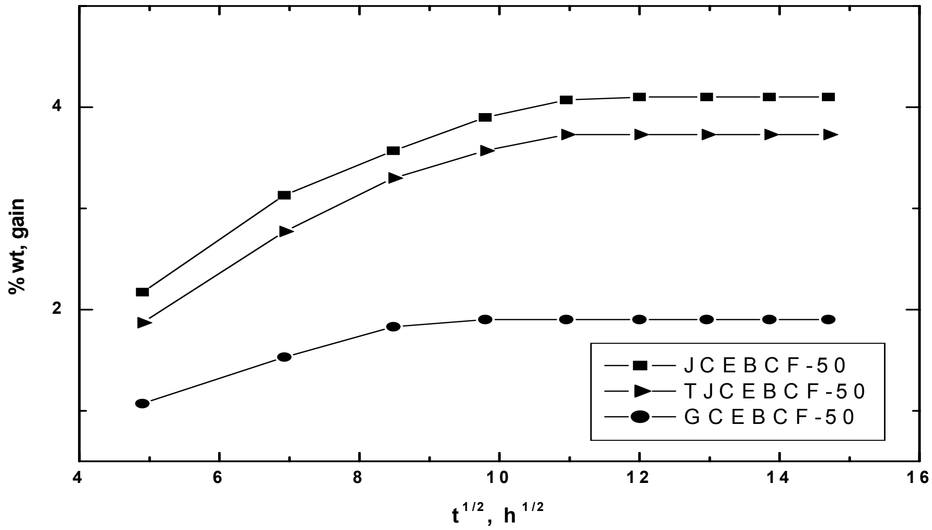


Fig. 3.26: The plots of % weight gain against $t^{1/2}$ for JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites in 10 % aq. NaCl at room temperature.

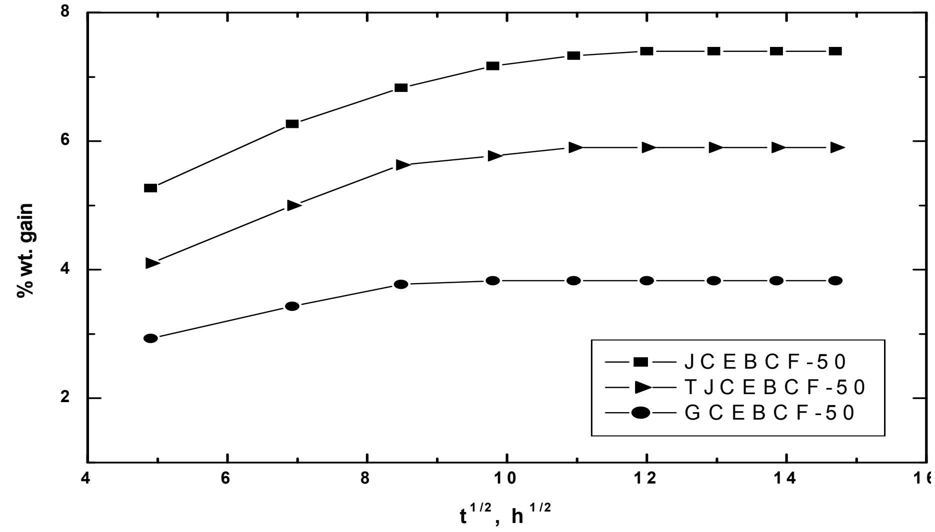


Fig. 3.27: The plots of % weight gain against $t^{1/2}$ for JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites in 10 % aq. HCl at room temperature.

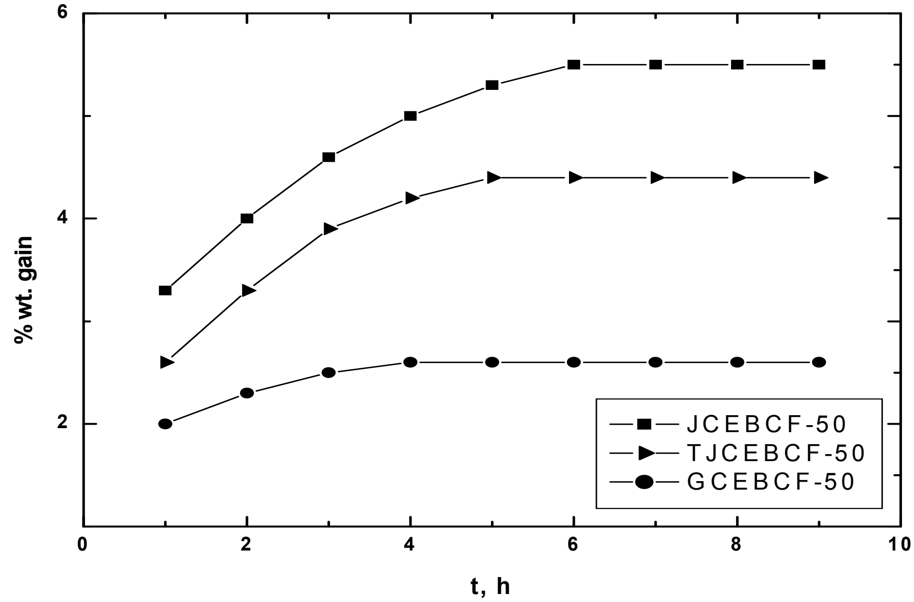
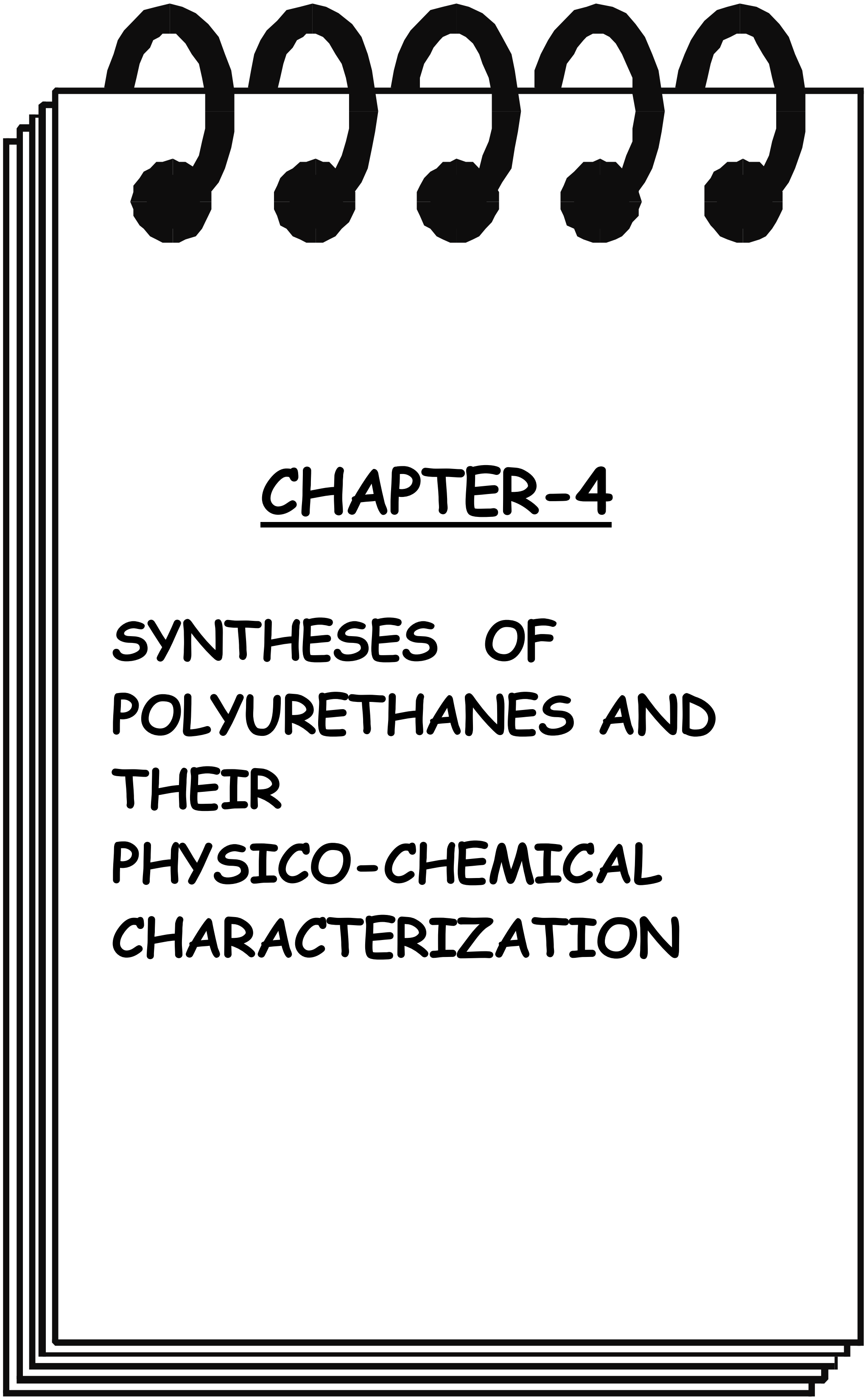


Fig. 3.28: The plots of % weight gain against time for JCEBCF-50, TJCEBCF-50 and GCEBCF-50 composites in boiling water.



CHAPTER-4

SYNTHESES OF POLYURETHANES AND THEIR PHYSICO-CHEMICAL CHARACTERIZATION

This chapter of the thesis describes the up to date literature survey on polyurethane resins and their applications; synthesis, preparation of the films, their densities and thermo-mechanical analyses, surface coating and chemical resistance are well-documented in this chapter and it is further subdivided into seven sections:

SECTION-I: INTRODUCTION

SECTION-II: SYNTHESES OF COPOLYURETHANES

SECTION-III: IR SPECTRAL CHARACTERIZATION OF COPOLYURETHANES

SECTION-IV: DENSITY MEASUREMENTS OF COPOLYURETHANE FILMS

SECTION-V: THERMAL, MECHANICAL AND ELECTRICAL PROPERTIES OF COPOLYURETHANE FILMS

SECTION-VI: WATER UPTAKE STUDY OF COPOLYURETHANE FILMS

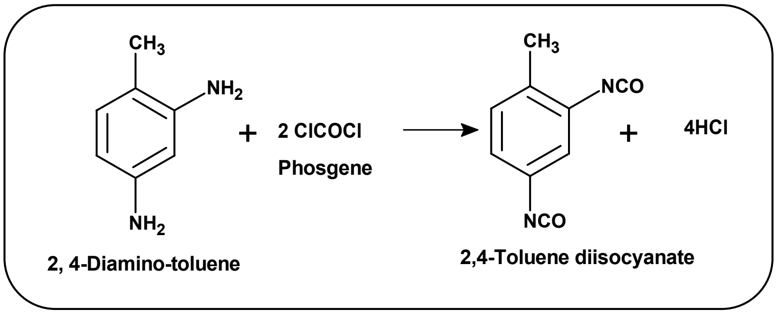
SECTION-VII: SURFACE COATING AND CHEMICAL RESISTANCE STUDY OF COPOLYURETHANES

SECTION-I: INTRODUCTION

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 (I).

---

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.



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

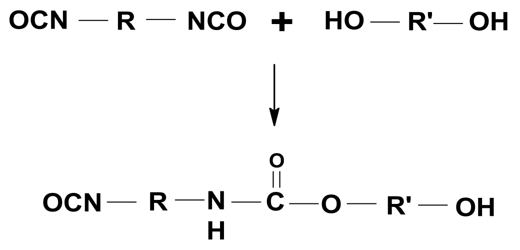
Polyurethane adhesives have developed reputation for reliability and high performance [3]. Polyurethane adhesive is widely used in footwear, packaging, automotive industries and furniture assembly [4].

Polyurethanes have been recognized as superior adhesives for metal bonding since 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. High reactivity of isocyanates with active hydrogens is the basis of urethane

---

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, “Strength and durability of one-part polyurethane adhesive bonds to wood.”, Forest Prod. J. **48**, 71-76, 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.

synthesis, polymerization proceeds by the reaction of a diisocyanate and diol to form a carbamate (or urethane) linkage (II):



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

(II)

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].

---

6. S. S. Voyutski, "Autohesion and adhesion of high polymers", Wiley Interscience, New York, 197-198, 1963.
7. F. H. Sexsmith, "Milestones in elastomer-to-metal bonding-II. The years 1935 to the present", Adhesives Age, **13**, 31-36, 1970.
8. M. M. Chehimi and J. F. Watts, "An XPS study of the steel-aromatic moisture-cured urethane interface", J. Adhesion Sci. Technol, **6(3)**, 377-393, 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. Jaisankar 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.

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 elasticity to PU materials [14].

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 [15, 16].

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

---

14. Z. S. Petrovic and J. Ferguson, “Polyurethane elastomers”, J. Prog. Polym. Sci., **16**, 695-836, 1991.
15. S. Desai, I. M. Thakore, B. D. Sarawade and S. Devi,” Effect of polyols and diisocyanates on thermo-mechanical and morphological properties of polyurethanes”, Eur. Polym. J., **36**, 711-720, 2000.
16. 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.

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

Shufen et al. [17] have studied on the thermal behavior of polyurethanes. They have reported thermal decomposition mechanism of polyurethane under different environmental conditions. Thermal decomposition and combustion reactions of polyether-polyurethane and polyester-polyurethane in air and nitrogen atmospheres were investigated by thermogravimetry analysis. Polyester-polyurethane was found to be more thermally stable than polyether – polyurethane.

Yeganeh et al. [18] have synthesized biodegradable elastomeric epoxy modified polyurethanes based on (ξ- caprolectone) and poly (ethylene glycol) as well as 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.

---

17. 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.
18. H. Yeganeh, M. M. Lakouraj and S. Jamshidi, "Synthesis and properties of biodegradable elastomeric epoxy modified PUs based on poly (ξ–caprolectone) and poly (ethylene glycol)", Eur. Polym. J., **41**, 2370-2379, 2005.

Asha et al. [19] have synthesized a new class of telechelic urethane methacrylic (TUMA) macromonomers by a two-step condensation of 1, 6-hexamethylenediisocyanate (HMDI) with polypropylene glycol (PPG) of various molecular weights and capped with hydroxyl ethyl methacrylate (HEMA). The structure of the telechelic urethanes were confirmed by ^{1}H, ^{13}C NMR and FTIR spectroscopy. Photopolymerization of these telechelic systems was investigated using 2, 2-diethoxy acetophenone as the photoinitiator at 5 wt. %. Trihydroxymethylpropane trimethacrylate (30 parts), PPG diacrylate (25 parts), ethylhexyl acrylate (20 parts) were mixed with the various telechelic urethane methacrylates (25 parts) for curing studies. The kinetics of the curing was monitored by following the disappearance of the methacrylic double bonds at 1628 cm^{-1} using IR spectroscopy. TUMAPPG-425 had the fastest cure rate among the telechelic urethane methacrylates. This could be accounted for by hydrogen bonding pre-association in these systems. The thermal properties of the cured films were studied using TGA measurements.

Rozman et al. [20] 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.

---

19. S. K. Asha, M. Thirumal, A. Kavitha and C. K. S. Pillai, “Synthesis and curing studies of PPG based telechelic urethane methacrylic macromonomers”, Eur. Polym. J., **41**, 23–33, 2005.
20. H. D. Rozman, G. S. Tay and A. Abu baker, “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”, Polym. Plast. Technol. Eng., **42**, 811-821, 2003.

Narayan et al. [21] 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. 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.

A review on structures and moisture permeability of polyurethane films was reported by Shibaya et al. [22]. 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 ΔH 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 ΔH and hydrogen bond concentration of urethane group by FTIR measurement decreased with increasing 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.

---

21. 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.
22. 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.

T. Hikita et al. [23] have demonstrated that the synthesis of a sequence ordered head to head or tail to tail (H–H or T–T) polyurethane (H–H or T–T content: 90%) can be achieved by direct polyaddition of symmetric monomer ethylene glycol with nonsymmetric monomer tolylene, 2,4-diisocyanate. A certain influence of constitutional regularity on the thermal properties of isomers was observed.

Pechar et al. [24] have synthesized the polyurethane networks (PUNs) using polyols derived from soybean oil, petroleum or a blend of the two inconjunction with diisocyanate. The soybean-based polyols (SBPs) were prepared using air oxidation or by hydroxylating epoxidized soybean oil. Some of the networks were subjected to several solvents to determine their respective swelling behavior and solubility parameters. Sol-fractions were also determined and DMA experiments were utilized to monitor the changes in storage modulus and tan δ with temperature for networks with sol and with the sol extracted. A linear relationship was noted between the hydroxyl number of a SBP and the glass transition temperature of its corresponding unextracted PU network within the range of hydroxyl numbers (i.e., 55-237 mg KOH/g) and glass transition temperatures (i.e., -21 to +83^{0}C) encountered in this work. This same linear relationship was realized between the weighted hydroxyl number of soy and petroleum-based polyol blends and the glass transition temperature of the resulting unextracted and extracted network PUs within the ranges utilized in this study (i. e., 44-57 mg KOH/g, -54-19^{0}C).

Eren et al. [25] have synthesized simultaneous interpenetrating polymer

---

23. T. Hikita, A. Mochizuki, K. Takeuchi, M. Asai and M. Ueda, “Synthesis and characterization of ordered polyurethanes from tolylene 2,4-diisocyanate and ethylene glycol”, High Perform. Polym., **13**, S247–S255, 2001.
24. T. W. Pechar , S. Sohn , S. Ghosh , C. E. Frazier , A. Fornof , T. E. Long and G. L. Wilkes, “Characterization and comparison of polyurethane networks prepared using soybean-based polyols with varying hydroxyl content and their blends with petroleum-based polyols”, J. Appl. Polym. Sci., **101**, 1432-1443, 2006.
25. T. Eren, S. Colak and S. H. Kusefoglu, “Simultaneous interpenetrating polymer networks based on bromoacrylated castor oil polyurethane”, J. Appl. Polym. Sci. **100**, 2947-2955, 2006.

networks (SINs) based on bromoacrylated castor oil polyurethane. In the first step, simultaneous addition of bromine and acrylate to the double bonds of castor oil was achieved. In the second step, bromoacrylated castor oil (BACO) was reacted with toluene diisocyanate (TDI), to form a prepolyurethane (BACOP). The prepolyurethanes were reacted with styrene (STY), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and 3-(acryloxy)-2-hydroxypropylmethacrylate (AHPMA) free radically, using the acrylate functional group to prepare the simultaneous interpenetrating polymer networks (SINs). 2, 2′-Azobis-(isobutyronitrile) (AIBN) was used as the initiator and diethylene glycol dimethacrylate (DEGDMA) was used as the cross linker. BACO and BACOP were characterized by IR ^{1}H-NMR and ^{13}CNMR techniques. Synthesized polymers were characterized by their resistance to chemical reagents, thermo gravimetric analysis and dynamic mechanical thermal analyzer (DMTA). All the polymers decomposed with 6-10% weight loss in a temperature range of 25-240^{0}C. MMA-type SIN showed the highest T_g (126^{0}C), while STY-type SINs showed the highest storage modulus (8.6×10^9 Pa) at room temperature, with respect to other synthesized SINs.

