Pathak, Urvish G., 2011, *"Studies on Novel Polyester Polyols and Their Biocomposite",* thesis PhD, Saurashtra University

STUDIES ON NOVEL POLYESTER POLYOLS AND THEIR BIOCOMPOSITE

A

THESIS

SUBMITTED TO THE SAURASHTRA UNIVERSITY

FOR

THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

THE FACULTY OF SCIENCE (CHEMISTRY)

BY

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UNDER THE GUIDANCE

OF

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

Date: -02-2011
Place: Rajkot.

(Mr. Urvish G. Pathak)

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

Date : -02-2011
Place : Rajkot

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ACKNOWLEDGEMENTS

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

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

I would like to extend my sincere thanks to my seniors as well as juniors - Dr. Niral, Dr. Sunil, Dr. Paresh, Dr. Vrajesh, Dr. Viren, Dr. Bharat, Dr. Pankaj, Dr. Sandip, Punit, Jignesh, Suresh, Pooja, Leena, Ritesh, Rizwan for their help and cooperation.

I also thankful to Dr. M. B. Patel, B. M. Gabhawala, Late Dr. Kandoi, J. M. Mehta, C. S. Patel, M. G. Rao, Dr. A. B. Pancholi and my colleagues (GNFC- Laboratory parivar) for continuous encouragement during my research work. I especially thankful to Mukesh Prajapati for providing stirrer and other lab equipments.

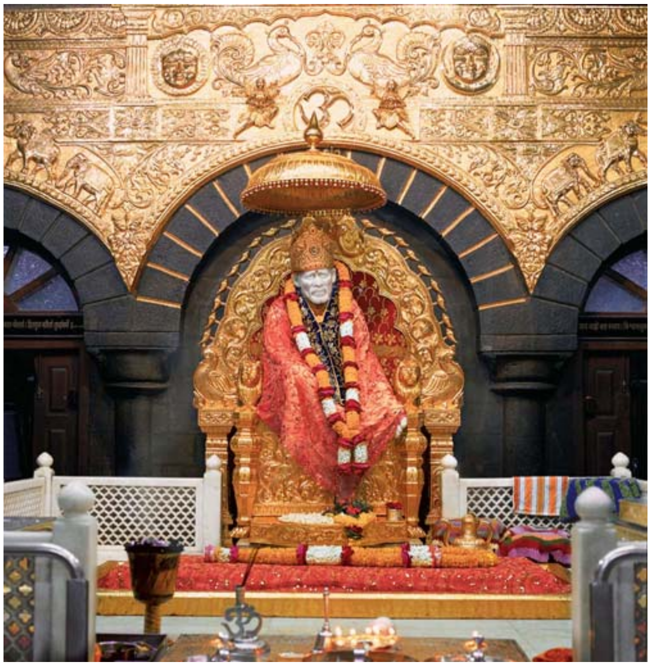
I thankful to my friends; Sumesh, Umesh, Bharat, Bonney and Himanshu for their appreciation, inspiration and motivation during the tenure of my research work.

I am also indebted to The Directors, RSIC–Chandigarh, ERDA-Vadodara and SICART- V. V. Nagar for instrumental facilities. I would like to extend my sincere thanks to Purvesh Vyas for their analytical help during my research work (Department of Physics, Sau. Uni.).

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

The never ending process of unsurpassable devotion, love and affection, which was showered upon me by my uncle Satishchandra, aunty Bhadraben, my father Ganpatishanker, mothor Shobhanaben, brother Snehal and his wife Darshana, my daughter (Jinal and Khushi), my son Atharva, my cousin (Harsh & Soham) who have enlightened my path and always boosted me to go ahead to reach the goal. Last but not the least; I would like to express my real sense of gratitude to my life partner Manisha (Minu) for her continuous support, understanding and loving care.

Urvish G. Pathak



Dedicated to

My guide & my family…

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SYNOPSIS

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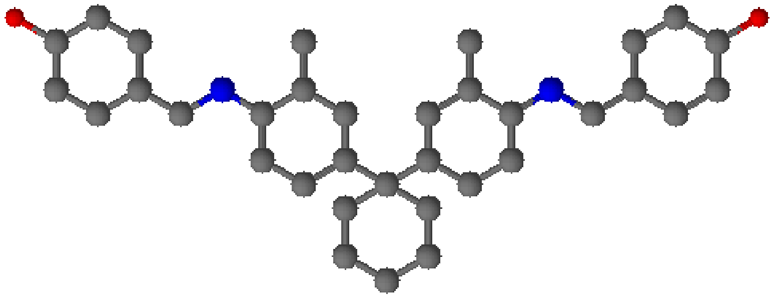
AND THEIR BIOCOMPOSITES



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SYNOPSIS OF THE THESIS TO BE SUBMITTED TO SAURASHTRA UNIVERSITY FOR THE DEGREE OF PHILOSOPHY IN THE FACULTY OF SCIENCE - CHEMISTRY

FACULTY	: **SCIENCE**
SUBJECT	: **CHEMISTRY**
TITLE OF THE THESIS	: **STUDIES ON NOVEL POLYESTER POLYOLS AND THEIR BIO-COMPOSITES**
NAME OF THE CANDIDATE	: **URVISHKUMAR G. PATHAK**
REGISTRATION NO.	: **3756**
DATE OF REGISTRATION	: **31st JULY - 2007**
NAME OF THE GUIDE	: **Dr. P. H. PARSANIA** **PROFESSOR & HEAD** **DEPARTMENT OF CHEMISTRY,** **SAURASHTRA UNIVERSITY,** **RAJKOT – 360 005**
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The work to be incorporated in the thesis entitled "Studies on novel polyester polyols and their bio-composites" is described as under.

GENERAL INTRODUCTION

Today polymers have replaced many traditional engineering materials like metals, wood, cement, etc. Polymers are used in various forms such as fibers, films, coating material and various fabricated or molded articles, which exhibit a wide range of properties in terms of strength, rigidity, flexibility, toughness, elasticity, resilience, optical clarity, chemical and solvent resistivity, etc.

Among all, nitrogen containing compounds like amino compounds are more useful. They find their usefulness as intermediates for synthetic fibers and medicines. Aromatic diamines are the important constituents for the syntheses of dyes, agrochemicals, varnishes, adhesive, coating materials, pesticides, fertilizers and in other applications. They are widely used in manufacturing thermally stable polyamides, amino and epoxy resins. They are also used as curing agents for epoxy resins and in the synthesis of variety of Schiff bases for various purposes [1-4].

The Schiff bases are products of reaction between aldehydes or ketones and aliphatic or aromatic primary amines in the presence of acid or base as a catalyst [5-8]. Schiff bases are most widely used as fine chemicals [9], medical substrates and ligands for metal complexes [10-13].

Epoxy resins are widely used for land, marine and space transportation, automobile and electrical components, rehabilitation 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 [14].

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benzofuran - 2, 9 dicarbaldehyde with various diamines “ Iranian Polymer Jounral, 12, 43 ,2003.

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Polyurethanes constitute a class of polymers with great versatility such as excellent abrasion resistance, hardness, enhanced chemicals and solvent resistance, flexibility, high cohesive strength and amenable curing speed [15-16], which permit the manufacturing the products ranging from expanded materials to highly compact materials. Polyurethane can be tailor made according to their application as adhesive, additives or a coating material [17].

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

CHAPTER-1: LITERATURE SURVEY ON MONOMERS, SCHIFF BASES, PHENOLIC/EPOXY RESINS AND POLYURETHANES.

CHAPTER- 2: SYNTHESES OF MONOMERS, SCHIFF BASES AND THEIR SPECTRAL CHARACTERIZATION.

CHAPTER-3: SYNTHESES OF PHENOLIC/EPOXY RESINS, THEIR COPOLY URETHANES AND PHYSICO-CHEMICAL CHARACTERIZATION.

CHAPTER-4: ULTRASONIC SPEED AND ALLIED PARAMETERS OF EPOXY RESINS SOLUTIONS.

CHAPTER-5: SYNTHESIS AND CHARACTERIZATION OF POLYESTER POLYOLS; SYNTHESIS OF POLYURETHANE COMPOSITES AND THEIR PHYSICO-CHEMICAL CHARACTERIZATION

CHAPTER-6: A BRIEF REVIEW OF THE WORK DONE

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CHAPTER 1: LITERATURE SURVEY ON MONOMERS, SCHIFF BASES, PHENOLIC/EPOXY RESINS AND POLYURETHANES

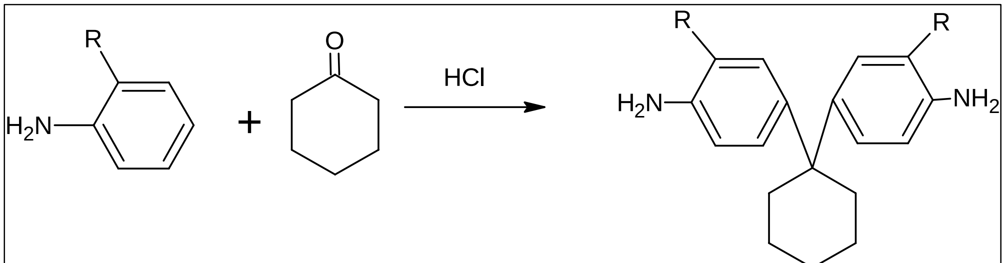
This chapter of the thesis describes the up to date literature survey on synthesis, characterization and applications of cardo diamines, Schiff bases, phenolic/epoxy resins, and polyurethanes in different fields of science and their applications in routine life.

CHAPTER 2: SYNTHESES OF MONOMERS, SCHIFF BASES AND THEIR SPECTRAL CHARACTERIZATION

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

SECTION– I: SYNTHESIS OF 1, 1' BIS (4-AMINOPHENYL) CYCLOHEXANE (BAPC)/ 1, 1' BIS (3-METHYL-4-AMINOPHENYL)CYCLOHEXANE (BAMPC)

BAPC/BMAPC(I) was synthesized by condensing 0.12 mol aniline/o-toludine hydrochloride and 0.05 mol cyclohexanone at 120°C for 2h and at 140-150°C for 24 h. BAPC and BMAPC were crystallized repeatedly from benzene - hexane system.



Where, R = H BAPC

R = CH_3, BAMPC

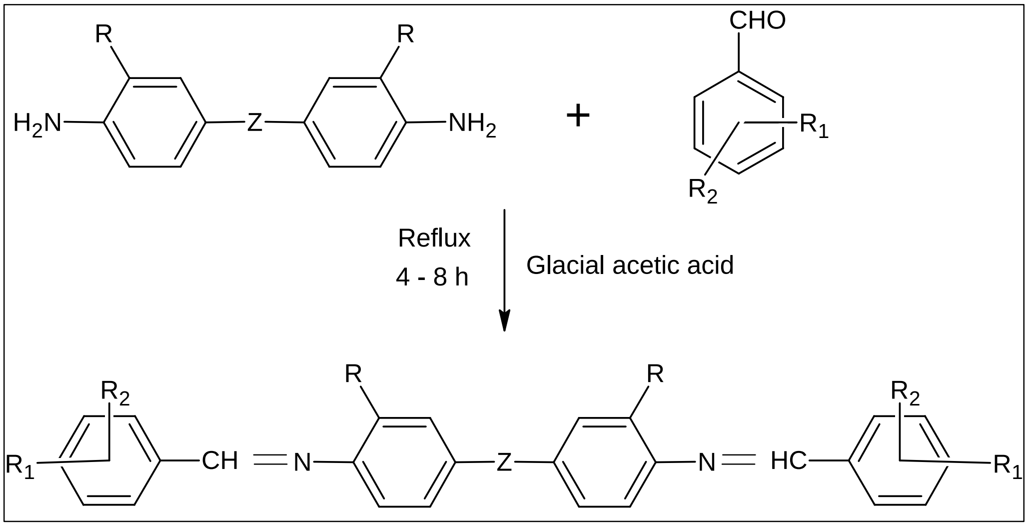
I

SECTION - II: SYNTHESES OF SCHIFF BASES

Schiff bases (II) were synthesized by condensing 0.01 mol different diamines and 0.021 mol substituted aromatic aldehydes using ethanol as a solvent and glacial acetic acid as a catalyst at reflux temperature for 4 - 8 h. The Schiff bases were isolated from chilled water, filtered washed well with sodium bisulfite solution, water and dried in an oven at 50°C. The Schiff bases were crystallized repeatedly from appropriate solvent and their purity were checked by TLC in appropriate solvent system at room temperature.

SECTION – III: SPECTRAL CHARACTERIZATION

The structure of the Schiff bases and polymers are supported by IR, ^{1}HNMR and Mass spectroscopic techniques.



II

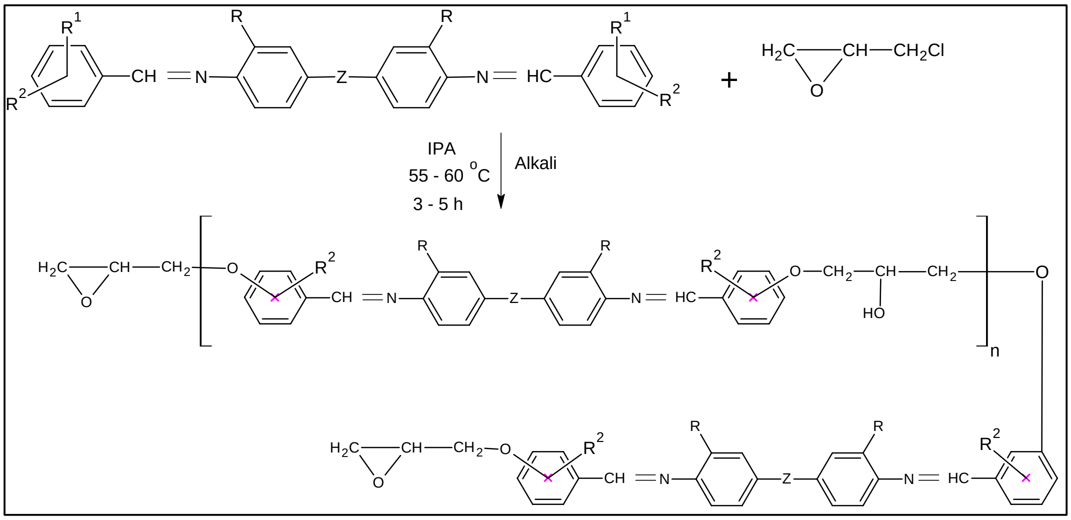
Schiff base	R	R_1	R_2	Z
SB-01	H	4-OH	H	O
SB-02	H	4-OH	H	CH_2
SB-03	H	4-OH	H	SO_2
SB-04	H	4-OH	H	Cyclohexyl
SB-05	H	2-OH	H	Cyclohexyl
SB-06	CH_3	4-OH	H	Cyclohexyl
SB-07	CH_3	2-OH	H	Cyclohexyl
SB-08	CH_3	4-OH	3-OCH3	Cyclohexyl

CHAPTER-3: SYNTHESES OF PHENOLIC/EPOXY RESINS, THEIR COPOLYURETHANES AND PHYSICO-CHEMICAL CHARACTERIZATION

This chapter is further subdivided into four sections.

SECTION – I: SYNTHESES OF EPOXY RESINS

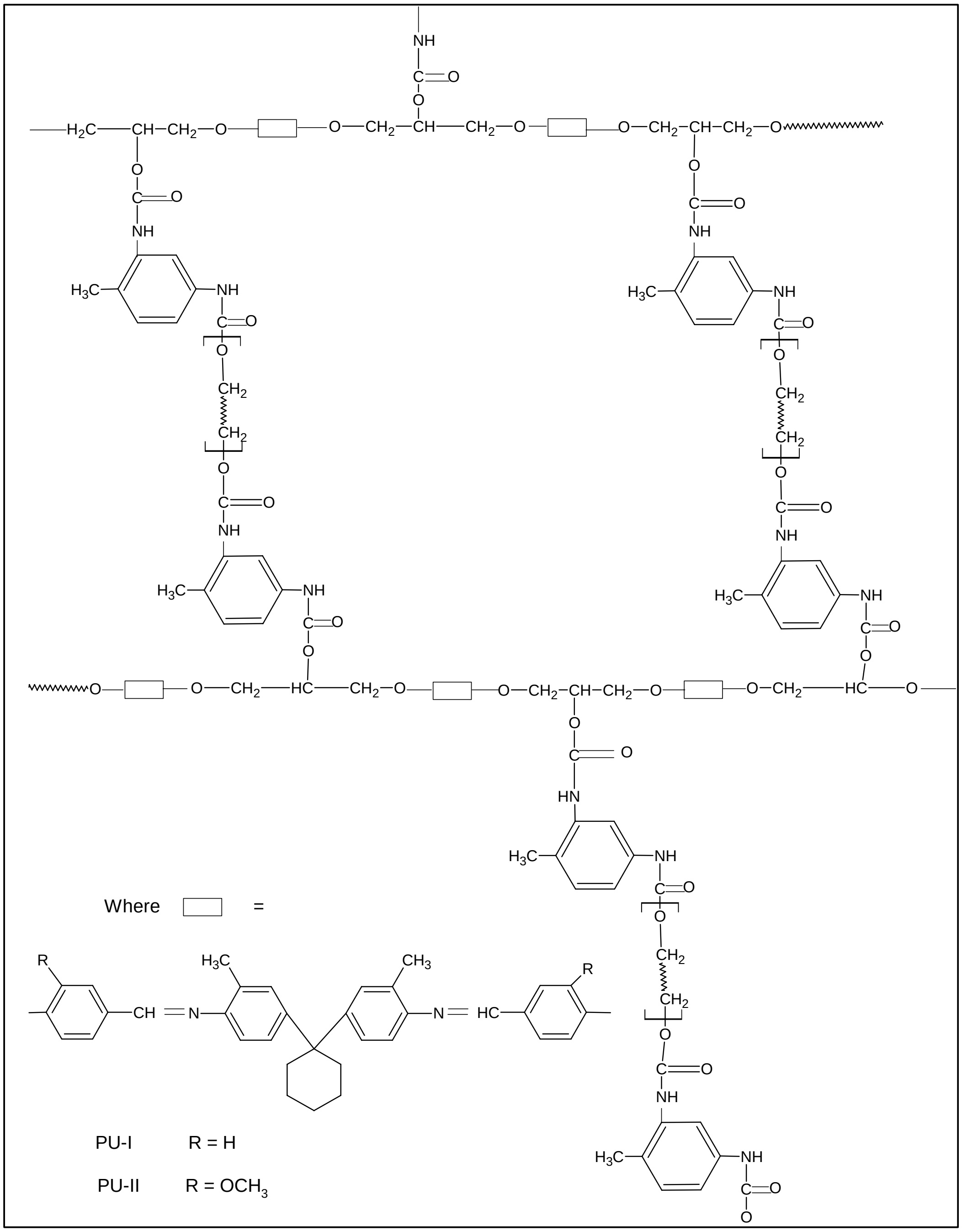
Epoxy resins (III) were synthesized by condensing different Schiff bases with epichlorohydrin by using isopropanol as a solvent and alkali as a catalyst at 55 to 60°C for 3 to 5h. The resins were isolated from water, filtered, washed well with distilled water and dried in an oven at 50°C. The resins are soluble in common solvents. Epoxy equivalents were determined by pyridinium hydrochloride method.



III

SECTION-II: SYNTHESES OF COPOLYURETHANE RESINS

Copolyurethanes (IV) were synthesized by reacting corresponding epoxy resin, PEG-600 and toluene diisocyante using chloroform as a solvent at room temperature. The resultant resin was poured into a leveled 15cm x 15cm glass mold and the solvent was allowed to evaporate with controlled rate at room temperature. After 24h, the film was peeled from the mold.



IV

SECTION-III: PHYSICO-CHEMICAL CHARACTERIZATION OF THE RESINS

This section describes the solubility behavior of the resins, determination of epoxy equivalents, hydroxyl values, molecular weights and molecular weight distribution and IR spectral analysis of the resins. The resins are also characterized DSC and TGA at 10^{O}C/min heating rate and in an N_2

atmosphere. Various thermal parameters are determined and discussed in light of structure property relationship.

Densities of polyurethane films are determined by floatation method and discussed in light of functional group. Chemical resistance of the films was determined against water and 10% each of aqueous acids, alkalis and salt solutions at room temperature by change in mass method at the interval of 24h. The effect of various reagents on PU films is discussed. It is also proposed to determine tensile strength, electric strength and volume resistivity of polymer films according to standard test methods. The data will be discussed in light PEG-600 concentration, degree of resin cure, etc.

CHAPTER-4: ULTRASONIC VELOCITY AND ALLIED PARAMETERS OF EPOXY RESINS SOLUTIONS

Recently ultrasonic has become the subject of extensive research because it finds applications in numerous fields of science like consumer industries, medical fields, engineering, process industries, etc. Knowledge of acoustical properties of solutions furnishes a wealth of information on molecular interactions occurring in the solutions, the nature and the strength of interactions. The density (ρ), viscosity (η) and ultrasonic speed (U) measurements on pure solvents (chloroform, 1,4-doixane and THF) and resins solutions are carried out at 35^{O}C. Various acoustical parameters such as isentropic compressibility (κ_s), specific acoustical impendance (Z), Rao's molar sound function (R), Van der wals constant (b), internal pressure (π), classical absorption coefficient $(\alpha/f^2)_{cl}$, viscous relaxation time (τ), solvation number (S_n), free volume (V_f) and intermolecular free length (L_f) are determined from U, ρ and η data and discussed in light of effect of solvent and concentration.

CHAPTER-5: SYNTHESIS AND CHARACTERIZATION OF POLYESTER POLYOLS; SYNTHESIS OF POLYURETHANE COMPOSITES AND THEIR PHYSICO-CHEMICAL CHARACTERIZATION

This chapter is further subdivided into five sections

SECTION–I: General introduction about polyurethanes , copolyurethanes and composites made from natural fibres.

SECTION–II: SYNTHESES OF EPOXY POLYESTER POLYOLS

To a 250ml three necked round bottomed flask, equipped with a condenser, thermometer and a mechanical stirrer, were placed into a thermostat bath and added 0.001mol ER-1/ER-3, 0.002mol fatty acids and 50ml 1,4-dioxane containing 2ml triethylamine as a catalyst. The reaction mass was brought to reflux and stirrered 3-3.5h so that desired acid values were achieved (<30 mg KOH/g of resin). Solid resins were isolated from cold water, filtered, washed well with water and dried in an oven at 50°C.

SECTION-III : CHARACTERIZATION OF EPOXY POLYESTER POLYOLS

Characterization of synthesized were done by Acid value, Hydroxyl value and IR spectra.

SECTION-IV : SYNTHESIS OF COMPOSITES

In order to prepare jute-polyurethane composites, polyurethane matrix material was 60% of woven jute fabric. Thus to a 250ml beaker UPER-1 / UPER-4 (39 / 38.3 g) was dissolve in 75ml chloroform. To this solution (11.7/11.5g) toluene diisocyanate in 25ml chloroform was added dropwise with stirring at room temperature for 5min. The resultant prepolyurethane solution was applied to 15cm x 15cm jute fabric with the help of smooth brush by hand lay up technique. The prepregs were allowed to dry in the sunlight for about 5 min. Eight such prepregs were stacked one over the other and pressed between the two preheated stainless steel plates under the hydraulic pressure of 30.4MPa at room temperature / 150°C for 8h under heating and 4h at room temperature using silicone spray as a mold releasing agent. Hereafter composites are designated as Compo-A and Compo-B respectively.

SECTION-V: PHYSICO-CHEMICAL CHARACTERIZATION OF COMPOSITES

The composites are characterized DSC and TGA at 10°C/min heating rate and in an N_2 atmosphere. Various thermal parameters are determined and discussed in light of structure property relationship. It is also proposed to determine tensile strength, electric strength and volume resistivity according to standard test methods. Chemical resistance of the composites was determined against water and 10% each of aqueous acid and alkali solutions at room temperature by change in mass method at the interval of 24h. The effect of various reagents on PU films is discussed.

CHAPTER-VI: A BRIEF REVIEW OF THE WORK DONE

This chapter describes comprehensive summary of the work done.

Signature of the guide	**Signature of the candidate**
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CHAPTER-1

CHAPTER-1: LITERATURE SURVEY ON MONOMERS (CARDO DIAMINES), SCHIFF BASES, EPOXY RESINS, EPOXY ESTER AND POLYURETHANES

General Introduction

The universe has unique characteristic – rotation and revolution. Human beings observed and learnt the nut and bolt of each and every element from them.

Historians frequently classify the early ages of man according to the materials that he used for making his implements and other basic necessities. The most well - known of these periods are the Stone Age, the Iron Age and the Bronze Age. From the ancient civilizations of Egypt and Babylonia he was employing a range of materials such as stones, woods, ceramics, glasses, skins and fibers.

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

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

Polymers are substances containing a large number of structural units joined by the same type of linkage. These substances often form into a chain-like structure. Polymers in the natural world have been around since the beginning of time. Starch, cellulose and rubber all possess polymeric properties. Man-made polymers have been studied since 1832. Today, the polymer industry has grown to be larger than the aluminium, copper and steel industries combined.

For living human body or any living things one necessary molecule is required, which is known as protein got synthesized in natural form by reacting simple chemical compounds like methane, ammonia and carbon dioxide. The protein is a natural polymer on which the life is supported. Polymers are also appeared in their other natural forms like wood, cotton, cellulose, starch, etc.

Over the many civilizations, however human beings have been finding different ways to meet their basic requirements. Once upon a time the need to cover the body was met by animal skins; it is being met by polyester today. As the time passes people had tried to develop synthetic polymers for different purposes. “The motivation behind all the research is necessity”.

However, polymers have obviously not been discovered overnight. They come out of long and pressuring study by a host of motivated scientists, whose work has enriched life. Today and also in forth coming days, the over all insight into polymer science and technology is so deep that a material scientists can create an almost limitless range of new materials.

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

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

Until the 19th century man’s inanimate possessions, his home, his tools, his furniture, were made from varieties of these classes of materials.

[A] Literature Survey on Cardo Diamines

Functional groups containing nitrogen atoms are responsible for their unique chemical reactivity patterns and play important role in the preparation of drugs, dyes, agrochemicals and molecules of life. There are many functional groups, which contain one or more nitrogen atoms. Some categories of compounds based on these functional groups include nitro compounds, amines, cyanides, isocyanides and diazo compounds. The chief commercial uses of amine compounds are found as intermediates in the synthesis of dyes, synthetic fibers and medicines, etc.

Diamines are the important constituents or intermediates in dyes, agrochemicals, varnish, coating, pesticides, fertilizers, etc. Their major applications are as a chain extender, liquid crystalline polymers, membranes, sensors, curatives, semiconductors, etc.

Yuko Ishihara [1] synthesized 3-3'-diamino-4-4'-diphenoxy benzophenone and its derivatives, and used as a monomer for a polyimide resin fiber reinforcement.

Toshiya [2] and Wen–Chung Chu [3] have synthesized diamino compounds which are used to prepare polyamide resin, for liquid crystal aligning film with a less image sticking, with a high voltage holding ratio from a low temperature to high temperature even under high humidity.

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1. Yuko Ishihara, "Aromatic dinitro and diamino intermediates", Yuko Ishihara, U.S. 5,710,334, 1998.
2. Toshiya Sawai, "Diamino compounds and methods for preparing them", U.S. 5,663,440, 1997.
3. Wen-Chung Chu, "Aromatic diamine derivatives, the preparation thereof and alignment film material containing same for liquid crystal display cell", U.S. 00884653 A1, 2004.

Yaw – Temg Chern and Ming – Hung Ju [4] have synthesized diamine from the reaction between 2, 6 di-tert-butyl phenol and 4-chloro nitro benzene in presence of K_2CO_3 in DMSO solvent. This intermediate was further treated with 2-fluoro 5–nitro benzene trifluoride and finally reduced in presence of 10% Pd – C catalyst. White crystals having m.p. is 120 – 122°C and the yield of 85 % achieved. The diamine was used for the synthesis of polyimide for pretilt angle of liquid crystals.

Singh and Rao [5] have synthesized various semiconductors based on aromatic diamines with various electron acceptors. Aromatic diamine such as benzidine with various acceptors name iodine, 2,3-dichloro, 5,6-dicyano, p-bezoquinone, tetra cyano quinodimethane and p-chloroanil were used for the said purpose. They posses low electrical conductivities and two thermal activation energies indicating mixed conductivity mechanism in which both the electrons and holes are charge carriers.

Diamines having different cardo groups (Latin meaning Loops) such as cyclo aliphatic moieties (cyclopentane, cyclohexane), cyclo aromatic moieties (anthraquinone, fluorenyl, norbornane, quinuclidine) are mostly used in the synthesis of amides, imides, Schiff bases, epoxy resins, poly urea, etc.

Korshak et al. [6] have synthesized a series of polymers containing bis(phenyl)fluorenes or bis(phenyl)phthalides as cardo groups and reported their physical properties.

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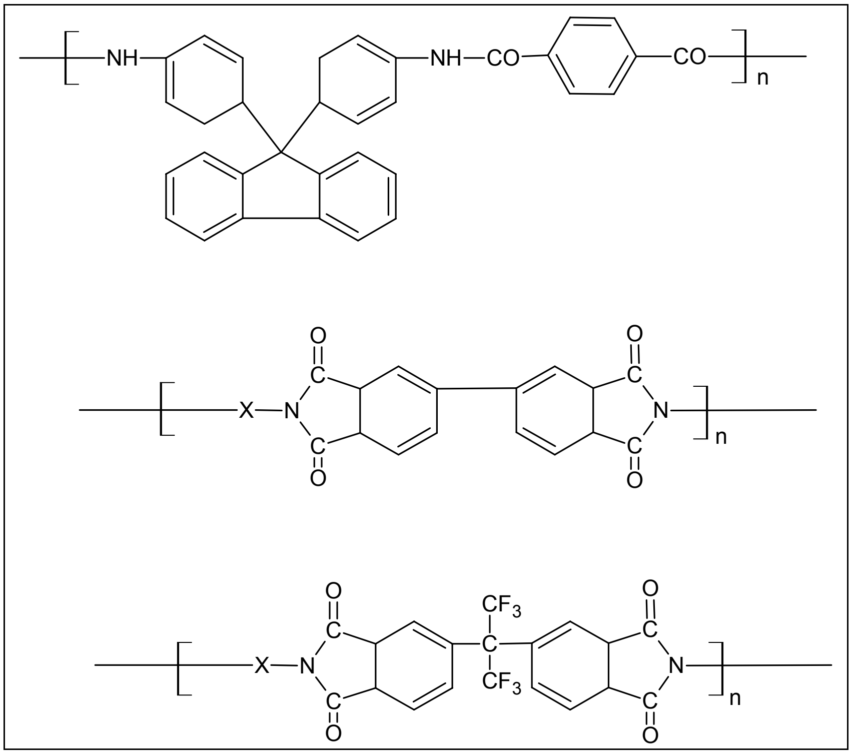
4. Yaw – Temg Chern and Ming – Hung Ju, “Conformation of polyimide backbone structure for determination of pretilt angle of liquid crystals”; Macromolecule, 42(1), 169 -179, 2009.
5. Ram Adhar Singh and O. Sundar Rao, “Synthesis and characterization of molecular semiconductor based on aromatic diamine with various electron acceptors”, Bull. Mater. Sci., 18, 541-548, 1994.
6. V. V. Korshak, S. V. Vinogradova and Y. S. Vygodskii, “Cardo polymers”, Macromol.. Sci- Rev. Macromol. Chem., C11, 45-142, 1974.

The phenyl fluorene based cardo polymers show high thermal stability, high solubility, high transparency, high refraction index and so on. [7, 8]. This good stability enables the preparation of an ultra thin layer as a membrane.



Aromatic diamines based on quinuclidine are widely used for the synthesis of thermally and chemically stable polyimides. Different drugs containing quinuclidine moieties are prepared, one of them namely phenacarol provides effective relief against allergies [9].

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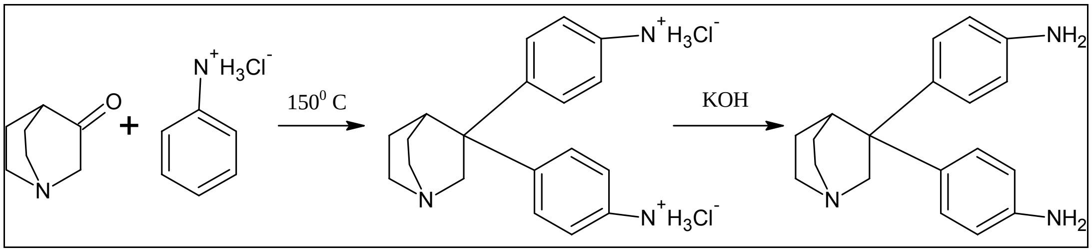
7. H. Andoh, B. T. Teramoto, “Polyarylate containing fluorine units: prepearation and properties”, Polym. Preprints Jpn., 31, 677-684,1990.
8. T. Teramoto, “Cardo polyamide membranes for CO_2 capture from flue gases”, Kogyo, Zairyo, 43, 79, 1995.
9. M. D. Mashkovskii and L. S. Meditsina, Moscow, 1, 312, 1984.

Vygodskii et al. [10] have reported synthesis of 3,3'-bis(4-aminophenyl) quinuclidine and its polymer.

22.83 g (0.22 mol) aniline hydrochloride and 10.0 g (0.1 mol) quinuclidione–3 mixture was heated at 150°C and then the reaction temperature was raised to 170°C.



At this temperature the reaction mixture was stirred for 3h. AQ hydrochloride was cooled to 140°C and 25-30 ml boiling water was added to obtain transparent deep red solution. The solution was refluxed with activated charcoal and filtered. AQ was precipitated by adding 20% KOH solution, filtered, washed repeatedly with ice water and dried at 50-60°C. AQ was crystallized by vacuum sublimation at 200°C. The yield was 43%.

IR spectrum showed absorption peak at 3380 and 3460 cm^{-1} due to primary NH_2 groups. ^{1}HNMR spectrum has shown a singlet at 5.62 ppm due to NH_2 groups, multiplet at 3.10 – 1.75 ppm due to quinuclidine moiety and at 7.00 - 6.56 ppm due to benzene ring.

Liaw et al. [11] have reported synthesis of new cardo diamine monomer 1,1'-bis[4-(4-amino phenoxy)phenyl] 4-tert butyl cyclohexane. This cardo diamine was prepared in three steps from 4-tert butyl cyclohexanone as under.

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10. Y. S. Vygodskii, N. A. Churochkina, T. A. Panova, Y. A. Fedotov, "Novel condensation functional polymers having highly basic groups", Reactive & Functional Polym., 30, 241-250, 1996.
11. D. J. Liaw, B.Y. Liaw, and C.Y. Chung, "Synthesis and characterization of new cardo polyamides and polyimides containing tert – butylcyclohexylidene units", Macromol. Chem. Phys. 201, 1887-1893, 2000.

1,1'-Bis(4-hydroxyphenyl)-4-tert-butylcyclohexane (BHBC)

A flask was charged with a mixture of 0.067 mol (10.4 g), 4-tertbutylcyclohexanone, 0.2mol (19g) phenol and 1mol 3-mercaptopropionic acid. Heat was applied and when the reaction mixture became liquid at 58°C, anhydrous hydrogen chloride was introduced until the solution became saturated. Stirring was continued at 60°C for 2 h, during which period white solid began to separate from the reddish-orange reaction mixture.

The solid mass was dispersed in 1L of water and the mixture was steam distilled to remove the excess phenol and 3-mercaptopropionic acid leaving an aqueous suspension. The solid residue was collected from the mixture by filtration and recrystallization from toluene twice gave 1,1'-bis(4-hydroxyphenyl) -4-tertbutylcyclohexane (BHBC). The yield was 74% and m. p. 181-182°C.