Kumar et al. [26] have prepared polyethylene glycol-400 (PEG) based polyurethane (PU) and polyacrylonitrile (PAN) semi-interpenetrating polymer networks (SIPNs) (PU/PAN; 90/10, 70/30, 60/40 and 50/50) by sequential polymerization method. The prepared SIPNs have been characterized by physico mechanical properties. The microcrystalline parameters such as crystal size, lattice disorder (g), surface (D_s) and volume (D_v) weighted crystal size of SIPNs were estimated using wide angle X-ray scattering studies, and quantification of the polymer network has been carried out on the basis of these parameters. The microstructural parameters were established using exponential, lognormal and reinhold asymmetric column length distribution functions and the results are compiled.

---

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

Rath et al. [27] have synthesized novel two component polyurethane sealant from hydroxyl terminated polybutadiene (HTPB) end capped with toluene diisocyanate (TDI) and polyoxypropylene triol. The 4, 4′-diamino-3, 3′-dichloro diphenyl methane (DADCDPM) and 4, 4′-diamino-3, 3′-dichloro triphenyl methane (DADCTPM) were used as chain extenders and fillers. Evaluation of mechanical properties and ageing studies indicated that the sealant possessed excellent mechanical properties and stability in different environments.

Chen et al. [28] 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.

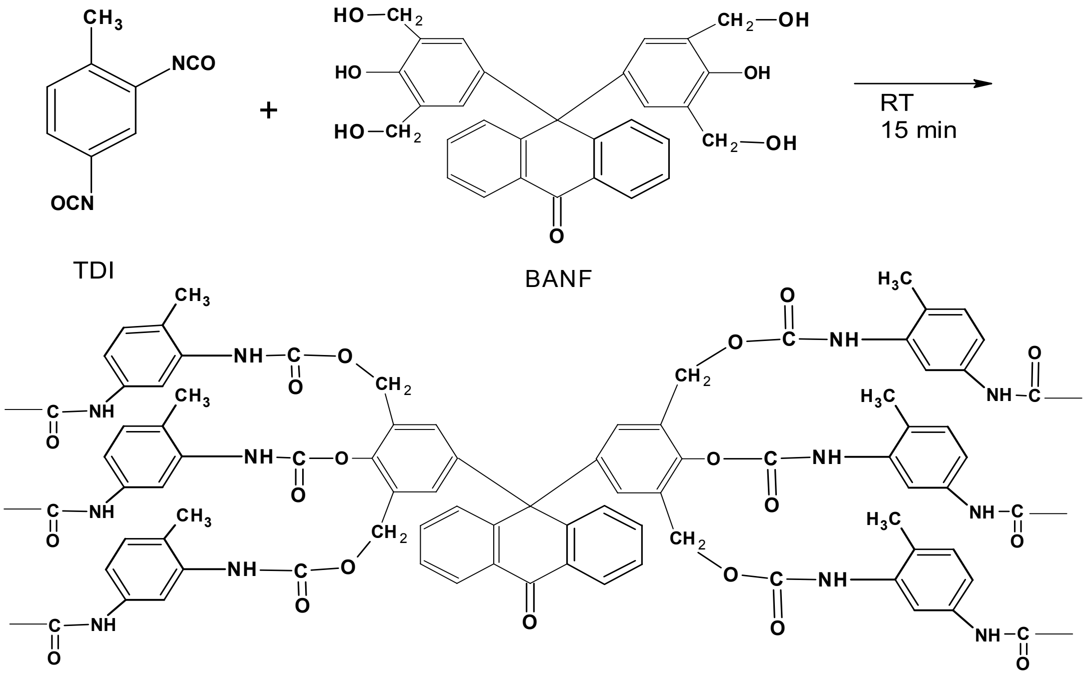
SECTION-II: SYNTHESES OF COPOLYURETHANES

(I) Synthesis and preparation of films of polyurethane of BANF-TDI (Scheme-I)

Into a 250 ml beaker, 0.0005M (0.249g) BANF was dissolved in 15 ml methyl ethyl ketone (MEK) at room temperature. To this solution 0.0015 M (0.261g) TDI in 5 ml MEK was added and the resultant solution was stirred manually for 15 min and poured into a leveled 15cm x 15cm glass mold. The solvent was allowed to evaporate with a controlled rate 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-400/600.

---

27. S. K. Rath, U. G. Suryavansi and M. Patri, “A novel polyurethane sealant based on hydroxy-terminated polybutadiene”, J. Appl. Polym. Sci., **99**, 884-890, 2006.
28. S. Chen, Y. Tian, L. Chen and T. Hu, “Epoxy resin/polyurethane hybrid networks synthesized by frontal polymerization”, Chem. of Mater., **18**, 2159-2165, 2006.



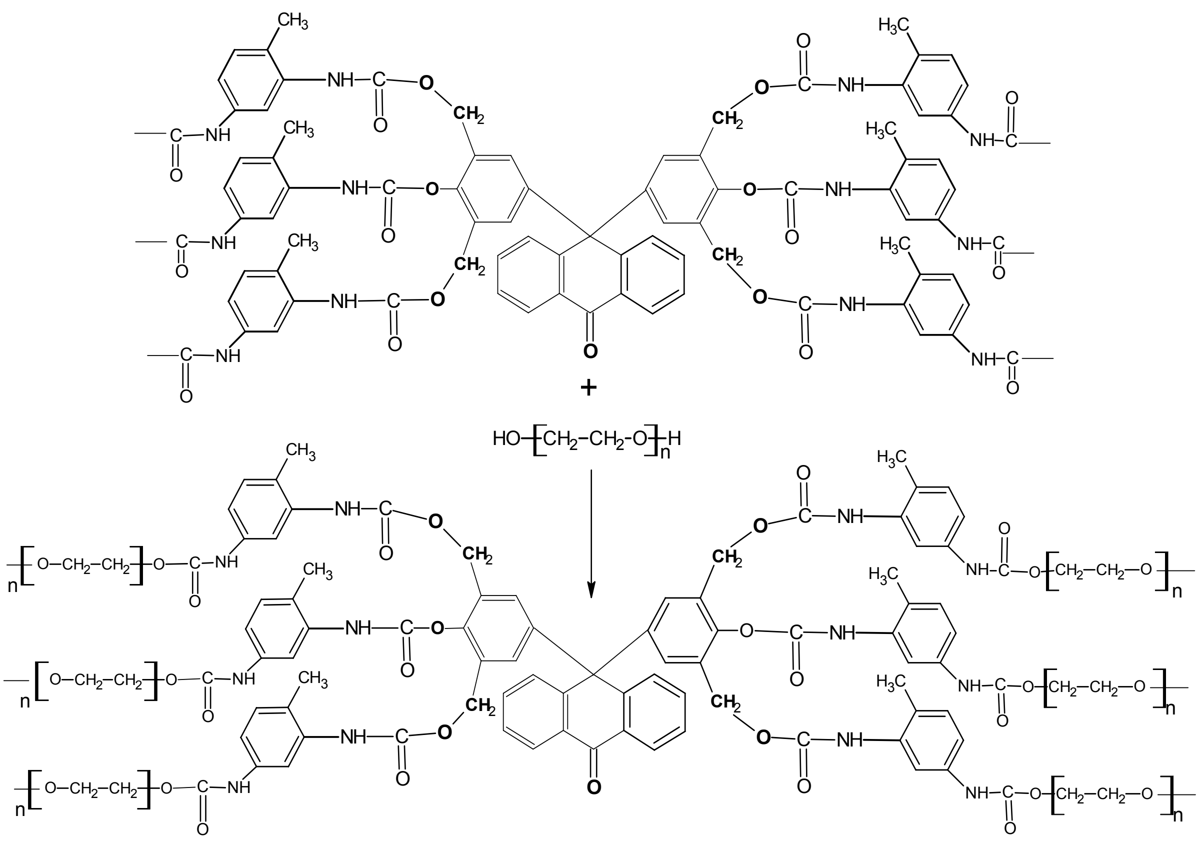
Scheme - I

(II) Synthesis and preparation of films of copolyurethanes of BANF-TDI-PEG-400/600 (Scheme-II)

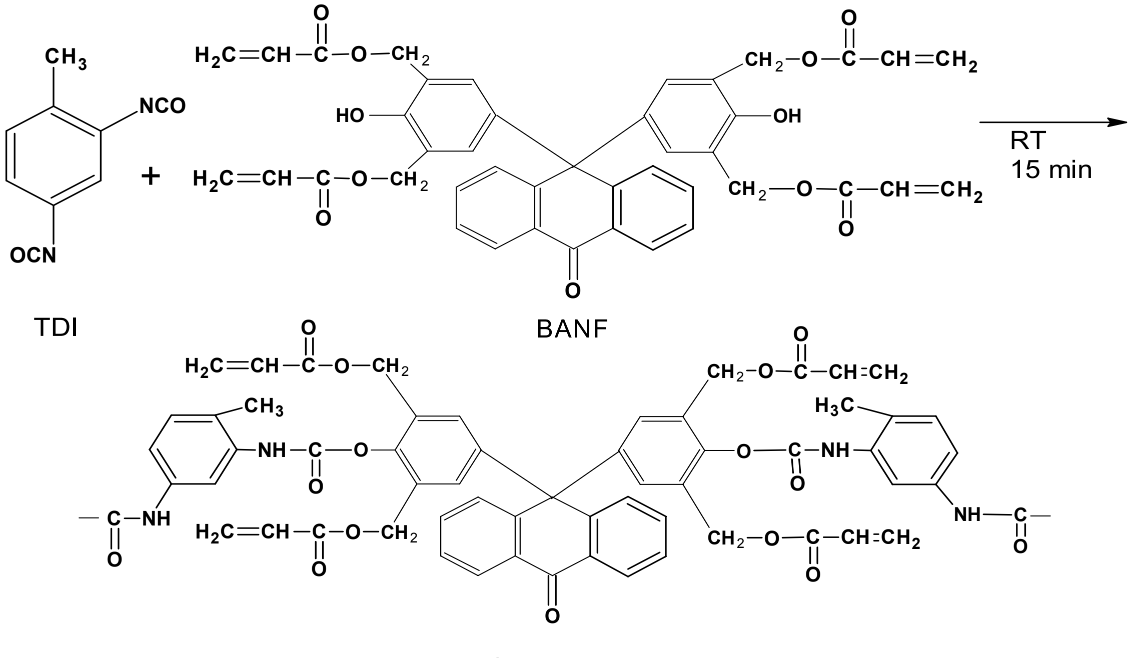
Into a 250 ml beaker, 0.0005M (0.249g) BANF was dissolved in 15 ml MEK at room temperature. To this solution 0.0015 M (0.261g) TDI in 5 ml MEK was added and the resultant solution was stirred manually for 15 min and to this prepolyurethane, 0.0015M (PEG-400)/ 0.0005M (PEG-600) in 5 ml MEK was added drop wise with stirring. After completion of the PEG addition, the mixture was stirred for 10 min and poured into a leveled 15 cm X 15 cm glass mold. The solvent was allowed to evaporate with controlled rate at room temperature. After 24 h, the film was peeled from the mold. Hereafter films are designated as BTP-400 and BTP-600.

(III) Synthesis and preparation of films of polyurethane of BANFA-TDI (Scheme-III)

Into a 250 ml beaker, 0.0005M (0.357g) BANFA was dissolved in 15 ml methyl ethyl ketone (MEK) at room temperature. To this solution 0.001 M (0.174g) TDI in 5 ml MEK was added and the resultant solution was stirred manually for 15 min and poured into a leveled 15cm x 15cm glass mold. The solvent was allowed to evaporate with a controlled rate 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-400/600.



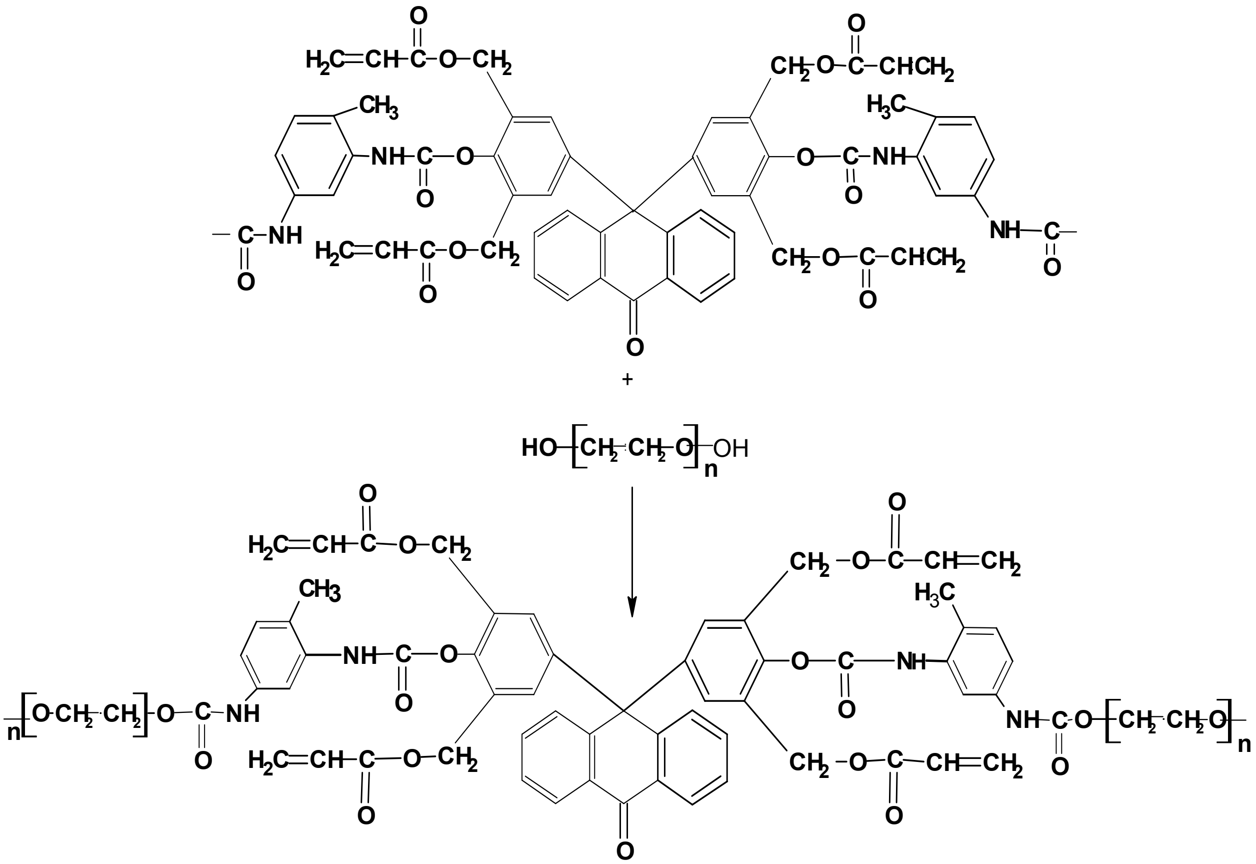
Scheme-II



Scheme-III

(IV) Synthesis and preparation of films of copolyurethanes of BANFA-TDI-PEG-400/600 (Scheme-IV)

Into a 250 ml beaker, 0.0005M (0.357g) BANFA was dissolved in 15 ml MEK at room temperature. To this solution 0.001 M (0.174g) TDI in 5 ml MEK was added and the resultant solution was stirred manually for 15 min and to this prepolyurethane, 0.0005M (PEG-400)/ 0.0002M (PEG-600) in 5 ml MEK was added drop wise with stirring. After completion of the PEG addition, the mixture was stirred for 10 min and poured into a leveled 15 cm X 15 cm glass mold. The solvent was allowed to evaporate with controlled rate at room temperature. After 24 h, the film was peeled from the mold. Hereafter films are designated as BTP-400 and BTP-600.



Scheme-IV

SECTION–III: IR SPECTRAL CHARACTERIZATION OF COPOLY- URETHANES

This section of the chapter includes IR spectral data of the copolyurethanes.

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.

Figs. 1-4 show IR spectra of BTP-400, BTP-600, BATP-400 and BATP-600, respectively. The observed characteristic bands (cm^{-1}) (Table 4.2) are 3669-3640 (-NH str.) 1990-1938 and 1780-1738 (urethane str.) and 1267-1244 (C-O-C str.) besides normal modes of alicyclic, alkyl and aromatic groups. The traces of the unreacted isocyanate groups may react with the moisture in the environment and ultimately converted into amino groups. Unreacted isocyanate and hence amino groups may affect the ultimate physico-chemical properties of the polyurethanes. Thus, IR spectral study supported the formation of copolyurethanes.