1,1'–Bis[4-(4–nitrophenoxy)phenyl]–4-tert-butylcyclohexane (BNPBC)

A mixture of 0.028 mol (9.2g) BHBC, 0.06 mol (9.44 g), p-chloro nitrobenzene, 0.07mol (9.7g) anhydrous potassium carbonate and 50ml anhydrous DMF was refluxed for 8h. The mixture was then cooled and poured into methanol. The crude product 1,1'-Bis[4-(4-nitrophenoxy)phenyl]-4-tert-butyl cyclohexane (BNPBC) was recrystallized from glacial acetic acid to give yellow needles (m.p. 190-191°C) in 94% yield. The characteristic IR absorption peaks of BNPBC are 1578 and 1334 cm^{-1} (NO_2) 1243 cm^{-1} (C-O-C). ^{1}HNMR ($CDCl_3$) showed following signals (ppm): 8.21-8.16 (m, 4H, aromatic H ortho to NO_2 groups); 7.46 (d, 2H, aromatic H ortho to cardo group); 7.26 (d, 2H, aromatic H ortho to cardo group); 7.03-6.94 (m, 8H, aromatic H meta to NO_2 and cardo group); 2.76-1.21 (m, 9H, cyclohexane group); 0.81 (9H,-CH_3).

1,1'-Bis [4-(4-aminophenoxy) phenyl] 4-tert-butylcyclohexane (BAPBC)

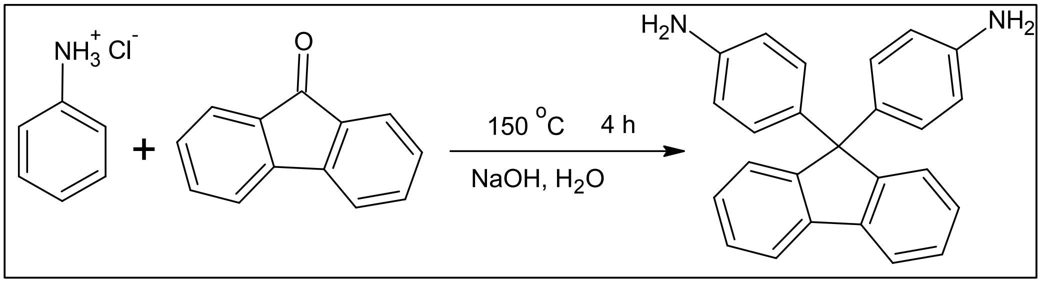
A 20 ml hydrazine monohydrate was added drop wise to a mixture of 0.014mol (7.98g) BNPBC, 160 ml ethanol, and a catalytic amount of 10% palladium on activated carbon (Pd/C, 0.06 g) at the boiling temperature.

The mixture became homogeneous after 1h and the reaction was refluxed for 24h. The mixture was then filtered to remove Pd/C. After cooling, the precipitated white crystals of 1, 1'–bis [4-(4–aminophenoxy phenyl]–4 –tert–butyl cyclohexane (BAPBC) were isolated by filtration and recrystallized from ethanol to give 83% yield (m.p. 171-172°C). The IR spectrum (KBr) of BAPBC exhibited characteristic absorptions at 3418, 3350 and 1613 cm^{-1} (N-H), and 1237 cm^{-1} (C-O-C).

BAPBC was reacted with various aromatic dicarboxylic acids and tetra dicarboxylic dianhydrides to produce polyamides and polyimides, respectively. Polyamides and polyimides imparted greater solubility, enhance rigidity as well as better thermo-mechanical properties.

Aromatic diamines are widely used for the synthesis of polyimides, which have been noted for their excellent characteristic properties. But their processability is poor, which limits their application area [12]. Therefore various efforts have been made to synthesize soluble polyimides without sacrifice of their excellent properties.

Xie Linghai et al. [13] have reported synthesis of 4,4'-(9-fluorenylidene)dianiline and fluorenone derivatives.



0.22 mol aniline hydrochloride and 0.1 mol 9-fluorenone mixture was heated at 150°C. At this temperature the reaction mixture was stirred for 4h. The resultant 4,4'-(9-fluorenylidene)dianiline hydrochloride was poured in distilled water and precipitated by adding NaOH solution and put it at room temperature for 4h, then filtered, washed repeatedly with water and dried.

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12. D. Wilson, H. D. Stenzenberger and P.M. Hergenrother, "Polyimide", Glasgow, U. K. 1991.
13. Xie Linghai, Huang Wei, Zhao Jianfeng, Chang Yongzheng, Lin Zongqiong and Qian Yan, "A process for preparing fluorenone derivatives" Assignee Nanjing University of Posts and Telecommunications, CN 101643381, 2010

By using diamines having cyclic ring between two benzene rings, the obtained polymer showed good thermal stability as well as solubility [14].

Choi et. al [15] have reported the synthesis of series of novel aromatic diamines containing cyclohexane moieties. They have also synthesized and characterized soluble polyimides from1,1'-bis(4-aminophenyl)cyclohexane derivatives.

1,1'-Bis (4-aminophenyl) cyclohexane (BACH)

BACH was prepared by the condensation of cyclohexanone and excess aniline. To a solution of 0.41mol (40.0g) cyclohexanone in 35% HCl aqueous solution in a 1L autoclave equipped with a mechanical stirrer was added 1.68mol (156.3g) aniline and the mixture was stirred at 120°C for 20h. After cooling, the solution was made basic with aqueous NaOH solution to pH 10, and the oily layer was separated and steam distilled to remove the unreacted excess aniline. The residual crude product was recrystallized from benzene to give 86.4g (79.4% yield) of light-yellow crystal (m.p. 112°C).

1,1'-Bis(4-aminophenyl)-4-methylcyclohexane (BAMC) and 1,1'-bis(4-amino phenyl)-3,3,5-trimethyl cyclohexane (BATMC) were prepared in a similar manner to that of BACH by reacting 4-methylcyclohexanone and 3,3,5-trimethyl cyclohexanone with aniline.

BAMC was recrystallized from isopropyl alcohol to give light yellow crystals (m.p. 158.8°C). BATMC was recrystallized from isopropyl alcohol (m.p. 46°C).

The structures of BACH, BAMC and BATMC were supported by elemental, IR, mass and NMR spectral data. They have also proposed the mechanism of diamines formation and was confirmed by the structural identification of a major by ^{1}HNMR. The dehydration reaction was faster than the substitution reaction of aniline and therefore diamine yield is low.

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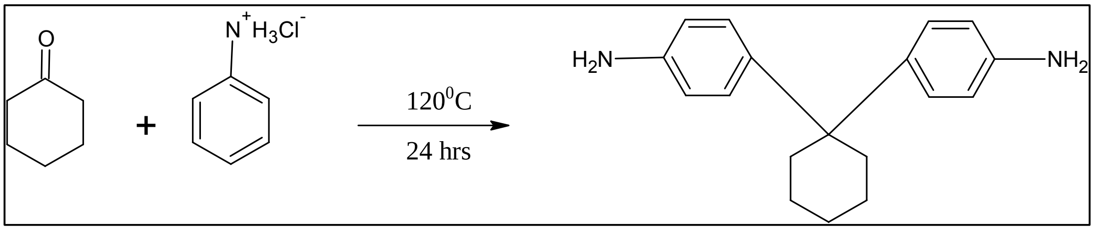
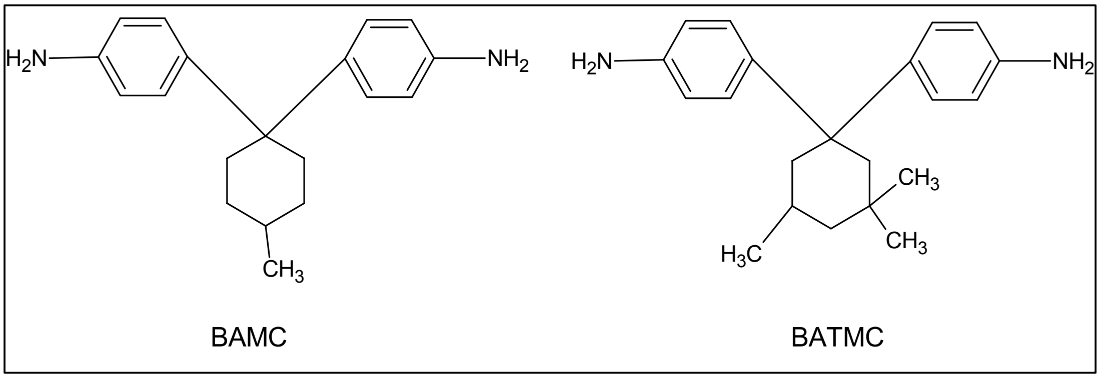
14. K. Y. Choi, M. H. Yi and M. Y. Tin, "Polymeric Materials Encyclopedia", CRC. Boca Raton, New York, London. Vol-7, 5379, 1996.
15. M. H. Yi, W. Hung, M. Y. Tin and K. Y. Choi, "Synthesis and characterization of soluble polyimides from 1, 1'-bis (4-amino phenyl) cyclohexane derivatives", Macromolecules, 30, 5606-5611, 1997.





Yi et al. [16] have reported the synthesis and characterization of soluble polyimides from aromatic diamines containing polycycloalkane structure between two benzene rings.

2,2’-Bis(4-aminophenyl)norbornane (BANB) and 2,2’-bis(4-amino phenyl) admantane (BAAD) were synthesized by HCl catalyzed condensation reaction of corresponding polycycloalkanone with aniline hydrochloride at 140-160°C for 20 h. The yields of diamines were 32-35% and the structures of diamines were supported by FTIR, ^{1}HNMR, ^{13}CNMR spectroscopy and elemental analysis.

To a 500ml four-neck flask equipped with a mechanical stirrer was placed 0.16mol (17.6g) of 2-norbornanone, 0.48 mol (45.0g) aniline and 0.32mol (41.5g) aniline hydrochloride and the mixture was stirred at 140-160°C for 2h. After cooling, the solution was made basic with aqueous NaOH solution to pH 10, and the purple oily layer was separated and steam distilled to remove the unreacted aniline and then recrystallized from ethyl acetate to give 15.0 g (35.2%) off white crystals of BANB (m.p. 202°C).

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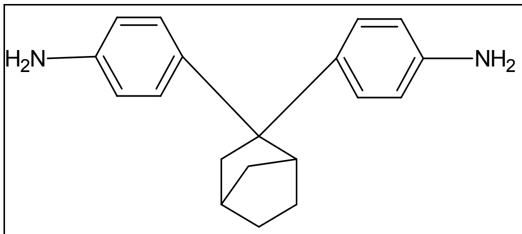
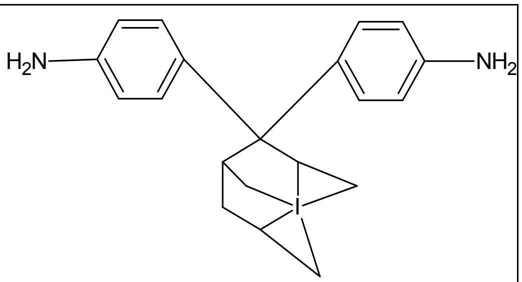
16. M. H. Yi, W. Huang, B. J. Lee, and K. Y. Choi, “Synthesis and characterization of soluble polyimides from 2, 2’-bis (4-aminophenyl) cycloalkane derivatives”, J. Polym. Sci. Part-A Polym. Chem., 37, 3449-3454, 1999.



BANB



BAAD

The structure of BANB was supported by MS, FTIR [3444 and 3359 cm^{-1} (NH str.), 1615 cm^{-1} (NH def)] spectral and elemental analysis.

Inoki et al. [17] have studied curing behavior and properties of epoxy resins cured with the diamines having heterocyclic ring. The diamines 2,3'- bis (4-amino phenyl) benzoquinoxaline (BABQ); 4,5-bis (4-aminophenyl)2-phenyl imidazole (BAPI), and 4,5- bis (4-amino phenyl) 2-methyl oxazole (BABQ) were prepared and used as curing agents. They have reported that DGEBA cured with aromatic diamine having heterocyclic ring, especially 2,3 bis (4-aminophenyl) quinoxaline (BAPQ) displayed both excellent bonding strength and thermal stability.

Commercially available diamines such as, 4,4'-diamino diphenyl sulfone (DDS), 4,4'-diamino diphenyl methane (DDM) or m-phenylene diamine possess high bonding strength at lower temperature, but fall at elevated temperature, while the epoxy resin cured with BAPQ has high bonding strength even at 180°C.

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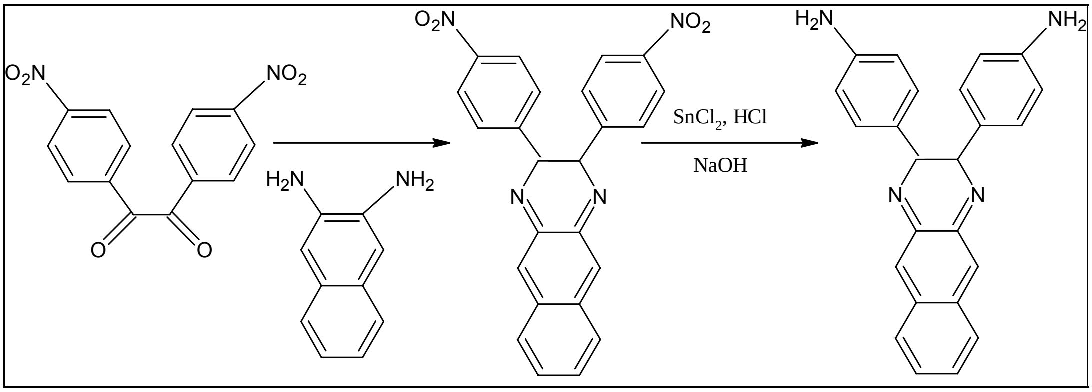
17. M. Inoki, S. Kimura, N. Daicho, Y. Kasashima F. Akutsu and K. Marushima, "Curing behavior and properties of epoxy resins cured with diamine having heterocyclic ring", J. Macromol. Sci- Part A, 39, 321-331, 2002.



Union Carbide Co. [18] has reported curing of polyepoxides with liquid glycol diamines ($H_2N(CH_2)_3O(C_nH_{2n}O)x\ (CH_2)_3NH_2$), where n is 2-5 and x is 1-11. The cured compounds have excellent impact strength and flexibility and are stable as protective coatings. Thus, 100 g of diglycidyl ether was mixed with 29.4g stoichiometric amount $H_2N(CH_2)_3O(CH_2CH_2O)_2(CH_2)_3NH_2$ for 5 min. The mixture was applied on cold-rolled steel and was cured by storing 7 days at room temperature.

Joshi et al. [19] have studied curing behavior and properties of epoxy resins of 1,1'-bis(4-hydroxy-phenyl) cyclohexane by using 50% pyromellitic dianhydride(PMDA), tetrachloro phthalicanhydride (TCP), bisphenol-C-formaldehyde resin (BCF), diamino diphenyl methane (DDM) and 1,1'-bis(4-amino phenyl)cyclohexane (DDC) as curing agents at 230°C/150°C.

PMDA, TCP and BCF cured resins are insoluble in all common solvents, while DDM and DDC cured resins are soluble in common solvents. BCF, PMDA, TCP and DDC cured samples are thermally stable up to about 350-365°C except DDM cured sample (275°C).

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18. Union Carbide Co. (by Norman H. Reinking.), "Liquid glycol diamine curing agent for polyepoxides", Brit. 904,403 -1962; Chem. Abstr. 58, 1643, 1963.
19. J. K. Joshi, S. T. Gadhia and P. H. Parsania, "Thermal properties of cured bisphenol –C–epoxy resins", J. Polym. Materials, 21, 133, 2004.

[B] Literature Survey on Schiff Bases

The chemistry of carbon-nitrogen double bonds has played a vital role in the progress of chemical sciences. Due to presence of a lone pair of electrons on the nitrogen atom and general electron donating character of the double bond, these compounds have found very large applications in the field of chemistry.

The compounds containing >C=N group are known as imines or azomethines or anils or ligands but generally they are known as "Schiff bases " in honor of German Chemist Hugo Schiff who have synthesized such compounds very first time [20,21].

The literature survey revealed that Schiff bases are useful as starting material in the synthesis of important drugs, such as antibiotic, antiallergic, anticancer, antiphologistics and antitumor, etc [22-24]. Schiff base compounds are widely used as fine chemicals, analytical reagents, corrosion inhibitors as well as ligands [25].

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20. H. Schiff, Ann. Chem. 131,118-119, 1864.
21. P. G. Cozzi, "Metal-Salen Schiff base complexes in catalysis: Practical aspects", Chem. Soc. Rev., 33, 410-421, 2004.
22. S. Patai, "The chemistry of the carbon nitrogen double bond", John Wiley and Sons Ltd., London 1970.
23. V. E. Kuzmin, A.G. Artemenko, R. N. Lozytska, A. S. Fedtchouk, V. P. Lozitsky, E. N. Muratov and A. K. Mescheriakov, "Investigation of anticancer activity of macro cyclic Schiff bases by means of 4-D QSAR based on simplex representation of molecular structure", SAR and QSAR in Environmental Research, 16, 219-230, 2005.
24. C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Ithaca Cornell Univ. 2nd ed., 1969.
25. A. P. Mishra, M. Khare and S. K. Gautam, "Synthesis, physico–chemical characterization and antibacterial studies of some bioactive Schiff bases and their metal chelates", Synth. React. Inorg. Metal Org. Chem., 32, 1485-1500, 2002.

Metal complexes synthesized from Schiff bases have been widely studied because of their industrial, antifungal and biological applications [26,27]. Schiff bases possess characteristic properties like manifest of thermal stabilities, abnormal magnetic properties, relevant biological properties, high synthetic flexibility, co-ordinating ability and medicinal utility. A wide range of Schiff bases have been synthesized and extensively studied [28,29]. The Schiff bases are the condensation products of aromatic or aliphatic aldehydes (e.g. benzaldehyde, cinamaldehyde, crotonaldehyde, etc.),with aliphatic or aromatic mono or diamines (e.g. aniline, aminophenols,1,2-ethanediamine, benzidine, diamino diphenyl methane , diamino diphenyl sulphone, etc.)[30-33].

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26. D. Y. Sabry, T. A. Youssef, S. M. El-Medani and R. M. Ramadan, “Reaction of chromium and molybdenum carbonyls with bis(salicylaldehyde)ethylene diimine Schiff base ligand”, J. Coord. Chem., 56, 1375-1381, 2003.
27. M. Nazimuddin, M. A. Ali, F. E. Smith and M. A. Mridha, “Preparation, characterization and antifungal activities of nickel(II) and copper(II) complexes of ONS ligands formed from acetyl acetone and alkyldithiocarbazates”, Trans. Met. Chem., 17, 74-78, 1992.
28. M. E. Hossain, M. N. Alam, J. Begum, M. A. Ali, F. E. Smith and R. C. Hynes, “The preparation, characterization, crystal structure and biological activities of some copper(II) complexes of the 2-benzoyl pyridine Schiff bases of 5-methyl and 5-benzyldithiocarbazate“, Inorg. Chimica Acta, 249, 207-213, 1996.
29. Y. P. Titan, C. Y. Duan and X. Z. You, “Crystal structures spectroscopic and nonlinear optical properties of metal complexes of Schiff base ligands containing nitrogen and sulphur donors”, Trans. Met. Chem., 23, 17-20, 1998.
30. Y. P. Titan, C. Y. Duan, Z. L. Lu and X. Z. You, “Crystal structures and spectroscopic studies on metal complexes containing NS donor ligands derived from 5-benzyldithiocarbazate and p-dimethylamino benzaldehyde”, Polyhedron, 15, 2263-2271, 1996.

Agarwal et al. [34] have proved that Schiff bases possess the unique characteristic of improving both anti wear and corrosion inhibition properties of a lubricant. Schiff bases derived from the reaction of an aromatic aldehyde such as salicylaldehyde and aromatic diamines can be added to a variety of lubricants and particularly lubricating oil greases in amount ranging up to about 5% by weight of the total composition.

They are very useful for high performance engines such as machinery aboard ship, submarines and particularly in the aircraft industry. The engines perform well at higher speeds, higher load and higher temperature and therefore life of lubricants and engine parts decrease, which can be prevented by using Schiff bases as additives in lubricating oils and greases

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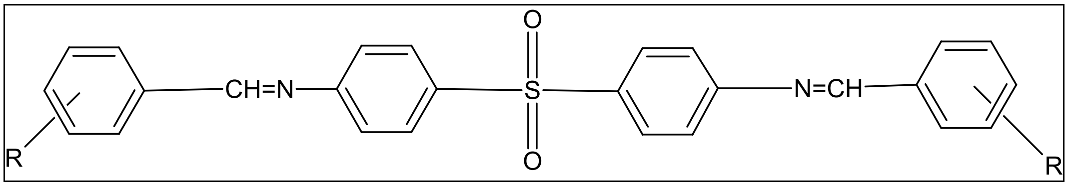
31. N. Parvathi and K. L. Omprakash, "Mixed ligand complexes of a novel Schiff base derived from benzimidazole 2-carboxaldehyde and ethylene diamine", J. Electro. Chem. Soc. India, 51, 96-98, 2002.
32. Saraii, Mahnaz, Entezami, Ali Akbar, "Synthesis and characterization of poly Schiff bases derived from 5a, 10b-dihydrobenzofuro-[2,3-B] benzofuran-2,9-dicarbaldehyde with various diamines", Iranian Polym. J., 12, 43-45, 2003.
33. K. Mishra, A. Power, P. Chopra, M. Sharma and R. Chatal, "Synthesis of novel bifunctional Schiff bases ligands derived from condensation of 1-(p-nitro benzyl)ethylene diamine and 2-(p-nitrobenzyl)-3-monooxo,1,4,7-triazaheptane with salicylaldehyde", New J. Chem., 27, 1054-1058, 2003.
34. V. S. Agarwal, K. S. Rajan and P. K. Sen, "Synthetic lubricating oil greases containing metal chelates of Schiff bases", U.S. 5,147,567, 1992.

Das et al. [35] have reported metal ion uptake behavior of chelating resins derived from formaldehyde and phenolic Schiff bases. They were synthesized by the condensation of 4, 4’- diamino diphenyl sulfone with ortho, meta and para - hydroxy benzaldehyde, respectively. The metal ion uptake behavior of these resins towards Cu^{+2}, Ni^{+2}, Co^{+2} and UO^{+2} ions in dilute aqueous media was studied. The optimum conditions for efficient uptake of metal ions were determined by varying the various parameters like contact time, size of sorbents, concentration of metal ion in the solution and pH of the reaction medium.

They have reported that out of three resins, resin containing –OH groups at meta position has a significant influence on the extent of metal ion uptake tendency. They have also reported that all these resins could be employed successfully to separate Cu^{2+} efficiently from binary mixture of Cu^{2+}-Ni^{2+} and Cu^{2+}-UO_2^{2+} at different pH values.



R = -OH at ortho, meta and para position, respectively.

Ray et al. [36] have reported metal ion uptake behavior of formaldehyde condensed resins of phenolic Schiff bases derived from the reaction of 4,4’-diamino diphenyl and 4,4’-diamino diphenyl methane with o-hydroxy benzaldehyde.

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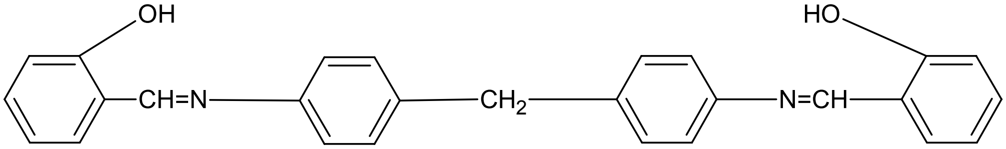
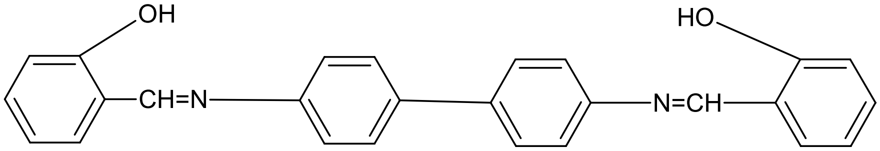
35. R. R. Das, S. Samal, S. Acharya, P. Mohapatra and R. K. Dey, “A comparative study on metal ion uptake behavior of chelating resins derived from the formaldehyde condensed phenolic Schiff bases of 4,4’-diamino-diphenyl sulfone and hydroxyl benzaldehydes”, Polym. Plast. Technol. Eng., 41, 229-246, 2002.
36. A. R. Ray, S. Samal, S. Acharya and R. K. Dey, “Studies of metal ion uptake behavior of formaldehyde condensed resins of phenolic Schiff bases derived from the reaction of 4,4’-diamino diphenyl and 4,4’-diamino diphenyl methane with o-hydroxy benzaldehyde”, Ind. J. Chem. Technol., 11, 695-703, 2004.

They have examined metal ion uptake characteristic of o-HB-DDM-HCHO and o-HB-DD-HCHO towards transition metal ions like Cu^{+2}, Ni^{+2} and UO_2^{+2} under both competitive and non-competitive conditions. The resin o-HB-DDM-HCHO is more effective in removing metal ions in comparison of o-HB-DD-HCHO.



o - HB DDM



0 - HB - DD

Several Schiff bases have been investigated as corrosion inhibitors for various metals and alloys in acidic media [37-39].

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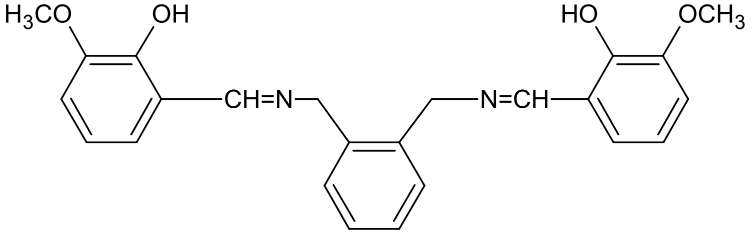
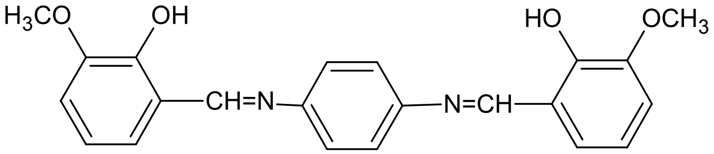
37. M. N. Desai, M. B. Desai, C. B. Shah and S. M. Desai, "Schiff base as corrosion inhibitors for mild steel in hydrochloric acid solutions", Corros, Sci., 26, 827-837, 1986.
38. H. Shokry, M. Yuasa, I. Sekine, R. M. Issa and G. K. Gomma, "Corrosion inhibition of mild steel by Schiff base compounds in various aqueous solutions, Part-1", Corros, Sci., 40, 2173-2186, 1990.
39. S. Li, S. Chen, S. Lei, H. Ma, R. Yu and D. Liu, "Investigation on some Schiff base as HCl corrosion inhibitors for copper", Corros, Sci., 41, 1273-1287, 1999.

Ma et al. [40] have reported that Schiff bases synthesized from 3-methloxy salicylaldehyde with aromatic diamines exhibited strong inhibition of copper corrosion in chloride solution at different pH. In addition these molecules are environmentally friendly. The chemical structures of two Schiff bases are



N-N' o-phenylene - bis(3-methoxy salicylidenimine)



N-N' p-phenylene - bis(3-methoxy salicylidenimine)

Kuzmin et.al [41] have reported anticancer activity of a set of macro cyclic Schiff bases based on 2,6-bis (2 and 4 formylaryl -oxy methyl) pyridines. They have derived correlation equation between the anticancer activity and structural parameters of the molecules studied.

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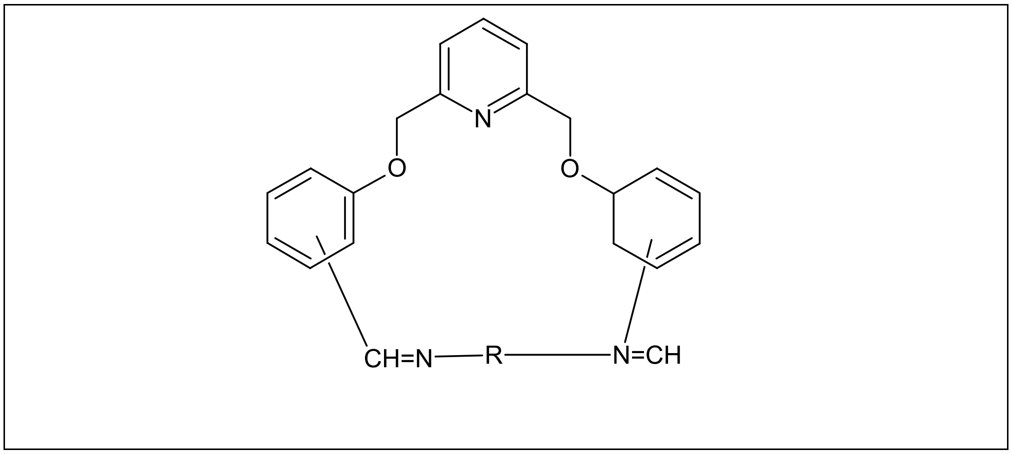
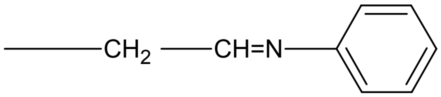
40. H. Ma, S. Chen, L. Niu, S. Zhao, S. Li and D. Li, "Inhibition of copper corrosion by several Schiff bases in aerated halide solutions", J. Appl. Electrochem., 32, 65-72, 2002.
41. V. E. Kuzmin, V. P. Lozitsky, G. L. Kamalov, R. N. Lozitskaya, A. I. Zheltvay, A. S. Fedtchouk and D. N. Kryzhanovsky, "Analysis of the structure-anticancer activity relationship in a set of Schiff bases of macro cyclic 2,6-bis(2 and 4-formylaryl oxymethyl)pyridines", Acta Biochimica, Polonica, 47, 867-875, 2000.

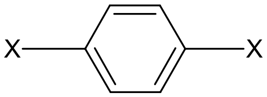


Where R= various aromatic and aliphatic diamines

They have proved that the increase in activity of the investigated Schiff bases towards leukemia and prostate cancer is caused by the presence of F1 fragments and the increased in number of F2 fragments lowered the activity both towards the CNS cancer and melanoma and so average activity towards nine tumors. Ortho-dialdehydes and aliphatic diamines macro cyclic Schiff bases containing two F1 fragments are the most effective, while the appropriate 4,4' derivatives and 1,4-phenylene diamine Schiff bases containing two F2 fragments give lower anticancer activity.



F_1

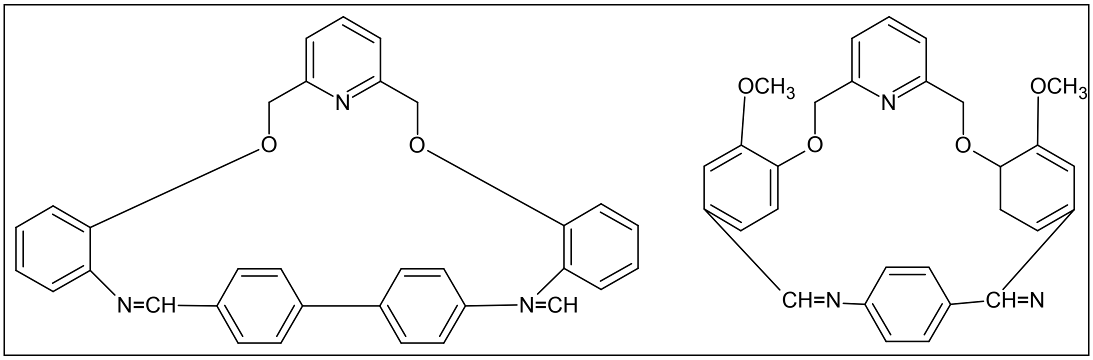


F_2

Where x = non aromatic carbon atom

Lozitsky et al. [42] have reported 4D-QSAR study and anticancer activity of macro cyclic Schiff bases. The Schiff bases were synthesized by the condensation of various aliphatic and aromatic diamines with 2,6-bis(2 and 4-formyl aryloxy methyl) pyridine derivatives. The results of biological activities showed that Schiff bases are active towards cell growth of the nine cell culture of human malignant tumors like leukemia, CNS cancer, prostate cancer, breast cancer, melanoma, small cell lung cancer, colon cancer, ovarian cancer and renal cancer.

They claimed that pyridine ring has a negative influence on anticancer activity, while the presence of the >C=N group with different substituent promotes anticancer activity. Para substituted phenyl with non-aromatic substituent prevent the activity.



Bhowon et al. [43] have reported antibacterial properties of Schiff bases and Schiff base metal complexes. The Schiff bases were derived from 2, 3-diamino pyridine and selected aldehydes namely, salicylaldehyde, 4-hydroxy benzaldehyde and 4-nitrobenzaldehyde.

The mixed Schiff bases of salicylaldehyde and p-hydroxy benzaldehyde were prepared by simple condensation in ethanol for 6h. The crystalline products were characterized by elemental, IR and NMR spectral analysis. These Bis Schiff bases displayed antibacterial properties against bacteria Pseudomonas aeruginosa and Salmonella.

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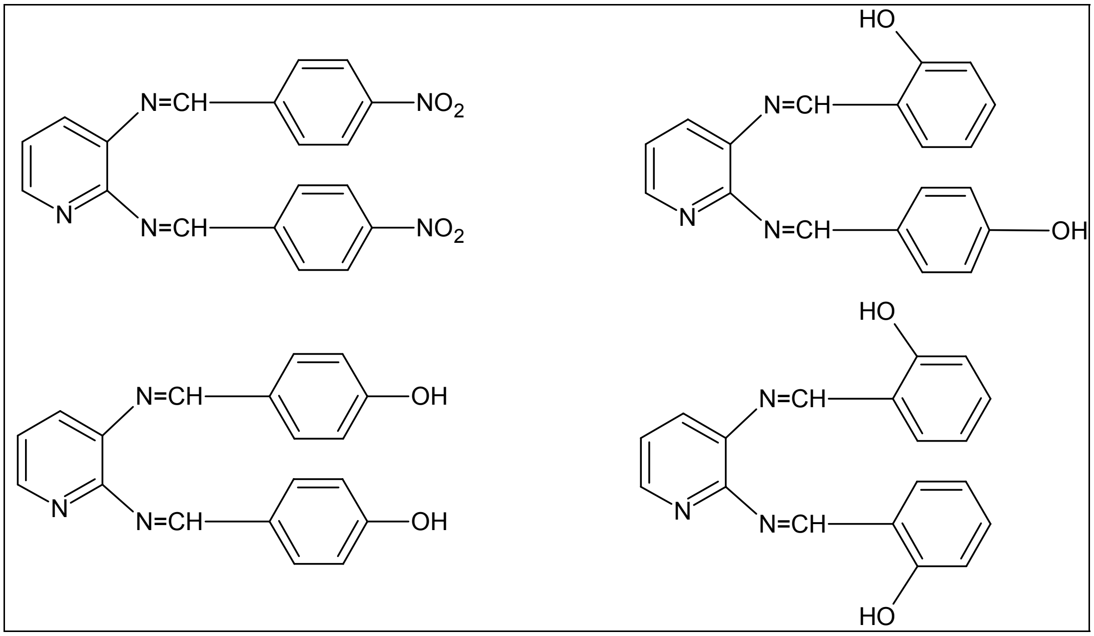
42. V. P. Lozitsky, V. E. Kuzmin, A. G. Artemenko, R. N. Lozytska, A. S. Fedtchouk, E. N. Muratov and A. K. Mescheriakov, “Investigation of anticancer activity of macrocyclic Schiff bases by means of 4D-QSAR based on simplex representation of molecular structure”, SAR and QSAR in Environmental Research, 16, 219-230, 2005

43. M. G. Bhowon, T. Jeewoth and H. L. Kam-Wah, “Synthesis, characterization and antibacterial properties of Schiff bases and Schiff base metal complexes from 2,3-diamino pyridine”, Transition Met. Chem., 4, 445-448, 1999.

The susceptibility is almost the same for both the microbes but inactive against Escherichia coli and Staphylococcus aureus. They have claimed that 2,3-diamino pyridine did not show activity against all these microbes, though all the Schiff bases have been found to be active against p. aeruginosa and Salmonella. Similarly Cu^{+2} and Ni^{+2} complexes of nitro Schiff base exhibited antibacterial activities against these two bacteria.



Kraicheva et al. [44] have reported synthesis and NMR spectroscopic study of three novel 5-methylfuryl containing Schiff bases. These three Schiff bases were synthesized by condensation of 5-methyl furfuraldehyde with appropriate mole ratio of 4,4'-diaminodiphenyl methane, 1,4-phenylene diamine and benzidine, respectively in diethyl ether with stirring at room temperature in nitrogen atmosphere for 4h. Schiff bases were recrystallized from cyclohexane.

They have also synthesized bis(amino phosphonates) of these three Schiff bases, which have biological properties and various applications in agro chemistry.

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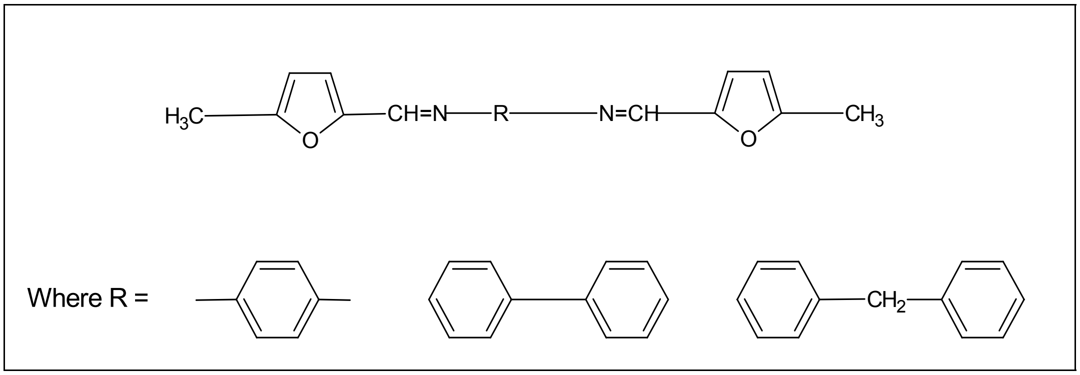
44. I. Kraicheva, P. Finocchiaro and S. Failla, "Synthesis and NMR spectroscopic study of new 5-methylfuryl containing Schiff bases and related Bis(amino phosphonates)", Phosphorus, Sulfur and Silicon, 179, 2345-2354, 2004.



Schiff bases play an important role in Inorganic Chemistry as they easily form stable complexes with the most metal cations [45-47]. Transition metal complexes of tetradentate Schiff base ligands find applications as model of certain metal enzymes, in catalysis and material chemistry [48].

In the field of co-ordination chemistry ortho-hydroxylated Schiff bases have received considerable attention [49]. The introductions of lateral polar hydroxy groups enhance the molecular polarizability as well as stabilizing the liquid crystalline compounds [50].

In addition Schiff base complexes are known to show antifungal activity, which is increased by the presence of hydroxy groups in the ligands [51].

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45. H. Temel and M. Sekerci, "Novel complexes of Manganese (II), Cobalt (II), Copper (II) and Zinc (II) with Schiff base derived from 1, 2-bis (p-amino phenoxy) ethane and salicylaldehyde", Synth. React. Inorg. Met. Org. Chem., 31,849-857, 2001.
46. H. Temel, U. Cakir and H. I. Urgas, "Synthesis and characterization of Zn (II), Cu(II) and Ni(II) complexes with bidentate Schiff base ligands, complexation studies and the determination of stability constant", Russ. J. Inorg. Chem., 46, 2022, 2001.
47. H. Temel, M. Sekerci, S. Ilhan and R. Ziyadanogullari, "Synthesis and characterization of new Cu (II), Ni (II), Co(II), and Zn(II) complexes with Schiff base", Spectroscopy Lett., 35 , 219-228, 2002.

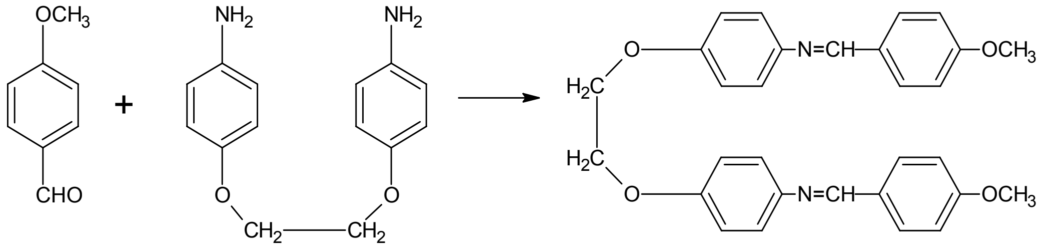
48. H. Temel, S. Ilhan and M. Sekerci, “Synthesis and characterization of a new bidentate Schiff base and its transition metal complexes”, Synth. React. Inorg. Met. Org. Chem., 32, 1625-1634, 2002.

49. H. Temel, U. Cakir, H. I. Urgas and M. Sekerci, “The synthesis, characterization and conductance studies of new Cu(II), Ni(II) and Zn(II) complexes with Schiff base derived from 1,2-bis(o-amino phenoxy) ethane and salicylaldehyde”, J. Coord. Chem., 56, 943-951, 2003.

50. G. Y. Yeap, S. T. Ha, P. L. Lim, P. L. Boey and W. A. K. Mahmood, “Synthesis and mesomorphic properties of Schiff base esters ortho-hydroxy, para-alkyloxy benzylidene-para substituted anilines”, Mol. Crystal. Liq. Cryst., 423, 73-84, 2004.

51. H. C. Lin, “Synthesis and characterization of some indium complexes of Schiff base”, Synth. React. Inorg. Met. Org. Chem., 23, 1097-1106, 1993.

Cakir et al. [52] have synthesized Cu(II), Ni(II), Zn(II) and Co(II) complexes of Schiff base derived from 4-methoxy benzaldehyde and 1,2-bis(4-aminophenoxy)ethane. Schiff base and its complexes were characterized by magnetic susceptibility, conductance measurements, elemental analysis, UV-Vis, ^{1}HNMR and IR spectral studies. Based on the physical and chemical data of spectral studies they have proposed structure of Schiff base and its complexes.



Temel [53] has reported Cu(II), Ni(II), and Zn(II) complexes with the Schiff base derived from 1,2-bis(o-amino phenoxy)ethane and 2-hydroxynaphthelin-1-carbaldehyde and are characterized by elemental analysis, magnetic measurement, ^{1}HNMR, UV–Visible and IR spectra, as well as conductance studies. Magnetic properties showed that Cu(II) Schiff base complex is a paramagnetic and its magnetic moment is 1.61 BM. Since Cu(II) complex is a paramagnetic and as a result its ^{1}HNMR spectrum could not be obtained, while Ni(II) and Zn(II) Schiff base complexes are diamagnetic and ^{1}HNMR spectra were obtained.

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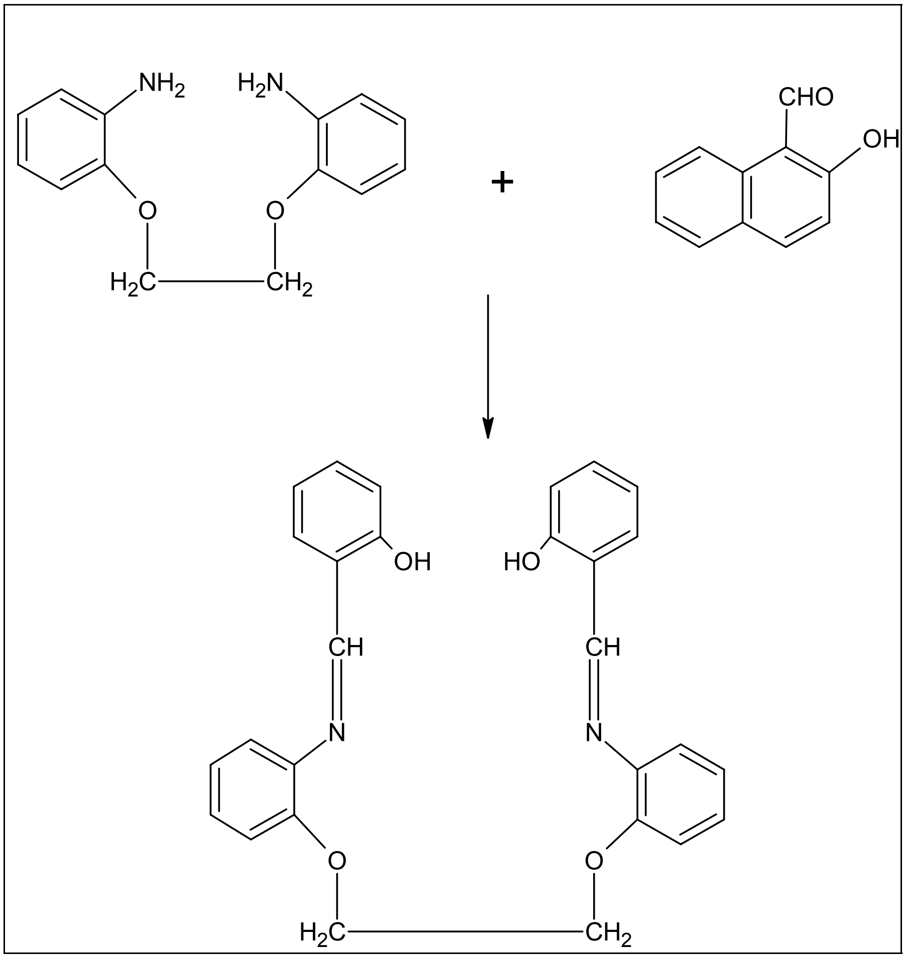
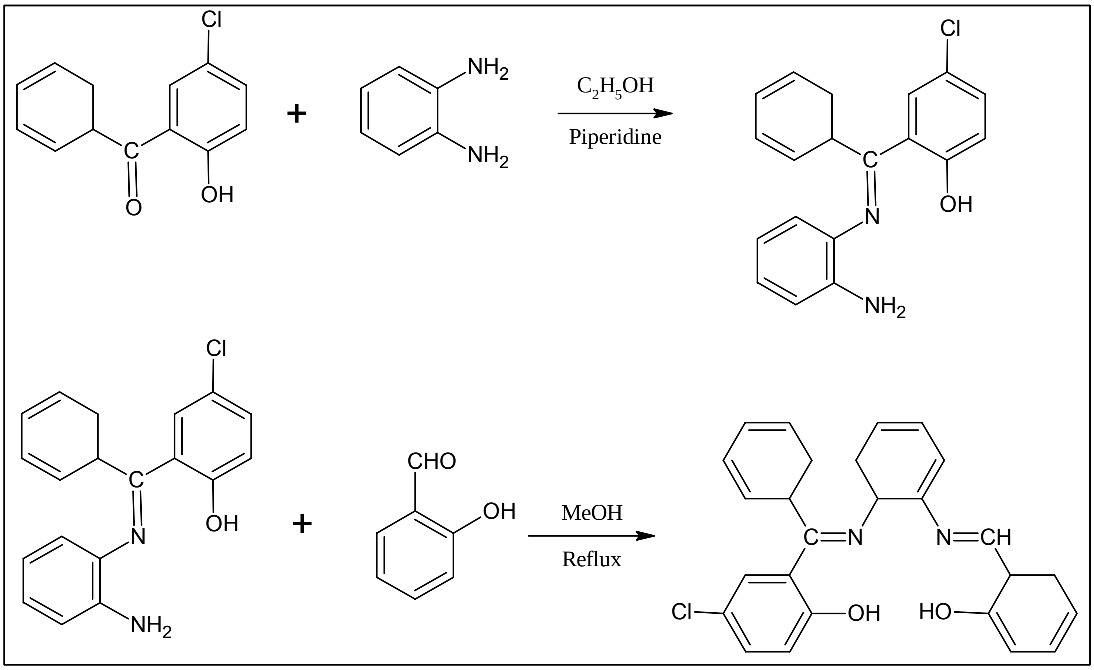
52. U. Cakir, H. Temel, S. Ilhan, and H. I. Ugras, "Spectroscopic and conductance studies of new transition metal complexes with a Schiff base derived from 4-methoxybenzaldehyde and 1,2-bis(p-aminopheoxy) ethane", Spectroscopy Lett., 36, 429-440, 2003.
53. H. Temel, "Synthesis and spectroscopic studies of new Cu(II), Ni(II), and Zn(II) complexes with n,n'-bis(2-hydroxy naphthelin-1-carbaldhydene) 1,2-bis(o-amino-phenoxy)ethane", J. Coord. Chem., 57, 723-729, 2004.

Conductivity studies showed that the complexes are non-electrolyte as shown by their molar conductivity measurements in DMF. Synthesis of the ligand n,n'-bis(2-hydroxy naphthelin-1-carbaldehydene)-1,2-bis(o-amino phenoxy)ethane



Bi and Fan [54] have reported that symmetric tetradentate Schiff base complexes are used extensively as macro cycle models [55], while asymmetric complexes are very important in biological systems and in industrial catalysis [56,57]. They have synthesized a new asymmetric tetradentate Schiff base ligands using 5-chloro-2-hydroxybenzophenone,o-phenylenediamine and salicylaldehyde. Five metal complexes of ligand have been prepared and characterized by elemental analysis, IR, UV spectra and molar conductance. Asymmetric Schiff base ligand was synthesized in two steps.



Patel et al. [58, 59] have reported synthesis of symmetric Schiff base known as n,n'-di(o-hydroxy phenyl) terephthalaldehyde diimine.

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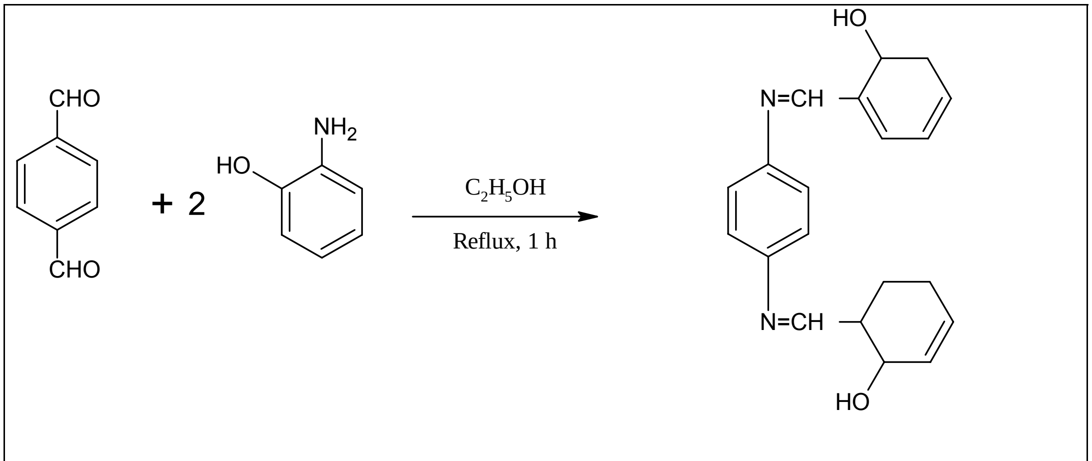
54. C. Bi and Y. Fan, "Synthesis and characterization of metal complexes with asymmetric tetradentate Schiff base ligands", Synth. Rea. Inorg. Met. Org. Chem., 34, 687-695, 2004.
55. K. E. Krakowiak and J. S. Bradshow, "Catalytic and anti microbial activities of new Ruthenium(II) unsymmetrical Schiff base complexes", Trans. Metal Chem., 27, 790-794, 2002.
56. E. Kwiatkowoski and M. Kwiatkowoski, "Metal complexes with unsymmetrical tetradentate Schiff base", Inorg. Chim. Acta, 82, 101-109, 1984.
57. W. George and D. M. Gokel, "Unsymmetrical Schiff base complexes of nickel (II) and palladium (II)", Inorg. Chim. Acta, 42, 197-202, 1980.
58. N. H. Patel, K. M. Patel, K. N. Patel and M. N. Patel, "Co-ordination chain polymers of transition metals with Schiff base", Synth. React. Inorg. Met -Org. Chem., 31, 1031-1039, 2001.
59. N. H. Patel, P. K. Panchal and M. N. Patel, "Synthesis and characterization and coordination polymers of trivalent lanthanides with a Schiff base", Synth. React. Inorg. Met.Org. and Nonmetal Chem., 35, 107-110, 2005.

They have also reported synthesis of Mn(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of Schiff base ligand and characterized by elemental analyses, IR and electronic spectra, magnetic measurements and thermo gravimetric analysis. The Schiff bases were derived from terephthalaldehyde and o-aminophenol.

They have noticed that when ethanolic solutions of terephthalaldehyde and o-aminophenol were mixed, a yellow crystalline solid was obtained immediately. The mixture was heated on a water bath for 1h and the ligand was filtered, washed successively with water and ethanol and dried in air. The ligand is insoluble in organic solvents like benzene, chloroform and acetone but soluble in DMF.



n-n' di (o- hydroxy phenyl) terephthaldehyde diimine

Cimerman et al. [60] have reported that Schiff bases play an important role in analytical chemistry because they are widely applicable in analytical determination of metal ions, as a solvent polarity indicators, spectroscopic and in tautomerism studies [61]. They have derived Schiff bases from amino pyridines and salicylaldehyde.

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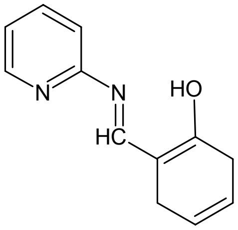
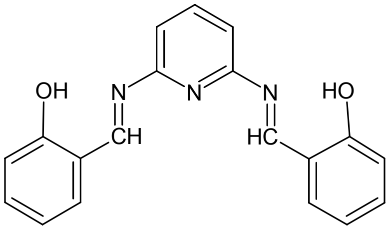
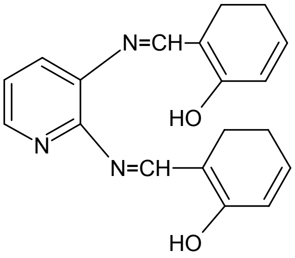
60. Z. Cimerman, S. Miljanic and N. Galic, “Schiff bases derived from amino pyridine as spectro fluorimetric analytical reagents”, Croatica Chemica. Acta. , CCACAA 73, 81-95, 2000.
61. E. Jungreis and S. Thabet, “Analytical Application of Schiff Bases” in H. A. Fluschka and A. J. Barnard, “Chelates in Analytical Chemistry”, Marcel Decker, New York, 2, 149-177, 1969.

These Schiff bases possess fluorescent characteristics. The fluoroscence of all the compounds is strongly pH dependent and find application in fluorimetry. It was shown that the quenching effect of Cu^{+2} on the fluorescence of n,n'-bis(salicylidene)-2-3 pyridine diamine can be used for copper determination. This procedure is simple and fast based on the correlation of structural properties, spectroscopic characteristics and complex formation capabilities of the condensation products of amino pyridines and salicylaldehyde.





n- n' Bis(salicylidene) 2,6 pyridine diimine



n- n' Bis(salicylidene) 2,6 pyridine diimine

The effect of the solvents and the substituents on the protonation constant of sixteen Schiff bases derived from salicylaldehyde and substituted anilines were studied under nitrogen atmosphere and at different percentages of dioxane, in dioxane-water media [62-63].

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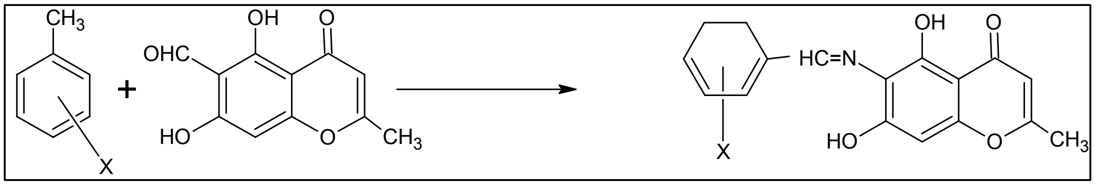
62. T. Gundaz and K. Esma, "Titration in non-aqueous media. Part VI, Effects of substituents on basicity or acidity of n-salycylidene 2-hydroxy aniline", Analyst, 112, 1057-1061, 1987.
63. T. Gundaz, E. Kilic, Ecanel and F. Koeseoglu, "Protonation constant of some substituted salicylidene anilines in dioxane-water mixture", Anal. Chem. Acta., 282, 489-495, 1993.

Sherif et al. [64] have reported potentiometric study on Schiff bases derived from the reaction of 5,7-dihydroxy-6-formyl-2-methyl benzopyran-4-one with some aromatic amines such as aniline, anthranilic acid, o-amino phenol, 5-chloro, 2-amino phenol and 4-amino 3-hydroxy benzene sulphonic acid. The effect of ionic strength at different temperatures and solvents on the ionization of this Schiff bases were studied. Various thermodynamic parameters such as Gibbs free energy, enthalpy and entropy for the ionization process were also determined.



Yang et al. [65] have reported microwave assisted condensation of salicylaldehyde and aryl amines without solvent with high yields, They have reported that solvent free organic synthesis mediated by microwave irradiation (M.W.) offers significant advantages such as economy, environmental friendly, simple work up procedure and high yields along with fairly mild conditions, while on the contrary in classical organic synthesis it is common to meet the problem of removing solvents especially in the case of aprotic dipolar solvents with high boiling points or the isolation of reaction products through liquid – liquid extraction.

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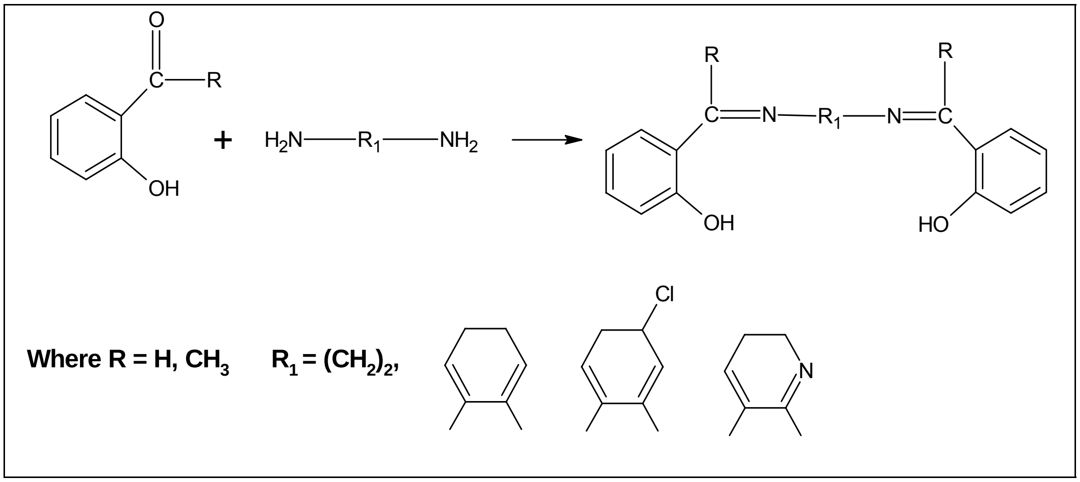
64. O. E. Sherif, Y. M. Issa and S. M. Abbas, “Thermodynamic parameters of some Schiff bases derived from 5,7-dihydroxy-6-formyl 2-methyl benzopyran-4-one”, J. Thermal Analy. and Calorimetry, 59, 913-926, 2000.
65. H. Yang, W. H. Sun, Z. Li and L. Wang, “Solvent free synthesis of salicylaldimines assisted by microwave irradiation”, Synthetic Communications, 32, 2395-2402, 2002.

Aghayan et al. [66] have synthesized tetra dentate Schiff bases using microwave activation under solvent free condition with and without support. They have proved microwave radiation enhanced chemical reaction in general and on organic supports. Microwave assisted reactions have gained popularity over the usual homogeneous and heterogeneous reactions. They can be conducted rapidly and provide pure products in quantitative yields without using solvent.



Where R = H, CH_3 $R_1 = (CH_2)_2$,

Gangani et al. [67] synthesized a series of new symmetric double Schiff bases of 1,1'-bis(4-aminophenyl) cyclohexane and substituted aromatic benzaldehyde via classical and microwave-irradiated techniques. The synthesis time is much shorter and yields of the Schiff bases are found to be better with the microwave-irradiation technique than classical technique. The purity of Schiff bases is checked by TLC.

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66. M. M. Aghayan, M. Ghassemzadeh, M. Hoseini and M. Bolourtchian, "Microwave assisted synthesis of the tetradentate Schiff bases under solvent free-and catalyst free condition", Synthetic Communication, 33, 521-525, 2003.
67. B. J. Gangani and P. H. Parsania, "Microwave irradiated and classical syntheses of symmetric double Schiff bases of 1,1'-bis(4-amino phenyl)cyclohexane and their physico-chemical characterization", Spectroscopic letters, 40, 97-112 , 2007.

The structures of Schiff bases are supported by FTIR, ^{1}H NMR, and MS techniques. The biological activity of Schiff bases is checked against Gram-positive and Gram-negative microbes. Schiff bases showed moderate antibacterial activity but showed moderate to excellent antifungal activity in comparison with chosen standard drugs.

Aghera et al. [68] synthesized novel symmetric double quinoline derivatives using the Vilsmeier–Haack reagent and symmetric double acetamides of 1, 1'-bis(R,4-aminophenyl)cyclohexane/methane. The structure of the intermediates (SDA-1 to SDA-3) and final products (SDQ-1 to SDQ-3) were supported by UV, FTIR, ^{1}HNMR, ^{13}CNMR and Mass. Compounds SDA-1 to SDA-3 and SDQ-1 to SDQ-3 possess moderate to good antibacterial and antifungal activities. They had also studied thermal behavior with TGA and DSC technique Schiff bases are thermally stable up to 173-272°C and followed single step or two step degradation. Different magnitudes of η, E and A suggested different degradation mechanisms [69].

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68. V. K. Aghera, J. P. Patel and P. H. Parsania, "Synthesis, spectral and microbial studies of some novel quinoline derivatives via Vilsmier-Haack reagent", ARKIVOC XII, 195-204, 2008.
69. V. K. Aghera and P. H. Parsania, "Effect of substituents on thermal behavior of some symmetric double schiff's bases containing a cardo group", J. Sci. and Ind. Res., 67, 1083-1087, 2008.

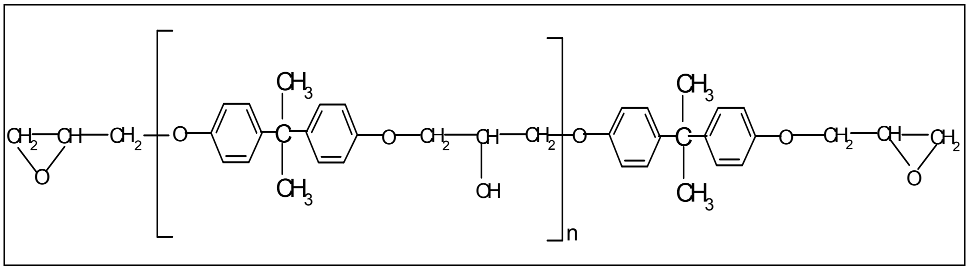
[C] Literature Survey on Epoxy Resins

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

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 from the 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.

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).



The resin can be obtained with different degrees of polymerization ranging from low viscosity liquids to high melting solids [70] as shown in Table 1.1

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

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

1) Resin viscosity (of liquid resin)
2) Epoxide equivalent
3) Hydroxyl equivalent
4) Average molecular weight
5) Melting point (of solid resin)
6) Heat distortion temperature (of cured resin)

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70. H. Lee and K. Neville, “Epoxy Resins in Their Application and Technology”, Mc Graw-Hill, New York, 1957.

Table – 1.1: Effect of reactant ratios on molecular weight

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

The epoxy resin can be converted into three dimensional infusible networks together by covalent bonds [71]. This conversion from a liquid or a 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 [72]. Many researchers have tried to modify the epoxy resin to improve its mechanical properties by reacting it with dienes [73], acrylates, etc.

This modification of epoxy resin is feasible due to highly reactive epoxy ring, which can also undergo ring opening reaction in the presence of acids [74] to yield polyester polyol containing a free hydroxyl group that can be utilized to produce polyurethanes.

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71. A. F. Yee, and R. A. Pearson, "Toughening mechanisms in elastomer modified epoxies: Part-1 Mechanical studies", J. Mater. Sci., 21, 2642-2474, 1986.
72. A. F. Yee, and R. A. Pearson, "Toughening mechanisms in elastomer modified epoxies: Part-2 Microscopic studies", J. Mater. Sci., 21, 2475-2488, 1986.
73. A. V. Cunliffe, M. B. Huglin, P. J. Pearce and D. H. Richards, "An anionically prepared flexible adhesive, 1: Synthesis", Polymer, 16, 654-658, 1975.
74. C. A. May, "Epoxy Resins- Chemistry and Technology", Marcel Dekker, New York, 1988.

To make an economic production of polyurethanes, efforts have been made to prepare polyester polyols from the low cost natural oils and their derivatives.

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

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

The commercial interest in epoxide resins was first made apparent by the publication of German patent 676,117 by I. G. Farben in 1939, which described liquid poly epoxides. In 1943 P. Casten filed US patent 2,324,483 covering the curing of the resins with dibasic acids. The Ciba Company subsequently exploited this important process. A later patent of Casten (US patent 2,444,333) covered the hardening of epoxide resins with alkaline catalyst used in the range 0.1–5%. This patent, however, became of somewhat restricted value as the important amine hardeners are usually used in quantities higher than 5%.

In the early stage of their development, epoxy resins were used almost entirely for surface coating. The developments in this field are due to the research work of S. O. Greenlee and described in a number of patents. These include work on the modification of epoxy resins with glycerol, the esterification with drying oil acids and reaction with phenolic and amino resins.

Wolfram et al. [75] have prepared phenolic composition, which is suitable for molding compositions. They have proposed the formation of resinous condensation product by reacting phenol or cresol with CH_2O in the presence of strong acid or base as a catalyst.

Greenlee [76] has prepared the rapid drying composition from diphenols and epichlorohydrin and esterified this product with Tall–oil.

Chemie produkte, GmbH [77] has reported the sealing composition for pipe joints and building materials. A typical composition consists of a mixture of an epoxy resin, a hardener and tar, which polymerized rapidly.

Lederman (Midland Chemical Corp.) [78] has reported varnish based on bisphenols. A wrinkle varnish or base comprising a blend of tung-oil varnish and fish-oil varnish is described. It gives a fine texture wrinkle finish, the good toughness and flexibility.

Petri et al. [79] have prepared epoxy resin foams from aqueous dispersions. An epoxy resin based on bisphenol-A, benzsulfohydrazide and dipropylene triamine were dispersed in water by using 2, 3-dibromopropyl phosphate as a dispersing medium. Rigid foam was obtained by this composition, which is suitable for architectural uses.

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75. A. Wolfram and H. Jhan, "Synthetic resins suitable for various uses", U.S. 2,322,990; 1943; Chem. Abstr. 38, 185, 1944.
76. S. O. Greenlee, "Tall-oil esters", U.S. 2,493,486; 1949, Chem. Abstr. 442,770, 1950.
77. Chemie Produkte, "Epoxy resins containing sealing compositions", Ger. 1,020,140; 1957, Chem. Abstr. 54, 179,704, 1957.
78. B. E. Lederman (Midland Chemical Co.) "Bisphenol-modified wrinkle varnish", Chem. Abstr. 53, 1779, 1959.
79. R. Petri, H. Reinhard and L. Keller, "Epoxy resin foams from aqueous dispersions", Ger. 1,080,774; 1960, Chem. Abstr. 55, 14982, 1961.

CIBA Ltd. [80] 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, difluro 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. [81] has reported curing of polyepoxides with liquid glycol diamines ($H_2N\ (CH_2)_3O\ (CnH_{2n}O)_x\ (CH_2)_3NH_2$), 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, 100 g of diglycidyl ether of 2,2'-bis(p-hydroxy-phenyl) propane was mixed with 29.4 g stoichiometric amount of $H_2N\ (CH_2)_3O\ (CH_2CH_2O)_2(CH_2)_3NH_2$ for 5 min. The mixture was applied on cold-rolled steel and was cured by storing 7 days at room temperature.

Minnesta Mining and Manufacturing Co. [82] has synthesized flexible adhesive film having honeycomb structure. Thus an epoxy resin mixture was prepared by heating 100 parts of glycidyl ether of bisphenol–A to 121°C, adding 2-parts fine SiO_2 and stirring at 149°C for 10-20 min. A mixture of 145 parts isophthaloyl dihydrazide, 10 parts MgO and 1 part dimethyl diocta decyl ammonium bentonite was added to epoxy mixture at 104°C and the resulting mixture was milled at 77°C to complete dispersion

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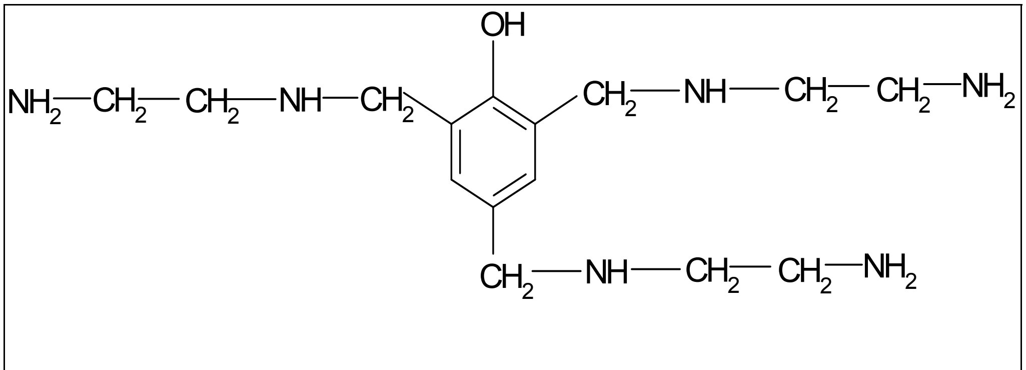
80. CIBA Ltd., "Epoxy resin containing coatings", Brit. 883,521, 1961; Chem. Abstr. 56 11746, 1962.
81. Union Carbide Co. (by Norman H. Reinking.), "Liquid glycol diamine curing agent for polyepoxides", Brit. 904,403; 1962; Chem. Abstr. 58, 1643, 1963.
82. Minnesta Mining and Manufacturing Co. "Flexible adhesive film", Ger. 1,100,213; 1961; Chem. Abstr. 58,11551, 1963.

Bremmer [83] 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°C under N_2 atmosphere with stirring. The composition was cured by triethyl amine.

Kogyo [84] has formulated epoxy resin composition hardened by phenol-blocked-phenol-polyamine–aldehyde reaction products at low temperature i.e. 10-15°C.



(I)

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

Castan and Gandillon [85] have reported esterified epoxy resin of phenol formaldehyde with long chain fatty acids, which may be unsaturated, and dehydration is affected with acid catalyst to produce rapid drying films. Co or Pb naphthenate were used.

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83. B.J. Bremmer (Dow Chemicals Co.), “Flame retardant epoxy resin”, U.S. 3,294,742; 1966; Chem. Abstr. 66,38487, 1967.
84. D. Kogyo. “Hardenable epoxy resin composition”, Japan 2,126,179; 1972; Chem. Abstr. 78, 137,425, 1973.
85. P. Castan and C. Gandillon, U.S. 3,028, 348; 1958; Chem. Abstr, 57, 11,338;1962.

The resulting films are relatively resistant to alkali. The use of saturated acids in the esterification step gives resins, which can be hardened in the kiln.