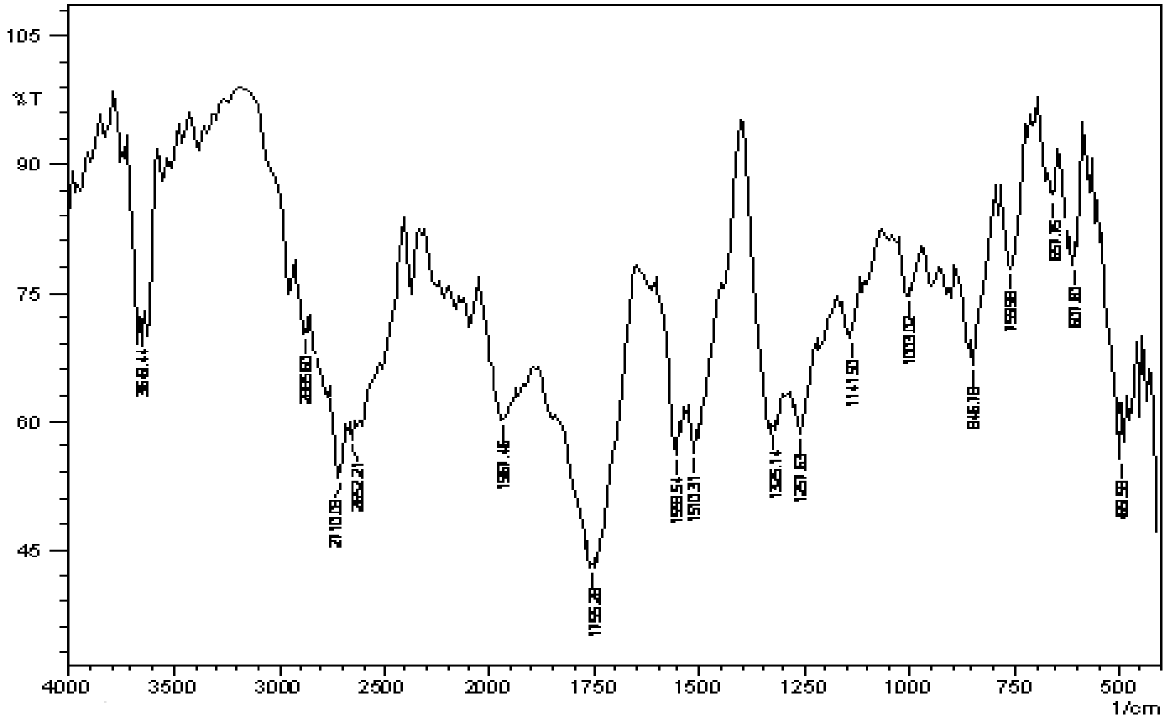


Fig. 4.1: IR spectrum of BTP-400

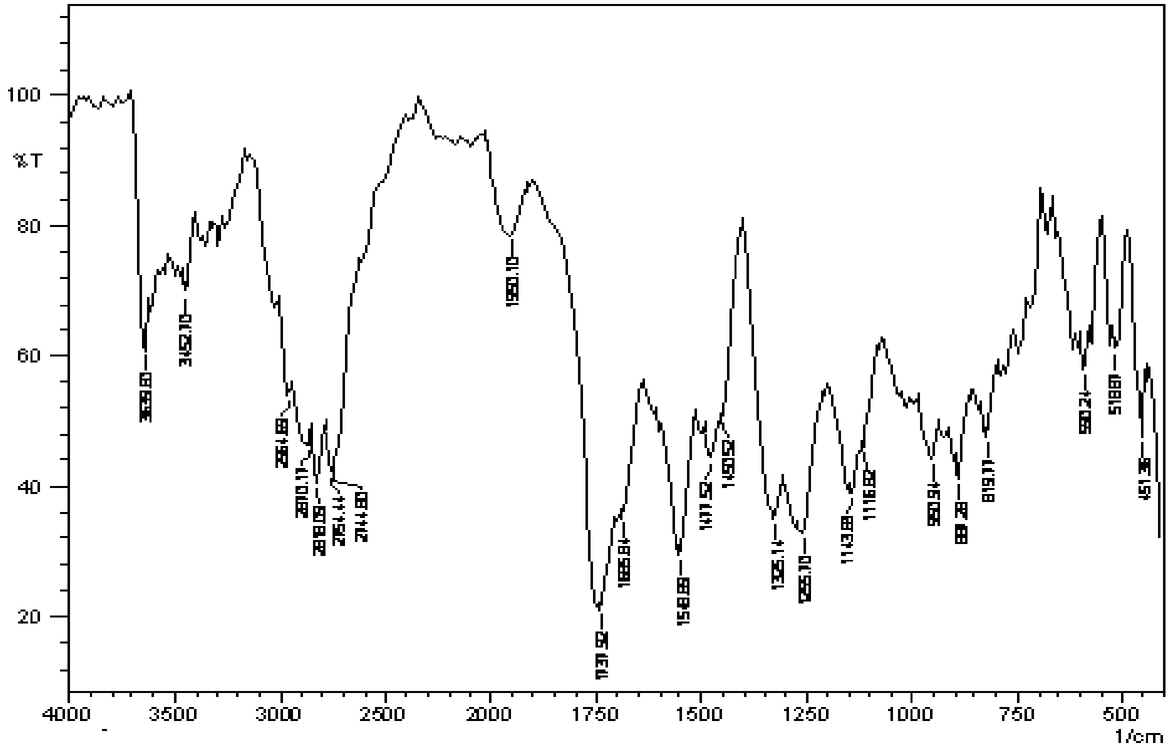


Fig. 4.2: IR spectrum of BTP-600

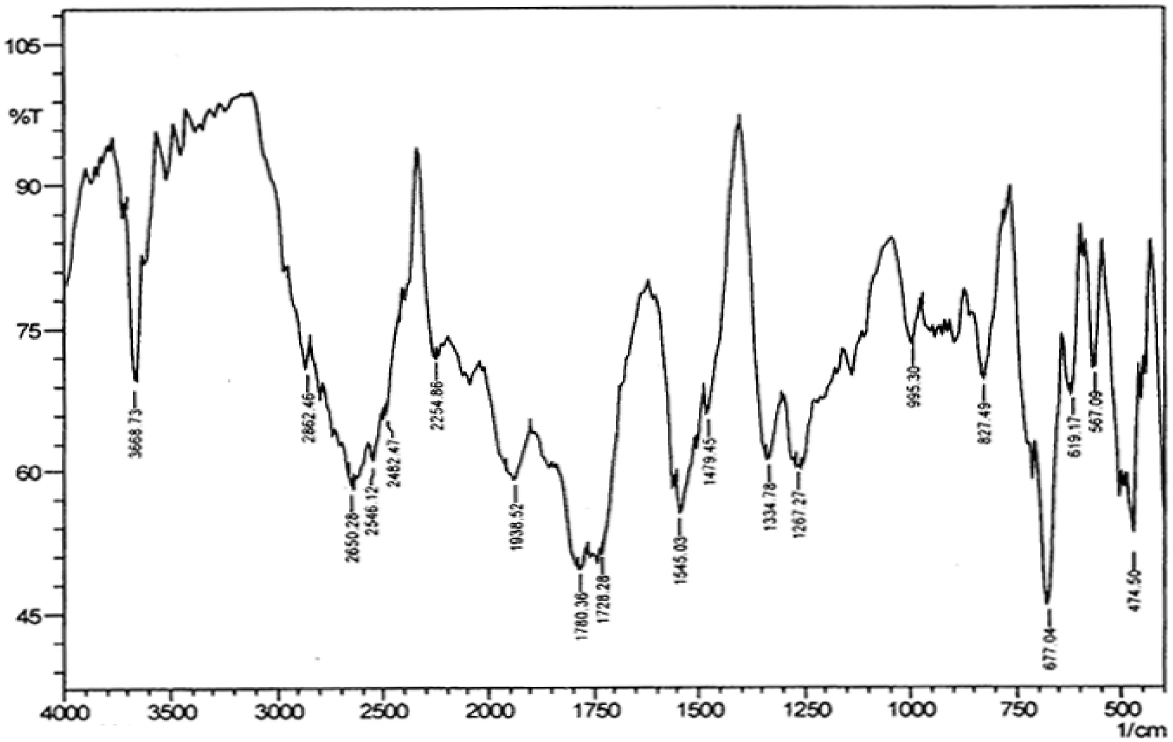


Fig. 4.3: IR spectrum of BATP-400

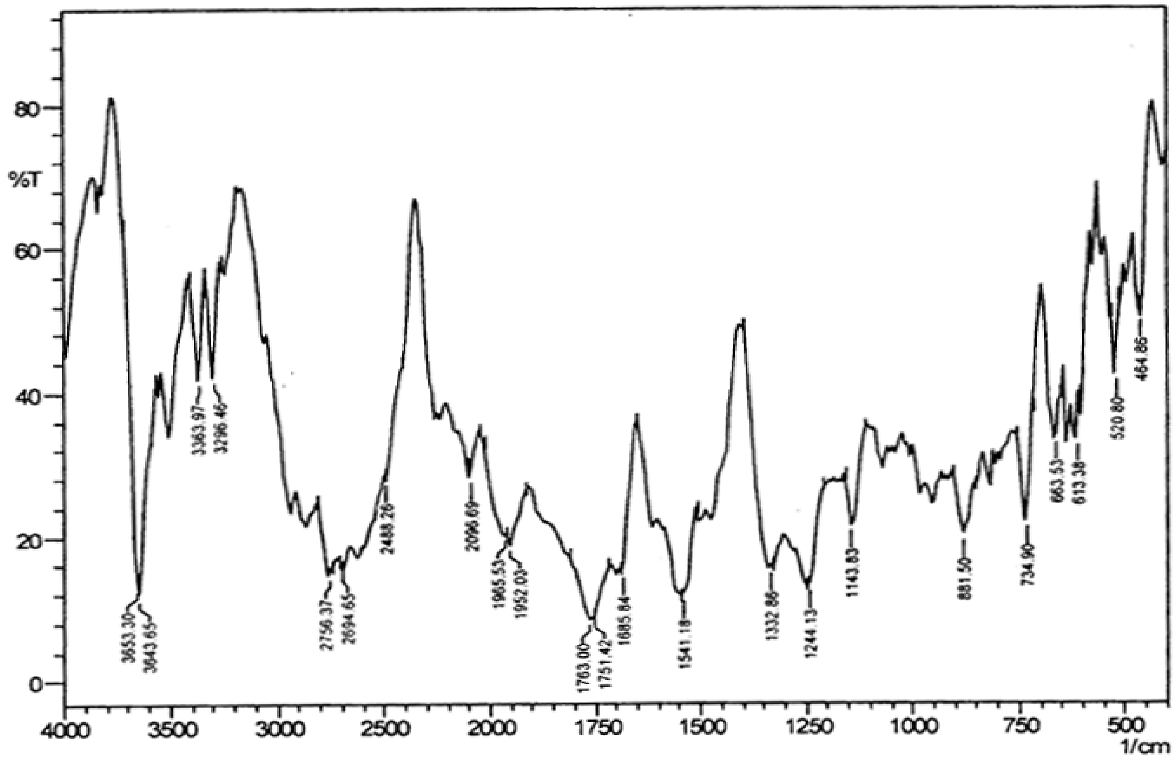
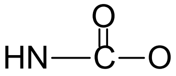
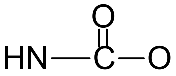
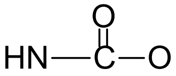
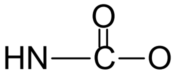


Fig. 4.4: IR spectrum of BATP-600

Table-4.2: The characteristic IR absorption frequencies of copolyurethanes

Resin	Absorption frequency, cm^{-1}	Type
BTP-400	3649.4	-NH and -OH str.
	1967.4 1755.2	 $HN-\overset{O}{\overset{\|}{C}}-O$ str.
	1257.6	C-O-C str.
BTP-600	3639.8	-NH and -OH str.
	1960.1 1737.9	 $HN-\overset{O}{\overset{\|}{C}}-O$ str.
	1255.7	C-O-C str.
BATP-400	3668.7	-NH and -OH str.
	1938.5 1780.3	 $HN-\overset{O}{\overset{\|}{C}}-O$ str.
	1267.2	C-O-C str.
BATP-600	3653.3 3643.6	-NH and -OH str.
	1965.5 1763.0	 $HN-\overset{O}{\overset{\|}{C}}-O$ str.
	1244.1	C-O-C str.

SECTION-IV: DENSITY MEASUREMENTS OF COPOLYURETHANE 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 [29-31]. 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. [32] the density of the polymer may be expressed as:

$$\rho = \mathrm{K.M} / \mathrm{N_A}\Sigma\Delta\mathrm{V} \qquad \ldots 4.1$$

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 ΔV_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.

$$\mathrm{K} = \mathrm{K_{int}} / \mathrm{K_{true}} = \frac{\mathrm{N_A}\Sigma\Delta\mathrm{V_i}}{\left(\mathrm{M}/\rho\right)} \qquad \ldots 4.2$$

---

29. H. F. Mark, N. C. Gaylord and N. F. Bikales, "Encyclopedia of Polymer Science and Technology", Vol. 12, Willey Inter science, New York, 1970.
30. C. Tanford, "Physical Chemistry of Macromolecules", John Willey and Sons, Inc. New York, 1961.
31. V. R. Govarikar, N. V. Vishvanathan and J. Sreedhar, "Polymer Science", Willey Eastern Ltd., 1986.
32. G. L. Slonimskii, A. A. Askadskii and A. I. Kitaigorodkii, Vysokomolekulyarnye, Soedineniya, Seriya A, **12**, 494-512, 1970.

Determination of density by floatation method

The densities of BTP-400, BTP-600, BATP-400 and BATP-600 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 [33].

The observed densities of BTP-400, BTP-600, BATP-400 and BATP-600 are 1.2137± 0.0006, 1.2026 ± 0.0008, 1.2343 ± 0.0005 and 1.2232 ± 0.0007 g/cm^3, respectively. From the observed density values, it is clear that the density has decreased with increasing of PEG in molecular weight the copolyurethanes. The observed decrease in density with increasing PEG molecular weight (soft segment) is mainly due to increase of the distance between two crosslink points (hard segment). Physical properties of PUs largely depend upon polymer chain structure, soft and hard segments. The observed decrease of density is due to increase of chain flexibility.

SECTION-V: THERMAL, 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. Copolyurethane films are analyzed by TGA and DSC at the heating rate of 10^0C and 20^0C min^{-1} in an N_2 atmosphere, respectively. The tensile strength, electric strength and volume resistivity of copolyurethane films were determined according to standard test methods and interpreted in terms of increasing molecular weight of PEG, degree of resin cure, etc.

Mechanical and electrical properties of copolyurethanes

---

33. 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.

Materials 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 the 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,and reduced maintenance, obviations of lubrications, weight savings, noise reduction and freedom from corrosion.

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, 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. [34] 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. [35] 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.

Kozakiewicz et al. [36] 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.

---

34. 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.
35. 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.
36. 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.

Bharadwaj et al. [37] have prepared polyurethane (PU) elastomers from castor oil based polyol, polyethylene glycol (PEG) of various molecular weights (200, 400 and 600) and toluene diisocyanate in the form of transparent sheets. The sorption, mechanical and thermal properties have been studied. The solubility parameter, molecular weight between two crosslinks and degree of crosslinking of PU samples were calculated from equilibrium swelling experiments. The kinetic study of swelling revealed that sorption is anomalous in nature in all the samples. Diffusion coefficient (D) and sorption coefficient (S) were found to decrease with an increase in chain length of PEG. The stress-strain data showed that the elastomers obtained using PEG-200 gave the best mechanical properties. The thermal degradation of all elastomers starts at ~250^{0}C, regardless of the PEG chain length. The values of activation energy of degradation were in the range of 600-725 kJ/mole.

Measurements

Tensile strength (ASTM D 638-91), volume resistivity (ASTM-D-257-92) and electric strength (ICE: 243-Pt.-1-1988) measurements were done respectively on a Universal Tensile Testing Machine Model No.1185 at a speed of 50mm/min, Hewlett Packard high resistance meter at 500V DC after charging for 60 sec, a high voltage tester (Automatic Mumbai) in air at 27^{o}C by using 25/75 mm brass electrodes. TGA and DSC thermograms of BTP-400, BTP-600, BATP-400 and BATP-600 were scanned on a Perkin Elmer TGA model No. Pyris-I; and Universal V-3.0G TA-instrument at the heating rate of 10^{0}C and 20^{0}C/min in nitrogen atmosphere, respectively.

Due to brittle nature of BANF-TDI and BANFA-TDI polyurethane films, mechanical and electrical properties were not tested. The tensile strength, electric strength and volume resistivity of BTP-400, BTP-600, BATP-400 and BATP-600 are reported in Table 4.3 from which it is clear that tensile strength and volume resistivity have decreased, while electric strength has increased with increasing chain length of PEG. Introduction of soft segments in the polymer chains increased elasticity and

---

37. V. Bharadwaj, K. Somani and S. Kansara, “The effect of chain length of polyethylene glycol on properties of castor oil based polyurethane elastormers”, J. Macromol. Sci.-Pure and Appl. Chem., **39**, 115-127, 2002.

decreased tensile strength. When the load is applied to the film, because of high flexibility of PEG-400/600, load is thrown away to the rigid segments of copolyurethanes and as a result stress is concentrated at the junction of rigid and soft segments resulting in rupture at low load. Thus, due to lack of mutual co-ordination between hard and soft segments resulted non-uniform stress distribution and hence caused decrease in tensile strength. Increase of electric strength and decrease of volume resistivity with increasing chain length of PEG are due to decrease in intermolecular interaction forces and increase in chain length flexibility. Besides these many more 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 electrical properties of the material, sample thickness, impurities, extent of ageing, etc affect the mechanical and electrical properties. Thus, the resultant structure of copolyurethanes affected both mechanical and electrical properties to a considerable extent.

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 surface [38]. The volume resistivity mainly depends on the presence of free charge and their mobility. Thus, increase in chain length of PEG in copolyurethane result decrease in tensile strength and volume resistivity and increase in electric strength. Fairly moderate tensile strength, good electric strength and volume resistivity of copolyurethanes indicated their usefulness as insulating, adhesive and coating materials.

Thermal analysis of copolyurethane 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 levels off. TGA curves are characteristic for a given polymer because of unique sequence of

---

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

Table-4.3: Mechanical and electrical properties of copolyurethanes

Copolyurethane films	Tensile strength, MPa	Electrical strength, kV/mm	Volume resistivity, Ω cm
BTP-400	11.36	16.09	1.89×10^{12}
BTP-600	10.21	26.89	1.63×10^{12}
BATP-400	18.0	18.5	4.6×10^{11}
BATP-600	16.7	20.0	4.4×10^{11}

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.

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 [39,40].

Chiang et al. [41] 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.

---

39. D. W. Levi, L. Reich and H. T. Lee, "Degradation of polymers by thermal gravimetric techniques", Polym. Eng. Sci., **5**, 135-141, 1965.
40. H. L. Friedman, U. S. Dept. Com., Office. Tech., 24 (1959); C.A. **55**, 26, 511, 1961.
41. 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.

Suresh et al. [42] 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 methane diisocyanate (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.

Thermal studies of intercross-linked networks based on siliconized polyurethane-epoxy/unsaturated polyester were reported by Prabhu and Alagar [43]. Epoxy and unsaturated polyester (UP) resins were modified with PU prepolymer and hydroxyl terminated polydimethylsiloxane (HTPDMS) using γ-aminopropyl triethoxysilane (γ-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 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 10 wt. % silicone into PU modified epoxy/UP systems improved their thermal stability due to the partial ionic nature, high bond energy and thermal stability of -Si-O-Si- linkage.

---

42. 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.
43. L. 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.

Lee et al. [44] 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 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).

Thermal analysis of polymers is of paramount importance especially for the study of degradation kinetics, degradation mechanism, bond strength, thermal stability and molecular architecture. It is also useful in designing materials for high temperature applications and for the identification purposes as well as processability. TGA provides qualitative and semi quantitative rapid comparison about thermal stability and degradation finger prints of polymers [45]. The characteristic temperatures for the assessment of the relative thermal stability of polymers are initial decomposition temperature (T_0), temperature of 10 % weight loss (T_{10}), temperature of maximum weight loss (T_{max}) and temperature of final decomposition (T_f). DTA or DSC technique provides much useful information about physico-chemical changes occurring during heating of the polymeric materials. Thermal analysis of polymers is useful in designing articles for specific applications.

DSC and TG thermograms of BTP-400, BTP-600, BATP-400, and BATP-600 were scanned without thermal treatment are presented in Figs. 4.5-4.8 (DSC) and

---

44. 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.
45. L. Reich, D. W. Levi., In: Peterlin, Goodman, Editors Macromolecular Reviews. New York: Wiley-Interscience, 1, 173 1968.