Nakahara et. al [86] have developed new type of epoxy resin containing a 4,4'-biphenylene moiety in the backbone (bis-EBP) and confirmed by elemental analysis, IR, and ^{1}HNMR.

In addition, to evaluate the influence of the 4, 4'-biphenylene group in the structure, an epoxy resin having a 1,4-phenylene group in place of the 4,4'-biphenylene moiety (bis-EP) was synthesized. The cured polymer obtained through the curing reaction between the new biphenyl-containing epoxy resin and phenol novolac was used for making a comparison of its thermal and physical properties with those obtained from bis-EP and bisphenol-A (4,4'-isopropylidenediphenyl)-type epoxy resin (bis-EA). The cured polymer obtained from bis-EBP showed markedly higher fracture toughness of 1.32 MPa $m^{1/2}$, higher glass transition temperature, lower moisture absorption, and higher thermal decomposition temperature.

Liu et al. [87] have prepared simultaneous interpenetrating polymer networks (IPNs) based on epoxy (diglycidyl ether of bisphenol-A) and unsaturated polyester (UP)using m-xylenediamine and benzoyl peroxide as curing agents. A single glass transition temperature for each IPN was observed with differential scanning calorimetry, which suggested good compatibility of epoxy and UP. This compatibility was further confirmed by the single damping peak of the rheometric dynamic spectroscopy.

Curing behaviors were studied with dynamic differential scanning calorimetry and the curing rates were measured with a Brookfield RTV viscometer.

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86. K. Nakahara, T. Endo and M. Kaji, "Synthesis of a bifunctional epoxy monomer containing biphenyl moiety and properties of its cured polymer with phenol novolac", J. Appl. Polym. Sci., 74, 690-698, 1999.
87. C. C. Liu, C. T. Lee and M. S. Lin, "Toughened interpenetrating polymer network materials based on unsaturated polyester and epoxy", J. Appl. Polym. Sci., 72, 585-592, 1999.

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

Sanariya et al. [88] have reported a convenient method for the preparation of epoxy resins based on bisphenol-C. The epoxy resins of bisphenol-C derivatives were synthesized by condensing corresponding derivative (0.5 moles) with epichlorohydrin (1.1 moles) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0 mol in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was ~ 75-80 %.

Kagathara et al. [89] have reported a convenient method for the preparation of epoxy resins based on halogenated bisphenol-C. The epoxy resins of bisphenols-C derivatives were synthesized by condensing corresponding derivative (0.5m) with epichlorohydrin (1.1 m) by using isopropanol (500 ml) as a solvent and sodium hydroxide (1.0m in 40 ml water) as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. Excess of solvent was distilled off and the viscous resin was isolated from distilled water. The resin was extracted from chloroform and evaporated to dryness to obtain pure resin. The yield was ~ 75-80 %.

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88. 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.
89. V. M. Kagathara, M. R. Sanariya and P. H. Parsania, “Selected Topics in Polymer Science.’ S.K. Dolui Edi., Prof. Sukumar Maiti, Polymer Award Foundation, Kolkata, 1-8, 2001.

Liu et al. [90] have reported combination of epoxy and novolac resins. In a typical study, a novel phosphorus-containing aralkyl 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 (159-170^{0}C), good thermal stability (>320^{0}C).

Vikarm Sarabhai Space Center [91] has reported phenolic resin prepared by treating HCHO with bisphenol / cardanol mixture in the presence of basic catalyst.

Aoki et al. [92] have reported the wood reinforced decorative molding board. In a typical formulation, wood was impregnated with an unsaturated polyester resin to prepare composites. Thus, a spruce veneer was immersed in unsaturated polyester containing 40% styrene and 1% benzoyl peroxide for 24 h to 95% pick-up of solution and 10 such veneers were laminated at 115^{0}C and 3 kg/cm^2 pressure under hydraulic press.

Joseph et al. [93] have developed composite boards from rice husk by coating and mixing the raw husks with water dispersible resin prepared by 1-step condensation of cardanol or cashew nut shell liquid with phenol formaldehyde using alkali as a catalyst. Coated husks were placed between hot pressing mats at 160-220°C. Thus, 8 kg husk was sprayed coated with 1.6 kg resin binder.

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90. 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 B, 40, 2329-2339, 2002.
91. Vikram Sarabhai Space Center, "Phenolic resins", Ind. Pat. 137,274; 1973; Chem. Abstr. 92, 59687, 1980
92. Aoki, Eiichi, Fujii, Nobuyoshi, Sasakuri, Hirokai, "Reinforcement and decorative molding of wood", Japan Kokai 77,125,607; 1977; Chem. Abstr. 88, 122864, 1978.
93. G. Joseph, Zoolagad, Shri Shankarya, Shivasangayya and Surender, "Composite boards from rice husk", Ind. Pat. 1,46,015; 1976; Chem. Abstr. 91, 212346, 1979.

Li et al. [94] have studied properties of sisal fiber and its composites. They have modified the surface morphology of fibers by coupling agents such as N-substituted methacrylic acid, gamma-methacryloxy propyl trimethoxy silane, neo-pentyl (diallyl) oxy tri (dioctyl) pyrophosphate titanate and neo pentyl (dially) oxy triacryl zirconate. They have also studied dynamic mechanical, electrical and ageing properties. They concluded that the modified sisal fiber reinforced composites are result of their good mechanical, environmental and economical properties.

Singh et al. [95] have fabricated jute fiber reinforced phenolic composites for the study of durability and degradation due to out door exposure. The physical and mechanical properties of jute composites have been studied under various humid, hydrothermal and weathering conditions. The ageing induced deterioration effect of their conditions on the dimensional stability, surface topology and mechanical properties of the composite was observed.

Joffe et al. [96] have studied the composites based on flex as a reinforcing fiber. They have fabricated natural fiber composites (NFC) and compared their mechanical properties with glass mat thermoplastics (GMT). The investigation showed that NFC have mechanical properties such as matrix/fiber compatibility, stiffness, strength and fracture toughness are as high as GMT or even higher in some cases. They have concluded that such a good mechanical properties in combination with light weight makes use of NFC very attractive for automotive industries

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94. Y. Li, Y. W. Mai and L. Ye, "Sisal fiber and its composite: A review of recent developments", Composite Sci. and Tech., 60, 2037-2055, 2000.
95. B. Singh, M. Gupta and Anchal Verma, "The durability of jute fiber reinforced phenolic composites", Composite Sci. and Tech., 60, 581-589, 2000.
96. R. Joffe, L. Wallstrom and L. A. Berflund, "Natural fiber composites based on flax matrix affects", Proceedings of International Scientific Colloquium, Modeling for Saving Resources, Riga, May 17, 2001

Biswas et al. [97] have described the importance of natural fibers for composite manufacturing. They have discussed the fabrication of jute-coir, jute-glass, jute-polyester composites, bamboo-mat veneered rice husk board and the use of cashew nut shell liquid as natural resin for biodegradable composites. The physical properties of composites were also measured.

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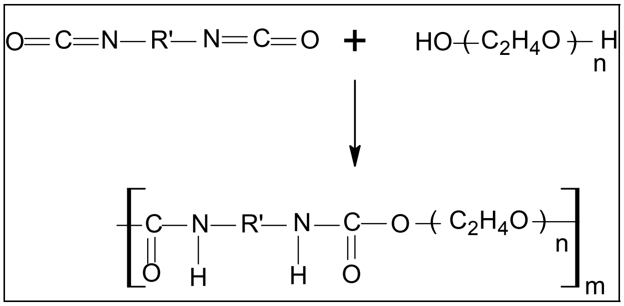
97. S. Biswas, G. Shrikanth and S. Nagia, "Development of natural fiber composites in India", Composite 2001 Convention and Trade Show, composite fabrication association, Oct. 3-6, 2001, Tampa, FL, USA.

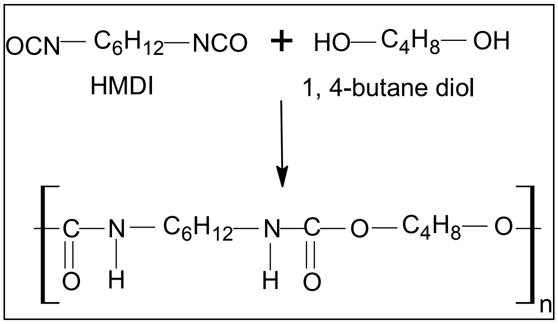
[D] Literature Survey on Polyurethane Resins, Films and Their Composites

Polyurethane resins are a very unique class of specialized materials, which are used industrially and on trade scale virtually in all sectors. Polyurethanes form an important class of polymers, whose structures and performances can be designed to meet the user's needs. Polyurethane resins are mainly produced by isocyanation of diisocyanate with polydiols of various molecular weights or other reactants containing hydrogen donors that are reactive with isocyanates.



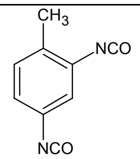
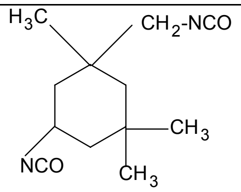
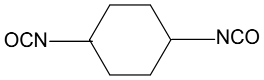
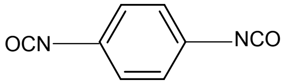
A urethane is essentially an ester of carbamic acid or substituted carbamic acid. The main advantage of polyurethane is that it can be tailor made to meet the diversified demands of modern technologies such as coatings, adhesives, foams, rubbers, reaction molding plastics, thermoplastic elastomers and composites.

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



The most commonly used isocyanates or the production of polyurethanes are listed in Table-1.2.

Table-1.2: The common diisocyanates used for the production of polyurethanes

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

The other component in the production of polyurethane is polyol. Polyols are hydroxyl terminated polyesters, polyether polyols, acrylic polyols and polyols based on natural oils.

[1] Polyester polyols

In addition to the typical linear and branched polyester oil modified polyesters are also used in these applications. The molecular weights vary between 500 and 5000.

[2] Polyether polyols

Linear and slightly branched polyethers with molecular weights ranging between 1000 and 2000 are preferably used. Polyethers are more resistant to hydrolysis, while polyesters are more resistance to oxidative degradation. The typical polyethers used in the coating sectors are liquid in nature.

[3] Other products with reactive hydroxyl groups

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

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

Polyurethane possesses a unique combination of performance and application properties with excellent abrasion resistance, flexibility, hardness, chemical resistance, UV light resistance and anti-microbial characteristics [98].

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98. M. X. Xu, W. G. Liu, Y. L. Guan, Z. P. Bi and K. D. Yao, “Study on phase behavior-impact strength relationship of unsaturated polyester/polyurethane hybrid polymer network”, Polym. Inter., 38, 205-209, 1995.

A great number of factors, which affect or influence the properties of polyurethane resins are nature of polyol and diisocyanate, crosslinking density, NCO/OH ratio, curing conditions, etc [99,100]. Polyurethane resins are characterized by a segmented structure, consisting of flexible segment, the polyol chains, hard segments with the difference, crystallizability, segmental length, intra and inter segment interactions such as H-bonding, overall compositions and molecular weight.

Over the last few decades polyurethanes are widely used as adhesive materials and have developed a reputation for reliability and high performance in many applications including footwear industry, packaging applications, plastic bonding, furniture assembly and the automotive industry. Polyurethanes are rapidly developing products of coating and paint industry because of unique combinations of performance and application properties such as excellent elasticity, high hardness, high scratch and abrasion resistance, excellent impact resistance, high water, solvent, acids and alkali resistance and resistance to degradation from light and weathering

The polyurethane coated fabrics find applications in inflatable structures, conveyer belts, protective coatings, biomaterials, etc [101,102].

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99. J. M. Buist, "Development in Polyurethane-1", Applied Science Publishers Ltd. London, 1978.
100. I. S. Lin, J. Biranowski and D. H. Lorenz, "Urethane Chemistry and Applications", K. N. Edwards, Ed; ACS Symposium Series, 172, Chapt. 34, p. 523, 1981.
101. J. A. Grapski and S. L. Cooper, "Synthesis and characterization of biocidal polyurethanes", Biomaterials, 22, 2239-2246, 2001.
102. A. Z. Okkema and S. L. Cooper, "Effect of carboxylate and/or sulphonate ion incorporation on the physical and blood contacting properties of polyetherurethane", Biomaterials, 12, 668-676, 1991.
103. R. Jayakumar, M. Rajkumar, R. Nagendran and S. Nanjundan, "Synthesis and characterization of metal-containing polyurethanes with antibacterial activity", J. Appl. Polym. Sci., 85, 1194-1206, 2002.

Polyurethanes are very appealing class of polymers for use in the biomedical field. This is because of their relatively good biocompatibility, their physical properties and the ease with which their properties can be tailored to end use. They are widely used in the development of medical devices, for tissue and blood contact such as mammary prosthesis, vascular catheters, artificial skins, vascular grafts, artificial heart diaphragms and valves. They can be biodegradable depending upon their chemical structures [103].

Recent years have shown a growing interest in the development of bio based products that can reduce the widespread dependence of fossil fuels. Indeed, the inevitable depletion of petroleum reverses with the attending high cost has prompted the researchers to develop polymers from cheap and renewable resources such as natural oils [104]. There are number of natural oils such as castor oil, linseed oil, sunflower oil, tung oil etc. are available in the market but among all of them castor oil and its derivatives are widely used due to its unique chemical structure [105,106].

Castor oil is a triglyceride of fatty acids, whose main constituent is ricinoleic acid, extracted from Ricinus Communis [107,108]. Commercial castor oil consists of triglycerides that contain 90% of ricinoleic acid and 10% of non-functional acid and it has an effective functionality of 2.7. Thus, castor oil acts as a polyol, which reacts with polyfunctional isocyanates to form polyurethanes, whose properties range from rigid polymers to elastomers.

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104. G. Scott, “Polymer and Environment” Cambridge: Royal Society of Chemistry; p27, 1999.
105. L. W. Barrett, L. H. Sperling, J. Gilmer and S. G. Mylonakis, “Crystallization kinetics of poly(ethylene terephthalate) in compositions containing naturally functionalized triglyceride oil”, J. Appl. Polym. Sci., 48, 1035-1050, 1993.
106. H. Q. Xi, X. D. Huang and G. G. Wang, “Electronic-ionic conducting interpenetrating polymer networks based on (castor oil-polyethylene glycol) polyurethane and poly(vinyl pyridine)”, Eur. Polym. J., 30, 1227-1230, 1994.

Because of unique structure of castor oil, it provides better water resistance and lower viscosity as compared to the polyols. Castor oil exhibits exceptional ability in pigment wetting and penetration due to the presence of ricinoleate. The castor oil based PU systems have been widely used in the telecommunication/ electrical industries, coatings, adhesives and sealants.

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

Some advantages of composite materials over traditional materials are.

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

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107. K. Othmer, “Encyclopedia of Chemical Technology” 4th Edition, John Wiley and Sons, Inc. New York, 5, 1979.
108. R. W. Johnson and E. Iritz, “Fatty Acids in Industries Process Properties Derivatives and Applications” Marcel Dekker, New York, p13, 1989.

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

Mehdizadeh et al. [109] have synthesized polyurethane elastomers based on difunctional castor oil and poly(propylene glycol), toluene 2,4-diisocyanate and 1,4-butane diol were prepared and cured using toluene diisocyanate dimer as cross linking agent. The elastomers were characterized by conventional methods. Physical, mechanical and thermal properties of the elastomers were studied. Investigation of these properties showed that the elastomers could be tailor made in order to fulfill industrial needs.

Kendagannaswamy et al. [110] have synthesized polyurethane elastomers using castor oil, 4,4'-methylene bis(phenyl isocyanate) (MDI) and toluene 2,4-diisocyanate (TDI) and study the effect of different aromatic diamines on the physico-mechanical and optical properties of polyurethane. The study showed that tensile strength and percent elongation were in the range of 13-24MPa and 76-32, respectively. Higher tensile strength was observed for 4,4'-diaminodiphenyl sulphone (DDS) than the 4,4'-diaminodiphenyl methane (DDM) chain extender. The properties imparted by the chain extenders were explained on the basis of the groups present in the diamines and changes have been interpreted by wide angle X-ray scattering data.

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109. M. R. Mehdizadeh and H. Yagnesh, "Synthesis and properties of isocyanate curable milliable polyurethane elastomers based on castor oil as a renewable resource polyol", Eur. Polym. J., 40, 1233-1238, 2004.
110. B. K. Kendagannaswamy, V. Annadurai, V. Siddaramaiah and R. Somashekar, "Physico-mechanical, optical and waxes studies on chain extended polyurethane", J. Mat. Sci.-Pure Appl. Chem., 37, 1617-1625, 2000.

Swada [111] has synthesized epoxy modified polyurethane resin for a coating comprising curing agent and an epoxy modified PU resin which is the byproduct of reacting a carboxyl group containing polyurethane polyol containing repeat units derived from reacting an isocyanate compound and a polyol with a hydroxyl carboxylic acid with an epoxy compound in such a proportion that the epoxy group falls in a range of 0.1 to 1 equivalent per equivalent of the carboxyl group.

Ashraf et al. [112] have synthesized polyurethane from linseed oil epoxy and have developed anticorrosive coatings from it. Trans hydroxylation of linseed oil epoxy was carried out in situ. It is further reacted with TDI to synthesize polyurethane. Structural elucidation was carried out using IR and NMR spectral data. Physico-mechanical and weather resistance performance of the coated samples were also studied and found that synthesized resin showed good performance in various corrosion tests.

Mao et al. [113] have studied the damping properties of epoxy resin / PU (EP/PU) semi interpenetrating polymer networks (IPNs) by dynamic mechanical analysis (DMA) method. It showed that the semi IPNs have excellent damping properties at ordinary temperature. The maximum value of tanδ is about 1 when the weight composition of EP/PU is 70/30. Tensile tests also indicate that the system has good tensile strength and elongation at break at this ratio. The effects of structure on the properties of semi-IPNs are discussed. Applied to the cavitation corrosion resistant coating, the semi-IPNs showed good cavitation corrosion resistance.

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111. H. Swada, “Epoxy-modified PU resin for a coating material.” GB 2,369,123A, 2002.
112. S. M. Ashraf, E. Sharmin, F. Zafar, A. Hasant and S. Ahmad, “Studies on ambient cured PU modified epoxy coatings synthesized from sustainable resource”, Prog. Cryst. Grow. Chara. Mater., 45, 83-88, 2002.
113. S. Mao and Y. Li, “Study on the properties and application of epoxy resin/PU semi-interpenetrating polymer networks”, J. Appl. Polym. Sci., 61, 2059-2063, 1996.

Opera et. al. [114] have synthesized epoxy urethane acrylate from epoxy resins, acrylic acid and 4,4’-diphenyl methane diisocyanate using two stage polymerization. The oligomer obtained was studied by IR spectra, ^{1}HNMR spectroscopy. The oligomer was cured using thermal treatment. All of these materials formed transparent films used for testing. The low molecular weight oligomers can be used as solvent less coating.

Kolekar and Athawale [115] have synthesized interpenetrating networks composed of glycerol modified castor oil based polyurethane (CG-PU) and PMMA. The effects of polyol modification change in NCO/OH ratio and PU/PMMA composition mechanical, chemical and thermal properties of IPNs were studied. It was found that among the three IPNs synthesized from (1) unmodified castor oil PU (2) glycerol modified castor oil PU (3) glycerol modified mixture of castor and linseed oil PU and PMMA, glycerol modified PU IPNs (CG-IPN) exhibited better tensile strength and chemical resistance. The detailed study of CG-IPNs revealed that tensile strength and hardness increased, while elongation decreased with increase in NCO/OH ratio. However, an exactly reverse trend was observed with increase in PU composition in PU/PMMA IPNs. The chemical resistance and thermal properties of the IPNs were unaffected by the change in NCO/OH ratio and PU/PMMA composition.

Prabu et al. [116] have prepared two different inter crosslinked networks (ICN) of siliconized polyurethane-epoxy / unsaturated polyester (UP) coatings.

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114. S. Opera, S. Vlad, A. Stanciu, M. Macoveanu, “Epoxy-urethane acrylate”, Eur. Polym. J., 36, 373-378, 2000.
115. S. Kolekar and V. Athawale, “Interpenetrating polymer networks based on polyol modified castor oil polyurethane and PMMA”, Eur. Polym. J. 34, 1447-1451, 1998.
116. A. A. Prabu and M. Alagar, “Mechanical and thermal studies of inter-crosslinked networks based on silicone- polyurethane-epoxy/unsaturated polyester coatings”, Prog. in Org. Coatings, 49, 236-243, 2004.

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

Whereas, the incorporation of 10% silicone into the PU modified epoxy/PU system, the thermal stability was increased due to the partial ionic nature, high energy and thermal stability of Si-O-Si linkages.

Joshi and Athwale [117] have synthesized polyurethane resins from chemoenzymatically modified castor oil and different isocyanates and studied the difference in hardness, flexibility, impact strength and chemical resistance when the different isocyanate precursors were used. The interesterification of castor oil and linseed oil was carried out near ambient temperature using lipase as a catalyst. The resultant interesterification product (IP) was reacted with isocyanates to form polyurethane resins. Polyurethane synthesized by this method is light in color and compared to conventional ones obtained from chemically catalyzed inter esterification reactions at high temperature.

Somani et. al [118] have developed high solids polyurethane coating formulation by reacting different castor oil based polyester polyols with aromatic as well as aliphatic isocyanate adducts in different NCO/OH ratios.

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117. K. R. Joshi and V. D. Athawale, “Structure-property relationship in polyurethane coatings synthesized from chemoenzymatically modified castor oil”, J. Polym. Mater., 21, 165-173, 2004.
118. K. Somani, S. Kansara, R. Parmar and N. Patel, “High solids polyurethane coatings from castor-oil-based polyester polyols”, Int. J. Polym. Mater., 53, 283-293, 2004.

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

Jayabalan et al. [119] have studied the effect of crosslinker on the stability of castor oil based aliphatic polyurethane potting compounds under thermal ageing, autoclaving, gamma radiation and sterilization. Two potting compounds, the first consisting of castor oil segments and an isocyanate cross linker, while second with the smaller castor oil segment and a polyether polyol as cross linker. The first potting compound undergoes degradation under sterilization conditions, while second undergoes cross linking under sterilization. A potting compound based on polyether polyol cross linker would be more promising for hollow fibers.

Lucas et al. [120] have prepared the thermoplastic polyurethane elastomers (TPUs) by reacting difunctional isocyanates with long or short chain polyesters or ethers containing terminal hydroxyl groups. Flexible hydroxyl polymers lower the tensile module and give high elongations. Typically thermoplastic of this type do not have both high strength and high elongation. By polymerizing specific cross linkable monomers, networks can be formed, which are usually clear and homogenous with broad glass transitions. Compared to the thermoplastic polyurethanes, they are stronger and give higher elongation at break. Additionally, improvement in solvent resistance is provided thorough cross linking.

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119. M. Jayabalan and P. P. Lizymol, "Studies on the effect of cross linker on the stability of castor-oil based aliphatic polyurethane potting compound", Polym. Degrad. Stab., 58, 251-255, 1997.
120. H. R. Lucas, W. E. Mealmaker and N. Giannopouos, "Novel polyurethanes with interpenetrating networks for the coating industry", Prog. in Org. Coat., 27, 133-144, 1996.

Huang et al. [121] have prepared polyurethane elastomers from bisphenol-S derivatives and studied the structure property relationship. The effect of soft segment of diol and the effect of structure of diisocyanate on the mechanical properties were also studied. The thermal properties of polyurethane elastomers were also investigated by using DSC and TGA analyses.

Ajitkumar et al. [122] have carried out the swelling experiments of interpenetrating networks (IPNs) of castor oil based polyurethane and unsaturated polyesters and calculated their solubility parameters. The kinetics of swelling and sorption has also been studied in chlorobenzene at 25°C. IPNs with various weight composition of PU and UPE (80:20, 50:50, 20:80) and having various cross linking density (NCO/OH 1.2, 1.5, 2.0) have been employed. The results revealed that, the sorption was anomalous in nature, while diffusion coefficient (D) was found to increase with both cross linking density and UPE content, whereas sorption coefficient showed reverse trend in all the cases. From the swelling studies, the molecule between two crosslink (Mc) and the number of chains per unit volume (N) and degree of cross linking were also calculated.

Jimenez et al. [123] have studied the effect of soft segment structure and molecular weight on the microphase separation in segmented

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121. C. C. Huang, B. Y. Liaw and D. J. Liaw, “Synthesis and properties of polyurethanes based on bisphenol-S derivatives”, Polymer, 39, 3529-3535, 1998.
122. 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”, Eur. Polym. J., 36, 2387-2393, 2000.
123. G. Jimenez, A. Shishido, M. Sumita and S. Asai, “Effect of the soft segment on the fatigue behavior of segmented polyurethanes”, Eur. Polym. J., 36, 2039-2050, 2000.

polyurethane (SPU) by means of differential scanning calorimetry, small-angle X-ray scattering, dielectric constant measurements, pulsed nuclear magnetic resonance and thermo luminescence. Possible changes in the structural properties of SPU after cyclic mechanical fatigue were monitored using the same technique described as above. Samples were divided into two series according to their soft segment structure, i.e. one is linear poly(tetramethylene glycol) (PTMG) and another with methyl group on the PTMG chain. Hard segment consisted of 4, 4'-diphenyl methane diisocyanate (MDI) and 1, 4-butane diol as chain extender in both the sets. It was found that the phase separation increased for both types of SPU as the soft segment molecular weight increased. Samples with methyl group showed little soft segment crystallization. Upon fatigue, samples with methyl group showed a better fatigue resistance.

Desai et al. [124] have synthesized polyester polyols using vegetable oil fatty acids having different characteristics (mainly in terms of hydroxyl functionality) and epoxy resin, using triethyl amine as a catalyst. Polyols were characterized by FTIR spectroscopy. PU adhesives were synthesized from it and used in bonding the rubber. Treatment of sulphuric acid on the non-polar styrene-butadiene rubber (SBR) surface was studied for the bond strength improvement via an increase in wettability of the rubber surface. Wettability was found by measuring the contact angle using Goniometer. Bond strength was evaluated by a 180^0 T-peel strength test. The surface modification and mode of bond failure were studied by scanning electron microscopy (SEM).

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124. S. D. Desai, A. L. Emanuel and V. K. Sinha, “Polyester-polyol based PU-adhesives; effect of treatment on rubber surface”, J. Polym. Research, 10, 141-149, 2003.

Somani et al. [125] have synthesized polyurethane adhesives from different polyester polyols. The polyester polyols were synthesized by reacting castor oil derivatives with glycols (diols), while adhesives have been synthesized by reacting different polyester polyols with diisocyanate adducts, in different NCO/OH ratios. The polyols and polyurethanes were characterized by FTIR spectroscopy. The effect of NCO/OH ratios, types of isocyanate adducts, and chain length of glycols were studied, by determining wood to wood adhesion strength, i.e. by lap shear strength measurements. The change in lap shear strength after being placed in cold water, hot water, acid or alkali solutions was tested. Thermal stability of PU adhesives was determined by TGA.

Bledzki et al. [126] have fabricated the polyurethane based composites reinforced with woven flax and jute fabrics with an evenly distributed microvoid foam structure. The influence on type of reinforcing fiber, fiber and microvoid content on the mechanical properties was studied. The investigation results for the static mechanical properties of the composites were described by approximate formulae. From the data it was found that increasing fiber contents includes an increase in the shear modulus and impact strength, while increasing the microvoid content in the matrix results in decreased shear modulus and impact strength. The woven flax fibers result in composites with better mechanical strength than the woven jute fiber composites.

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125. K. P. Somani, S. S. Kansara, N. K. Patel and A. K. Rakshit, "Castor oil based PU adhesives for wood to wood bonding", Inter. J. Adhes., 23, 269-275,2003.
126. A. K. Bledzki, W. Zhang and A. Chate, "Natural-fibre-reinforced polyurethane microfoams", Comops. Sci. Technol., 61, 2405-2411, 2001.

Yeo et al. [127] have fabricated the polyurethane composites with rice husk (RH) and polyethylene glycol (PEG-200) as a polyol. The effect of % RH (by weight), % of RH hydroxyl groups and RH sizes on tensile, flexural and impact properties were investigated. For most tests, properties increased as the % RH and % RH hydroxyl groups was increased but after the exceeding a threshold value, the properties started to decrease. This phenomenon was attributed to two factors, (i) % RH (by weight) or % RH OH groups (ii) amount of homogeneous PU matrix. The size of RH also played a significant role in the properties, which could be detected by scanning electron microscope (SEM) analysis. DMF immersion and water absorption tests, showed that as the % of RH increased DMF immersion decreased, while water absorption increased due ability of RH OH groups to absorb water.

Tay et. al [128] have fabricated oil palm empty fruit bunch composites with polyethylene glycol (PEG) molecular weight (MW) of 200 (PEG-200), 400 (PEG-400), polypropylene glycol (PPG) with MW of 400 (PPG-400) used as polyols. The effect of isocyanate (NCO) / hydroxyl (OH) ratio and PPG-400/ PEG-400 ratio on the impact strebgth, dimensional stability (immersion test), and thermal behavior were investigated. The study revealed that, as NCO/OH ratio was increased from 0.8 to 1.1 the impact strength and enthalpy increased, while swelling of composites either in water or DMF and onset and peak temperatures decreased. While for NCO/OH ratio above 1.1 the onset and peak temperature increased, while enthalpy decreased due to formation of allophanates. Thermal behavior of the composites made from the glycol mixture was predominantly influenced by the PPG -400.

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127. Y. S. Yeo, G. S. Tay, A. Abubakar and H. D. Rozman, "The mechanical and physical properties of PU composites based on rice husk and PEG", Polymer Testing, 22, 617-623, 2003.
128. G. S. Tay, A. Abubakar and H. D. Rozman, "Oil palm EFB-PU composites: The extent of NCO/ glycol ratio, glycol type and glycol mixture on the impact strength, dimensional stability and thermal properties", Polym. Plast. Technol. Eng., 42, 811-826, 2003.

Tay et al. [129] have fabricated the oil palm EFB-PU composites and investigated the effect of isocyanate (NCO)/ glycol (OH) ratio, glycol type and mixtures [polyethylene glycol PEG-400 (MW- 400) and polypropylene glycol (MW-400)] on the flexural properties. Composites made with PEG-200 exhibited higher flexural properties than with PEG-400 and PPG-400. The flexural properties were also found to be influenced by the PPG-400/ PEG-400 ratio.

Wolcott et al. [130] have fabricated ligno cellulosic fiber reinforced PU composites using difunctional and trifunctional poly(propylene oxide) based polyol. The mechanical properties of the composites were found to depend on the type of fiber and accessibility of hydroxyl functionality on the fiber. Dynamic mechanical analysis, swelling behavior and scanning electron micrographs of failure surfaces all provided the evidence of a substantial interface in the composites that directly impacted to the performance properties. Trifunctional polyols generally increased the strength and stiffness, regardless of fiber type. The data suggested that synthetic polyol functionality and relative accessibility of the internal polymer structure of the fiber wall are dominant factors in determining the extent of interphase development.

Shamekhi and Yeganeh [131] have prepared versatile polyurethane material suitable as insulating coatings.

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129. G. S. Tay, A. Abusamah and H. D. Rozman, “The effect of glycol type, glycol mixture and isocyanate/glycol ratio on flexural properties of oil palm Empty Fruit Bunch(EFB)-PU composites”, J. Wood Chemi. Technol., 23, 249-260, 2003.
130. M. P. Wolcott, J. M. Nassar and T. G. Rials, “Interfacial contributions in lignocellulosic fiber reinforced PU- composites”, J. Appl. Polym. Sci. 80, 546-555, 2001.
131. 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.

Novel kinds of polyhydroxy compounds (PHCs) were prepared via transesterification reaction of poly(ethylene terephthalate) using 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, while crosslink density of the samples was determined via equilibrium swelling method and by using Flory-Rehner equation. Effects of crosslink density on electrical, physical, mechanical, and dynamic mechanical (DMTA) properties of the polyurethane coatings were investigated.

Chen et al. [132] have prepared a series of water-resistant composites from a mixture of soy dreg (SD), castor oil, and 2,4-toluene diisocyanate (TDI) by a one-step reactive extrusion (REX) process. The structure and properties of the composites were characterized by FTIR, SEM, DSC, dynamic mechanical analysis, tensile testing, and swelling experiments. The results indicated that the toughness of the composites prepared from castor oil based polyurethane and SD was significantly improved.

In this case, TDI played an in situ compatibilization role through the cross linking reaction of $—NCO$ groups with $—NH_2$, $—NH—$, and $—OH$ groups in SD and castor oil. With an increase in the molar ratio of $—NCO$ groups of TDI and $—OH$ groups of castor oil, the degree of crosslinking, tensile strength, glass-transition temperature, water resistivity, and solvent resistivity of the composites increased. With an increase in the SD content of the composites, the tensile strength and solvent resistivity of the composites increased because of the reinforcement of the cellulose component in SD.

Parsania et al. [133-137] attempted lot of work related to carry out polyurethane composites based on natural fibers as well as glass fibers. The results show encouraging working deeply in these fields.

132. Y. Chen, R. Deng, H. Liang and L. Zhang, “Toughened composites prepared from castor oil based polyurethane and soy dreg by a one-step reactive extrusion process”, J. Appl. Polym. Sci., 101, 953-960, 2006.

133. S. I. Mawani and P. H. Parsania, “Synthesis and comparative physico-chemical study of polyester polyols based polyurethanes of bisphenol-A and bisphenol-C epoxy resins”, Polym. Plastic Techno. & Engg., 46, 605-611, 2007.

134. S. I. Mawani, N. M. Mehta and P.H. Parsania, “Synthesis and physicochemical study of bisphenol-C-formaldehyde-toluene diisocyanate polyurethane–jute and jute–rice husk/wheat husk composites”, 101, 2363-2370, 2006

135. P. J. Vasoya, and P. H. Parsania, “Synthesis and characterization of novel Bisphenol-C-formaldehyde-acrylate-toluene diisocyanate-PEG-400 copolyurethanes”, Polym. Plast. Techno. Eng., 47, 635-642, 2008.

136. P. J. Vasoya, V. A. Patel, B. D. Bhuva and P. H. Parsania, “Synthesis and physico-chemical study of high performance cardo copoly(ether-sulfone-sulfonates)”, Polym. Plast. Techno. Eng., 47, 826-835, 2008.

137. V. A. Patel, P. J. Vasoya, B. D. Bhuva and P. H. Parsania, “Preparation and physico-chemical study of hybrid glass-jute (treated and untreated) bisphenol-C based mixed epoxy-phenolic resins composites”, Polym. Plast. Techno. Eng., 47, 842-846, 2008.

CHAPTER-2

CHAPTER-2: SYNTHESES OF MONOMERS, SCHIFF BASES AND THEIR SPECTRAL CHARACTERIZATION

This chapter of the thesis describes the syntheses of monomers, Schiff bases and their spectral characterization. This chapter is further subdivided into three sections.

SECTION-1: Syntheses of Monomers
SECTION-2: Syntheses of Schiff bases
SECTION-3: Spectral Characterization

SECTION-1: Syntheses of Monomers

[1] Synthesis of 1,1’-bis (4-amino phenyl) cyclohexane (BAPC)

Aromatic diamines can be synthesized by acid catalyzed condensation of aniline hydrochloride and cyclic ketones [1-3]. Thus, 0.23 mol (29.79 g) aniline hydrochloride and 0.10 mol (9.8 g) cyclohexanone were condensed with stirring at 120°C for 2h and then at 140-150°C for 24h. The resultant solution was cooled to 120°C and 50ml boiling water was added to get deep red solution. The solution was refluxed with activated charcoal for 15 min and filtered off charcoal and resinous mass. The clear blood red solution was made alkaline by using 10% NaOH solution. Product was filtered, washed well with distilled water and dried in an oven at 50°C. It was crystallized 3 times from chloroform-n-hexane system to obtain light brown needle shaped crystals. The yield was 28 % and m. p. 114°C.