Figs. 4.9 - 4.12 (TGA). DSC transition temperatures, T_0, T_{10}, T_{max}, T_f, decomposition range, % weight loss and % residual weight at the end of the reaction are reported in Table 4.4. From Figs. 4.9-4.12 it is observed that no T_g is detected clearly. Exothermic transition at 76.8^{0}C (BTP-400), 70.5^{0}C (BTP-600), 89.0^{0}C (BATP-400) and 97.3^{0}C (BATP-600) is due to some physical change and it is further confirmed no weight loss over that temperature (Figs. 4.9-4.12). Other endothermic transitions at 221.4 and 339.3^{0}C for BTP-400, 230.4 and 342.9^{0}C for BTP-600, 245.3 and 357.0^{0}C for BATP-400 and at 247.3 and 354.5^{0}C for BATP-600 are due to degradation of copolyurethanes and are further confirmed by weight loss in corresponding TG thermogram over that temperature in Figs. 4.9-4.12. Copolyurethanes are thermally stable up to about 100-120^{0}C. BTP-400, BTP-600, BATP-400 followed single step degradation while BATP-600 followed two step degradation involving ~34-55% weight loss and ~21-33% residual weight at 600^{0}C indicating formation of highly thermally stable compound. Decomposition of urethane linkages led to formation of carbon dioxide, carbon monoxide, alcohols, amines, aldehydes, etc. [46]. From Table-4.4, it is observed that thermal stability increased a little with increase of PEG molecular weight, but T_{max}, % weight loss and % residue are increased considerably. Similarly endothermic transitions also increased with increasing PEG molecular weight.

Kinetic parameters such as energy of activation (E_a), frequency factor (A), order of reaction (n) and entropy change (ΔS^*) are determined according to Anderson-Freeman method [47].

$$\Delta \ln dW/dt = n \,\Delta \ln W - (E_a/R)\,\Delta (1/T) \quad .....4.3$$

$$A = E_a\beta / RT^{2}\; e^{E_a/RT} \quad .....4.4$$

$$\Delta S^* = R \ln (Ah/kT) \quad .....4.5$$

Where β is the heating rate, R is the gas constant, h is the Planck's constant, T is the temperature and k is the Boltzmann constant. Other symbols have their own usual meaning. The detail calculations according to Eqn 4.3 for BTP-400, BTP-600,

---

46. B. K. Kendagannaswamy, Siddaramaiah, "Chain-extended polyurethanes - synthesis and characterization", J. Appl. Polym. Sci., **84**, 359-369, 2002.
47. D. A. Anderson, E. S. Freeman, "Kinetics of the thermal degradation polystyrene and polyethylene", J. Polym. Sci., **54**, 253-260, 1961.

BATP-400 and BATP-600 are presented in Tables 4.5-4.8 and the plots of ΔlndW/dt against Δ lnW are presented in Figs 4.13 and 4.14. The least square values of above mentioned parameters along with regression coefficients (R^2) are reported in Table 4.9 from which, it is clear that BTP-400 and BTP-600 copolyurethanes followed second order (2.3-2.4) degradation kinetics, while BATP-400 and BATP-600 copolyurethanes followed fractional order (1.4-1.5) order degradation kinetics. The activation energy has decreased with increasing PEG molecular weight in the copolyurethane chains. In accordance with theory higher is the value of E higher is the magnitudes of A. On the basis of E_a and A values we can say that BTP-400 is some what more rigid than that of BTP-600. Similarly BATP-400 is some what more rigid than that of BATP-600. The entropy change ΔS* for BTP-400, BTP-600, BATP-400 and BATP-600 was determined at their respective T_{max} according to equation 4.5 and is also reported in Table 4.5. The large and positive magnitudes of ΔS* for BTP-400 has confirmed less ordered transition state than individual polymer molecules, while large and negative magnitudes of BTP-600, BATP-400 and BATP-600 confirmed highly ordered transition states.

Degradation process is a complex process and involves a variety of reactions such as chain cleavage, branching, rearrangement, cross-linking, etc. Selective degradation occurs from weak points in the chains and consequently formation of free radials result, which further undergo a variety of reactions and degrade at higher temperature (>600^0C) to form low molecular weight substances. Increasing PEG molecular weight did not affect thermal stability much but it has increased T_{max}, % weight loss and % residue considerably.

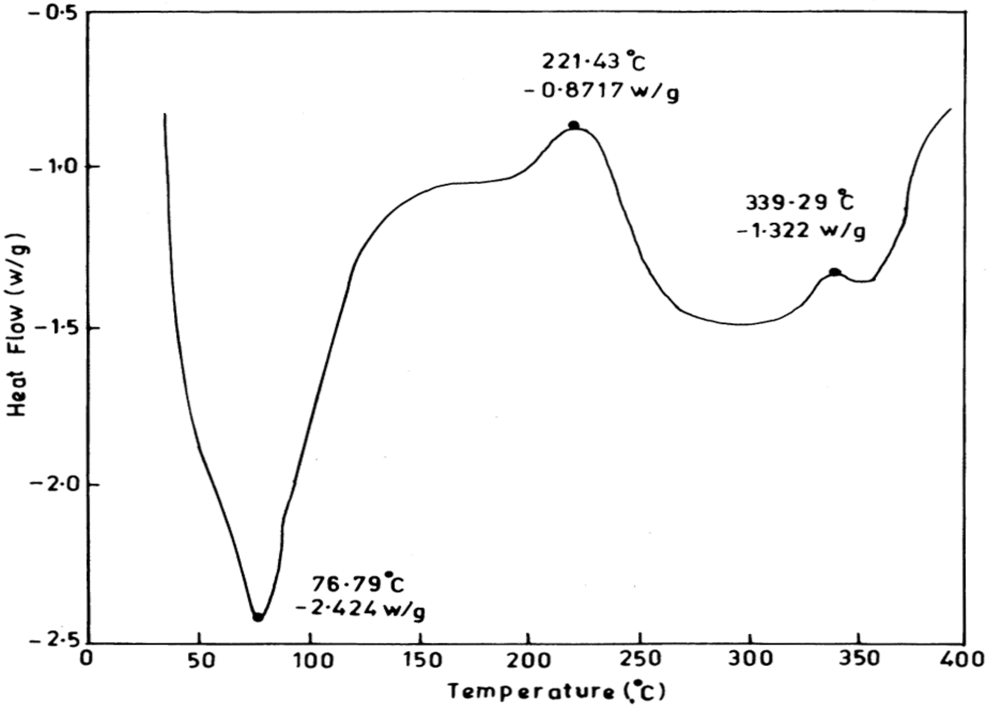


Fig. 4.5: DSC thermogram of BTP-400 at the heating rate of 20^{0}C/min in an N$_2$ atmosphere

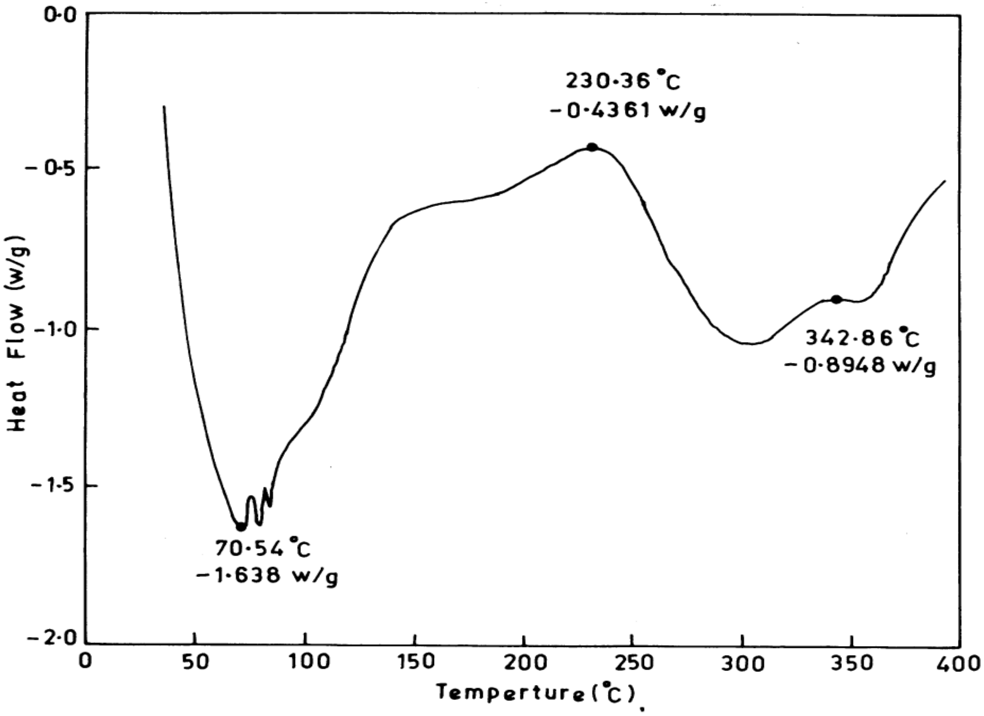


Fig. 4.6: DSC thermogram of BTP-600 at the heating rate of 20^{0}C/min in an N$_2$ atmosphere

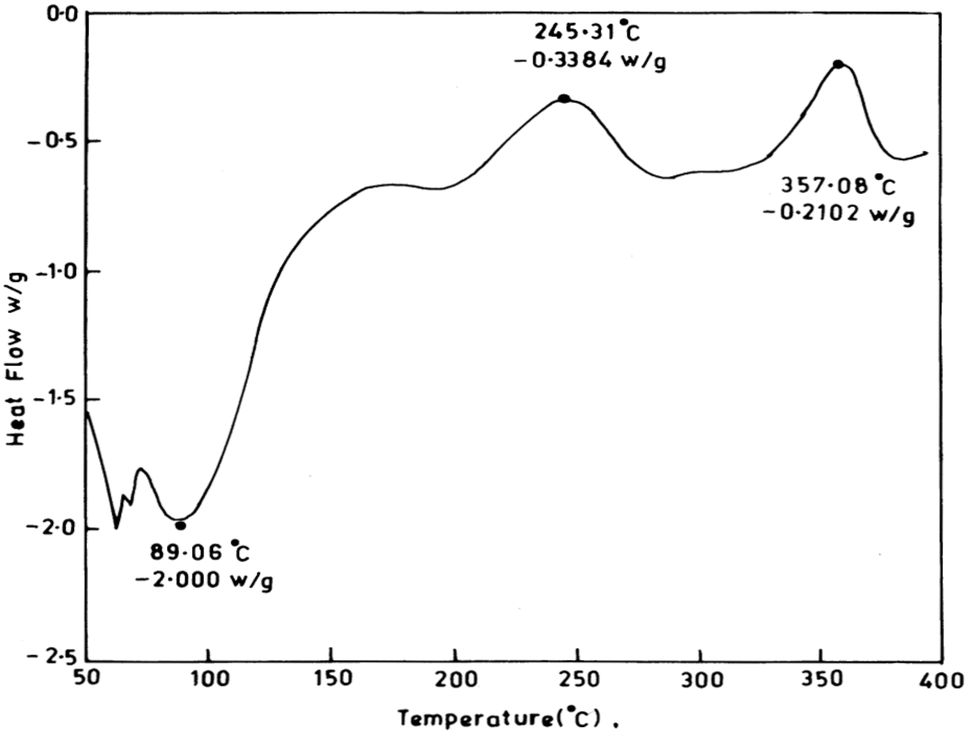


Fig. 4.7: DSC thermogram of BATP-400 at the heating rate of 20^{0}C/min in an N$_2$ atmosphere

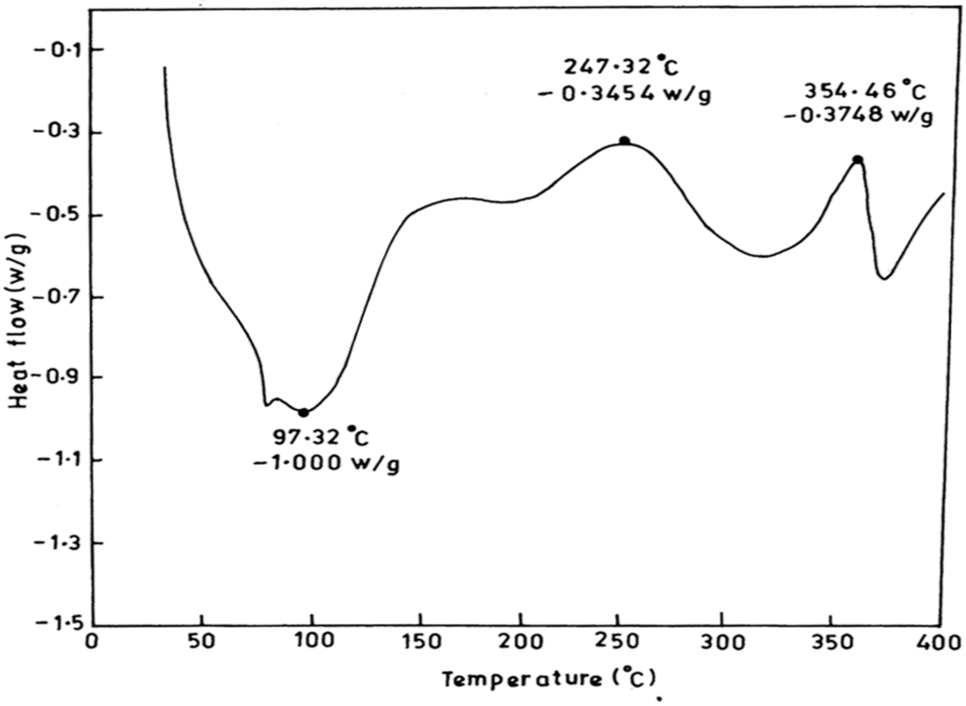


Fig. 4.8: DSC thermogram of BATP-600 at the heating rate of 20^{0}C/min in an N$_2$ atmosphere

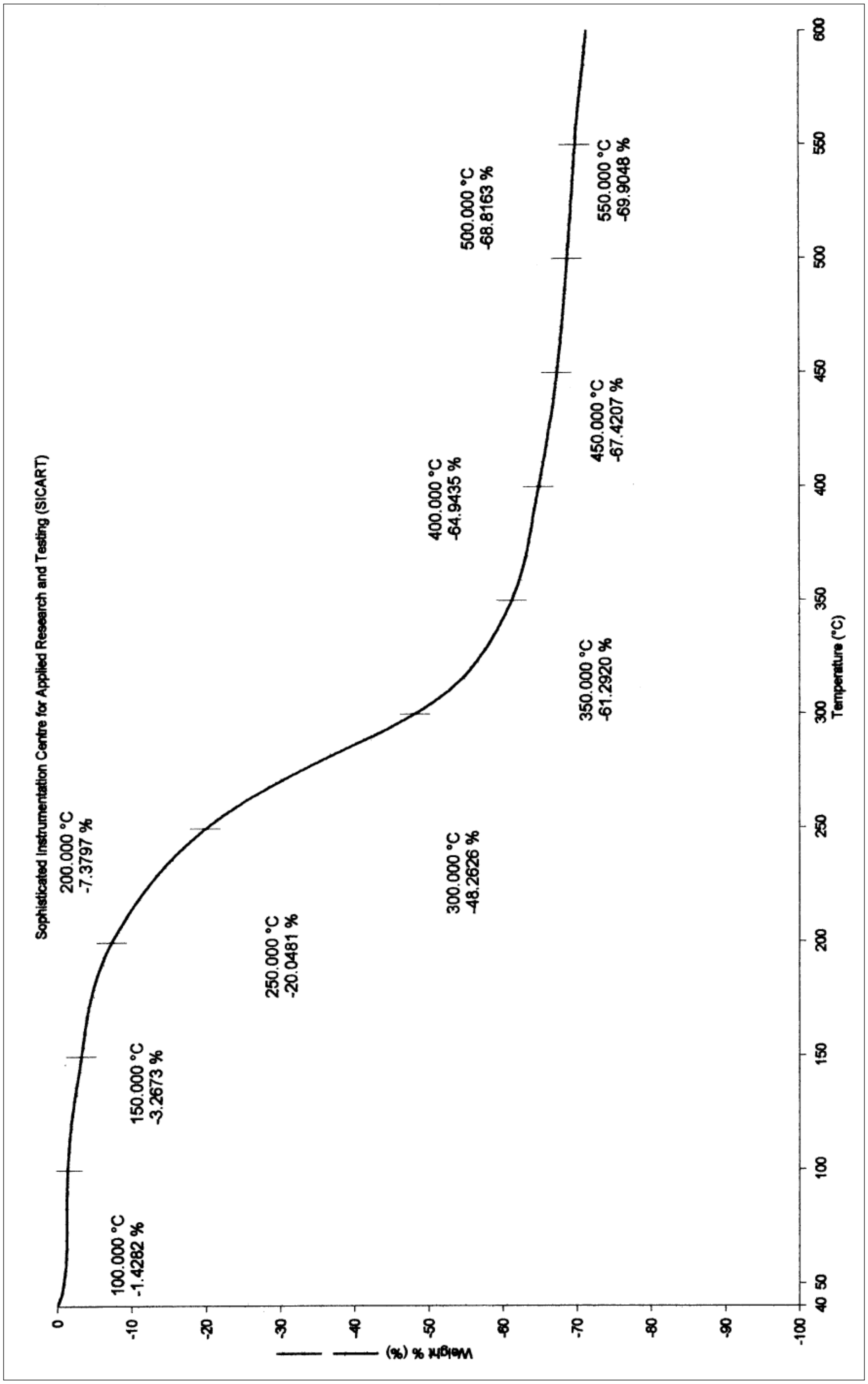


Fig. 4.9: TG thermogram of BTP- 400 at the heating rate of 10^0C/min in an N_2 atmosphere

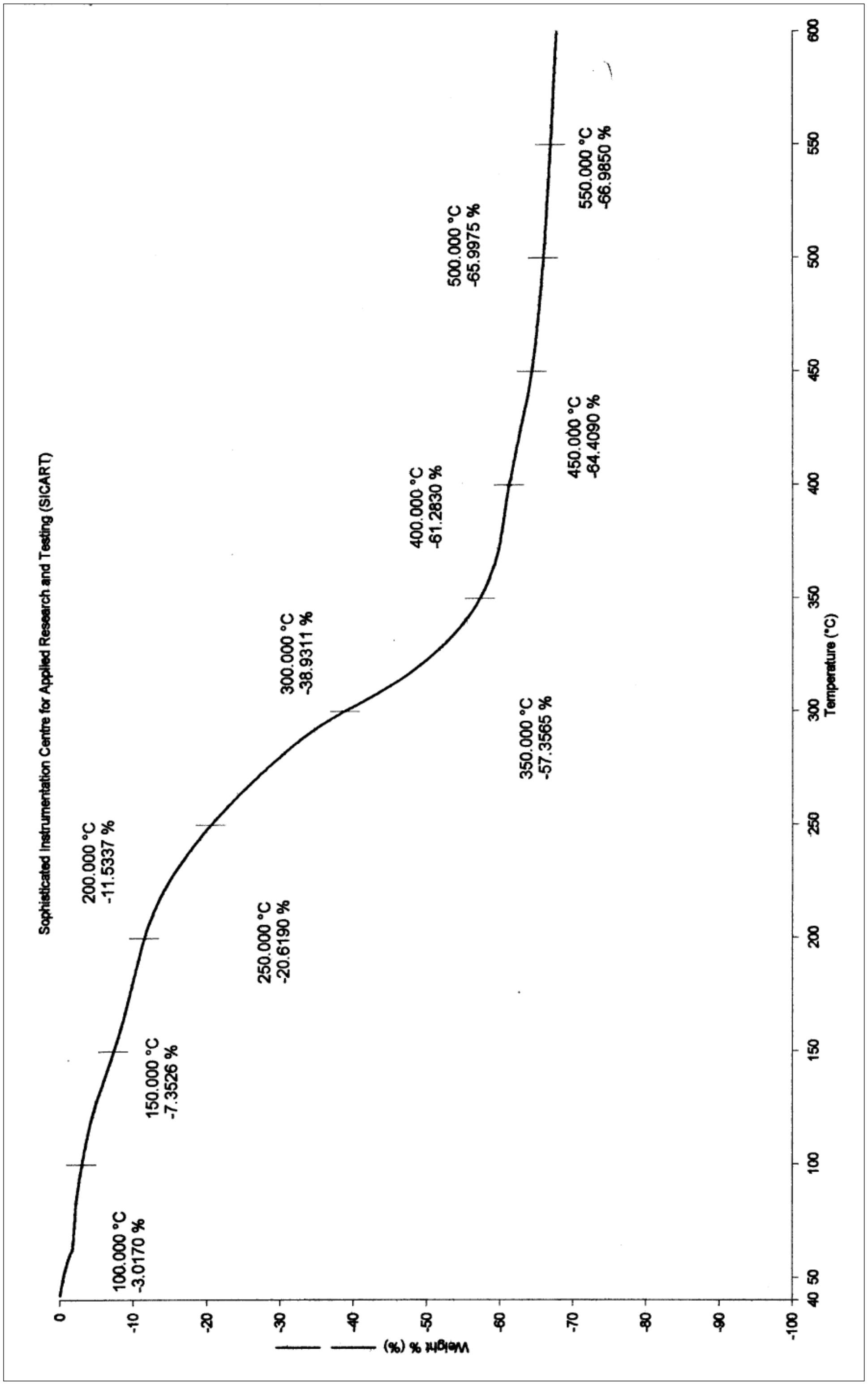


Fig. 4.10: TG thermogram of BTP- 600 at the heating rate of 10^0C/min in an N_2 atmosphere

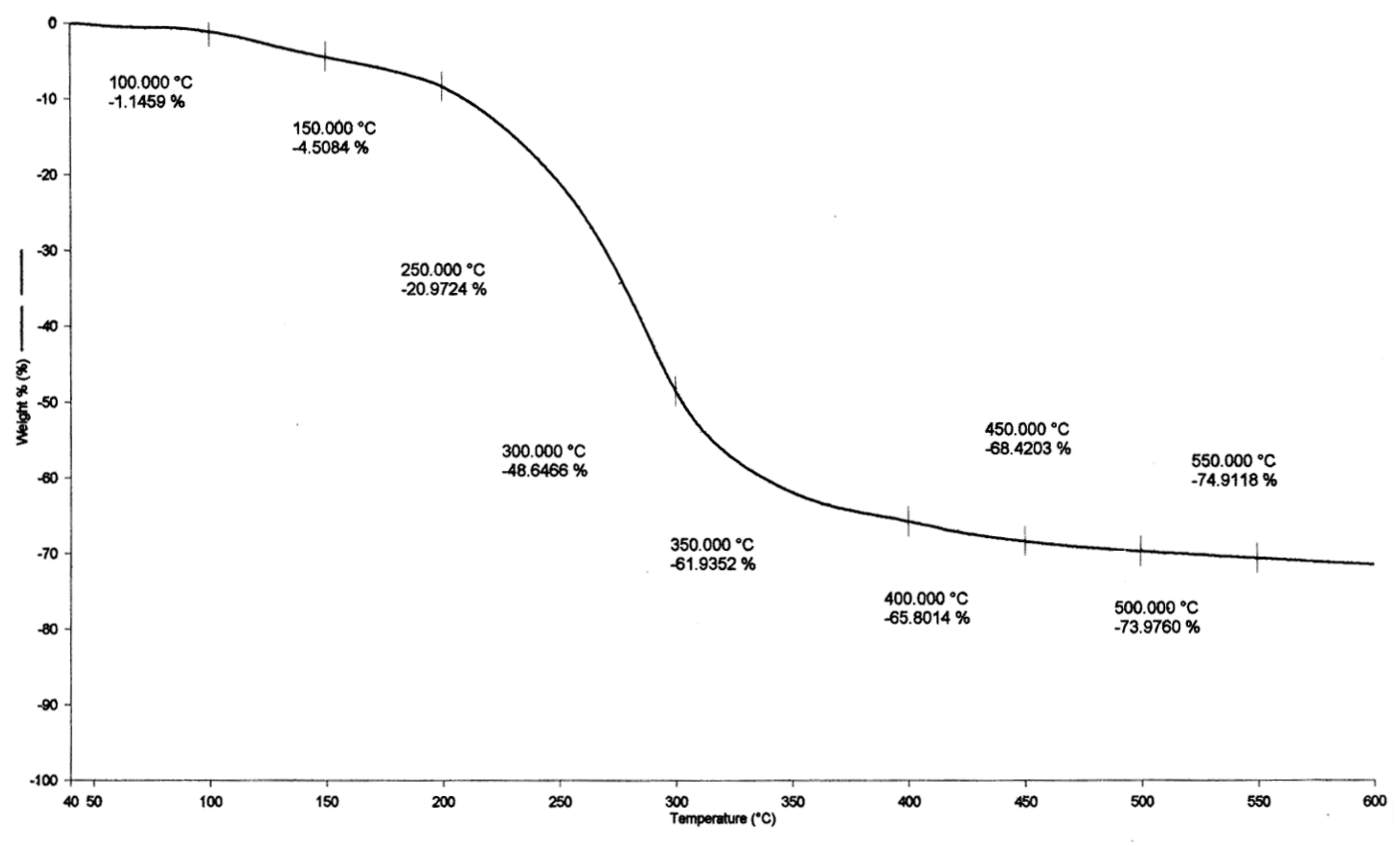


Fig. 4.11: TG thermogram of BATP- 400 at the heating rate of 10^0C/min in an N_2 atmosphere

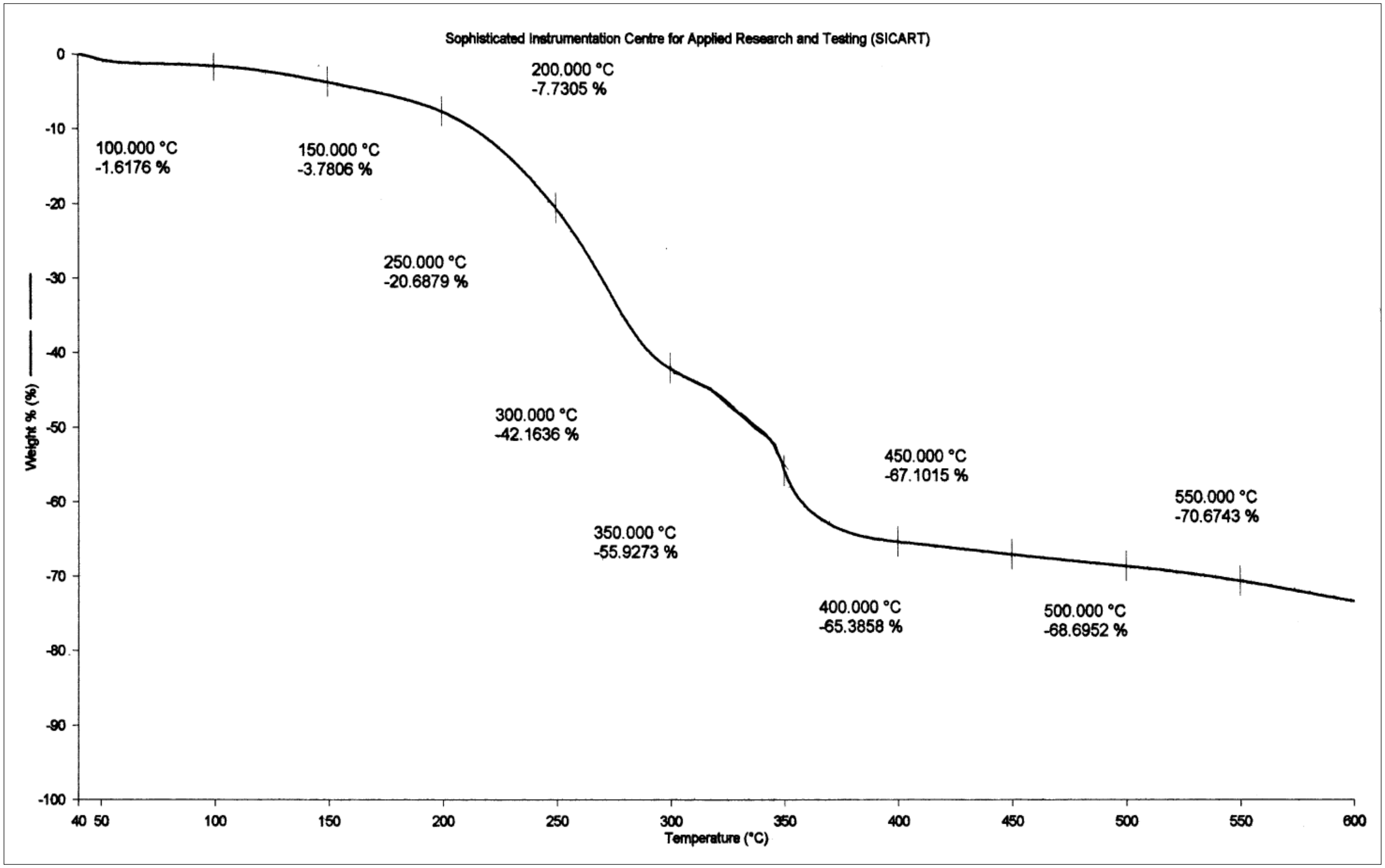


Fig. 4.12: TG thermogram of BATP- 600 at the heating rate of 10^0C/min in an N_2 atmosphere

Table 4.4 DSC and TGA data of copolyurethanes

Co-polyure-thane	Transition Temp., °C	T_0, °C	T_{10}, °C	T_f, °C	T_{max}, °C	Decompn. Range, °C	% wt. loss	% Residue
BTP-400	76.8 (Exo) 221.4 (Endo) 339.3 (Endo)	114.9	212.8	475.5	275.6	115-478	34.4	28.6
BTP-600	70.5 (Exo) 230.4 (Endo) 342.9 (Endo)	119.1	182.9	460.6	300.0	119-461	41.0	32.5
BATP-400	89.0 (Exo) 245.3(Endo) 357.0(Endo)	102.1	258.5	414.9	287.2	102-415	39.9	21.8
BATP-600	97.3 (Exo) 247.3 (Endo) 354.5 (Endo)	125.6 310.7	211.7 342.8	304.3 391.5	343.6	126-304 311-392	54.9	26.6

Table 4.5: The calculation scheme for BTP-400 by Anderson-Freeman method

$10^3/T$	% wt. loss	W	lnW	dw\dt	lndw/dt	ΔlnW	Δlndw/dt
1.72	52.32	16.3	2.791	3.92	1.366	-0.177	-0.170
1.74	49.16	19.46	2.968	4.65	1.536	-0.166	-0.127
1.76	45.64	22.98	3.134	5.28	1.663	-0.150	-0.092
1.78	41.91	26.71	3.285	5.79	1.756	-0.132	-0.058
1.80	38.12	30.5	3.417	6.14	1.814	-0.115	-0.027
1.82	34.38	34.24	3.533	6.31	1.842	-0.099	0.001
1.84	30.8	37.82	3.632	6.3	1.840	-0.084	0.028
1.86	27.45	41.17	3.717	6.12	1.811	-0.071	0.057
1.88	24.4	44.22	3.789	5.78	1.754	-0.059	0.088
1.90	21.68	46.94	3.848	5.29	1.665	-0.049	0.120
1.92	19.31	49.31	3.898	4.69	1.545	-0.040	0.154
1.94	17.29	51.33	3.938	4.02	1.391	-0.032	0.188
1.96	15.6	53.02	3.970	3.33	1.202	-0.026	0.213

Table 4.6: The calculation scheme for BTP-600 by Anderson-Freeman method

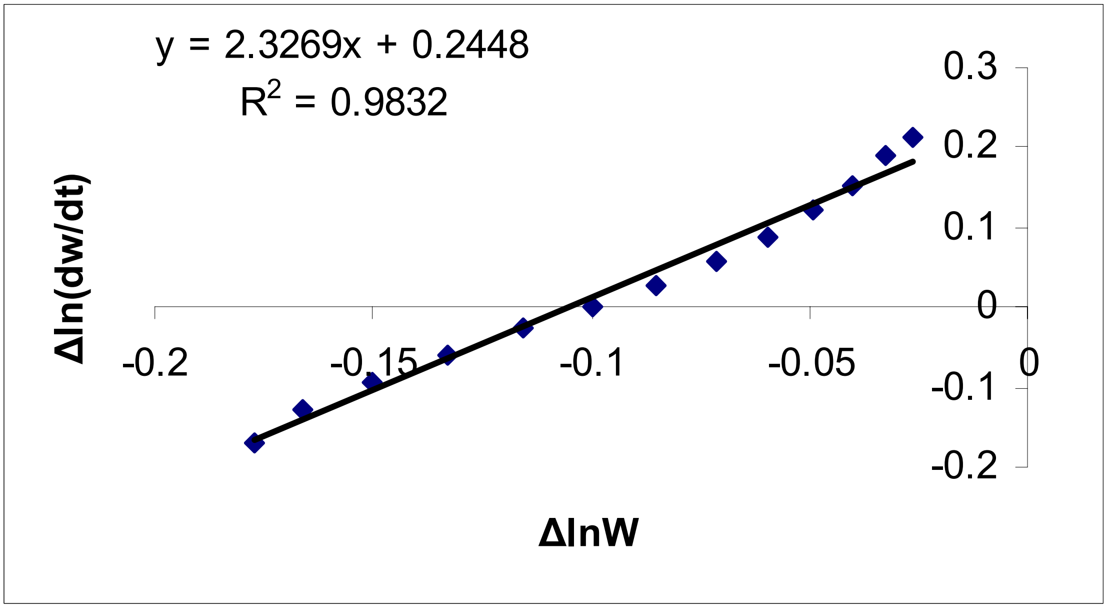
10^3/T	% wt. loss	W	lnW	dw\dt	lndw/dt	ΔlnW	Δlndw/dt
1.72	44.16	21.36	3.061	4.92	1.593	-0.071	-0.030
1.73	42.58	22.94	3.132	5.07	1.623	-0.066	-0.011
1.74	41.00	24.52	3.199	5.13	1.635	-0.062	0.003
1.75	39.43	26.09	3.261	5.11	1.631	-0.057	0.015
1.76	37.88	27.64	3.319	5.03	1.615	-0.053	0.024
1.77	36.37	29.15	3.372	4.91	1.591	-0.049	0.035
1.78	34.89	30.63	3.421	4.74	1.556	-0.045	0.043
1.79	33.47	32.05	3.467	4.54	1.512	-0.041	0.047
1.80	32.10	33.42	3.509	4.33	1.465	-0.038	0.052
1.81	30.79	34.73	3.547	4.11	1.413	-0.035	0.057

Table 4.7: The calculation scheme for BATP-400 by Anderson-Freeman method

10^3/T	% wt. loss	W	lnW	dw\dt	lndw/dt	ΔlnW	Δlndw/dt
1.75	50.11	17.13	2.840	5.74	1.747	-0.108	-0.049
1.76	48.15	19.09	2.949	6.03	1.796	-0.100	-0.035
1.77	46.13	21.11	3.049	6.25	1.832	-0.093	-0.023
1.78	44.05	23.19	3.143	6.40	1.856	-0.085	-0.010
1.79	41.97	25.27	3.229	6.47	1.867	-0.078	0
1.80	39.90	27.34	3.308	6.47	1.867	-0.071	0.007
1.81	37.86	29.38	3.380	6.42	1.859	-0.064	0.018
1.82	35.89	31.35	3.445	6.30	1.840	-0.059	0.025
1.83	33.98	33.26	3.504	6.14	1.814	-0.052	0.034
1.84	32.17	35.07	3.557	5.93	1.780	-0.047	0.041
1.85	30.45	36.79	3.605	5.69	1.738	-0.042	0.048
1.86	28.84	38.40	3.648	5.42	1.690	-0.038	0.054
1.87	27.34	39.90	3.686	5.13	1.635	-0.034	0.062
1.88	25.95	41.29	3.720	4.82	1.572	-0.030	0.066
1.89	24.68	42.56	3.750	4.51	1.506	-0.026	0.073

Table 4.8: The calculation scheme for BATP-600 by Anderson-Freeman method

$10^3/T$	% wt. loss	W	lnW	dw\dt	lndw/dt	ΔlnW	Δlndw/dt
1.59	60.56	4.96	1.601	3.87	1.353	-0.296	-0.159
1.60	58.85	6.67	1.897	4.54	1.512	-0.254	-0.076
1.61	56.92	8.60	2.151	4.90	1.589	-0.209	-0.016
1.62	54.92	10.6	2.360	4.98	1.605	-0.168	0.032
1.63	52.98	12.54	2.528	4.82	1.572	-0.133	0.075
1.64	51.19	14.33	2.662	4.47	1.497	-0.104	0.116
1.65	49.61	15.91	2.766	3.98	1.381	-0.079	0.160
1.66	48.30	17.22	2.846	3.39	1.220	-0.059	0.198
1.67	47.24	18.28	2.905	2.78	1.022	-0.044	0.229
1.68	46.41	19.11	2.950	2.21	0.792	-0.032	0.244