[2] Syntheses of 1, 1’-bis (3-methyl 4-amino Phenyl)cyclohexane (BAMPC)

0.23 mol (33.0 g) o-toluidine hydrochloride and 0.10 mol (9.8 g) cyclohexanone were condensed with stirring at 120°C for 2h and then at 140-150°C for 9h. The resultant solution was cooled to 120°C and 50ml boiling water was added to get deep red solution. The solution was refluxed with activated charcoal for 15 min and filtered off charcoal and resinous mass. The clear blood red solution was made alkaline by using 10% NaOH solution.

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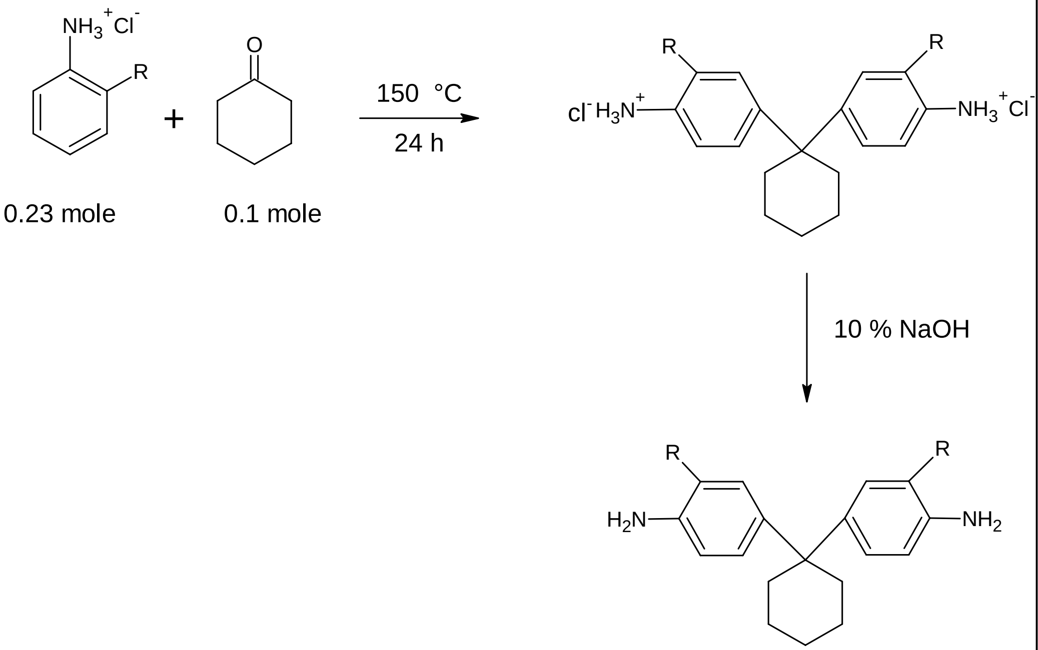
1. M. H. Yi, W. Huang, M. Y. Jin and K. Y. Choi, “Synthesis and characterization of soluble polyamides from 1,1’ bis (4-aminophenyl) cyclohexane derivatives“, Macromolecules, 30, 5606 - 5611, 1997.
2. Y. S. Vygodskii, N. A. Churochkina, T. A. Panova and Y. A. Fedotov, “Novel condensation functional polymers having highly basic groups”, Reactive & Functional Polymers, 30, 241 - 250, 1996.
3. M. H. Yi, W. Huang, B. J. Lee and K. Y. Choi, “Synthesis and characterization of soluble polyimides from 2,2’-bis (4-aminophenyl) cycloalkane derivatives”, J. Polym. Sci. – Part A Polym. Chem., 37, 3449 - 3454, 1999.

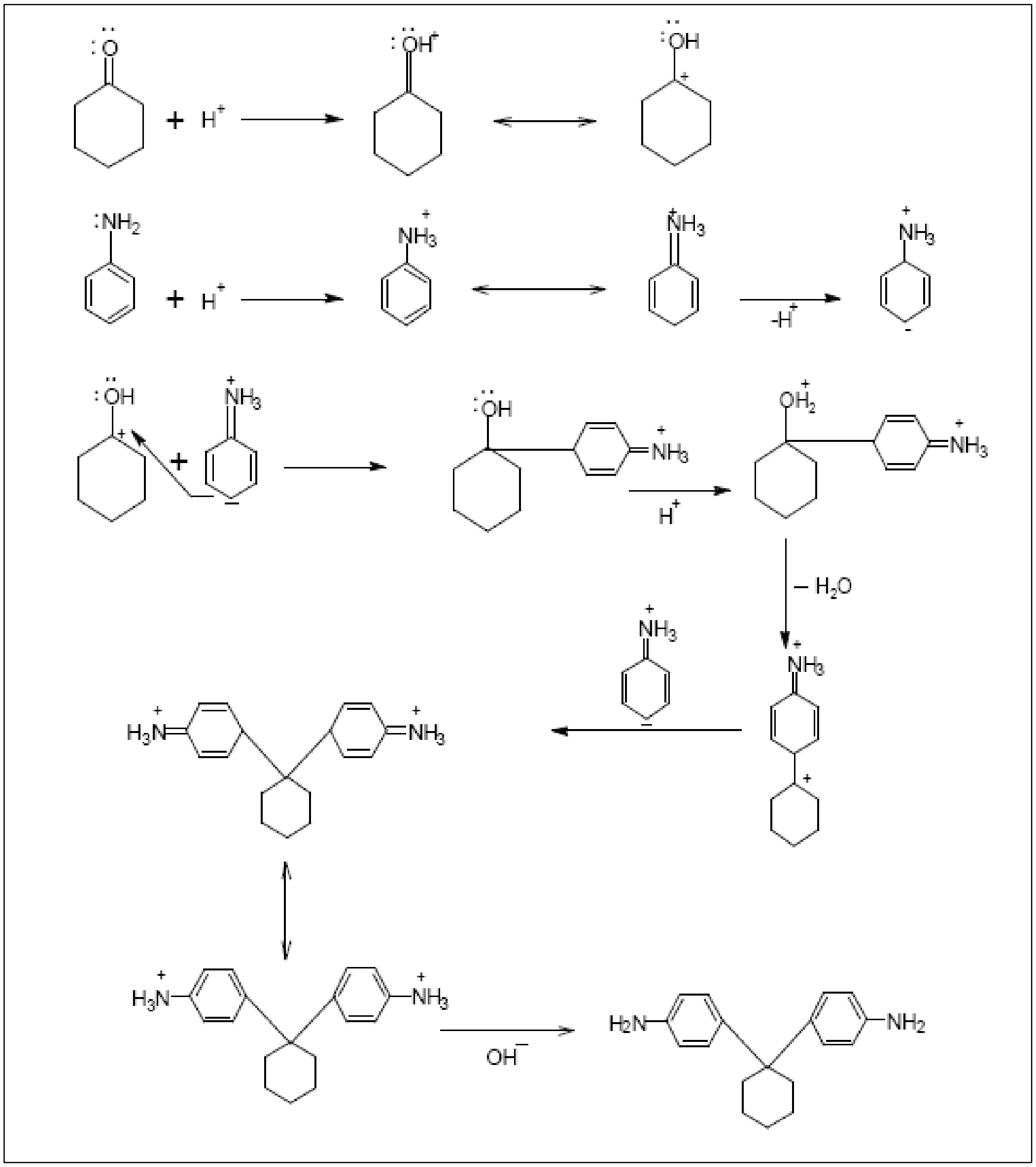
Product was filtered, washed well with distilled water and dried in an oven at 50°C. It was crystallized from toluene to harvest light brown needle shaped crystals. The yield was 34% and m.p. 162°C.

The general structure and reaction mechanism of cardo diamine is under



BAPC R = H

BAMPC $R=CH_3$


H⁺
-H⁺
H⁺
– H₂O
OH⁻

SECTION-2: Syntheses of Schiff Bases

Two different methods are available for the synthesis of Schiff bases: microwave irradiation and classical methods.

Solvent free microwave irradiation synthesis has become popular over usual homogeneous and heterogeneous reactions due to environmental friendly, economic and rapid reaction rates [4]. This technique provides pure products in quantitative yields [5, 6].

Schiff bases were synthesized by condensation of cardo diamine and substituted aromatic aldehydes in ethanol using glacial acetic acid as a catalyst at reflux temperature.

Thus, into a 100 ml RBF, 0.01mol BAPC/BAMPC was dissolved in 35 ml ethanol containing 2 ml glacial acetic acid. To this solution 0.02 mol aldehyde was dissolved in 20 ml ethanol and was added dropwise and refluxed for 4-8h. The product was isolated from chilled water, filtered, washed well with sodium bisulfite to remove excess aldehyde then with water and dried at 50°C in an oven. The Schiff bases are soluble in common solvents like $CHCl_3$, CCl_4, benzene, THF, DMF, DMSO, 1, 4-dioxane, etc. The Schiff bases were crystallized 3 times from appropriate solvent systems and analytical data are summarized in Table-2.1.

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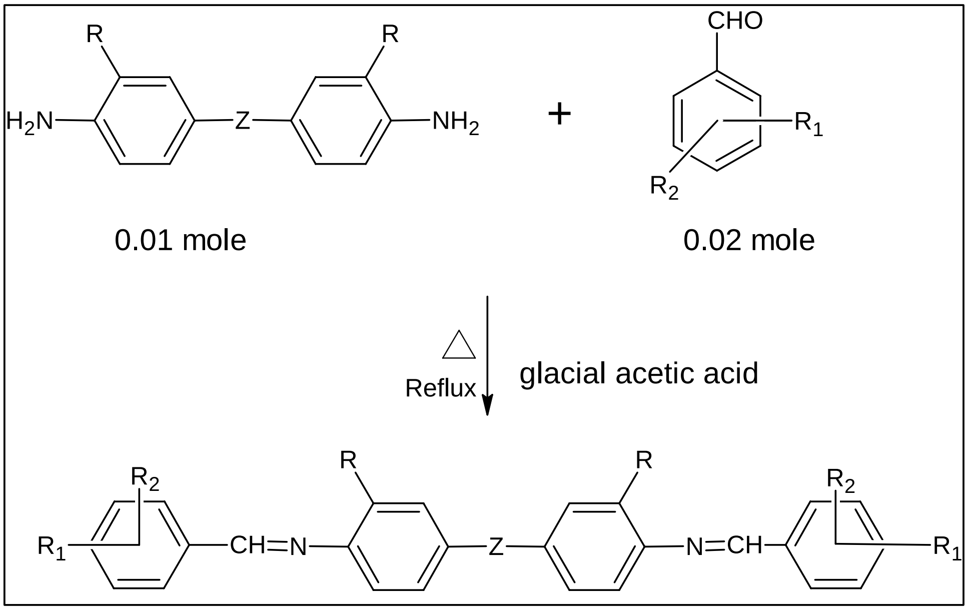
4. R. S. Varma, A. K. Chatterjee and M. Varma, “Alumina mediated deacetylation of benzaldehyde diacetate. A simple deprotection method“, Tetrahedron Lett., 34, 3207 - 3210, 1993.
5. M. Xia, S. H. Wang and W. Yuan, “Lewis acid catalyzed electrophilic substitution of indole with aldehydes and Schiff bases under microwave solvent free irradiation”, Synth. Commun., 34, 3175-3182, 2004 .
6. M. M. Aghayan, M. Ghassemzadeh, M. Hoseini and M. Bolourtchian, “Microwave assisted synthesis of the tetradentate Schiff bases under solvent free and catalyst free condition”, Synth. Commun., 33, 521-525, 2003.

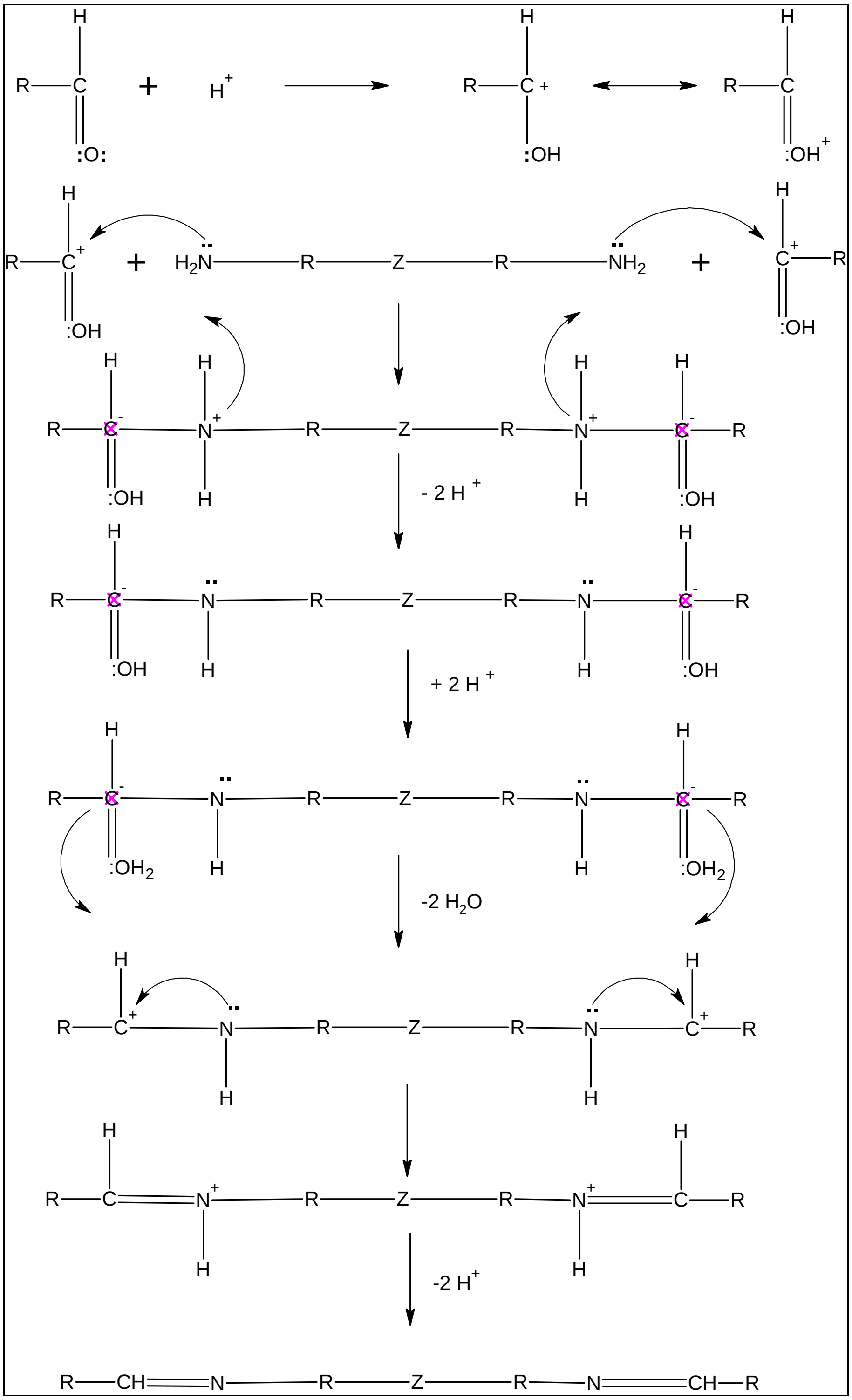


Schiff base	**Z**	**R**	**R_1**	**R_2**
SB-01	CH_2	H	4-OH	H
SB-02	Cyclohexyl	H	4-OH	H
SB-03	Cyclohexyl	H	2-OH	H
SB-04	Cyclohexyl	CH_3	4-OH	H
SB-05	Cyclohexyl	CH_3	2-OH	H
SB-06	Cyclohexyl	CH_3	4-OH	3-OCH_3

Table-2.1: Analytical data and experimental details.

Sample	M.F.	M.W.	m.p., ^0C	Reaction time, h	Yield, %
BAPC	$C_{18}H_{22}N_2$	266	114	24	28
BAMPC	$C_{20}H_{26}N_2$	294	162	18	34
SB-01	$C_{27}H_{22}N_2O_2$	406	138	5	81
SB-02	$C_{32}H_{30}N_2O_2$	474	245	4.5	68
SB-03	$C_{32}H_{30}N_2O_2$	474	240	5	70
SB-04	$C_{43}H_{43}N_2O_2$	502	128	6	82
SB-05	$C_{43}H_{43}N_2O_2$	502	92	8	78
SB-06	$C_{36}H_{38}N_2H_4$	562	136	2	88

The reaction mechanism for the formation of Schiff bases is explained as under



Normally an acid catalyst is added for imine formation. Without an acid catalyst, the reaction is very slow, though in some cases it may still take place (oximes, for example, will form without acid catalysis, but form much faster with it). It is important to notice that acid is not needed for the addition step in the mechanism (indeed, protonation of the amine means that, this step is very slow in strong acid), but is needed for the elimination of water later on in the reaction. Imine formation is in fact fastest at about pH 4–6 at lower pH, too much amine is protonated and the rate of the first step is slow; above this pH the proton concentration is too low to allow protonation of the OH leaving group in the dehydration step.

SECTION-3: Spectral Characterization

This section includes IR spectral characterization of BAPC, BAMPC and SB-01 to SB-06.

IR Spectral Characterization

Information about the structure of a molecule could frequently be obtained from its absorption spectrum. The atomic and electronic configuration of a molecule is responsible for the position of absorption bands. The most structural information of organic molecules could be obtained from their IR spectra. The masses of the atoms and the forces holding them together are of such magnitude that usual vibration of organic molecules interacts with electromagnetic radiation so as to absorb and radiate in the IR region. During the absorption, it is necessary for the molecule to undergo a change in a dipole moment. IR spectroscopy is an excellent method for the qualitative analysis because except for optical isomer, the spectrum of a compound is unique. It is most useful for the identification, purity and gross structural detail. This technique is faster than any other analytical method.

Clougherty et. al [7] observed that for Ar-CH=N-Ar types of Schiff bases frequency range is 1631-1613 cm^{-1} for -CH=N- group. They reported Infrared study of Schiff bases of R-Ph-C=N-Ph-R' types in various solvents namely C_6H_6, CCl_4, CH_2Cl_2 and CH_3CN. They have concluded that there aren't any significant effects of solvent on position of –CH=N- band, but the intensity of band increases by electron donating group and decrease by electron withdrawing group.

The IR spectra were scanned on a Shimadzu-8400 FTIR spectrometer over the frequency range from 4000–400 cm^{-1} by KBr pellet method and are presented in Figs.-2.1 to 2.8. The characteristic IR absorption frequencies (cm^{-1}) are summarized in Tables- 2.1 to 2.4.

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7. L. E. Clougherty, J. A. Sousa, G. M. Wyman, "-C=N stretching frequency in infrared spectra of aromatic azomethines", J. Org. Chem., 22, 462, 1957.

IR characteristic band due to -CH=N- is observed in the range of 1690-1635 cm^{-1} as an intense sharp band, while C-N str. band is observed in the range of 1360-1310 cm^{-1}. C-H symmetric and asymmetric absorption bands due to $-CH_2-$, $-CH_3$ and $-OCH_3$ groups are observed in the range of 2930-2920 and 2870-2860 cm^{-1}, while $-CH_2-$ scissoring bands are observed in the range of 1480-1440 cm^{-1}.

Other spectral studies like ^{1}HNMR, mass spectral are not summarized in this work because Aghera et al.[8] had already worked on Schiff bases.

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8. V. K. Aghera and P. H. Parsania, “Effect of substituents on thermal behavior of some symmetric double Schiff’s bases containing a cardo group”, J. Sci. and Ind. Res., 67, 1083-1087, 2008.

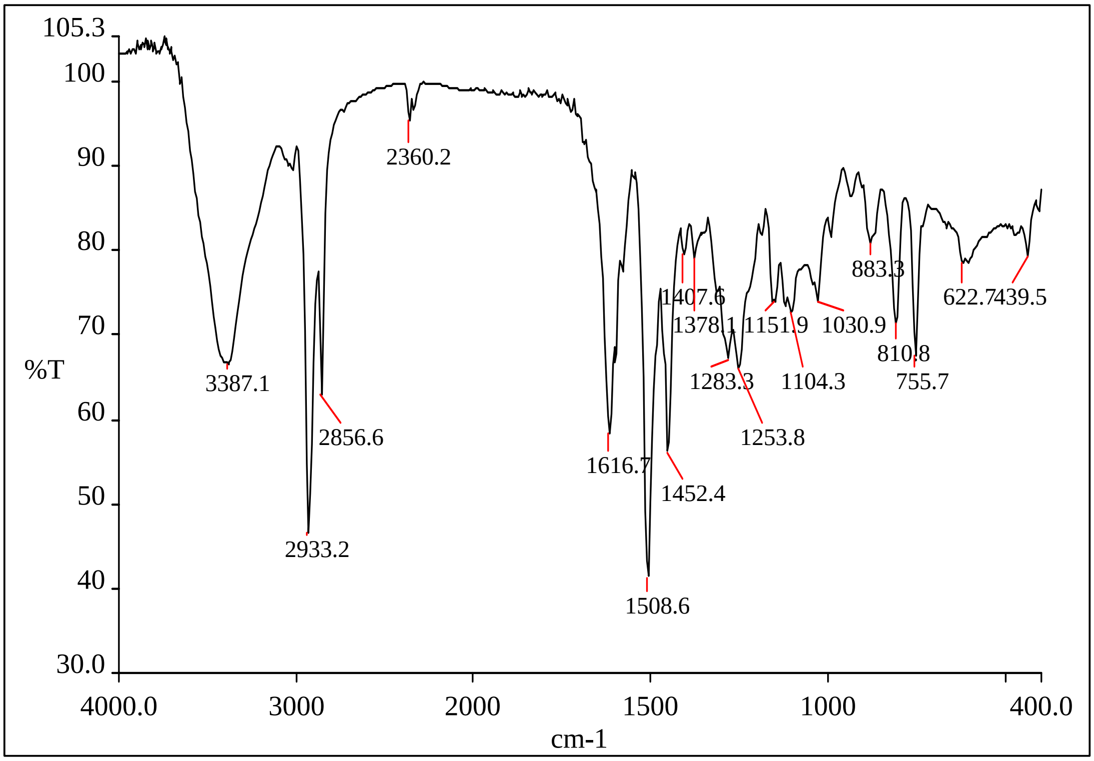

Fig. 2.1 : IR (KBr pellet) spectrum of BAPC

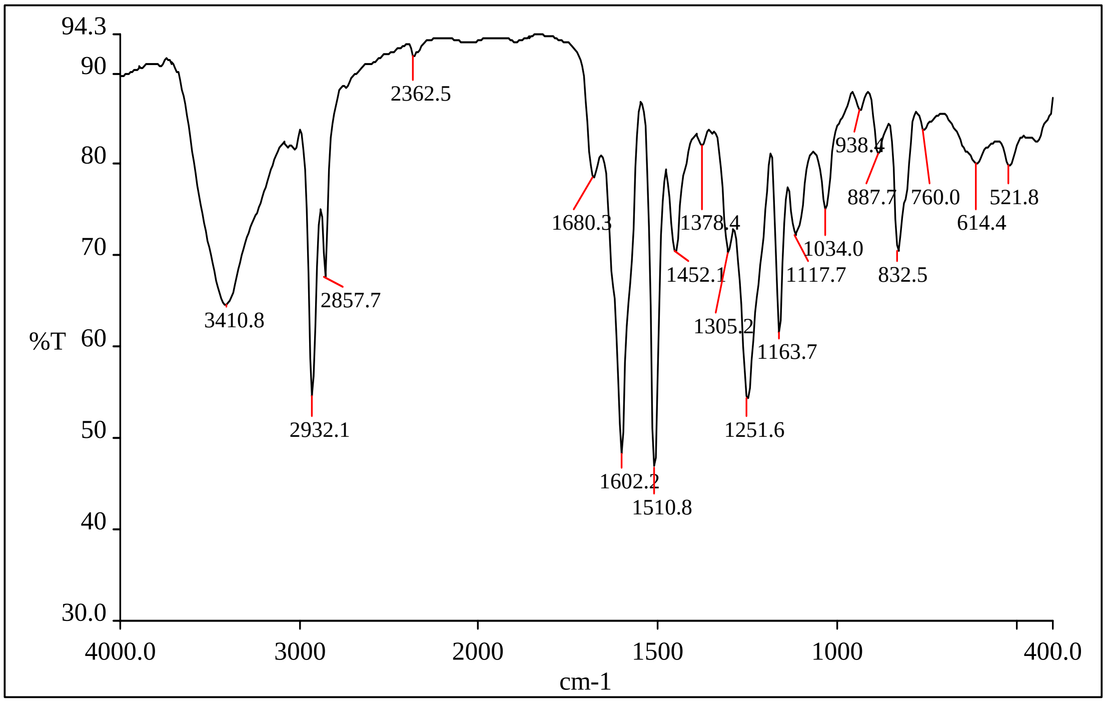

Fig. 2.2: IR (KBr pellet) spectrum of BAMPC

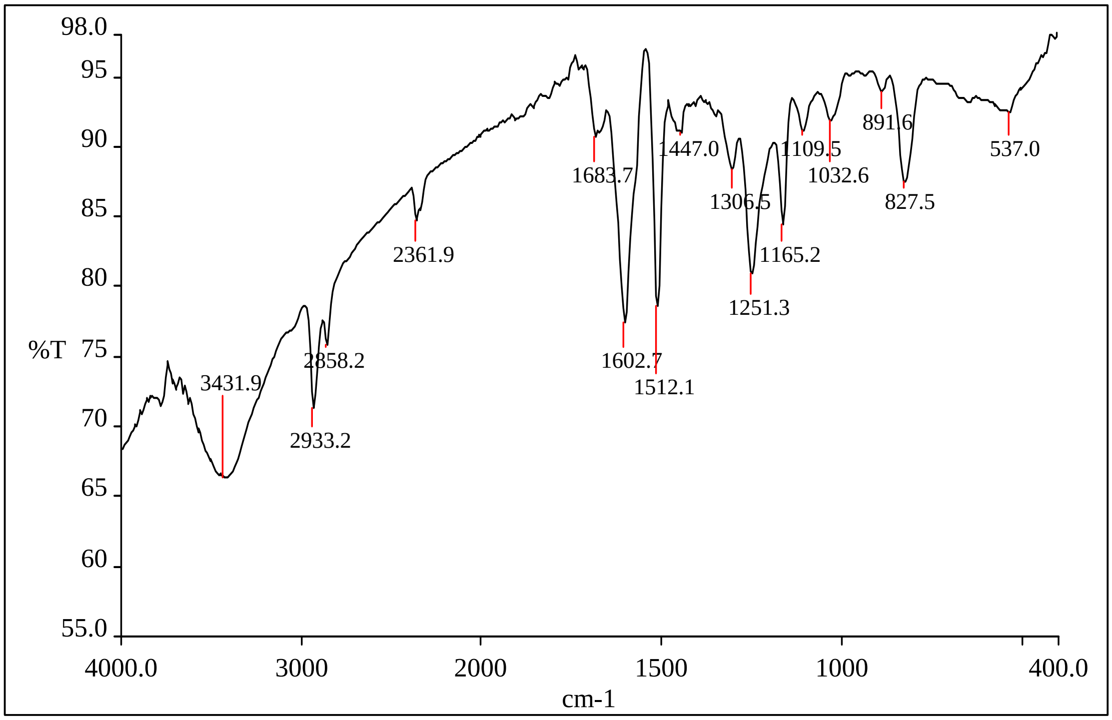

Fig. 2.3: IR (KBr pellet) spectrum of SB-01

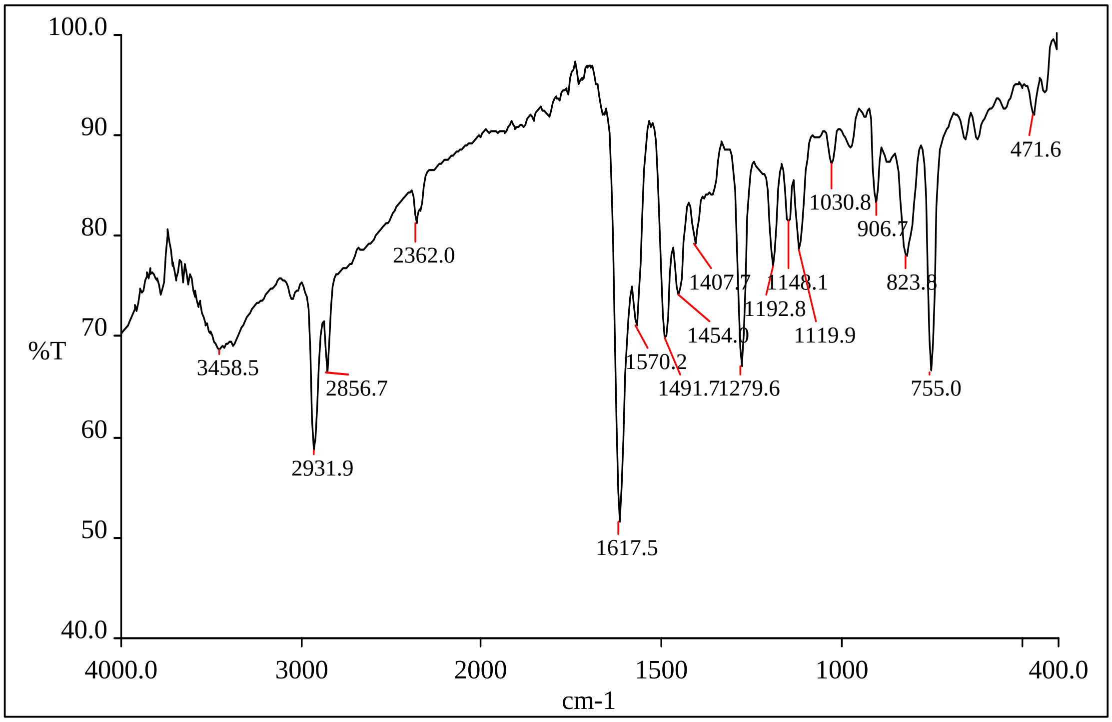

Fig. 2.4: IR (KBr pellet) spectrum of SB-02

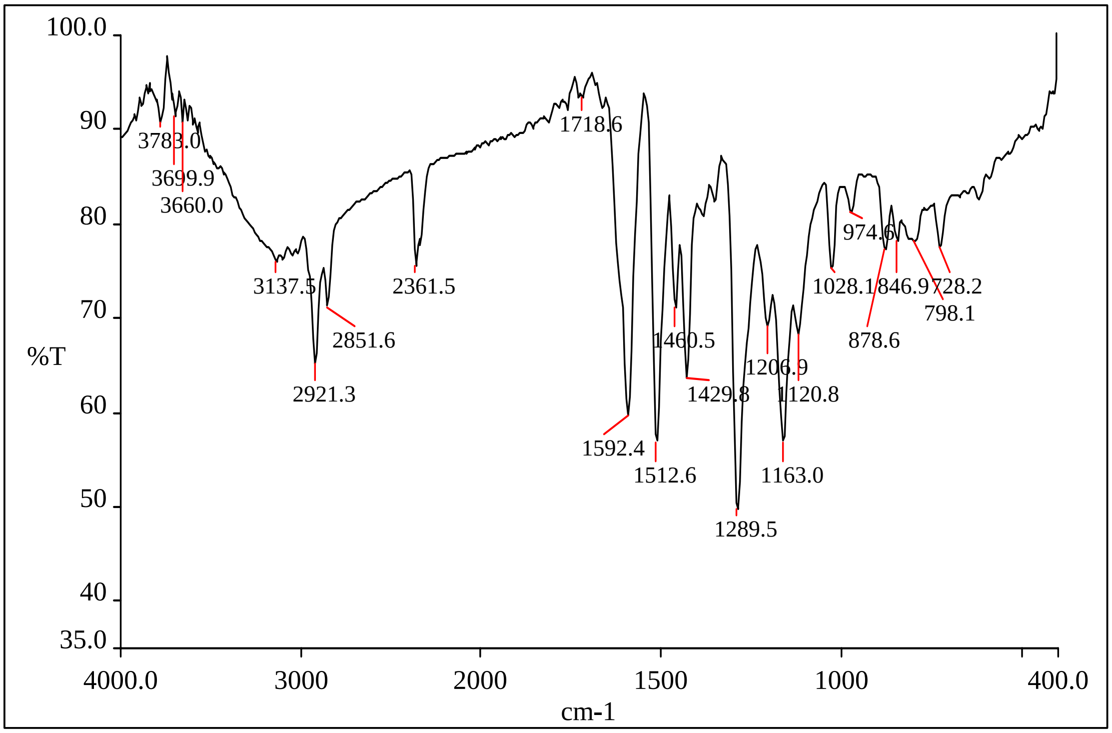

Fig. 2.5: IR (KBr pellet) spectrum of SB-03

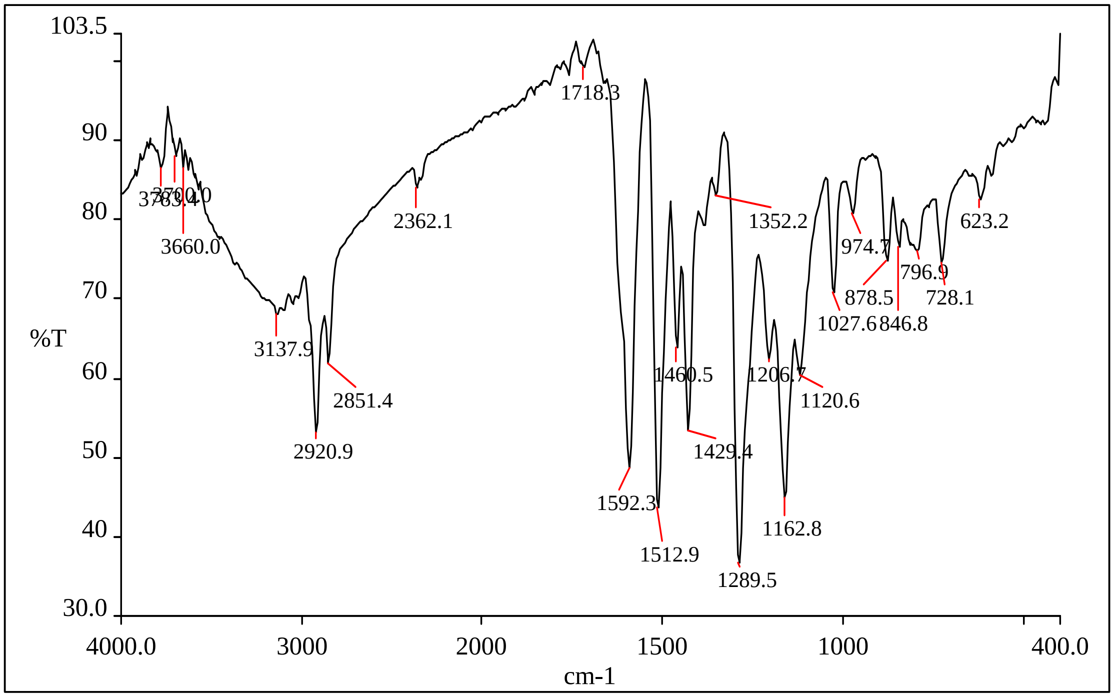

Fig. 2.6: IR (KBr pellet) spectrum of SB-04

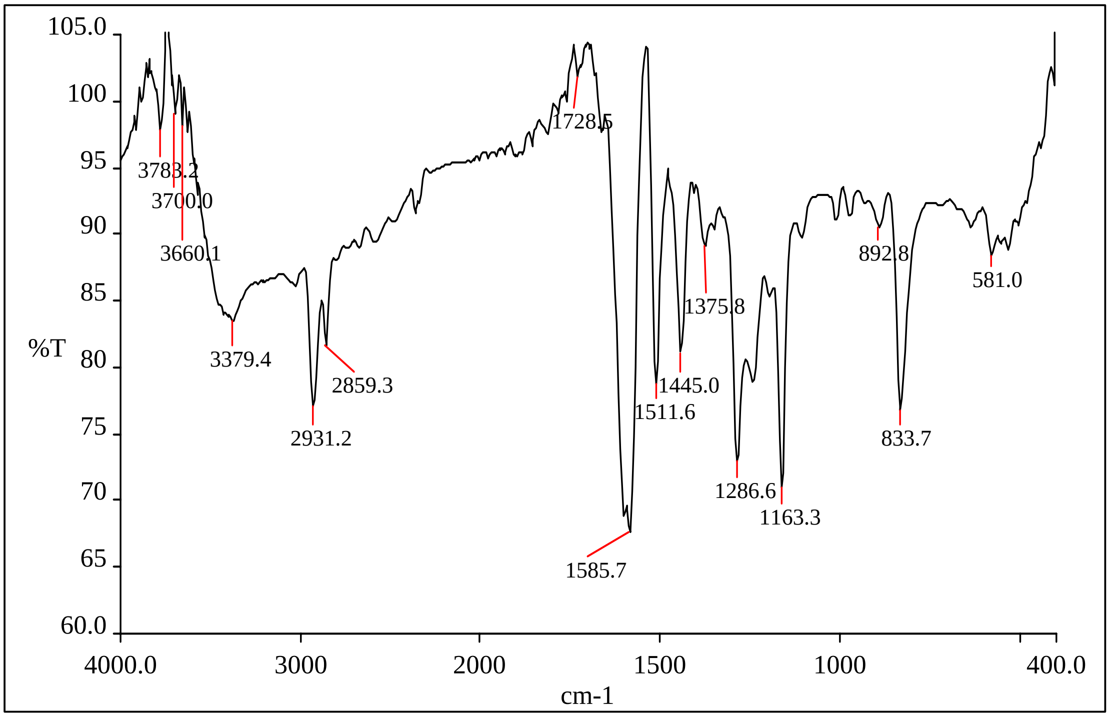

Fig. 2.7: IR (KBr pellet) spectrum of SB-05

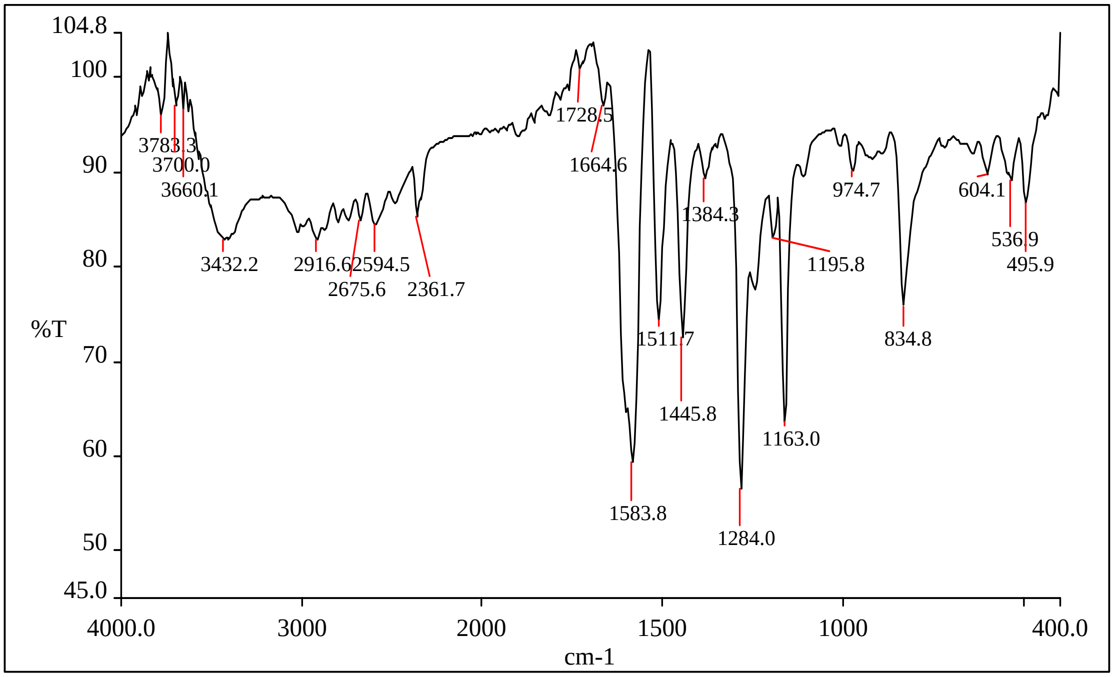

Fig. 2.8: IR (KBr pellet) spectrum of SB-06

Table-2.1: The characteristic IR absorption frequencies (cm^{-1}) of BAPC and BAMPC

Types	Group vibration mode	Observed IR Frequencies, (cm^{-1})		Expected Frequencies (cm^{-1})
		BAPC	BAMPC	
Alkane (-CH_3 & -CH_2-)	C-H asym. str.	2933	2932	2930-2920
	C-H sym. str.	2857	2858	2870-2860
	C-H scis.	1452	1452	1480-1440
	C-H twist-wag	1254	1252	1250
Aromatic trisub.	C=C ring str	-	1602	1579 ± 6
	C-H i.p.def.	-	1252	1250-950
	C-H o.o.p. def.	-	833	820-835
Aromatic monosub & disub	C=C str	1617	1603	1604 ± 3
		1507	1511	1510-1480
		1452	1451	1452 ± 4
	C-H i.p.def.	1152	1164	1180-1160
		1104	1118	1130-1110
	C-H o.o.p. def.	883 811	888 833	900-860 865-810
Amine (-NH_2)	-N-H str.	3387	3411	3400-3350
	C-N vib.	1378	1378	1360-1310

Table-2.2: The characteristic IR absorption frequencies (cm^{-1}) of SB-01 and SB-02

Types	**Group vibration mode**	**Observed IR Frequencies, (cm^{-1})**		**Expected Frequencies (cm^{-1})**
		SB-01	SB-02	
Alkane ($-CH_3$ & $-CH_2-$)	C-H asym. str.	2933	2932	2930-2920
	C-H sym. str.	2858	2857	2870-2860
	C-H scis.	1447	1454	1480-1440
	C-H twist-wag	1251	1280	1250
Aromatic trisub.	C=C ring str	-	-	1579 ± 6
	C-H i.p.def.	-	-	1250-950
	C-H o.o.p. def.	-	-	820-835
Aromatic monosub & disub	C=C str	1603	1618	1604 ± 3
			1570	1510-1480
		1447	1454	1452 ± 4
	C-H i.p.def.	1165	1193	1180-1160
		1110	1120	1130-1110
	C-H o.o.p. def.	892 828	907 824	900-860 865-810
Imine	N=CH sym	1684	1618	1690-1635
	C-N vib.	1307	1305	1360-1310
R	Ar-OH str	3432	3459	3550-3400
	Ar-OH def	1307	1407	1410-1310
	C-O str.	1165	1193	1230-1140
Ether	C-O-C str	1251	1280	1260-1200

Table-2.3: The characteristic IR absorption frequencies (cm^{-1}) of SB-03 and SB-04

Types	Group vibration mode	Observed IR Frequencies, (cm^{-1})		Expected Frequencies (cm^{-1})
		SB-03	SB-04	
Alkane ($-CH_3$ & $-CH_2-$)	C-H asym. str.	2921	2921	2930-2920
	C-H sym. str.	2852	2851	2870-2860
	C-H scis.	1461	1461	1480-1440
	C-H twist-wag	1290	1290	1250
Aromatic trisub.	C=C ring str	-	1592	1579 ± 6
	C-H i.p.def.	-	1207	1250-950
	C-H o.o.p. def.	-	847	820-835
Aromatic monosub & disub	C=C ring str	1592	1592	1604 ± 3
				1510-1480
		1461	1461	1452 ± 4
	C-H i.p.def.	1163	1163	1180-1160
		1121	1121	1130-1110
	C-H o.o.p. def.	879 847	879 847	900-860 865-810
Imine	N=CH sym	1592	1592	1690-1635
	C-N str	1353	1352	1360-1310
R	Ar-OH str	3138	3138	3550-3400
	Ar-OH def	1405	1429	1410-1310
	C-O str.	1163	1163	1230-1140
Ether	C-O-C str	1207	1207	1260-1200

Table-2.4: The characteristic IR absorption frequencies (cm^{-1}) of SB-05 and SB-06

Types	Group vibration mode	Observed IR Frequencies, (cm^{-1})		Expected Frequencies (cm^{-1})
		SB-05	SB-06	
Alkane ($-CH_3$ & $-CH_2-$)	C-H asym. str.	2931	2917	2930-2920
	C-H sym. str.	2859	2855	2870-2860
	C-H scis.	1445	1446	1480-1440
	C-H twist-wag	1253	1252	1250
Aromatic trisub.	C=C ring str	1586	1584	1579 ± 6
	C-H i.p.def.	1253	1252	1250-950
	C-H o.o.p. def.	834	835	820-835
Aromatic monosub & disub	C=C ring str	1586	1584	1604 ± 3
				1510-1480
		1445	1446	1452 ± 4
	C-H i.p.def.	1163	1163	1180-1160
		1121	1121	1130-1110
	C-H o.o.p. def.	893 834	890 835	900-860 865-810
Imine	N=CH sym	1664	1665	1690-1635
	C-N str	1376	1384	1360-1310
R	Ar-OH str	3379	3432	3550-3400
	Ar-OH def	1376	1384	1410-1310
	C-O str.	1163	1196	1230-1140
Ether	C-O-C str	1240	1241	1260-1200

CHAPTER-3

CHAPTER-3: SYNTHESES OF PHENOLIC/EPOXY RESINS, THEIR COPOLYURETHANES AND PHYSICO-CHEMICAL CHARACTERIZATION.

This chapter of the thesis describes the synthesis of epoxy resins, their copolyurethanes and physico-chemical characterization. This part is further subdivided into four sections:

SECTION – 1: General Introduction
SECTION – 2: Synthesis of Epoxy Resins
SECTION – 3: Synthesis of Copolyurethane
SECTION – 4: Physico-Chemical Characterization

SECTION – 1: General 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 wide range of high performance applications from paper coatings to the protection of equipment in industrial plants [1].

Polyurethane 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.

Polyurethanes are polymers that contain the urethane (carbamate) linkage (-NH-CO-O-). Polyurethanes have revealed an unusual versatility; their chemistry, as well as chemistry of related intermediates (isocyanates among them), have 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. Polyurethane adhesives are widely used in footwear, packaging, automotive industries and furniture assembly [3]. Polyurethanes have been recognized as superior adhesives for metal bonding since 1940s [4]. 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 high performance paints for vehicles. High reactivity of isocyanates with active hydrogens is the basis of urethane synthesis. Polymerization proceeds by the reaction of a diisocyanate and diol/diamine to form a carbamate (or urethane) linkage. The resulting polymer is rich in polar functional groups that are potentially capable of strong interaction with metal oxide surface to provide excellent adhesion [5-7].

In recent decades, a wide variety of PU have been synthesized and studied regarding compatibilization [8,9], miscibility [10], morphology, rheology and dynamic mechanical properties [11].

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.
2. X. Tassel, D. Barbry and L. Tighzert, “A new blocking agent of isocyanates”, Eur. Polym. J., 36, 1745-1751, 2000.
3. 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.
4. S. Buchan, “Rubber to metal bonding”, C. Lockwood, London, 206-211, 1948.
5. S. S. Voyutski, “Autohesion and Adhesion of High Polymers”, Wiley Interscience, New York, 197-198, 1963.
6. F. H. Sexsmith, Adhesives Age, June, 31-36, 1970.
7. M. M. Chehimi and J. F. Watts, “The estimation of acid-base interactions by x-ray photo electron spectroscopy”, J. Adhesion Sci. Technol., 6, 377-393, 1992.
8. 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.
9. S. N. Jaisonkar and G. Radhakrishnan, “Effect of compatibilizer on morphology and mechanical properties of TPU/SAN blends”, Polym. Eng. Sci., 40, 621-629, 2000.
10. 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.
11. 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 [12].

The composition, concentration and NCO / OH molar ratio in the hard segment can affect the structure, organization, flexibility of the hard segment and the soft segment, micro-phase separation and mechanical properties of PU [13,14].

There are three major types of polyurethane elastomers. One type is based on ether or ester type prepolymers that are chain-extended and crosslinked using polyhydroxy compounds or amines. 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 reaction of diisocyanate with a dihydroxy ester or ether type prepolymer, or a diacid. 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 3.1, which suggests continuing growth of polyurethane consumption.

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12. Z. S. Petrovic and J. Ferguson, “Polyurethane Elastomers”, J. Prog. Polym. Sci., 16, 695-836, 1991.
13. 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.
14. 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-3.1: Worldwide consumption of polyurethanes by end-user market.

No.	Different application	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

The first synthesis of polyurethane by frontal polymerization has been successfully carried out by Stefano Fiori et al. [15]. Namely, the two reactants (1,6-hexamethylene diisocyanate and ethylene glycol) and the catalyst (dibutyltin dilaurate) were mixed together at room temperature in the presence of an additive (pyrocatechol, necessary for extending pot life), dimethyl sulfoxide (as the solvent), and a filler (fumed silica, added for stabilizing the propagating front).

Anjanapura [16] et al. synthesized waterborne polyurethane (WPU). These coatings have received increased attention in recent coatings technology development because they evolve only water instead of volatile organic compounds during the drying process. They could be utilized effectively in electronic devices as coatings for antistatic or electromagnetic shielding if they could be modified for improved conductivity.

Since the urethane group is polar, it is characterized as a hard segment. Fully hard segmented polyurethane could not be processed because the urethane group undergoes decomposition at around 250°C. To make the polyurethane flexible, it is common practice that they are manufactured as segmented polyurethane [17], where one of the segments is comprised with flexible ether or ester groups.

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15. Stefano Fiori, Alberto Mariani, Laura Ricco and Saverio Russo, “First synthesis of a polyurethane by frontal polymerization”, Macromolecules, 36, 2674-2679, 2003.
16. Anjanapura V. Raghu, Yu Rok Lee, Han Mo Jeong, Cheol Min Shin, “Preparation and physical properties of waterborne polyurethane-functionalized graphene sheet nanocomposites”, Macromol. Chem. Phys., 209, 2487–2493, 2008.
17. Thiyagarajan Shanmugam, A. Sultan Nasar, “Novel hyperbranched poly(aryl ether urethane)s using AB2-type blocked isocyanate monomers and copolymerization with AB-type monomers”, Macromol. Chem. Phys., 209, 651–665, 2008.

Metal-containing polyurethane and polyurea is the subject of extensive research as these polymers exhibit low viscosity, liquid crystalline properties and unusual thermal properties. Metals are usually incorporated into polyurethane chain by means of ionic bond or through coordination. Natarajan et al. [18] reported that the introduction of heterocyclic group into the polyurethane backbone increases the overall thermal stability (10–85 wt. % loss) of polyurethane from 279–345°C to 385–414°C. Study of polymers-containing metals in the main chain or side chain is one of the most active frontiers of current chemical research

Since the synthesis of metal-containing isocyanate is difficult, metal-containing diols are commonly used for the synthesis of metal-containing polyurethanes. Klein et al. [19] used bis (diacetylcarbinol)-beryllium as a diol component for the preparation of metal-containing polyurethanes.

The temperature dependence of hydrogen bonding in 2,4-TDI and 2,6-TDI based polyurethanes was investigated by Paik Sung et al. [20] to resolve hydrogen bonded and non-bonded NH and carbonyl. The fraction of hydrogen bonded carbonyl was used as a measure of the extent of inter-urethane hydrogen bonding. The onset temperature for dissociation of both hydrogen bonded NH and carbonyl in 2,6-TDI polymers occurs at 65°C, independent of urethane content and well below the melting temperature of crystalline hard segment structure (130 to 170°C).

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18. Natarajan Senthilkumar, A. Raghavan and A. Sultan Nasar, “Novel metal-containing polyurethane elastomers prepared using tetradentate Schiff base metal complexes”, Macromol. Chem. Phys., 206, 2490–2500, 2005.
19. R. M. Klein and J. C. Bailar, Jr., “Preparation and reduction of bis-(3-nitro-2,4 pentaediono)-beryllium”, Inorg. Chem., 2, 1187-1190, 1963.
20. C. S. Paik Sung and N. S. Schneider, “Temperature dependence of hydrogen bonding in toluene diisocyanate based polyurethanes”, Macromolecules, 10, 452-458, 1977.

Polymers are frequently used not only as structural components but also as matrix materials, i.e., as carriers for other chemicals. Examples are polymer matrices for pigments (in paints and coatings), for high energy compounds (in explosives and propellants), and for drugs (in controlled-release pharmaceuticals). For some applications it is desirable to have a matrix material that retains its physical properties under one set of environmental conditions, but that can be deliberately degraded in a controlled fashion by changing the conditions. Kenley et al. [21] investigated polymers that feature useful structural or matrix properties at ambient temperature but that convert to soluble materials on heating. To do so they prepared the difunctional azo compound named azo bis[(3-hydroxypropyl)diisobutylmethane] (BHPA) and characterized its homolytic decomposition kinetics in solution and after incorporation into a cross-linked polyurethane.

Various thermoanalytical techniques such as DTA, DSC, thermomechanical analysis, and thermal expansion measurements have been employed in the study of morphology and intermolecular bonding in polyurethane block polymers [22,23].

New biodegradable polyurethanes containing azo-linked polymeric prodrugs of 5-aminosalicylic acid (5-ASA) in the main chain were prepared by Mahakam et al. [24]. Reacting 1,6-hexamethylenediisocyanate(HDI) with 3,3'-azobis(6-hydroxy benzoic acid) (ABHB) and 5-[4-(hydroxyl phenyl) azo] salicylic acid (HPAS) as azo derivatives of 5-ASA. To estimate the hydrolytic behavior of these polymers, they were hydrolyzed at physiological condition (aqueous buffer solution, pH=8.5 and pH=1 at 37°C).

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21. R. A. Kenley, and G. E. Manser, "Degradable polymers. Incorporating a difunctional azo compound into a polymer network to produce thermally degradable polyurethanes", Macromolecules, 18, 127-131, 1985.
22. R. W. Seymour and S. L. Cooper, "Thermal analysis of polyurethane block polymers", Macromolecules, 6, 48-53, 1973.
23. Pil Joong Yoon and Chang Dae Han, "Effect of thermal history on the rheological behavior of thermoplastic polyurethanes", Macromolecules, 33, 2171-2183, 2000.

Elena et al. [25] synthesized a series of polyurethane-urea using diamine as chain extenders, either heterocyclic or aromatic diamine. The polymers containing equal amounts of urethane and urea groups presented better behavior on tensile tests at simple uniaxial tension, at room temperature.

Biocompatible and biodegradable polyurethanes have been investigated as scaffolds for tissue engineering applications [26]. To avoid the toxic diamine decomposition products from aromatic diisocyanates, aliphatic diisocyanates, such as methyl 2,6-diisocyanatohexanoate (lysine methyl ester diisocyanate, or LDI), have been used by Guelcher et al. [27] to synthesize biodegradable polyurethanes. Porous polyurethane scaffolds have been prepared from LDI and polyols by incorporating a porogen (e.g., salt or gelatin) or water, which reacts with isocyanate to form carbon dioxide, a biocompatible blowing agent. In vitro and vivo studies have demonstrated that porous polyurethane scaffolds prepared from LDI and polyester (or polyether) polyols degrade to non-toxic by-products and support the migration of cells and growth of new tissues.

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24. M. Mahakam, M. G. Assadi, R. Zahedifar and M. Ramesh, “Linear type azo-containing polyurethanes for colon-specific drug delivery”, J. Bioactive and Compatible Polym., 19, 45-55, 2004.
25. Elena Scor¸ Tanu, Cristina Prisa-Cariu, A. A. Caraculacu and Maria Brum-A, “New heterocyclic polyurethane-ureas based on 4,4-dibenzyl diisocyanate, Part 1: Influence of oxadiazole structure on mechanical properties”, High Perfor. Polym., 18, 127-143, 2006.
26. Jakov Stamenković, Suzana Cakić,Sandra Konstantinović, Sonja Stoilković, “Catalysis of the isocyanate-hydroxyl reaction by non-tin catalysts in water-borne two component polyurethane coatings”, Working and Living Environm. Protection, 2, 243 – 250, 2004.
27. S. A. Guelcher, V. Patel, K. Gallagher, S. Connolly, J. E. Didier, J. Doctor and J. O. Hollinger, “Synthesis of polyurethane foam scaffolds for bone tissue engineering”, Bone Tissue Engineering Center, Dept. of Biomedical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890

SECTION – 2 : Synthesis of Epoxy Resins

This section of the thesis describes the synthesis of epoxy resins. Solvents that are used in the synthesis are purified as per the standard procedure [28].

Epoxy resins (Scheme-I) were synthesized by condensing corresponding 0.01mol Schiff base with 0.022mol epichlorohydrin by using 100ml isopropanol as a solvent and 0.03mol sodium hydroxide in 15ml water as a catalyst. The reaction mixture was stirred at reflux temperature for 4h. The excess of solvent was distilled off and the resin was isolated from distilled water, filtered, washed well with water and dried in an oven at 50°C. The resins were purified three to four times from chloroform-n-hexane system. The yield was ~ 80 %. The resins are found soluble in common organic solvents like chloroform, 1,2-dichloroethane, 1,4-dioxane, tetrahydrofuran, DMF, DMSO, etc.

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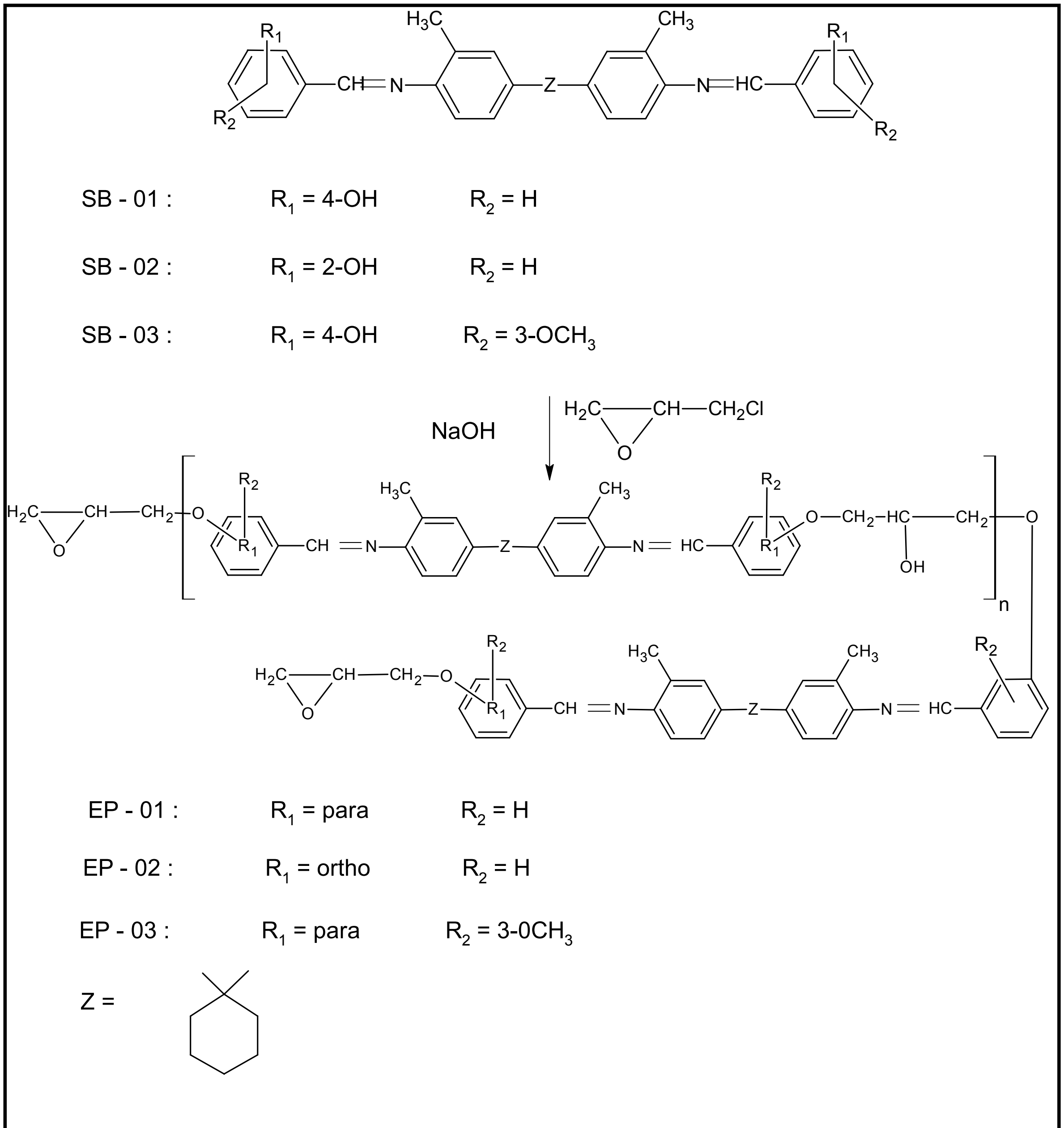
28. C. A. Weissberger and E. S. Proskauer, “Techniques of Organic Solvents”, Interscience, New York, 1955.



SB - 01 : R_1 = 4-OH R_2 = H

SB - 02 : R_1 = 2-OH R_2 = H

SB - 03 : R_1 = 4-OH R_2 = 3-OCH_3

EP - 01 : R_1 = para R_2 = H

EP - 02 : R_1 = ortho R_2 = H

EP - 03 : R_1 = para R_2 = 3-0CH_3

Scheme -I

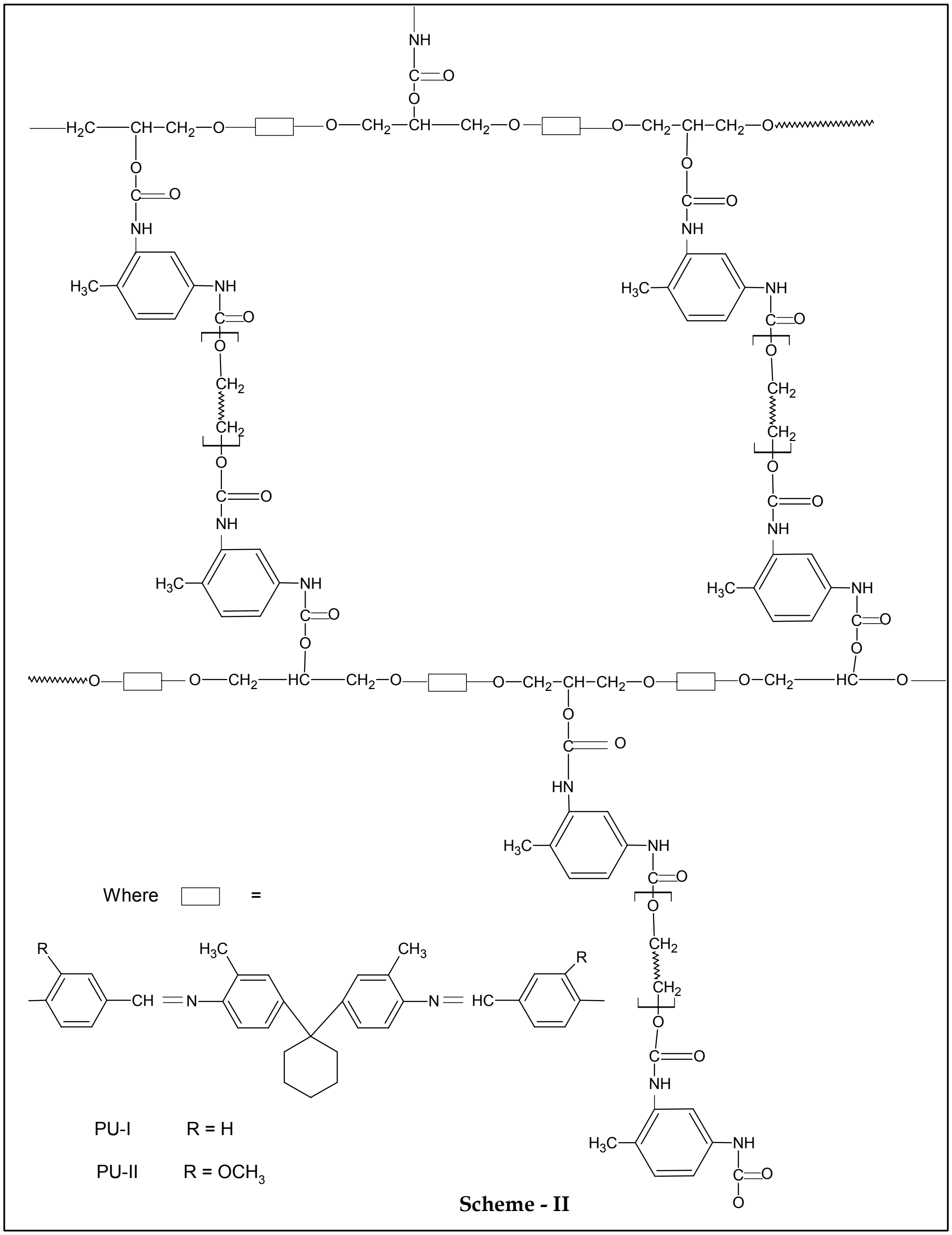
SECTION – 3: Synthesis of Copolyurethane Resins

Into a 250ml beaker, 0.001mol (5.152g/2.29g/5.4g) EP-01/EP-02/EP-03 was dissolved in 15ml chloroform at room temperature. To this solution 0.0045mol (0.783g) TDI in 5ml chloroform was added and the resultant solution was stirred manually for 15 min and poured into a leveled 15cm x 15cm glass mold. The solution was allowed to dry with a controlled evaporation of chloroform at room temperature. The resultant PUs were obtained in powdered form.

In order to improve their elasticity, an attempt has been made by copolymerizing them with PEG-200 and PEG-400. The films were found brittle but with PEG-600 films were obtained successfully.

Thus, into a 250ml beaker, 0.0005mol EP-01/EP-2/EP-03 was dissolved in 15ml chloroform at room temperature. To this solution 0.0005mol (0.3g) PEG-600 in 5ml chloroform was added drop wise with stirring. 0.0045mol(0.783 g) TDI in 5ml chloroform was added dropwise and the resultant solution was stirred manually for 15 min at room temperature and poured into a leveled 15cm x 15cm glass mold. The solution was allowed to evaporate with a controlled rate at room temperature. After 24h, the film was peeled from the mold. The film obtained from EP-02 found brittle in nature. Herewith the film obtained from EP-01 and EP-03 are designated as PU-I and PU-II.

General structure of copolyurethane is shown in Scheme-II.



Scheme - II

SECTION – 4: Physico-Chemical Characterization

SECTION – 4.1: Solubility behavior of the resins

The solubility consideration is of prime importance [29-31] in solution processing during the casting of films, manufacturing of fibers and adhesive materials and also during the use of polymers under conditions, which expose them to attack by potential solvents either in industry or in the house hold applications.

The solubility of liquids in polymer strongly depends on crystallinity. Crystallinity decreases the solubility of polymers markedly increases since the process of solution involves overcoming the heat and entropy factors associated with crystallization as well as those of the intermolecular interactions in intermolecular interactions in the amorphous regions.

When we introduce the polar groups among the polymer chain, solubility of that polymer decreases, since strong polymer-polymer bonds usually develop. The situation is complicated however, by factors such as the arrangement and bulkiness of the groups, which in turn influence crystallinity. The solubility of a polymer may improve or grow worse with increasing temperature.

Dissolution of a polymer is a slow process and occurring in two stages. First, solvent is slowly imbibed into the polymer to produce a swollen gel. In the second stage, the gels gradually disintegrate into a true solution. Only the second stage is materially speed up by agitation. If the polymer is cross linked by primary valance bonds or strong hydrogen bonds or is highly crystalline, only swelling may take place.

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29. J. H. Hildebrand, R. L. Scott, “The Solubility of Non-Electrolytes”, 3rd Ed. Reinhold, New York, 1950.

30. F. W. Billmeyer, “Textbook of Polymer Science” 4th Ed., John Willey and Sons., New York, 1994.

31. P. J. Flory, “Principles of Polymer Chemistry” Cornell University Press, Ithaca, New York, 1962.

In order to test the solubility of a given polymer, approximately 50 mg of polymer sample was placed in a series of test tubes containing about 5ml of solvents and kept them aside for sometime. Gradual disintegration of swollen gel indicated the formation of true solution. EP-01, EP-02 and EP-03 are soluble in chloroform, 1,2-dichloroehtane, dichloromethane, 1,4-dioxane, N-N' dimethyl formamide, dimethylsulfoxide, tetrahydrofuran, acetone, isopropyl alcohol, methyl ethyl ketone, dimethyl acetamide.

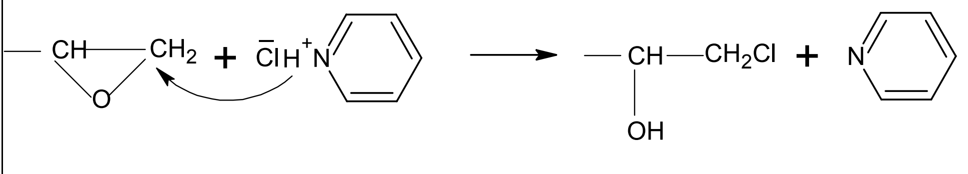
SECTION – 4.2: Determination of epoxy equivalent

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 resin.

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, acetone or 1-4 dioxane 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 to 806 cm^{-1} for terminal epoxy groups; from 847 to 775 cm^{-1} for internal epoxy groups and from 769 to 752 cm^{-1} for triply substituted epoxy group [32]. The epoxide equivalent may be determined from changes in intensity as related to change in molecular weight using the absorption band of the epoxy group at 912 or 862 cm^{-1} in comparison to aromatic bands at 1610 cm^{-1}.

Greenlee [33] 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 reflux temperature for 20 min and back titrating the excess pyridine hydrochloride with 0.1 N sodium hydroxide by using phenolphthalein as an indicator and considering that 1 HCl is equal to 1 epoxide group.



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

Jungnickel et al. [34] 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. The precision and accuracy are somewhat better, due to the reduction of side reactions.

Burge and Geyer [35] have also described an extensive procedure for the determination of epoxide equivalent. A weighed sample of an epoxide compound containing 2-4 milliequivalents of epoxy group, is placed into a 250 ml round bottomed flask, and 25 ml of 0.2 N pyridinium chloride in pyridine was added. The solution was swirled and if necessary, heated gently until the sample was dissolved completely and refluxed for 25 min, cooled and then added 50 ml of methyl alcohol and 15 drops of phenolphthalein indicator and titrated with 0.5 N methanolic NaOH till pink end point. The epoxide equivalent was calculated according to following relationship:

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32. J. Bomstein, “Infrared spectra of oxarine compounds. Correlation with structure”, Anal. Chem. 30, 544-546, 1958.
33. S. O. Greenlee (Devoe & Raynolds Co. New York), “Phenol aldehyde and epoxide resin compositions”, U.S. 2,502,145: 1949; Chem. Abst 44, 5614, 1950.
34. J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss, “Organic Analysis (J. Mitchell Jr., ed.)”, 1, 127, Interscience, New York, 1953.
35. R. E. Burge, Jr. and B. P. Geyer, “Analytical Chemistry of Polymers” (G. M. Hline, ed.) Vol. XII/1, Interscience, New York, 1959.

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

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

The number 0.016 is the miliequivalent weight of oxygen in grams. The epoxide equivalent of the resins under study was determined according to above mentioned method. Average of three measurements for EP-01 to EP-03 is 1220, 680 and 1060, respectively.