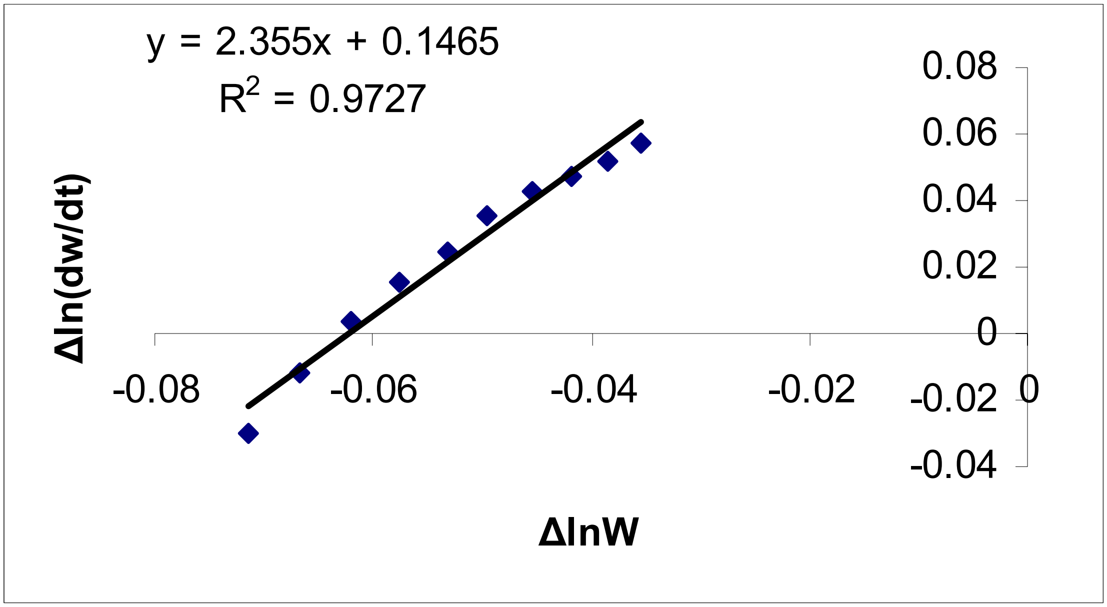
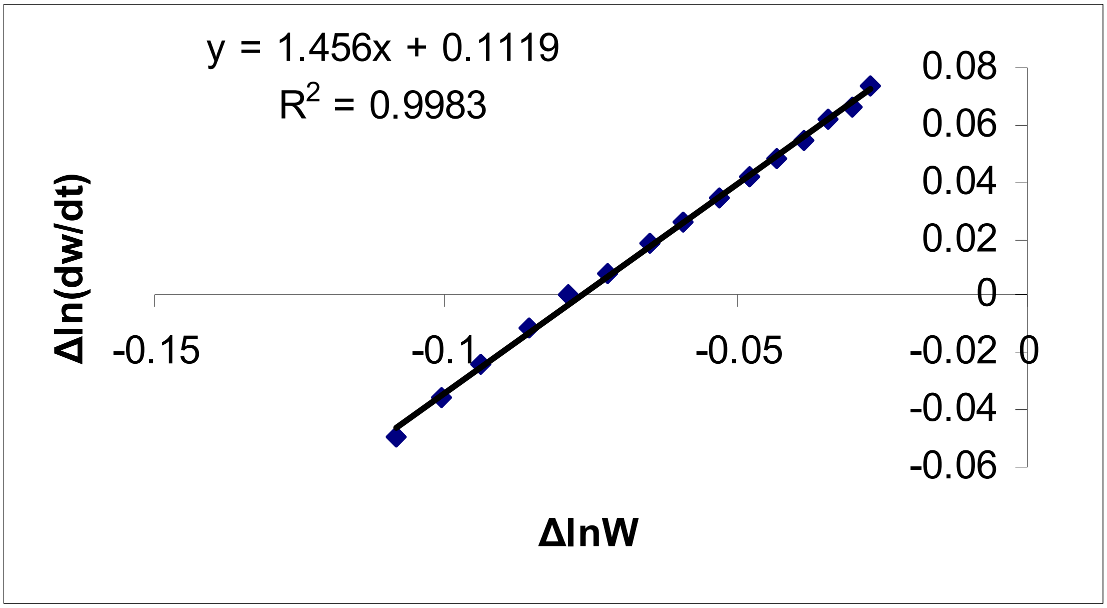


Fig. 4.13: The Anderson-Freeman plots for BTP-400 and BTP-600



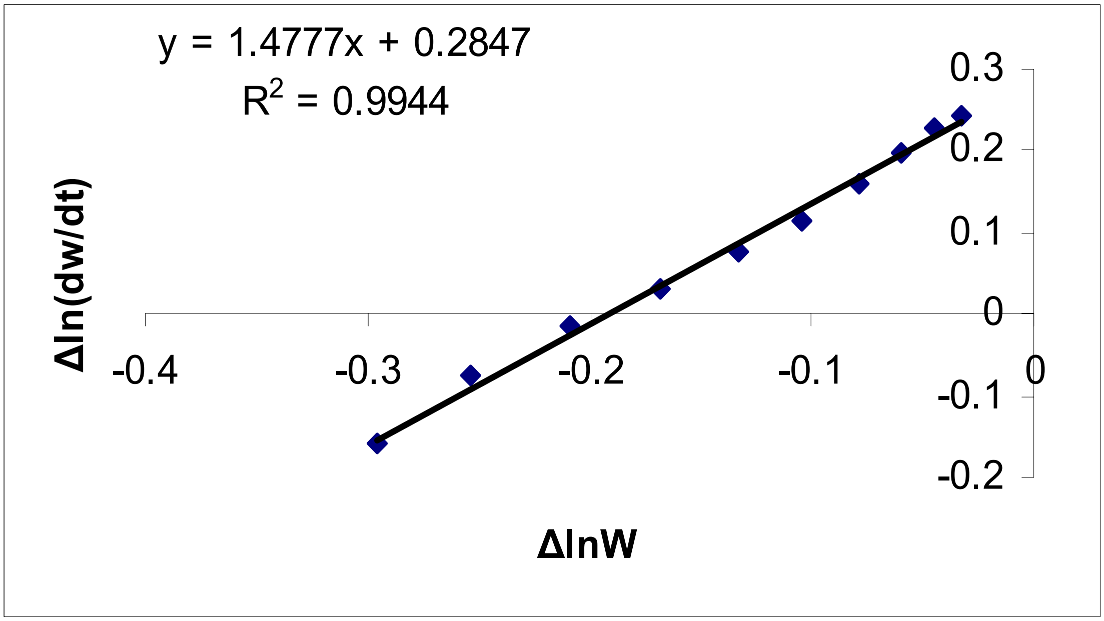


Fig. 4.14: The Anderson-Freeman plots for BATP-400 and BATP-600

Table 4.9: Kinetic parameters of copolyurethanes

Copolyurethane	n	E_a, kJ	A, S^{-1}	ΔS^*, JK^{-1}	Regression coefficient, R^2
BTP-400	2.3	194	$3.8X10^{16}$	67.4	0.983
BTP-600	2.4	125	$1.8X10^{9}$	-72.8	0.973
BATP-400	1.5	113	$5.4X10^{7}$	-121.2	0.998
BATP-600	1.4	96	$2.2X10^{6}$	-110.3	0.997

SECTION-VI: WATER UPTAKE STUDY OF COPOLYURETHANE FILMS

Polymeric materials absorb moisture in humid atmosphere and when immersed in water. The extent of water uptake 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 uptake 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 [48]. 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 water uptake of the material is determined by averaging the change in mass of several specimens.

Ajithkumar et al. [49] have performed equilibrium swelling experiments of interpenetrating polymer networks (IPNs) based on castor oil-based polyurethanes (PU) and unsaturated polyester (UPE) in various solvents, in order to calculate their solubility parameter. The kinetics of swelling and sorption were also studied in chlorobenzene at 25^0C. IPNs with various weight compositions of PU and UPE (80:20, 50:50 and 20:80) (NCO/OH ratio) viz. 1.2, 1.5 and 2.0 were used in the study. The results were found to vary with the weight compositions of the components of the samples. The sorption behavior also varies with the hydroxyl number (mol. wt.) of the polyol used in the preparation of PU. The sorption was anomalous in nature in all the cases. The diffusion coefficient (D) increased with both an increase in NCO/OH ratio and UPE content, whereas the sorption coefficient (S) showed a reverse trend in all the samples studied.

---

48. L. R. Bao and A. F. Yee, “Effect of temperature on moisture absorption in bismaleimides resin and its carbon fiber composites”, Polymer, **43**, 3987-3996, 2002.
49. S. Ajithkumar, N. K. Patel and S. S. Kansara, “Sorption and diffusion of organic solvents through interpenetrating polymer networks (IPNs) based on polyurethane and unsaturated polyester”, Euro. Polym. J., **36**, 2387–2393, 2000.

Somani et al. [50] have studied the equilibrium swelling of polyurethanes (PU) in various solvents in order to calculate their solubility parameter. The kinetics of swelling and sorption were also been studied in 1,4-dioxane at 30^0C. The PU was synthesized by reacting a novel polyol (castor oil derivative and epoxy based resin, EpxR) and one of the polyethylene glycols (PEG 200, PEG 400, PEG 600) with different weight compositions, with a toluene diisocyanate (TDI) adduct (derived from toluene diisocyanate and R60 polyol). Different NCO/OH ratio viz. 1, 1.3 and 1.7 were employed in the study. The results were found to vary with the weight composition of polyol components, as well as the crosslink density of the samples. The sorption behavior was also found to vary with the molecular weight of polyethylene glycol employed in the preparations of the polyurethanes. Kinetic studies of swelling revealed that the sorption was anomalous in nature. The diffusion coefficient (D) increased with an increase in the NCO/OH ratio and decreased with an increase in chain length of polyethylene glycol. The sorption coefficient (S) decreased with an increase in crosslink density (NCO/OH) and increased with increasing polyethylene glycol (i.e., PEG 200, PEG 400, and PEG 600) moieties in the polyurethanes.

Water uptake of BTP-400, BTP-600, BATP-400 and BATP-600 films against various reagents at room temperature was determined according to change in weight method:

$$\%\Delta M = \left[{(M_2 - M_1)}\big/{M_1}\right] X100 \qquad \ldots 4.6$$

Where ΔM is the change in weight, M_1 is the initial weight and M_2 is the weight after chemical treatment with time.

Water uptake study of BTP-400, BTP-600, BATP-400 and BATP-600 films was tested against various reagents (water, 10% each of aq. HCl, HNO_3, H_2SO_4, NaOH, KOH and NaCl) at room temperature at the interval of 24h by change in

---

50. K. P. Somani, N. K. Patel, S. S. Kansara and A. K. Rakshit, “Effect of chain length of polyethylene glycol and crosslink density (NCO/OH) on properties of castor oil based polyurethane elastomers”, J. Macromol. Sci. Pure and Appl. Chem., **43**, 797-811, 2006.

weight method (Figs. 4.15-4.18). Equilibrium % weight gain and equilibrium time data are reported in Table 4.6 from which it is clear that BTP-600 has higher water uptake tendency as compared to BTP-400. Similarly BATP-600 has higher water uptake tendency as compared to BATP-400 due to long PEG chain length and hence this increased solvation tendency. From Table 4.10, it is also observed that the nature of strong electrolytes have affected water structure and hence water uptake tendency via H-bond formation due to presence of amino, urethane and ether groups [50-51]. Strong electrolytes break water structure and hence result increase in diffusivity. The observed water absorption order is HCl > H_2SO_4 > HNO_3 > KOH > NaOH > NaCl > H_2O. Absorbed water induces irreversible changes namely chemical degradation and cracking, while hydrophilic polar groups are responsible for blistering. Cracking and blistering cause high water absorption [48]. Thus, copolyurethanes possess excellent hydrolytic stability against water, saline, alkaline and acidic environments.

SECTION-VII: SURFACE COATING AND CHEMICAL RESISTANCE STUDY OF COPOLYURETHANES

This section of the chapter describes the surface coating application of polyurethane resin on different substrates such as copper, mild steel and aluminium. The chemical resistance of coated samples is tested against water, acid and salt 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 its appearance. They may be applied as liquids, gases or solids.

Ancient painted walls, to be seen at Dendera-Egypt, although exposed for many ages to the open air, still possess a perfect brilliancy of color, as vivid as when painted, perhaps 2000 years ago. The Egyptians mixed their colors with some gummy substance and applied them detached from each other without

---

50. 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**, 2824-2832, 2002.
51. 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.: Appl. Sci. Manuf., **35**, 1267-1276, 2004.

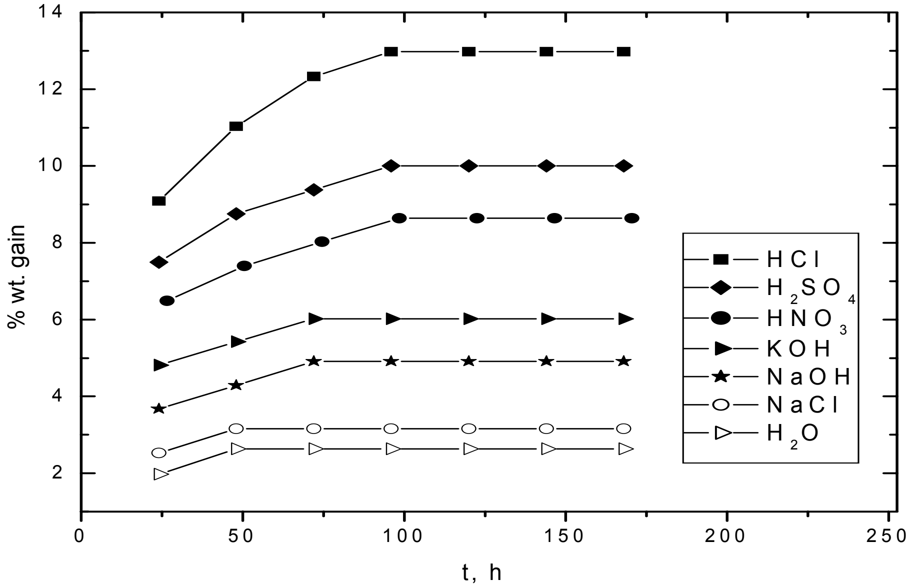


Fig. 4.15: Plots of % weight gain with time in different reagents for BTP-400

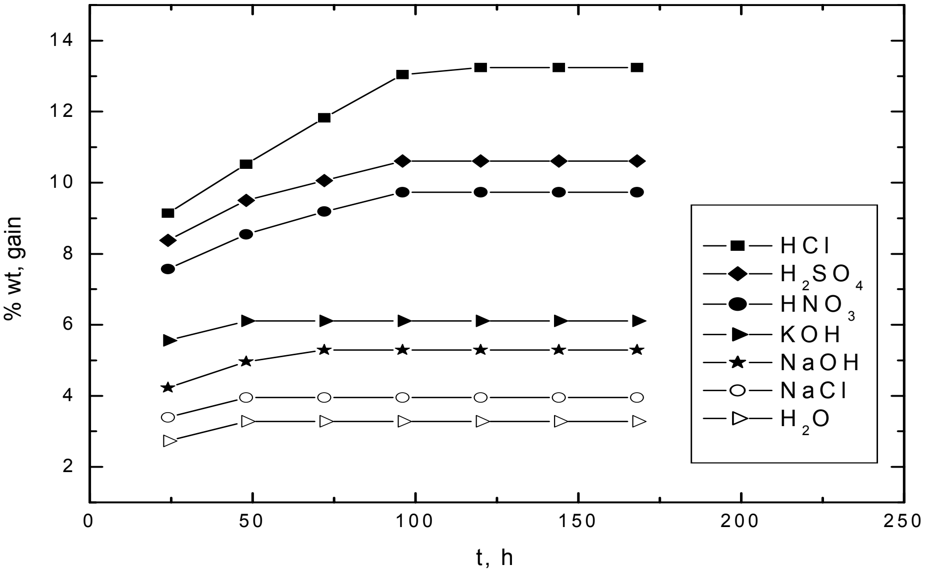


Fig. 4.16: Plots of % weight gain with time in different reagents for BTP-600

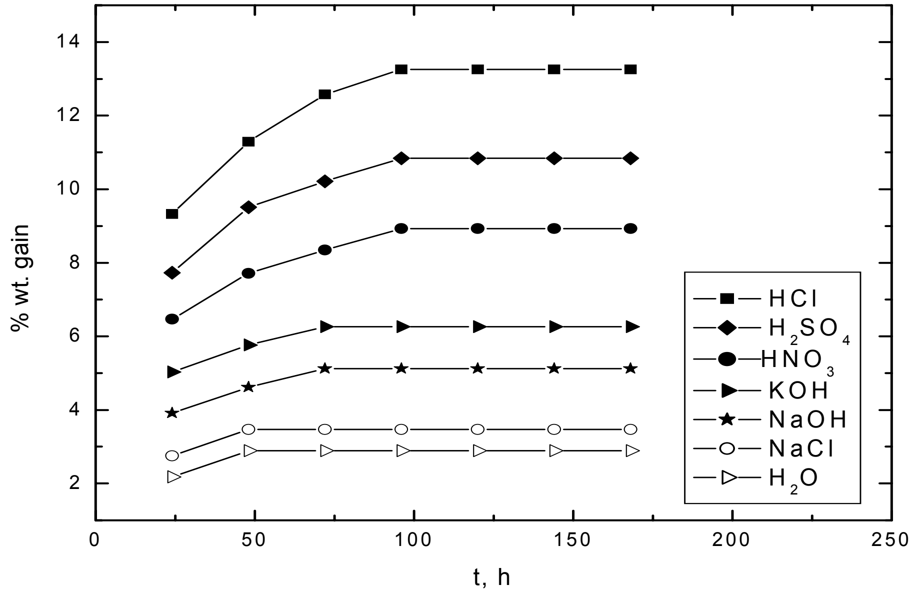


Fig. 4.17: Plots of % weight gain with time in different reagents for BATP-400

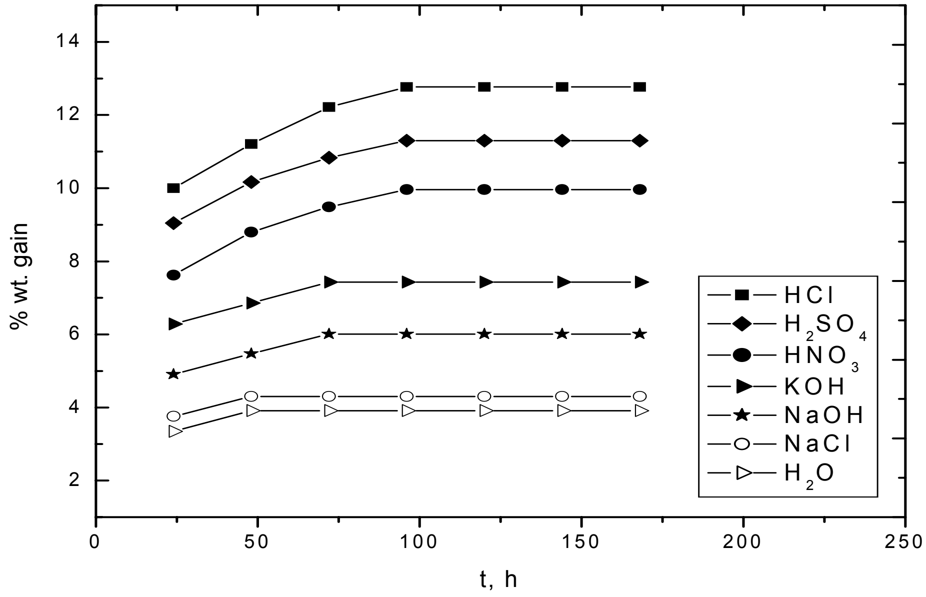


Fig. 4.18: Plots of % weight gain with time in different reagents for BATP-600

Table 4.10: Equilibrium % weight gain and time data for copolyurethane films

Reagent	Equilibrium time, h				Equilibrium % weight gain			
	BTP-400	**BTP-600**	**BATP-400**	**BATP-600**	**BTP-400**	**BTP-600**	**BATP-400**	**BATP-600**
H_2O	48	48	48	48	2.6	3.3	2.9	3.9
NaCl	48	48	48	48	3.2	3.9	3.5	4.3
NaOH	72	72	72	72	4.9	5.3	5.1	6.0
KOH	72	72	72	72	6.0	6.1	6.3	7.4
HCl	96	96	96	96	13	13.4	13.3	13.7
H_2SO_4	96	96	96	96	10	10.6	10.9	11.3
HNO_3	96	96	96	96	8.6	9.7	8.9	10.3

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 natural sources were the basis for the polymers and film forming materials used in paint and varnishes. Paint making at that time was a typical craft, with artists and painters mixing their own paints from 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 top coats have greatly increased the life of coated article. Coatings have also triggered the development in the field of marine, automobile, architectural, maintenance and fiber optics coatings. Also specifically coatings that control absorption or emission for temperature control, aircraft coatings that withstand the effect of UV radiation, absorption and the impact of air and dirt [52].

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.

---

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

- 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.

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-natural 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 [53].

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.

---

53. R. D. Deanin, “Polymer Structure, Properties and Applications”, Cabners books, division of Cabners publishing company, Inc., 1972.

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.

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 top coats by Mercedes Benz in 1989 show 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-4.11.

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 a way 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 [54]. The pot life can be affected by type of polyol and polyisocyanate, NCO/OH ratio, temperature, solvent, level of catalyst, etc.

---

54. M. Drukenbrod, Technically speaking: “Polyurethane coatings for the present and the future”, Oct.-1993.

Table-4.11: 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

A one component coating is supplied with all the raw materials in the same pack. Two main types are available: moisture cured and blocked polyurethanes.

Other radiation curing processes such as UV and electron beam can also be used to cure polyurethanes, blocked with specific protecting groups, polyurethane acrylates.

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

- Excellent mechanical properties

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

- Excellent chemical resistance

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

- High reactivity

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

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 two isomeric forms, 2,4- and 2,6-TDI, and is usually supplied commercially as a 80/20 blend of the two [55].

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 4.12.

---

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

Table-4.12: 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

Shamekhi and Yaganeh [56] have prepared versatile polyurethane material suitable as insulating coatings from novel kinds of polyhydroxy compounds (PHCs) via transesterification reaction of poly(ethylene terphthalate), different molecular weight of poly(ethylene glycol)s (PEGs), and castor oil. The final networks were prepared via crosslinking of PHCs with a novel blocked isocyanate curing agent (BPI) made from trimethylol propane (TMP), toluene diisocyanate (TDI) and *N*-methyl aniline (NMA). Polyols and curing agent were characterized by conventional methods and the curing condition was optimized via gel content measurements. Curing kinetic of the polyurethane network formation was investigated by differential scanning calorimetric method and the kinetic parameters were derived. Crosslink density of the samples was determined via equilibrium swelling method and by using Flory equations. Effects of crosslink density on electrical, physical, mechanical and dynamic mechanical (DMTA) properties of the polyurethane coatings were investigated.

Ismail and Hussain [57] have formulated adhesion of polyurethane (PU) coatings based on toluene diisocyanate, poly(propylene glycol) (PPG) 2000, polyethylene adipate (PEA) 2000 and castor oil (CO). The coatings were applied to glass slides with and without novolac primer (due to the high functionality of castor oil, the resultant PU coatings have limited shelf life). The studies showed that satisfactory adhesion strengths were achievable for immediate bonding. Furthermore, it was found that the adhesion of polyurethane to glass surfaces was increased by using a thin layer of novolac primer.

Polus et al. [58] have prepared polyurethane coatings by the "prepolymer mixing" method in two steps. The synthesis of the urethane prepolymer was carried out in presence of stannous 2-ethyl hexanoate. The obtained prepolymer was

---

56. E. A. Ismail and M. H. M. Hussain, “Improvement of polyurethane adhesion to glass using novolac primer”, J. Adhe. and Technol., **16**, 1509-1513, 2002.
57. M. A. Shamekhi and H. Yeganeh, “Novel polyurethane insulating coatings based on polyhydroxyl compounds, derived from glycolysed PET and castor oil”, J. Appl. Polym. Sci., **99**, 1222-1233, 2006.
58. I. Polus, “Synthesis of polyurethane coating components with IPDI and TMDI”, Holz als Roh- und Werkstoff, **61**, 238-240, 2003.

exposed to the reaction with branched polyester polyols. This reaction was carried out in presence of the catalysts: DABCO, TEA and stannous 2-ethyl hexanoate. In the synthesis of polyurethanes the aliphatic diisocyanates with linear (TMDI) and cyclic (IPDI) structures were used. The polyurethanes obtained using these diisocyanates was oxidized. The changes in the quality were monitored by determining some properties of the cured coating, such as hardness, flexibility and scratch resistance.

Duffy et al. [59] have conducted studies on ternary blends consisting of poly(propylene oxide) and poly(methyl methacrylate co *n*-butyl methacrylate) blended with either poly(hexamethylene adipate) or poly(hexamethylene sebacate). These ternary blends formed the basis for preparation of high performance polyurethane-based hot-melt adhesives and coatings. Changes in polyester structure were found to strongly alter the miscibility behavior. Binary interaction parameters for the five polymer pairs were determined experimentally, permitting calculation of the phase behavior of the ternary polymer blends. Results predicted by the model were in excellent agreement with experimental observations. The influence of miscibility in the melt on the morphology development was also discussed.

Gite et al. [60] have synthesized polyurethane coatings from monoglycerides (MGs) of four oils (castor, linseed, soybean and sesame). These coatings were applied in the form of thin films on tin plates and analysed for various coating properties such as gloss, scratch resistance, flexibility properties and physicochemical tests. A highly cross-linked product was obtained due to the higher functionality associated with MGs compared with their molecular weight. The trimer

---

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

also imparted cross-linking due to its trifunctionality, and a hard yet flexible, tough, glossy polyurethane coating was obtained.

Wounters et al. [61] have prepared polyurethane coatings with different network compositions in well-defined model systems as well as commercially-available formulations. The properties, such as glass-transition temperature, hardness and surface free energy, of the model network were tuned by the choice of the ingredients. All coatings were studied with respect to their bulk properties as well as their surface properties. It was found that by the addition of a fluorinated additive, the surface free energy of the coating was lowered by approximately 15mNm^{-1}, leaving the bulk properties intact. It was also shown that these polyurethane coatings were able to adapt their surface free energy in a reversible manner when exposed to water. The magnitude and rate of surface rearrangement was strongly dependent on the network density of the coating. The effect of coating properties on the formation of a biofilm and subsequent adhesion of diatoms was studied on a selection of the coatings used in this study, and the results obtained are discussed.

Synthesis of copolyurethanes of BANF-TDI-PEG-400/600 (Scheme-II) and BANFA-TDI-PEG-400/600 (Scheme-IV) are described in section-II of this chapter.

Hereafter copolyurethanes are designated as BTP-400, BTP-600, BATP-400 and BATP-600. The resultant solution was applied on each of 5 cm x 1 cm copper, steel and aluminium plates by means of a smooth brush. All the plates were allowed to dry at room temperature for 24 h. A very fine coating was observed on plates with good adhesion to the substrates.

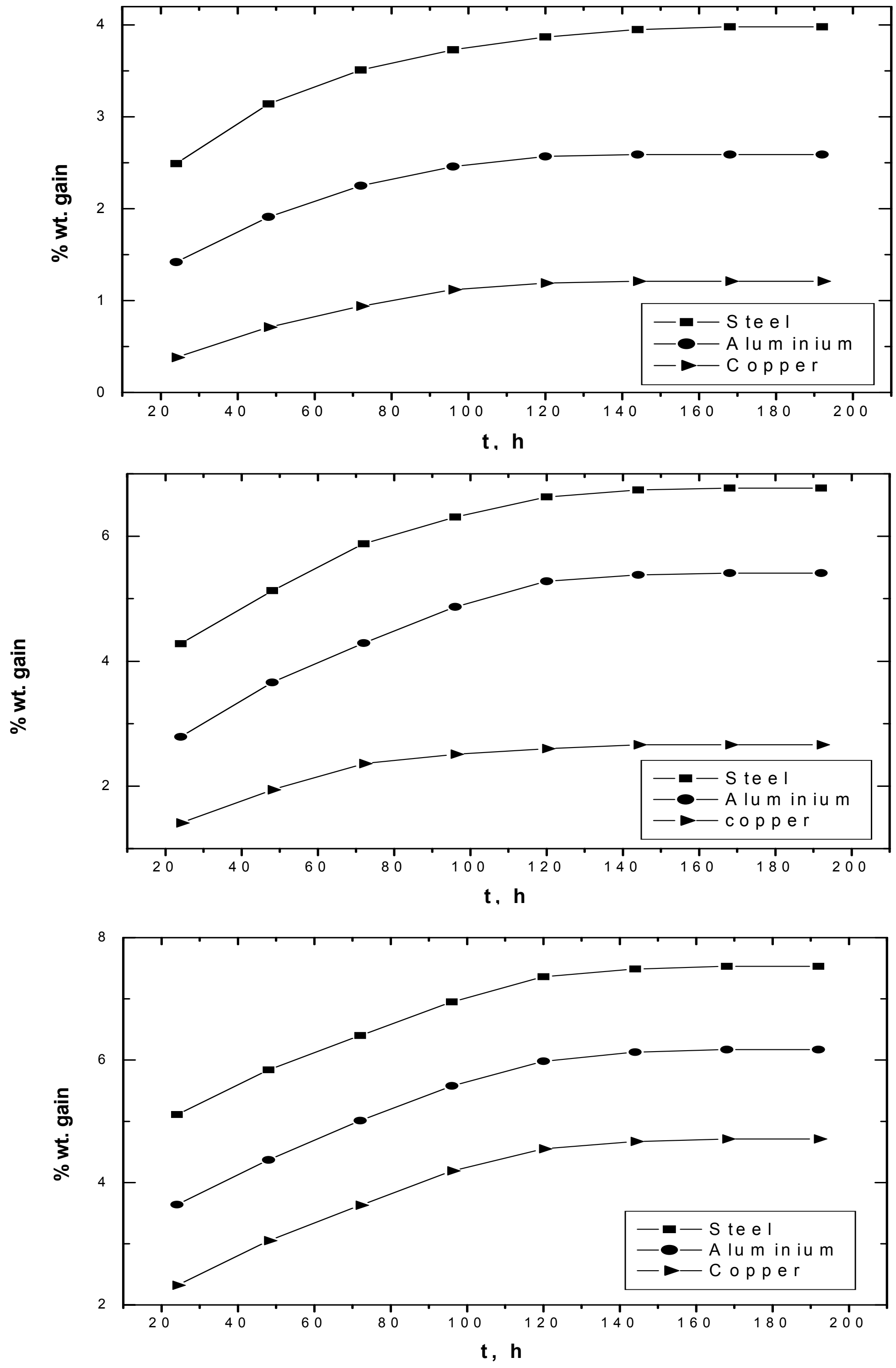
Chemical resistance of coatings

All the coated plates were subjected to chemical resistance by immersing in distilled water, 10% each of aq. NaCl and HCl solutions. These immersed plates were observed after every 24h by change in weight method. The % weight gained by BTP-400, BTP-600, BATP-400 and BATP-600 coated plates of copper, steel and aluminium with the passage of time is shown in Figs. 4.19-4.30, respectively from which it is clear that the % weight increased with time till equilibrium was established

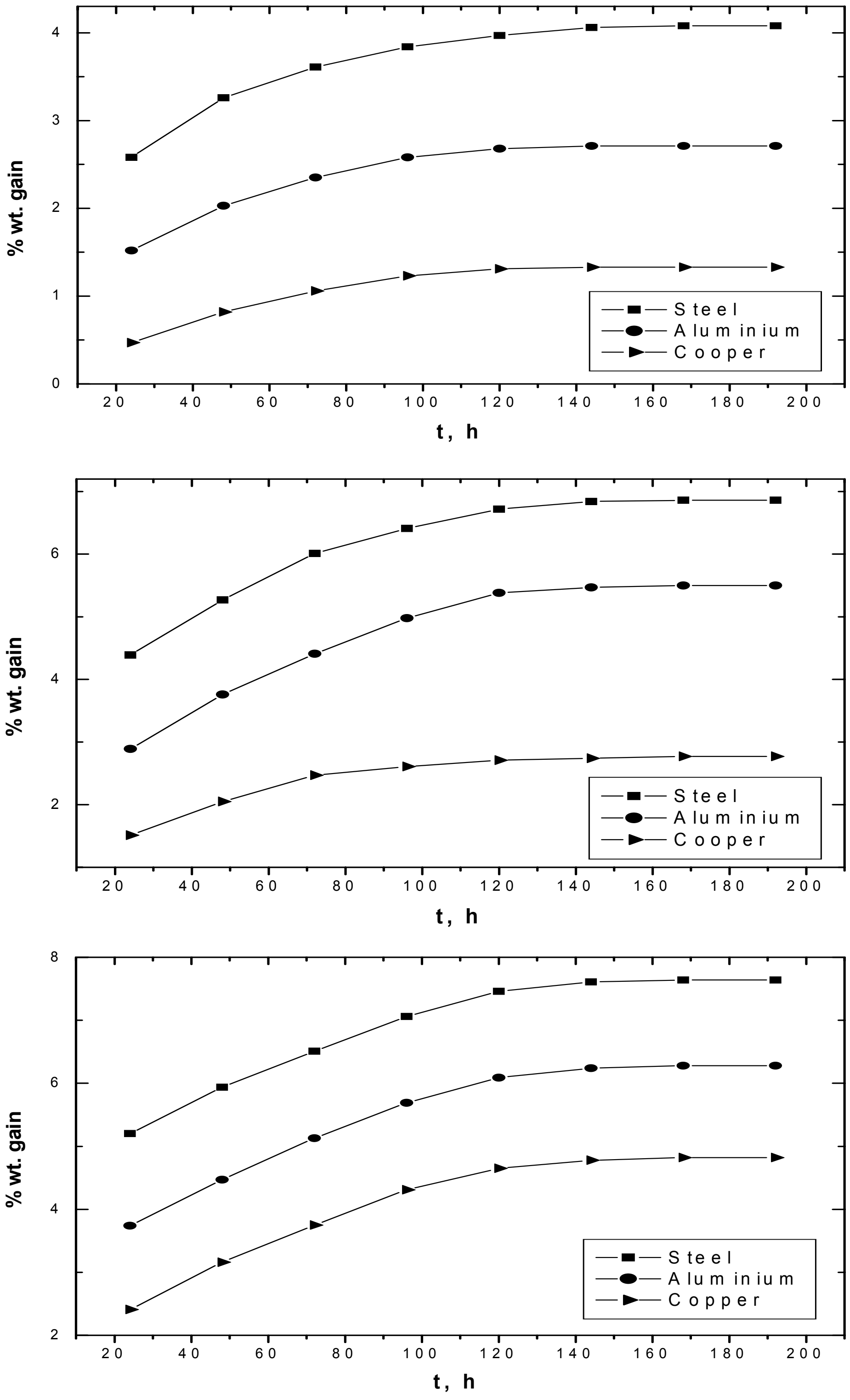
---

61. M. Wouters, J. Zanten, T. Vereijken, D. Bakker, J. Klijnstra, “Fluorinated polyurethane coatings with adaptable surface properties”, Surface Coatings International Part B: Coatings Trans., **89**, 23-30, 2006.

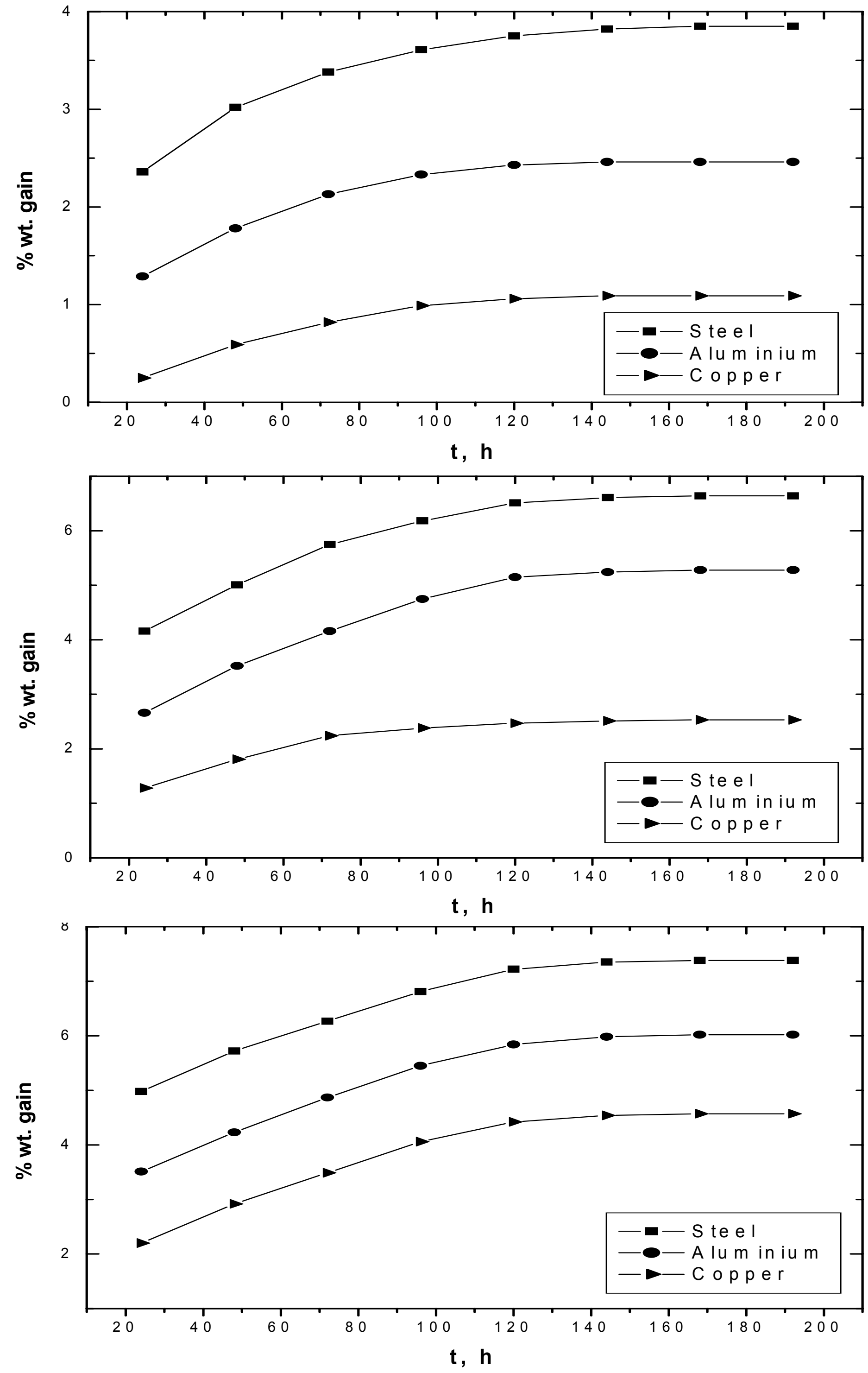
and then after it remained practically constant. Equilibrium % weight gain and equilibrium time data are reported in Table 4.13 from which it is clear that BTP-600 coated plates have somewhat higher water uptake tendency as compared to BTP-400 coated plates in all environments. Similarly BATP-600 coated plates have higher water uptake tendency as compared to BATP-400 coated plates in all environments. All the coated plates have high water uptake tendency in saline and acidic media. The nature of strong electrolytes affected water structure and hence water uptake tendency via H-bond formation due to presence of amino, urethane and ether groups. Strong electrolytes break water structure and formed hydrated ions. Absorbed water induces irreversible changes namely chemical degradation and cracking, while hydrophilic groups cause blistering. Cracking and blistering cause high water absorption. Coating material possesses excellent hydrolytic stability against water, saline and acidic environments indicating their usefulness in harsh conditions. Thus, coated plates showed good hydrolytic stability in different environments.