SECTION–4.3: Spectral characterization of the resins and copolyurathanes

This section includes IR and NMR spectral characterization of resins

[A] IR spectral characterization

Information about the structure of a molecule could frequently be obtained from its absorption spectrum. The atomic and electronic configuration of a molecule is responsible for the position of absorption bands. The most structural information of organic molecules could be obtained from their IR spectra. The masses of the atoms and the forces holding them together are of such magnitude that usual vibration of organic molecules interacts with electromagnetic radiation so as to absorb and radiate in the IR region. During the absorption, it is necessary for the molecule to under go a change in a dipole moment. IR spectroscopy is an excellent method for the qualitative analysis because except for optical isomer, the spectrum of a compound is unique. It is most useful for the identification, purity and gross structural detail. This technique is faster than any other analytical method.

IR (KBr pellets) spectra of EP-01 to EP-03, PU-I and PU-II were scanned on Shimadzu FTIR–8400 spectrometer over the frequency range of 4000 – 400 cm^{-1} and are presented in Figs. 3.1 to 3. 5.

IR absorption frequencies (cm^{-1}) of all these samples are assigned and reported in Tables-3.2 to 3.3 respectively for epoxy resins and CPUs.

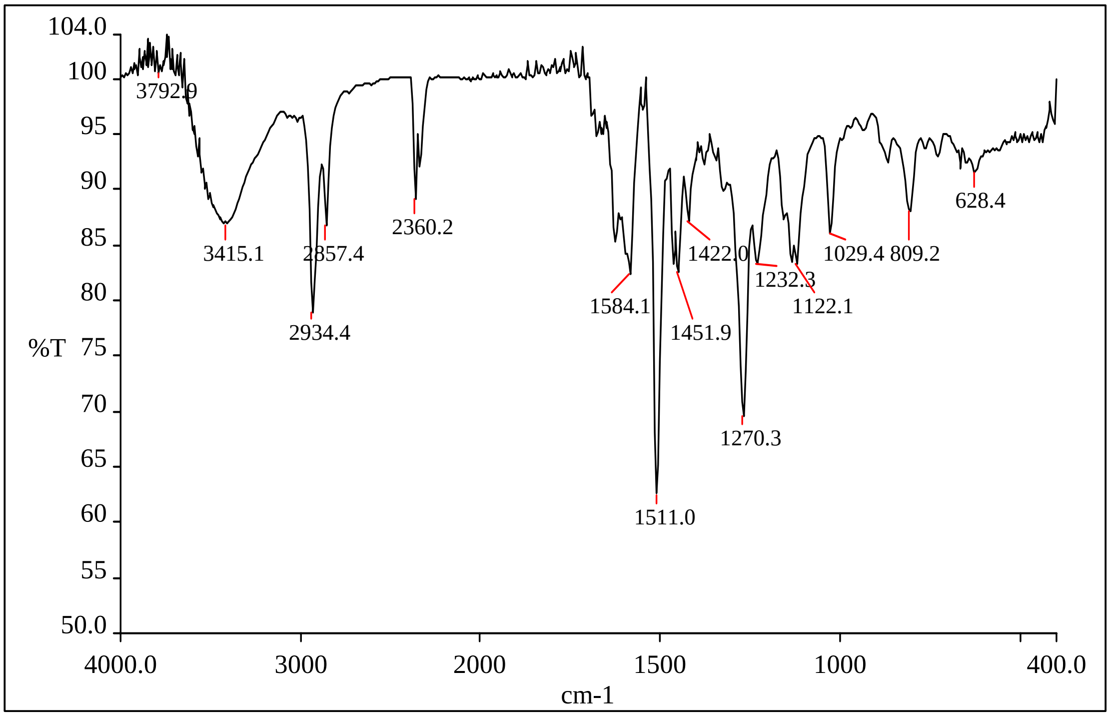


Fig.- 3.1: IR spectrum of EP-01

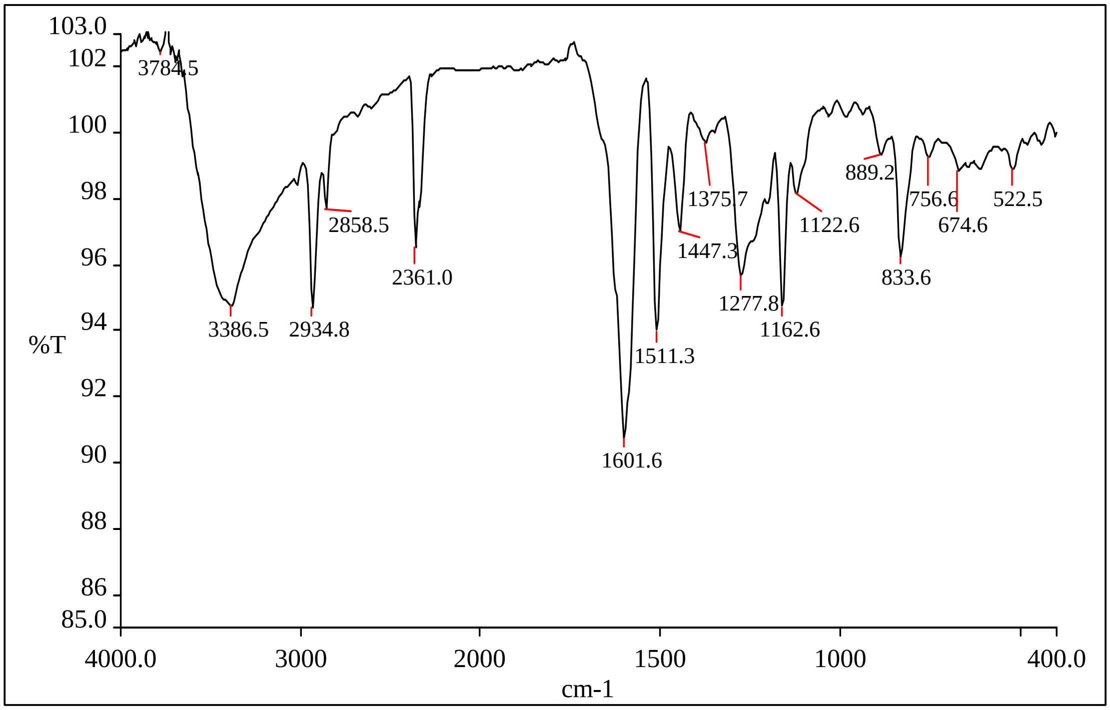


Fig. - 3.2: IR spectrum of EP-02

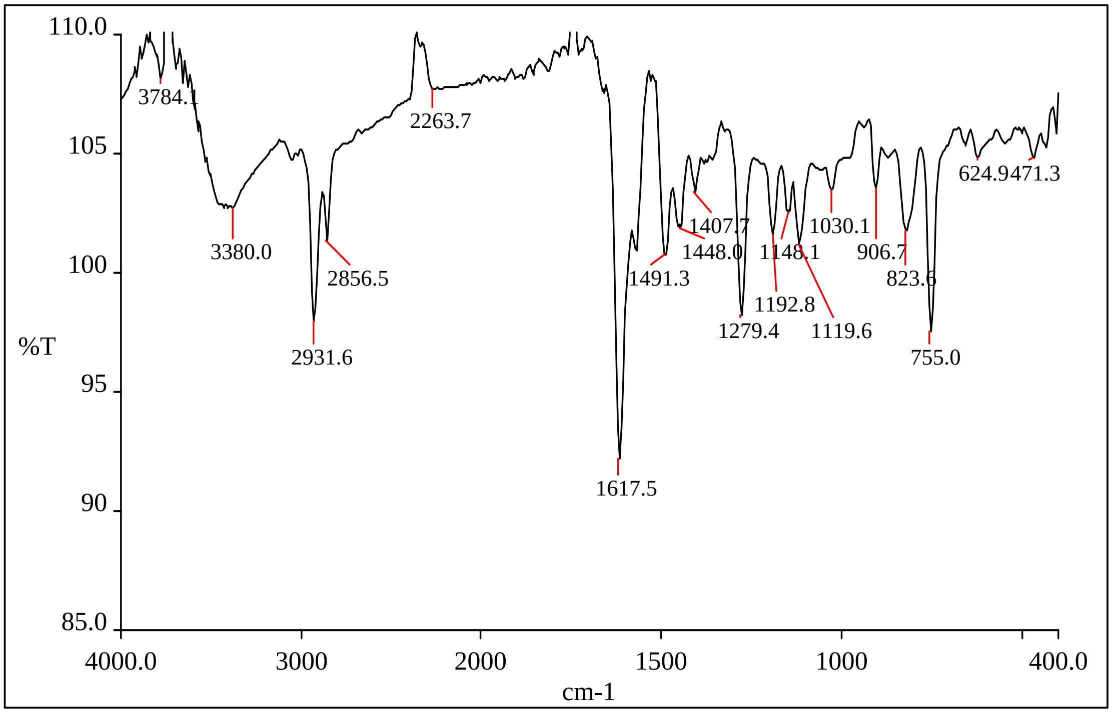


Fig. - 3.3: IR spectrum of EP-03

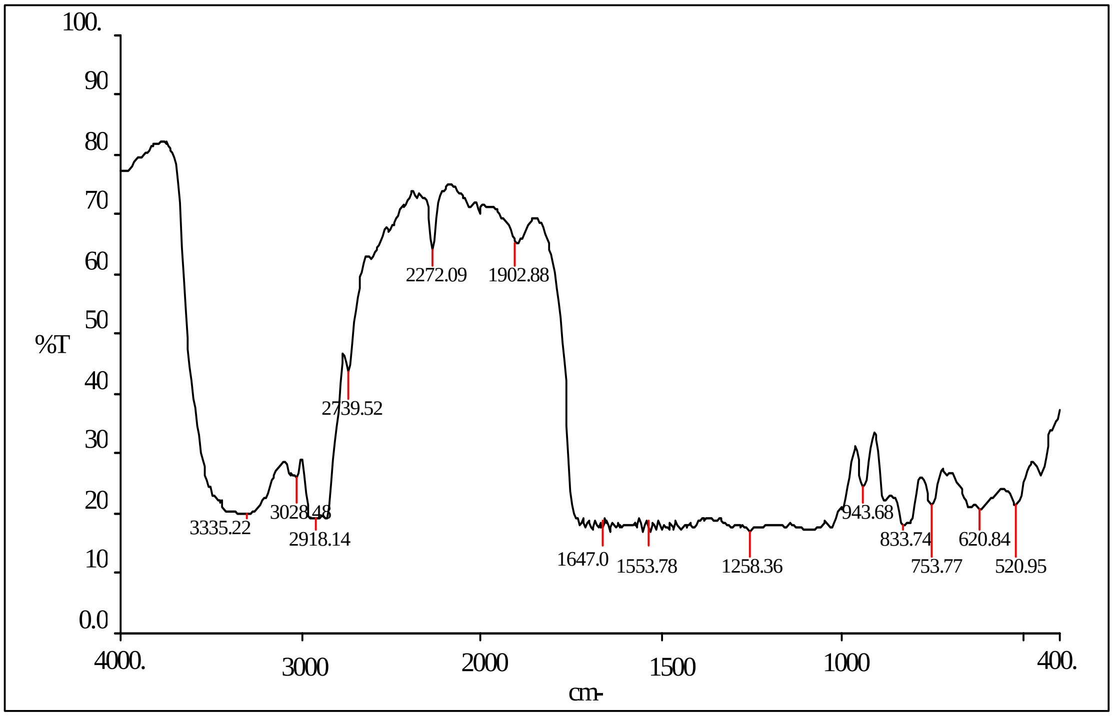


Fig. - 3.4: IR spectrum of PU – I

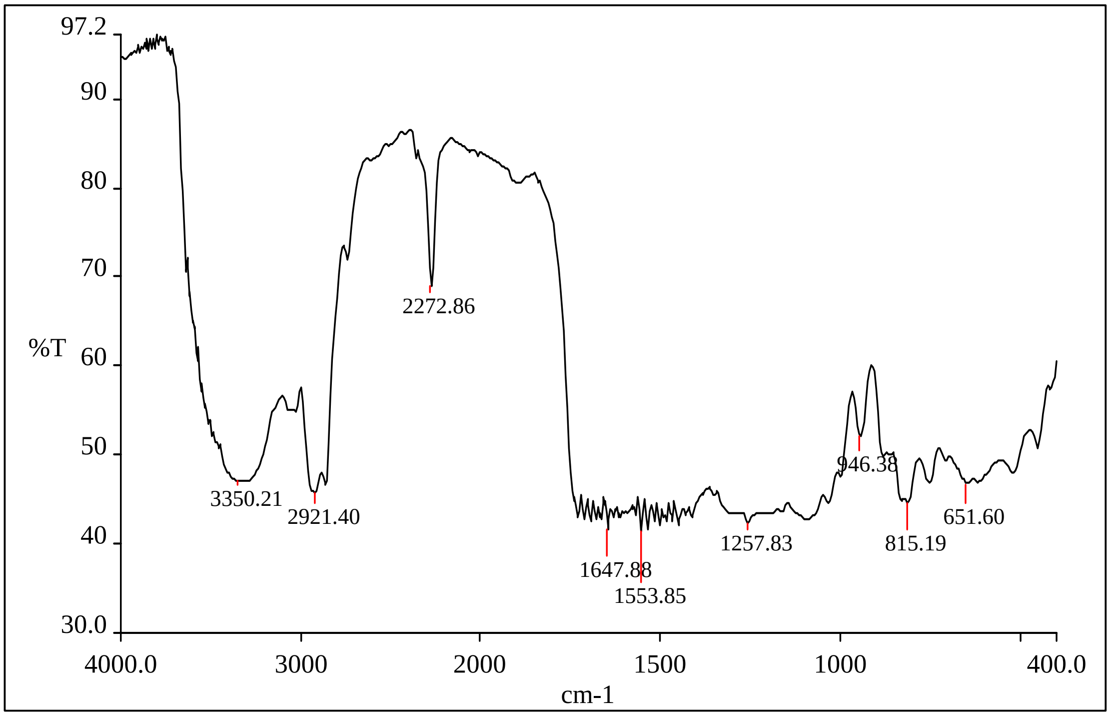


Fig. - 3.5: IR spectrum of PU – II

Thus, IR spectral study supported the formation of epoxies and copolyurethanes.

Table-3.2: The characteristic IR absorption bands (cm^{-1}) of epoxies

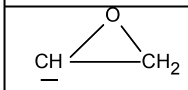
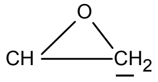
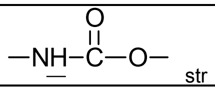
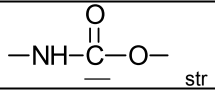
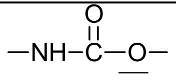
Types	Group vibration mode	Observed IR Frequencies, (cm^{-1})			Expected Frequencies (cm^{-1})
		EP-01	EP-02	EP-03	
Alkane ($-CH_3$ & $-CH_2-$)	C-Hasym. str.	2934	2935	2932	2930-2920
	C-H sym. Str.	2857	2859	2857	2870-2860
	C-H scis.	1452	1447	1448	1480-1440
	C-H twist-wag	1270	1252	1279	1250
Aromatic trisub.	C=C ring str	1584		1580	1579 ± 6
	C-H i.p.def.	1232	1252		1250-950
	C-H o.o.p. def.	833	834	824	820-835
Aromatic monosub & disub	C=C ring str	1605 1511	1602 1511	1618 1491	1604 ± 3 1510-1480
		1452	1447	1448	1452 ± 4
	C-H i.p.def.				1180-1160
		1122	1123	1148	1130-1110
	C-Ho.o.p. def.	885 809	889 834	907 824	900-860 865-810
Imine	N=CH sym	1645	1602	1618	1690-1635
	C-N str	1313	1320	1316	1360-1310
	C-O-C str	1232	1252	1256	1260-1200
 		3013	3009	3012	3002
$O-CH_2$		2924	2935	2932	2924
terminal epoxy		809	834	824	877 - 806
internal epoxy		752	757	755	847 -775

Table-3.3: The characteristic IR absorption bands (cm^{-1}) of PU-I and PU-II

Types	Group vibration mode	Observed IR Frequencies, (cm^{-1})		Expected Frequencies (cm^{-1})
		PU-I	PU-II	
Alkane ($-CH_3$ & $-CH_2-$)	C-Hasym. str.	2918	2921	2930-2920
	C-H sym. Str.		2868	2870-2860
	C-H scis.	1458	1462	1480-1440
	C-H twist-wag	1258	1258	1250
Aromatic trisub.	C=C ring str	1553	1554	1579 ± 6
	C-H i.p.def.	1258	1258	1250-950
	C-Ho.o.p. def.	834	830	820-835
Aromatic monosub & disub	C=C ring str	1608	1609	1604 ± 3
		1494	1490	1510-1480
				1452 ± 4
	C-H i.p.def.			1180-1160
				1130-1110
	C-H o.o.p. def.	907 834	900 815	900-860 865-810
Imine	N=CH sym	1647	1648	1690-1635
	C-N str			1360-1310
	 $-N\underline{H}-\overset{\overset{O}{\|}}{C}-O-$ str	3335	3350	3350-3400
	 $-NH-\underline{\overset{\overset{O}{\|}}{C}}-O-$ str	1647	1648	1740-1690
	 $-NH-\overset{\overset{O}{\|}}{C}-\underline{O}-$ and $-C-\overline{O-C}$ str	1258	1258	1350-1260

[B] NMR spectral characterization of epoxy resins

This part of the chapter includes NMR spectral data of epoxy resins.

Some nuclei spin about their axes in a manner to that electrons spin. In the presence of an externally applied magnetic field, a spinning nucleus can only assume a limited number of stable orientations. Nuclear magnetic resonance occurs when a spinning nucleus in a lower energetic orientation in a magnetic field absorbs sufficient electromagnetic radiation and excites to a higher energetic orientation. The excitation energy varies with the type and environment of the nucleus. NMR spectroscopy can be used for the quantitative chemical analysis [36-38].

The NMR spectra of epoxy resins were scanned on a Bruker FTNMR (400MHz) spectrometer by using $CDCl_3$ as a solvent and TMS as an internal standard and are presented in Figs.3.6 to 3.8.

The chemical shifts and types of protons of EP-01 to EP-03 are reported in Table-3.4. The integrated areas under the NMR peaks have revealed the labeled protons in each epoxy. The solvent $CDCl_3$ appeared at about 7.25-7.24 ppm either as a separate peak or overlapped with peak due to aromatic protons. Thus, NMR spectral data indicated expected number and types of the protons in a given epoxy molecule. The integrated area of each signal of epoxy polymer furnished the knowledge on the agreement of protons with theoretical protons. Thus, IR and NMR spectra supported the structure of the resins.

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36. V. M. Parikh, “Absorption Spectroscopy of Organic Molecules”, Addission Wesley Pub., p. 243-258, 1978.
37. R. M. Silverstein, G. C. Bassler and T. C. Morrill, “Spectrometric Identification of Organic Compounds”, 6th Ed. John Willey and Sons, New York, 1996.
38. C. N. Rao, “Chemical Applications of Infrared Spectroscopy”, Academic Press, New York, p. 317-333, 1963.

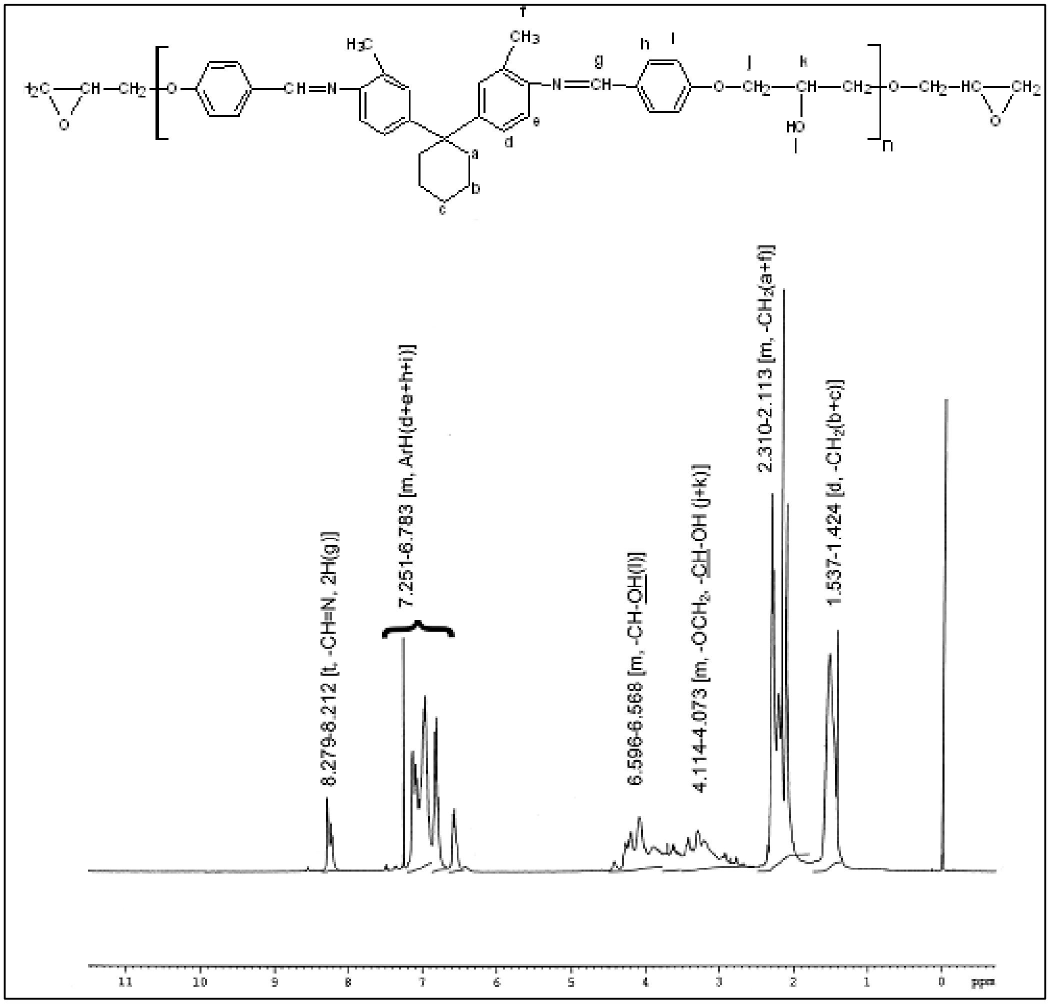

Fig. 3.6: NMR Spectrum of EP-01

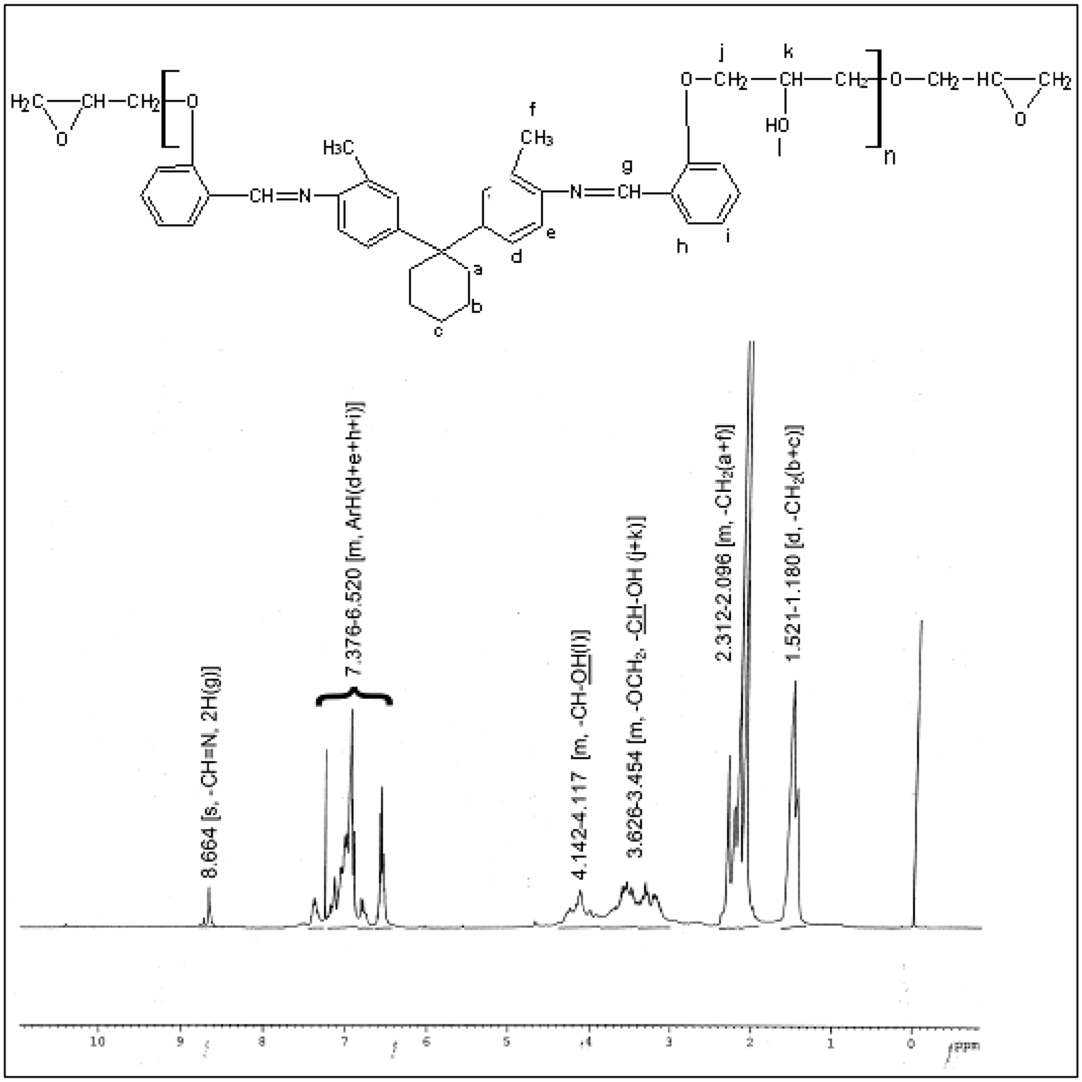

Fig. 3.7: NMR Spectra of EP-02

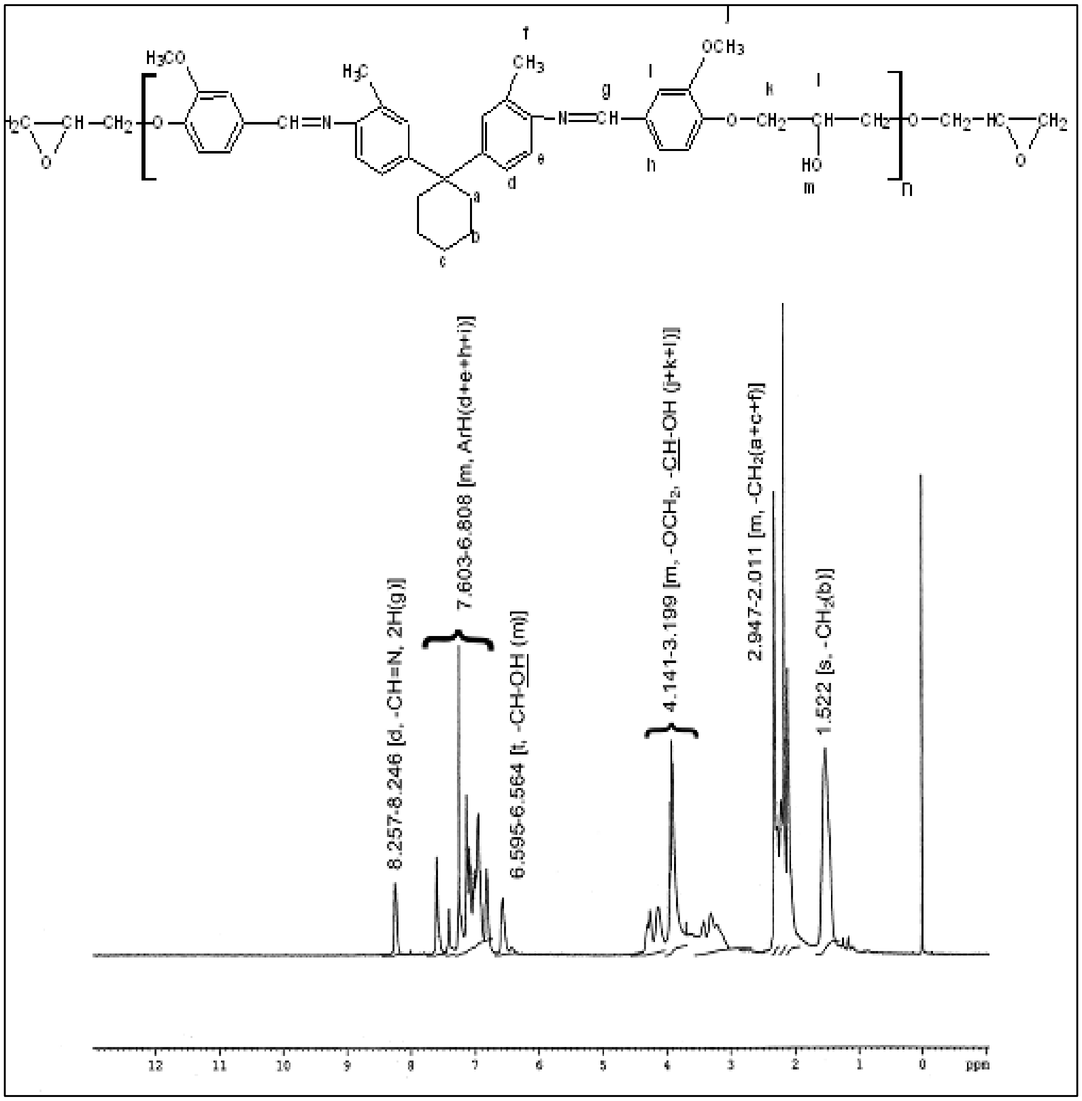

Fig. 3.8: NMR Spectra of EP-03

Table-3.4: NMR chemical shifts of EP–01 and EP-02

Sample	NMR chemical shift, ppm
EP-01	8.279-8.212 [t, -CH=N, 2H(g)] 7.251-6.783 [m, ArH(d+e+h+i)] 6.596-6.568 [m, -CH-$\underline{\mathrm{OH}}$(l)] 4.114-4.073 [m, -OCH$_2$, -$\underline{\mathrm{CH}}$-OH (j+k)] 2.310-2.113 [m, -CH$_2$(a+f)] 1.537-1.424 [d, -CH$_2$(b+c)]
EP-02	8.664 [s, -CH=N, 2H(g)] 7.376-6.520 [m, ArH(d+e+h+i)] 4.142-4.117 [m, -CH-$\underline{\mathrm{OH}}$(l)] 3.626-3.454 [m, -OCH$_2$, -$\underline{\mathrm{CH}}$-OH (j+k)] 2.312-2.096 [m, -CH$_2$(a+f)] 1.521-1.180 [d, -CH$_2$(b+c)]
EP-03	8.257-8.246 [d, -CH=N, 2H(g)] 7.603-6.808 [m, ArH(d+e+h+i)] 6.595-6.564 [t, -CH-$\underline{\mathrm{OH}}$ (m)] 4.141-3.199 [m, -OCH$_2$, -$\underline{\mathrm{CH}}$-OH (j+k+l)] 2.947-2.011 [m, -CH$_2$(a+c+f)] 1.522 [s, -CH$_2$(b)]

SECTION–4.4: Thermal analysis of epoxy resins and their copolyurethanes

A major driving force for the growth and interest in the thermally stable polymers is attributable to their extensive applications such as space exploration, terrestrial transportation, modern communication, energy saving, environmental protection, public health, microbiology, medicine, aeronautics and in supersonic applications. Considerable research work has been undertaken on thermally stable polymers [39], which may be useful for high temperature applications.

Increased emphasis on occupational safety and consumer protection has generated significant interest in analytical methods to evaluate safe processing, storage, shipping and safety conditions for a wide variety of materials. Thermal techniques particularly differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) have been proven useful for evaluating kinetic parameters of various reactions and materials [40].

Studies on thermal behavior of polymers are of paramount importance from both scientific and practical point of views. Scientific studies help to reveal the molecular structure such as the sequence and arrangement of repeating units and side groups in the polymers as well the nature of the chain ends and of the cross links between chains. The kinetics of degradation is very useful in determining the strength of various bonds in polymer structure [41, 42].

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39. J. H. Flynn and L. A. Wall, “A quick, direct method for the determination of activation energy from thermogravimetric data”, J. Polym. Sci., Part-B, Polym. Letter, 4, 323-328, 1966.
40. T. Ozawa, “Kinetic analysis of deviate curves in the thermal analysis”, J. Therm. Anal., 2, 301-324, 1970.
41. H. E. Kissinger, “Reaction kinetics in different thermal analysis”, Anal. Chem. 29, 1702-1706, 1957.
42. H. C. Anderson, “Thermal degradation of epoxide polymers”, J. Appl. Polym. Sci., 6, 484-488, 1962.

Thermal degradation of cross linked resins in controlled atmosphere has studied by Bouajila et al. [43]. 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.

Effect of various operating parameters

1. Atmosphere

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

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43. 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.

4. Sample size

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

5. Rate of heating

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

Physical transformation [44] such as glass transition, cold crystallization and crystallization from melts, crystallization disorientation, and melting can be studied by differential scanning calorimetry (DSC) and differential thermal analysis (DTA).

DSC provides useful information about crystallinity, stability of crystallites, glass transition temperature, cross linking, kinetic parameters such as the activation energy, the kinetic order, frequency factor, entropy change and heat of polymerization. DSC is a method where by the energy necessary to establish a zero transition occurs, the energy input to the sample is compensated by an increased energy input to the sample in order to maintain a zero temperature difference. The energy input is precisely equivalent in magnitude to the energy absorbed during the transition in direct calorimetric measurement. The combination of programmed and isothermal techniques has been used for characterizing unresolved multi step reactions in polymers [45].

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44. Bo Lin, H. Zhang and Y. Yang, “Synthesis and thermal analysis of linear triblock copolymers based on methacrylate ester”, J. Thermal Ana. and Calorimetry, Vol-102, 2010.
45. Y. Li, Yi Cheng, Y. Ye and Ruiqi Shen, “Supplement on applicability of Kissinger’s equation in thermal analysis”, J. Thermal Ana. and Calorimetry ,102, 605-608, 2009.

DTA is more versatile and gives data of more fundamental nature than TGA. This technique involves recording of difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a programmed heating rate. Any transition, which the polymer sample undergoes, will result in absorption or liberation of energy by the sample with a corresponding deviation of its temperature from that of the reference. In DTA, as soon as the sample reaches the temperature of the change of its state (chemical or physical), the differential signal appears as a peak. The number, position, shape and nature (exothermic or endothermic)of the DTA peaks give information about glass transition temperature, crystalline rearrangement, melting, curing, polymerization, crystallization, decomposition of polymer, etc.

Thermo Gravimetric Analysis (TGA)

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

There are three types of thermogravimetry namely

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

Most of the studies of polymers are generally carried out with dynamic thermogravimetry. Normally sample starts losing weight at a very slow rate up to a particular temperature and thereafter, the rate of loss becomes large over narrow range of temperature. After this temperature the loss in weight levels off. TGA curves are characteristic for given polymers because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at the rates that are function of the polymer structures.

The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evaluation of volatile products in the formation of heavier reaction products. Pyrolysis of many polymers yields TG curves, which follow relatively simple sigmoidal curves. In such a case weight of sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction gets completed. The shape of the curve depends on the kinetic parameters: reaction order (n), frequency factor (A) and activation energy (Ea). The values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation [46-47].

Reich and Levi [48] have described several temperature characteristics for qualitative assessment of relative thermal stability of polymers:

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

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.

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46. Leo Reich, "Kinetic parameters in polypropylene degradation from DTA traces", J. Appl. Polym. Sci., 10, 465-472, 1966.
47. C. Bouster, P. Vermande, J. Veron, "Study of the pyrolysis of polystyrenes. I: Kinetics of thermal decomposition." J. Ana. and Appl. Pyrolysis, 1, 297-313, 1980.
48. L. Reich and D. W. Levi, Macromol. Rev.Eds. Peterlin Goodman Willey Interscience, New York, 173, 1968.