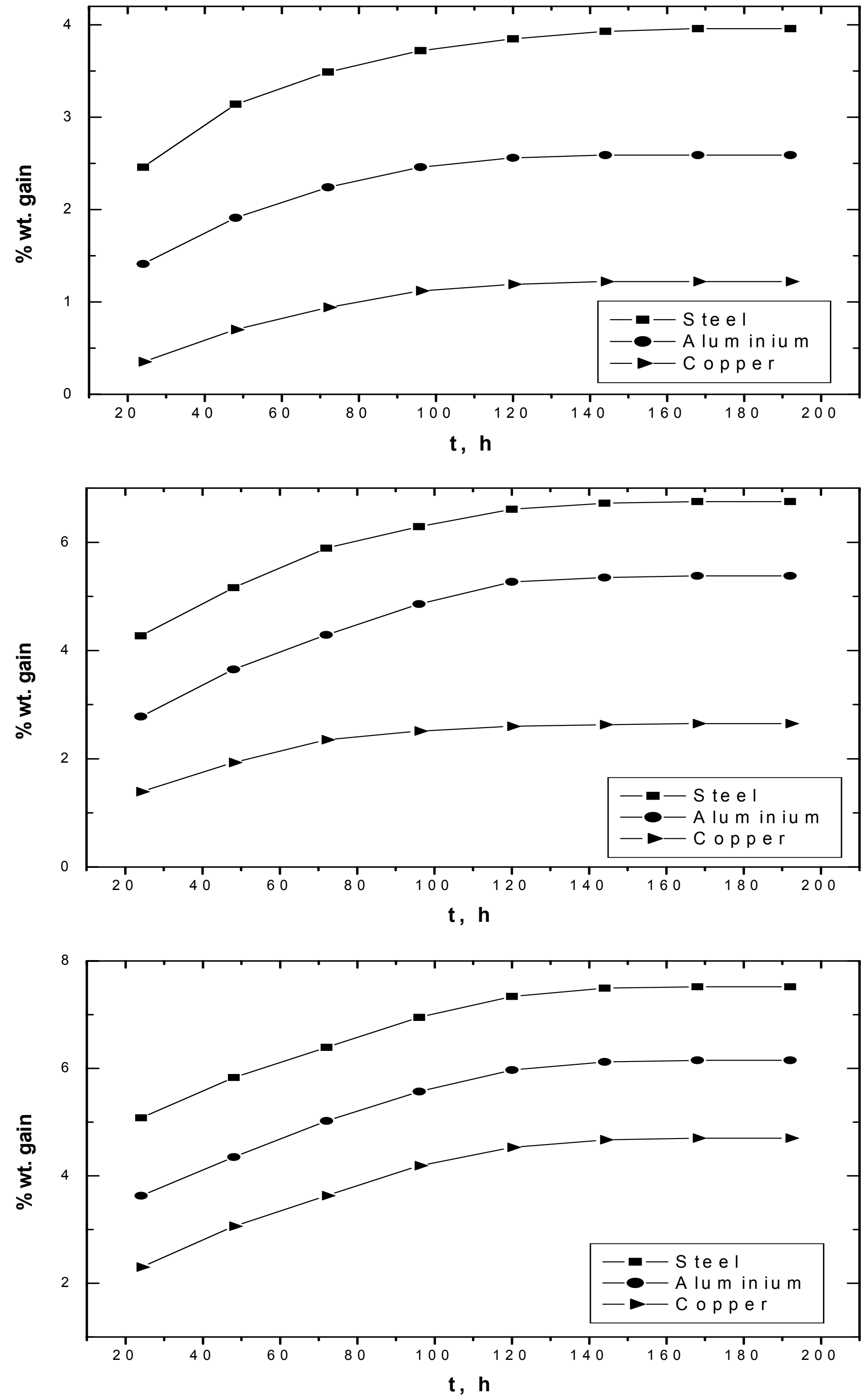
Figs. 4.19-4.21: Plots of % wt. gain with time for steel, aluminium and copper coated plates in water, 10 % NaCl and 10 % HCl for BTP-400, respectively at room temperature.



Figs. 4.22-4.24: Plots of % wt. gain with time for steel, aluminium and copper coated plates in water, 10 % NaCl and 10 % HCl for BTP-600, respectively at room temperature.



Figs. 4.25-4.27: Plots of % wt. gain with time for steel, aluminium and copper plates in water, 10 % NaCl and 10 % HCl for BATP-400, respectively at room temperature.



Figs. 4.28-4.30: Plots of % wt. gain with time for steel, aluminium and copper plates in water, 10 % NaCl and 10 % HCl for BATP-600, respectively at room temperature.

Table 4.13: Coating study of BTP-400, BTP-600, BATP-400 and BATP-600

Material	Medium	Equilibrium time, h	Equilibrium % wt. change		
			Copper	Steel	Aluminium
BTP-400	Water	144	1.21	3.95	2.59
	10 % aq. NaCl	168	2.66	6.77	5.41
	10 % aq. HCl	168	4.71	7.53	6.17
BTP-600	Water	144	1.33	4.06	2.71
	10 % aq. NaCl	168	2.77	6.86	5.50
	10 % aq. HCl	168	4.82	7.64	6.28
BATP-400	Water	144	1.09	3.82	2.46
	10 % aq. NaCl	168	2.53	6.64	5.28
	10 % aq. HCl	168	4.57	7.38	6.02
BATP-600	Water	144	1.22	3.93	2.59
	10 % aq. NaCl	168	2.65	6.75	5.38
	10 % aq. HCl	168	4.70	7.52	6.15

CHAPTER-5

A BRIEF REVIEW OF THE WORK DONE

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

CHAPTER-1

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

CHAPTER-2

This chapter deals with the syntheses of bisphenol-C based epoxy resin, self cured bisphenol-formaldehyde resin and its modification by acrylic acid, maleic anhydride, and boric acid and phosphorus oxychloride. The resins are characterized by IR spectral data. Kinetics of thermal degradation of the resins has been studied by TGA and DSC.

CHAPTER-3

This chapter of the thesis elaborates the fabrication of jute, sisal, glass and carbon fiber hybrid composites of bisphenol-C based mixed epoxy-phenolic resins. The mechanical and electrical properties of the composites are determined according to standard test methods. For JEBCF-10 to JEBCF-50, tensile strength has increased with BCF content in the composites, while a little change is observed in flexural strength except JEBCF-50. Increase in tensile strength indicated increase in interfacial bond strength through cross-linking and H-bonding. BCF possesses self curing property and it can also react with epoxy and hydroxyl groups of jute fibers to form covalent and H-bonds and hence improvement in interfacial bond strength. Electric strength has decreased with increasing amount of BCF content in the composite, while volume resistivity has increased with BCF content upto 30 wt. % and then it is decreased. Decrease in electric strength with increasing BCF content in composites is probably due to brittle nature of the cross-linked matrix material, which may not sustain electrical force. Due to formation of covalent and H-bonds between mixed matrix material and between jute fibers and matrix, volume resistivity is improved considerably. Decrease in volume resistivity of the composite above 30 wt. % indicated polar nature of the composites due to more number of free phenolic and jute OH groups.

Tensile strength (42.2%), flexural strength (13.9%), electric strength (400%) and volume resistivity (123.5 %) of TJEBCF-50 have increased on alkalization and acrylation of jute fibers as compared to JEBCF-50 composite.

Tensile strength (28.73%), flexural strength (34.84%), electric strength (43.54%) and volume resistivity (143.90 %) of TJG-50 have increased on alkalization and acrylation of jute fibers as compared to UJG-50 composite.

Tensile strength (33.7%), flexural strength (37.3%), electric strength (36.9%) and volume resistivity (42.5 %) of TSG-50 have increased on alkalization and acrylation of sisal fibers as compared to USG-50 composite. The increase in tensile strength, flexural strength, electric strength and volume resistivity after alkalization and acrylation are due to change in chemical composition, crystallinity, strength and surface modification of the fibers.

JCEBCF-10 to JCEBCF-50 possess 5.13-10.0 MPa tensile strength, 5.06-17.0 MPa flexural strength, 1.82 to 1.60 kV/mm electric strength and 3.16 to 5.90 x 10^{12} ohm cm, resistivity. Tensile and flexural strengths of the composites have increased with increase in BCF content in the hybrid matrix material indicating increasing interfacial bonding and toughness of the hybrid materials. BCF can also undergo self curing and react with hydroxyl and epoxide group to form network structure. Decrease in electric strength with increasing BCF content in the composites indicated increase in degree of cross-linking density and brittleness, which may not sustain electrical force. Decrease in volume resistivity with BCF content (up to 30 %) indicated formation of more number of polar groups as a result of reactions among polar groups of reinforcing fibers and matrices. Increase in volume resistivity above 30 % BCF content in the composites indicated increase in cross-linking due to self curing of BCF besides curing between EBC and BCF resins and hence formation of non-polar groups, which resulted in decrease in volume resistivity.

Tensile strength, flexural strength, electric strength and volume resistivity have increased by 46.50, 13.71, 24.40 and 15.15 %, respectively of TJCEBCF-50 on alkalization and acrylation of jute fibers as compared to JCEBCF-50 composite. In comparison to JCEBCF-50 and TJCEBCF-50 mechanical properties of GCEBCF-50 are somewhat higher due to high mechanical properties of glass fibers.

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. Equilibrium water content has decreased with increasing BCF content in the composite. Decrease in water uptake tendency of the composite with increasing amount of BCF in mixed material is due to self curing of BCF and reactions of OH groups of jute with EBC and BCF resulting in hydrophobic groups (methylene and ether linkages) indicating increase in cross-linking density i.e. hydrophobicity.

The acrylation is successfully implemented for jute and sisal fibers by acrylic acid that produced water repellency by partial replacement of hydrophilic –OH groups by vinyl ester groups. It showed 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 and sisal composites is relatively higher than that of treated one.

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 syntheses and coating applications of copolyurethanes, BANF-TDI-PEG-400/600 and BANFA-TDI-PEG-400/600 copolyurethanes were characterized by IR spectral data, thermal, 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 steel, aluminium and copper plates was carried out according to change in mass method. Copolyurethane films possess good thermal, 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 molecular weight of PEG (BTP-400: $\rho = 1.2137 \pm 0.0006$ g/cm^3, BTP-600: $\rho = 1.2026 \pm 0.0008$ g/cm^3, BATP-400: $\rho = 1.2343 \pm 0.0005$ g/cm^3 and BATP-600: $\rho = 1.2232 \pm 0.0007$ g/cm^3). Tensile strength and volume resistivity of Copolyurethane films have decreased, while electric strength has increased with increasing molecular weight of PEG. Thus, density and electric strength have decreased, while tensile strength and volume resistivity have increased with increasing molecular weight of PEG. Increasing molecular weight of PEG in copolyurethane films resulted in increasing of water uptake tendency. Copolyurethane films may find their excellent coating application under relatively concentrated (10%) acidic (HCl, H_2SO_4 and HNO_3), alkaline (NaOH and KOH) and saline environments.

Achievements

Manuscript published/accepted/communicated

1. Effect of temperature on ultrasonic velocity and thermodynamic parameters of cardo aromatic polysulfonate solutions. P. J. Vasoya, N. M. Mehta, **V. A. Patel** and P. H. Parsania, Journal of Scientific & Industrial Research, 66, 841-848, 2007.
2. Preparation, mechanical, electrical and water absorption behavior of jute composites of bisphenol-C based mixed epoxy-phenolic resins. **V. A. Patel**, P. J. Vasoya and P. H. Parsania, Journal of Polymer Materials, 24, 255-261, 2007.
3. Preparation, mechanical and electrical properties and water absorption study of novel bisphenol-C-formaldehyde-acrylate treated and untreated jute composites, P. J. Vasoya, **V. A. Patel** and P. H. Parsania, Polymer Plastics Technology and Engineering, 47, 53-57, 2008.
4. Synthesis and characterization of novel bisphenol-C-formaldehyde-acrylate-toluene diisocyanate-PEG-400 copolyurethane, P. J. Vasoya, **V. A. Patel** and P. H. Parsania, Polymer Plastics Technology and Engineering. Accepted.
5. Preparation and physico-chemical study of sandwich glass-jute-bisphenol-formaldehyde resins composites, N. M. Mehta, P. J. Vasoya, **V. A. Patel** and P. H. Parsania, Indian Journal of Engineering and Material Science: Accepted.
6. Synthesis and characterization of polysulfonate of 9,9'-bis(4-hydroxy phenyl)anthrone-10 and 4,4'-disulfonyl chloride diphenyl ether, P. J. Vasoya, **V. A. Patel**, B. D. Bhuva and P. H. Parsania, Polymer Plastics Technology and Engineering: Accepted.
7. Preparation, mechanical, electrical and water absorption study of jute-carbon hybrid composites of bisphenol-C based mixed epoxy-phenolic resins, **V. A. Patel**, B. D. Bhuva and P. H. Parsania, Journal of Reinforced Plastics and Composites: Accepted.
8. Preparation and physico-chemical study of hybrid glass-jute (treated and untreated) bisphenol-C based mixed epoxy-phenolic resins composites, **V. A. Patel**, P. J. Vasoya, B. D. Bhuva and P. H. Parsania, Polymer Plastics Technology and Engineering: Accepted.

9. Preparation and physico-chemical study of glass-sisal (treated-untreated) hybrid composites of bisphenol-C based mixed epoxy-phenolic resins, **V. A. Patel** and P. H. Parsania, Journal of Reinforced Plastics and Composites: Communicated.
10. Performance evaluation of treated-untreated jute-carbon and glass-carbon hybrid composites of bisphenol-C based mixed epoxy-phenolic resins, **V. A. Patel**, B. D. Bhuva and P. H. Parsania, Journal of Reinforced Plastics and Composites: Communicated.
11. Densities, thermal, mechanical and electrical properties and water absorption study of PEG-400/600-9,9’-bis(4-hydroxy phenyl)anthrone-10 -formaldehyde -toluene diisocyanate copolyurethanes, **V. A. Patel**, B. D. Bhuva, J. P. Patel and P. H. Parsania, Journal of Polymer Materials: Communicated.
12. The effect of PEG chain length on physico-chemical properties of 9, 9’-bis (4-hydroxy phenyl) anthrone-10-formaldehyde-acrylate-toluene diisocyanate copolyurethanes, **V. A. patel**, B. D. Bhuva, J. P. Patel and P. H. Parsania, Journal of Elastomers and Plastics: Communicated.
13. A comparative study of boron-containing phenolic resins and kinetics of thermal degradation **V. A. Patel** and P. H. Parsania, Polymer Plastics Technology and Engineering: Communicated.
14. Performance evaluation of alkali and acrylic acid treated and untreated jute composites of mixed epoxy-phenolic resins, **V. A. Patel**, P. J. Vasoya and P. H. Parsania, Polymer Plastics Technology and Engineering: Communicated.

Conferences/ Workshop/Seminar/Symposium participated and paper presented

1. * XXII Gujarat Science Congress, Bhavnagar University, Bhavnagar (March 9, 2008).
2. National Workshop on “Management & Use of Chemistry Databases & Patent Literature”, Department of Chemistry, Saurashtra University, Rajkot (February 27-29, 2008).
3. *International Seminar on “Frontiers in Polymer Science and Technology (POLY-2007)”, Guwahati (November 1-3,2007).

4. Seminar on “New Frontiers in Pharmaceutical Process Chemistry and related Topics”, Department of Chemistry, Saurashtra University, Rajkot (March 5, 2007).
5. *National symposium on “Advances in Polymer Science & technology”, jointly organized by Catalysis Society of India, Indian Institute of Chemical Engineering and Indian Chemical Society, Vadodara (March 17, 2007).
6. *XXI Gujarat Science Congress, Hemchandracharya North Gujarat University, Patan (March 11, 2007).
7. *National Seminar on “Novel Trends in Polymer Science & Technology (NSNTPST)”, jointly organized by UGC Funded Center of Excellent in Applied Polymer and Department of Chemistry, S. P. University, V. V. Nagar (March 8-9, 2007).
8. *2nd National Conference on “Thermodynamics of Chemical & Biological Systems”, Organized by Department of Chemistry, V. N. South Gujarat University, Surat (October 30- November-1, 2006).
9. National seminar on “Recent Advances in Chemical Science and Approach Towards Green Chemistry”, Saurashtra University, Rajkot, INDIA (October 11-13, 2006).
10. National seminar on “E-resources in Chemical Synthesis and Natural Products”, Department of Chemistry, Saurashtra university, Rajkot, INDIA. (March 2-3, 2006).
11. *Natoinal Conference on “Thermodynamics of Chemical & Biological Systems”, Guru Nanak Dev University, Amritsar (December 28-30, 2005).
12. *“Polymer Materials: Present Status and Future Prospects and Fourth Polymer Foundation Award Function”, Ahmedabad Textile Industry’s Research Association, Ahmedabad (December 10-11, 2005).
13. Workshop on “Nanotechnology Opportunities and Challenges”, Saurashtra University, Rajkot (October 17, 2005).
14. Regional Workshop on “An approach to Analytical Instruments Commonly used in Chemical Industries”, Department of Chemistry, Bhavnagar University, Bhavnagar (September 28, 2005).

(* paper presented)