For the estimation of kinetic parameters from TG traces, several so called exact methods have been proposed. All these methods involve the two assumptions that thermal and diffusion barriers are negligible and that Arrhenius equation is valid.

Since small quantities of materials are employed in TG studies, thermal and diffusion barriers would be negligible. Since the shape of any TG curve is dependent on the nature of apparatus and the way in which it is used. Most kinetic treatments are based on relationship of the type.

$$\frac{dC}{dt} = kf(C) \qquad \ldots 3.1$$

Where,

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

f (C) = temperature independent function of C

The constant k is generally assumed to have the Arrhenius from

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

C is defined as the conversion with respect to initial material

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

where

W_o = Initial weight of the material

W = weight of the material at any time.

The residual weight fraction is given by

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

and the rate of conversion is given by

$$\frac{dC}{dt} = -(1/W_o)\frac{dW}{dt} \qquad \ldots 3.4$$

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

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

Where

n = order of the reaction

Upon substituting Eqns. 3.2 and 3.5 into Eqn. 3.1

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

OR

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

Where,

β = Rate of heating

Methods of single heating rate

1. Freeman-Carroll [49] and Anderson-Freeman methods [50]

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

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

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

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

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

---

49. E. S. Freeman and B. Carroll, “The application of thermoanalytical techniques of the reaction kinetics: The thermogravimetric evaluation of the kinetic of decomposition of calcium oxalate monohydrate.” J. Phys. Chem., 62, 394-397, 1958.
50. D. A. Anderson and E. S. Freeman, “The kinetics of thermal degradation of polystyrene and polyethyl-ene”, J. Polym. Sci., 54, 253-260, 1961.

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2. Sharp-Wentworth method [51]

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

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

where,

C = fraction of polymer decomposed at temperature T,

β = rate of heating, A = Frequency factor and

E_a = the activation energy of the process.

The plot of log [(dC/dt)/ (1-C)] against 1/T would be a straight line, with slope equal to –(Ea/2.303 R) and the intercept equal to log (A/β).

3. Chatterjee method [52]

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

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

Where,

W_1 and W_2 are the sample weights.

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51. J. H. Sharp and S. A. Wentworth, “Kinetic analysis of the thermogravimetric data”, Anal. Chem., 41, 2060-2062, 1969.
52. P. K. Chatterjee, “Application of thermogravimetric techniques to reaction kinetic”, J. Polym. Sci., 3, 4253-4262, 1965.

4. Horowitz -Metzger method [53]

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

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

Where,

C = fraction of the compound decomposed at time t,

E_a= activation energy, Ts= Temperature at which the rate of decomposition is maximum θ = T-Ts

The frequency factor A and entropy change ΔS* can be determined respectively according to Eqns. 3.12 and 3.13.

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

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

where k_b is Boltzmann constant.

Use of multiple heating rates

1. Anderson method

Anderson [54] and Friedman [55] have developed the methods based on multiple heating rates. These methods are based on the fact that as the heating rate increases, TG curve tends to shifts to higher temperature range, since at lower temperature decomposition occurs for a shorter time interval range, since at lower temperature decomposition occurs for a shorter time interval.

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53. H. H. Horowitz and G. Metzger, Anal. Chem., 35, 1464, 1963.
54. H. C. Anderson, J. Polym. Sci., C6, 175, 1964.
55. H. L. Friedman, "Kinetics of thermal degradation of char-forming plastic from thermogravimetry- Application to a phenolic plastic", J. Polym. Sci., C6, 183, 1964.

The relation is

$$\ln R_t = \ln A + n \ln (1-C) - \frac{E_a}{RT} \qquad \text{... 3.14}$$

where $R_t = \beta\, dC / dT$ The plot of ln R_t against 1/T would be a straight line with slope equal of -Ea / R at a fixed degree of conversion. In order to evaluate the values of n and A, Eqn. 3.15 can be employed by considering $1/T = 1/T_o$ when ln R_t = 0

$$\frac{E_a}{RT_o} = \ln A + n \ln (1-C) \qquad \text{… 3.15}$$

According to Eqn. 3.15, the plot of Ea/RTo against ln(1–C) would be a straight line with slope equal to n and intercept equal to ln A.

2. Friedman method

Friedman has developed the following Eqn. 3.16:

$$\ln\left(\frac{dC}{dt}\right) = \ln A + n \ln (1-C) - Ea/RT \qquad \text{... 3.16}$$

According to Eqn. 3.16, the plot of ln(dC/dt) against 1/T for various constant values of C at each heating rate would be a straight line with slope equal to –Ea/R and

$$\text{Intercept} = \ln A + n \ln(1-C) \qquad \text{... 3.17}$$

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

Ozawa has developed the following Eqn. 3.18:

$$\log \int_0^C \frac{dC}{(1-C)^n} \approx \log \frac{AE_a}{RT} - \log \beta - 2.315 - 0.4567\left(\frac{E}{RT}\right) \qquad \text{… 3.18}$$

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).

TG and DSC thermograms of EP-01, EP-02, EP-03, PU-I and PU-II were scanned on a Perkin Elmer TGA Model-Pyris-1 and Shimadzu DSC-60 respectively at the heating rate of 10^0C/mm in an N_2 atmosphere over the temperature range from 50 to 600^0C.

DSC thermograms of EP-01, EP-02, EP-03 are shown in Figs. 3.9 to 3.11 and DSC transitions are summarized in Table-3.7. Endothermic transition for EP-01 at 96°C is due to melting of the resin and exothermic transition at 225°C is due to some physical change probably due to curing reaction. Endothermic reaction at 79°C (EP-02) is due to melting of resins and confirmed no weight loss over temperature range 79-96°C in corresponding TG thermogram of the resins (Fig.-3.14).

From Fig.-3.14, it is evident that all the three resins are thermally stable up to about 238-266°C and followed two step decomposition. Initial decomposition temperature (T_0), decomposition range, temperature of maximum weight loss (Tmax), % weight loss involved and % residue left above 500°C are summarized in Table-3.5.

Observed thermal stability order is EP-03>EP-02>EP-01. First step involved about 41-46 % weight loss, while second step involved about 8-27 % weight loss. About 22-30 % residue left above 500°C confirming formation of highly thermally stable products.

Associated 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. The least square values of E_a, A, n and ΔS^* along with regression coefficients (R^2) are reported in Table-3.5, from which it is observed that resins followed either integral or fractional order degradation kinetics. EP-02 followed complex degradation reaction. Both E_a and A varied in accordance to n. Higher the magnitude of E_a, higher is the value of A. Observed order of E_a is EP-02> EP-03> EP-01. The entropy change ΔS^* for each resin was calculated using corresponding T_{max}. A large and negative magnitudes of ΔS^* confirmed that transition state is much more in orderly state than those of individual resin molecules and vice versa. Degradation reaction is a complex process, which involves a variety of reactions such as cross-linking, branching, rearrangement and decomposition of segments. Azomethine, ether, hydroxyl and methoxy linkages in epoxies are weak linkages, which degrade selectively and form free radicals. These radicals further recombine to form new product, which may degrade at elevated temperatures. Relatively high amounts (22-30 %) of residue above 500°C, confirmed formation of highly thermally stable products.

Thermal decomposition of epoxies usually starts with the scission of the polymer chain through a six membered ring transition state. It is believed that this scission is mostly heterolytic and not a free radical process [56-57]. However this is not yet resolved. Kinetic analysis has shown that the thermal decomposition of epoxies is a complex process with activation energy varying from 100-250 kJ/mole. The observed activation energy (66-255 kJ/mol) for epoxies containing glycocidic linkage, cyclo aliphatic ring and imine linkage are similar with general range (100-250 kJ/mol).

DSC thermograms of PU-I and PU-II at the heating rate of 10°C/min in nitrogen atmosphere are presented in Figs. 3.12 and 3.13, respectively. Broad endothermic transition for PU-I (91°C) and for PU-II (95°C) is due to glass transition temperature. Initial decomposition temperature (T_0), decomposition range, temperature of maximum weight loss (Tmax), % weight loss involved, % residue left at 500°C are reported in Table-3.6. PU-I (215°C) is slightly more thermally stable than that of PU-II (205°C). Tmax and % weight loss are considerably more than that of PU-I.

Associated kinetic parameters such as energy of activation (Ea), frequency factor (A) and degradation order (n) were determined according to Anderson-Freeman method. Least square values of Ea, A and n alongwith regression coefficients (R^2) are reported in Table-3.6 from which it is clear that

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56. Jovan Mijovic, "Cure kinetics of neat v/s reinforced epoxies", J. Appl. Polym. Sci., 31, 1177-1187, 2003.
57. Z. S. Petrovic and Z.Z. Zavargo, "Reliability of methods for determination of kinetic parameters from thermogravimetry and DSC measurements", J. Appl. Polym. Sci., 32, 4353-4367, 1986.

both the copolyurethanes followed fractional order degradation kinetics. Higher is the value of Ea, higher is the value of A. The entropy change (ΔS^*) was determined using corresponding Tmax and also reported in Table-3.6. Large and negative value of ΔS^* indicated that transition state is more in orderly state than individual polyurethane molecules.

Urethane, ether, methyl and methoxy groups are weak linkages in polyurethane molecules, which degrade selectively and form free radicals. These radicals further combined and degrade at elevated temperatures. Degradation reaction is a complex reaction and involved a variety of reactions such as branching, rearrangement, crosslinking, etc. Considerable residue (20-29 %) above 500°C indicated formation of highly cross linked products. Somewhat high % residue for PU-II is due to methoxy group, which led to increasing cross linking density.

TG thermograms of PU-I and PU-II are presented in Fig.-3.15 from which it is clear that PU-I followed single step decomposition, while PU-II followed two steps decomposition.

The detail calculation for epoxies, PU-I and PU-II are reported in Tables-3.8 to 3.15 respectively. The plots of $\Delta \ln dW/dt$ against $\Delta \ln W$ are presented in Fig. 3.16 to 3.23.

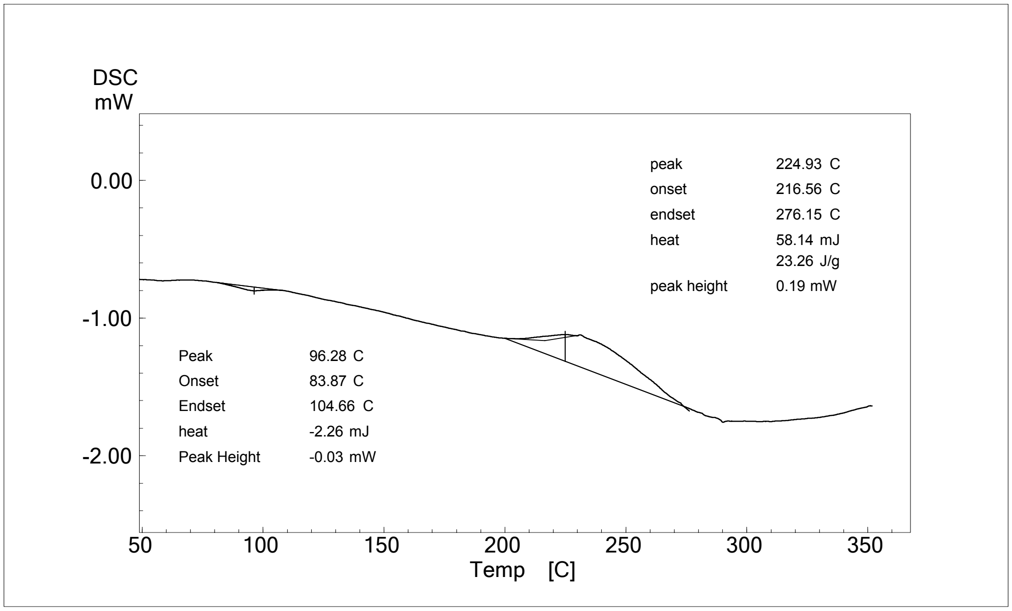

Fig. 3.9: DSC thermogram of EP-01 at the heating rate of 10°C/min in an N_2 atmosphere

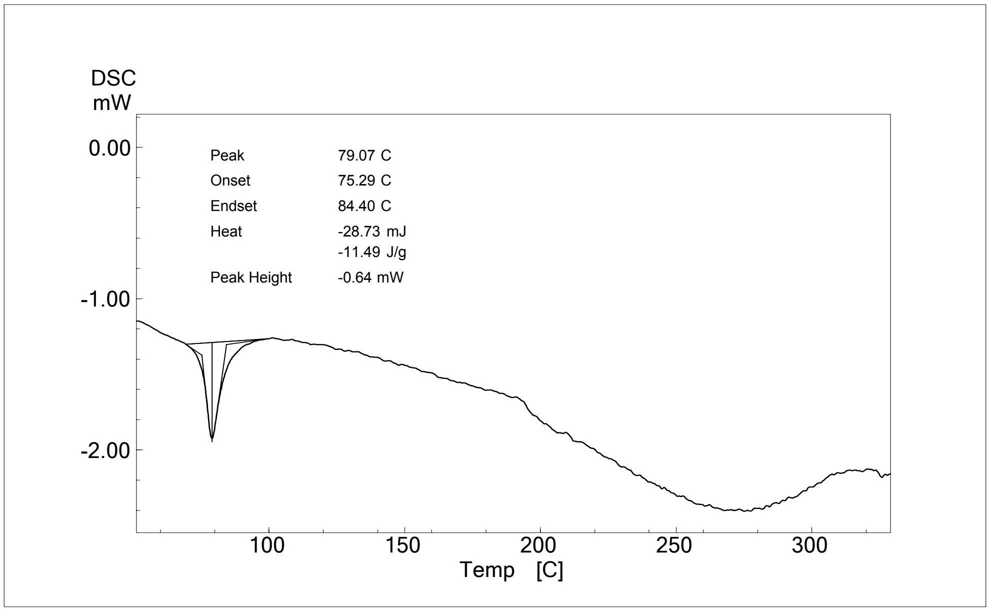

Fig. 3.10: DSC thermogram of EP-02 at the heating rate of 10°C/min in an N_2 atmosphere

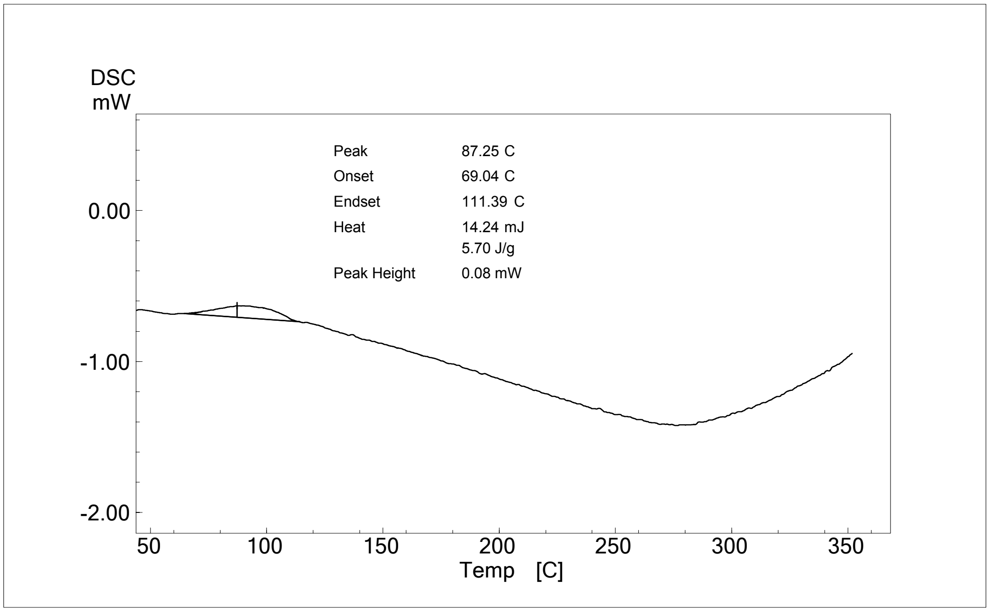

Fig. 3.11: DSC thermogram of EP-03 at the heating rate of 10°C/min in an N_2 atmosphere

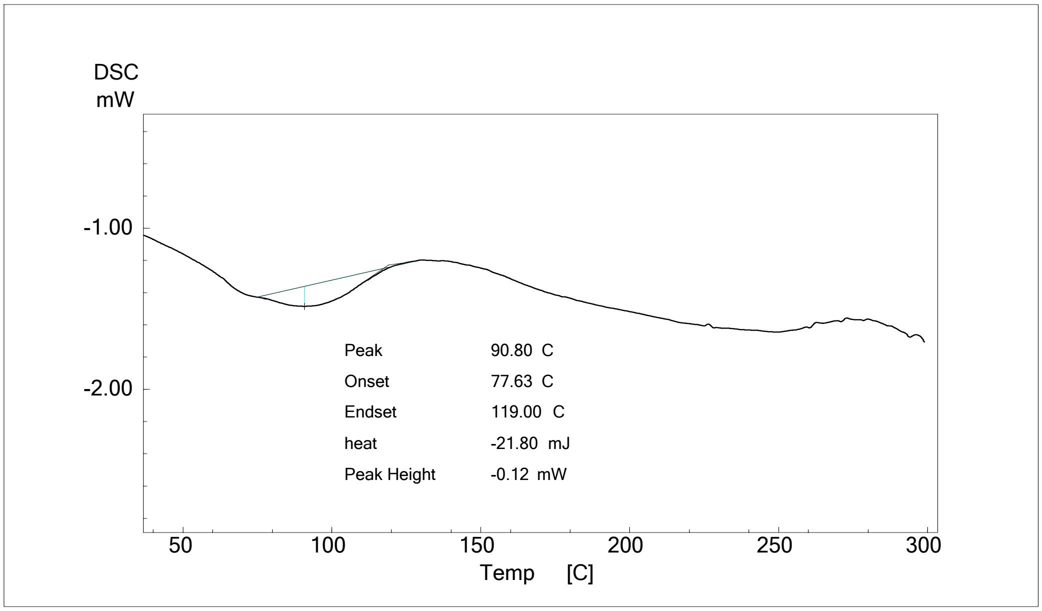

Fig. 3.12: DSC thermogram of PU-I at the heating rate of 10°C/min in an N_2 atmosphere

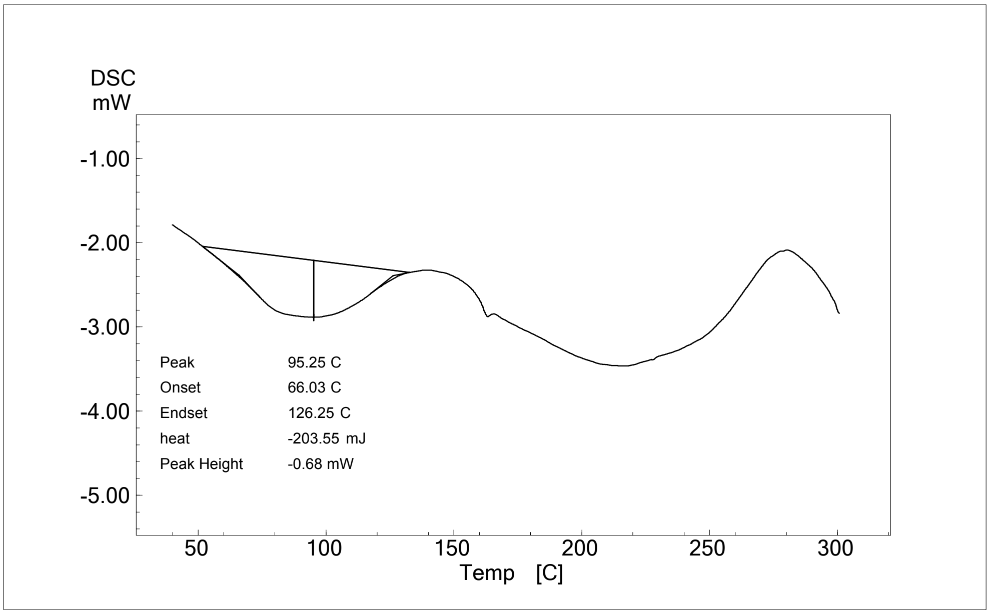

Fig. 3.13: DSC thermogram of PU-II at the heating rate of 10°C/min in an N_2 atmosphere

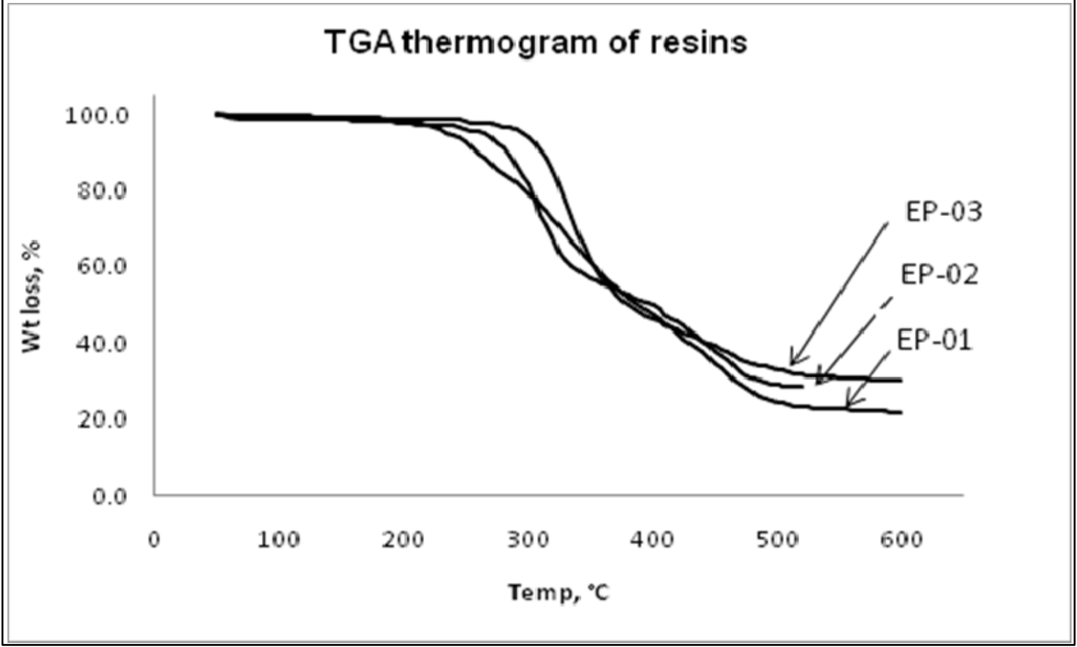

Fig. 3.14: TG thermogram of EP-01, EP-02 and EP-03 at the heating rate of 10°C/min in an N_2 atmosphere

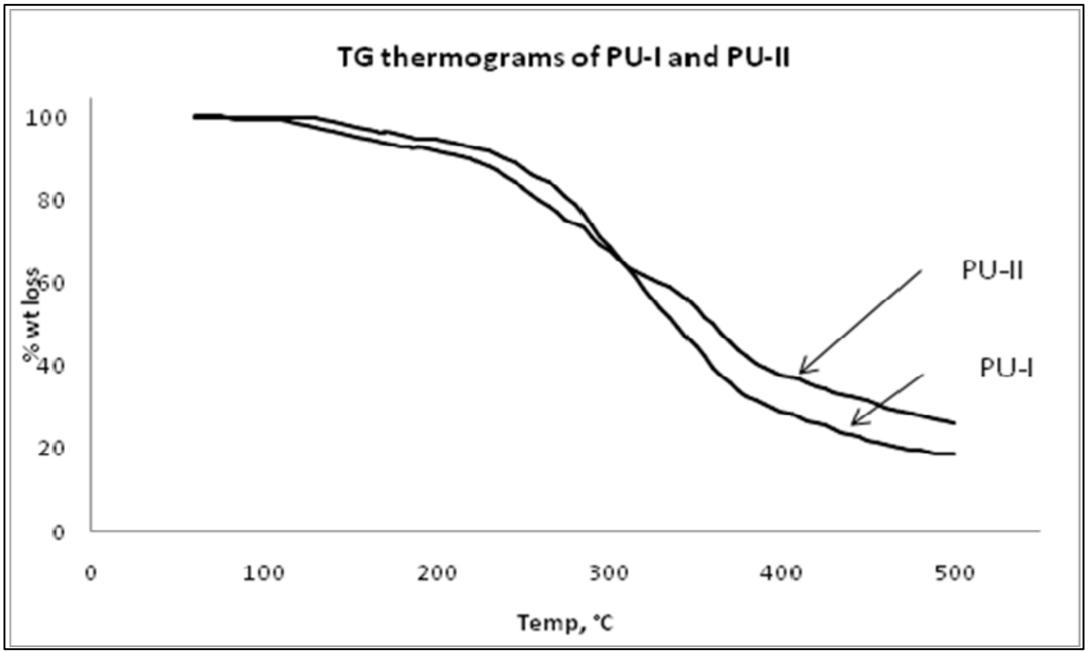

Fig.3.15: TG thermogram of PU-I and PU-II at the heating rate of 10°C/min in an N_2 atmosphere

Table-3.5: TG data of epoxy resins.

Parameter	Epoxy resin		
	EP-01	EP-02	EP-03
IDT,^{o}C	238	257	266
Decomposition range, ^{0}C	240-380 385-500	260-350 360-430	290-380 400-480
T_{max}, ^{0}C	332 450	306 438	335 415
% Wt.loss	41 27	46 12	45 8
% Residue at 500^{0}C	22	30	30
E_a, kJ mol^{-1}	73 66	255 69	165
n	1.2 0.5	5.1 1.2	1.7
A,s^{-1}	7992 141	1.41×10^{21} 318	1.70×10^{12}
ΔS^* JK^{-1} mol^{-1}	-176 -211	154 -204	-19
R^2	0.987 0.992	0.997 0.985	0.977

Table-3.6: TG data of copolyurethanes.

Parameters	Copolyurethane	
	PU-I	PU-II
IDT,^{o}C	215	205
Decomposition range, ^{0}C	215-395	218-335 335-410
T_{max}, ^{0}C	305	245 360
% Wt.loss	64	25 23
% Residue at 500^{0}C	20	29
E_a, kJ mol^{-1}	36.4	28.5 177
n	0.66	0.4 1.5
A,s^{-1}	4.26	1.59 3.79×10^{12}
ΔS^* JK^{-1} mol^{-1}	-238	-246 -10
R^2	0.984	0.980 0.978

Table-3.7: DSC transitions of epoxy resins and copolyurethanes

Name	Type	Peak temp, ° C	Heat of Transition, ΔH, J/g^{-1}	ΔH, kJmol^{-1}
EP-01	Endotherm	96	-0.8	-2.26
	Exotherm	225	23.3	58.14
EP-02	Endotherm	79	-11.5	-28.73
EP-03	Exotherm	87	5.7	14.24
PU-I	Endotherm	91	-8.7	-21.8
PU-II	Endotherm	123	-81.5	-203.6

Table-3.8: Detail calculations for EP-01 according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	∆lnW	∆lndW/dt
Step - 01							
1.76	19.22	2.680	33.6	3.515	0.986	0.027	-0.058
1.75	20.12	2.840	32.7	3.487	1.044	0.030	-0.055
1.74	21.09	3.000	31.73	3.457	1.099	0.034	0.330
1.72	23.26	3.304	29.56	3.386	1.195	0.041	-0.040
1.71	24.44	3.439	28.38	3.346	1.235	0.044	-0.035
1.7	25.67	3.560	27.15	3.301	1.270	0.048	-0.029
1.69	26.94	3.663	25.88	3.253	1.298	0.052	-0.022
1.68	28.26	3.745	24.56	3.201	1.320	0.056	-0.016
1.67	29.6	3.807	23.22	3.145	1.337	0.061	-0.010
1.66	30.98	3.845	21.84	3.084	1.347	0.066	-0.004
1.65	32.37	3.859	20.45	3.018	1.350	0.071	0.002
1.63	35.2	3.817	17.62	2.869	1.339	0.084	0.015
1.62	36.62	3.761	16.2	2.785	1.325	0.091	0.021
1.61	38.03	3.683	14.79	2.694	1.304	0.099	0.027
1.76	19.22	2.680	33.6	3.515	0.986	0.027	-0.058

Table-3.9: Detail calculations for EP-01 according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
Step – 02							
1.46	55.46	2.186	20.05	2.998	0.782	0.056	-0.033
1.45	56.56	2.259	18.95	2.942	0.815	0.062	-0.043
1.44	57.70	2.358	17.81	2.880	0.858	0.070	-0.046
1.43	58.89	2.47	16.62	2.810	0.904	0.079	-0.044
1.42	60.15	2.581	15.36	2.732	0.948	0.090	-0.038
1.41	61.47	2.68	14.03	2.641	0.986	0.104	-0.029
1.4	62.86	2.758	12.65	2.538	1.015	0.121	-0.017
1.39	64.30	2.804	11.21	2.417	1.031	0.141	-0.002
1.38	65.77	2.811	9.74	2.276	1.034	0.166	0.014
1.37	67.26	2.771	8.25	2.110	1.019	0.198	0.034
1.36	68.75	2.679	6.76	1.912	0.985	0.240	0.058
1.35	70.19	2.529	5.32	1.672	0.928	0.296	0.086
1.34	71.55	2.32	3.96	1.375	0.842	0.378	0.125
1.33	72.90	2.047	2.71	0.998	0.716	0.506	0.179

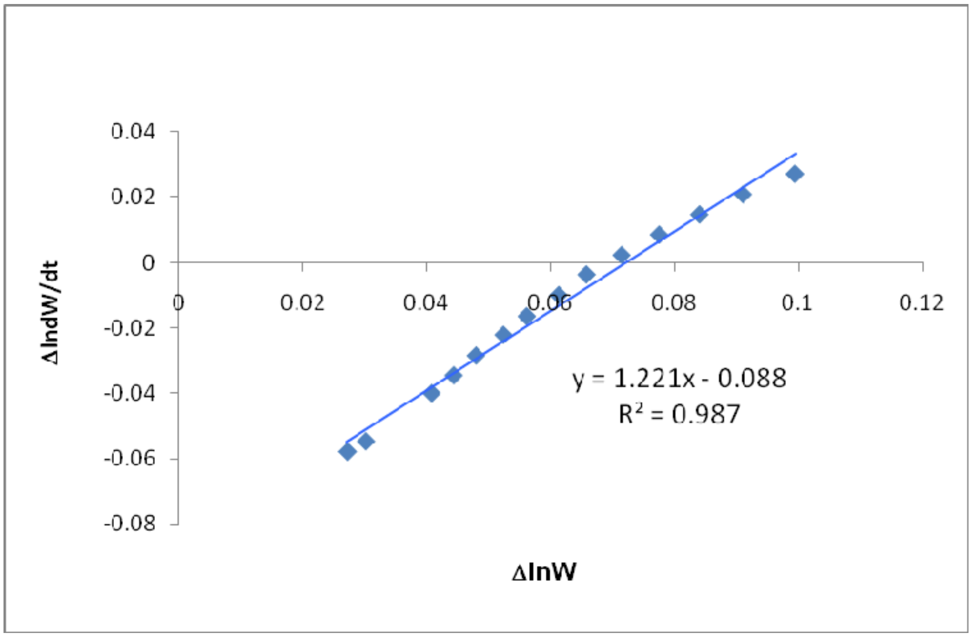

Fig.3.16 : The Freeman-Anderson plots of EP-01 (step-1)

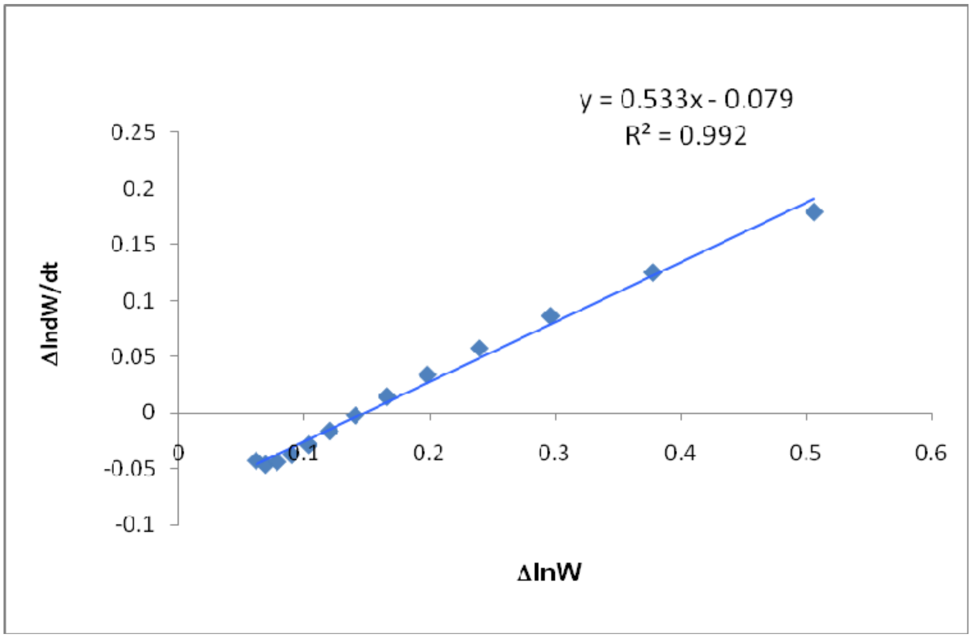

Fig.3.17 : The Freeman-Anderson plots of EP-01 (step-2)

Table-3.10: Detail calculations for EP-02 according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	∆lnW	∆lndW/dt
Step -01							
1.84	5.57	1.782	52.64	3.963	0.578	0.013	-0.235
1.83	6.27	2.253	51.94	3.950	0.812	0.018	-0.223
1.82	7.21	2.816	50.99	3.932	1.035	0.023	-0.190
1.81	8.39	3.404	49.82	3.908	1.225	0.028	-0.165
1.8	9.76	4.015	48.45	3.881	1.390	0.032	-0.139
1.79	11.30	4.612	46.91	3.848	1.529	0.037	-0.114
1.78	12.99	5.168	45.22	3.811	1.642	0.041	-0.091
1.77	14.81	5.662	43.40	3.771	1.734	0.045	-0.071
1.76	16.73	6.078	41.49	3.725	1.805	0.049	-0.052
1.75	18.72	6.4	39.49	3.676	1.856	0.053	-0.033
1.74	20.77	6.617	37.439	3.623	1.890	0.057	-0.016
1.73	22.85	6.724	35.36	3.565	1.906	0.061	0.001
1.72	24.95	6.715	33.26	3.504	1.904	0.065	0.018
1.71	27.04	6.592	31.17	3.440	1.886	0.068	0.036
1.7	29.10	6.358	29.11	3.371	1.850	0.072	0.055
1.69	31.11	6.019	27.10	3.300	1.795	0.074	0.075
1.68	33.05	5.586	25.16	3.225	1.720	0.077	0.095

Table-3.11: Detail calculations for EP-02 according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
Step –02							
1.43	55.78	2.544	14.37	2.6654	0.9337	0.090	-0.023
1.42	57.02	2.604	13.14	2.5753	0.9570	0.106	-0.011
1.41	58.34	2.634	11.82	2.4694	0.9685	0.125	0.001
1.4	59.72	2.632	10.43	2.3443	0.9677	0.149	0.014
1.39	61.16	2.595	8.99	2.1957	0.9536	0.178	0.029
1.38	62.63	2.520	7.52	2.0176	0.9243	0.216	0.048
1.37	64.09	2.403	6.06	1.8015	0.8767	0.192	0.070
1.36	65.15	2.240	5.00	1.6092	0.8065	0.414	0.101
1.35	66.85	2.025	3.31	1.1954	0.7056	0.458	0.144
1.34	68.06	1.753	2.09	0.7372	0.5613	0.656	0.212

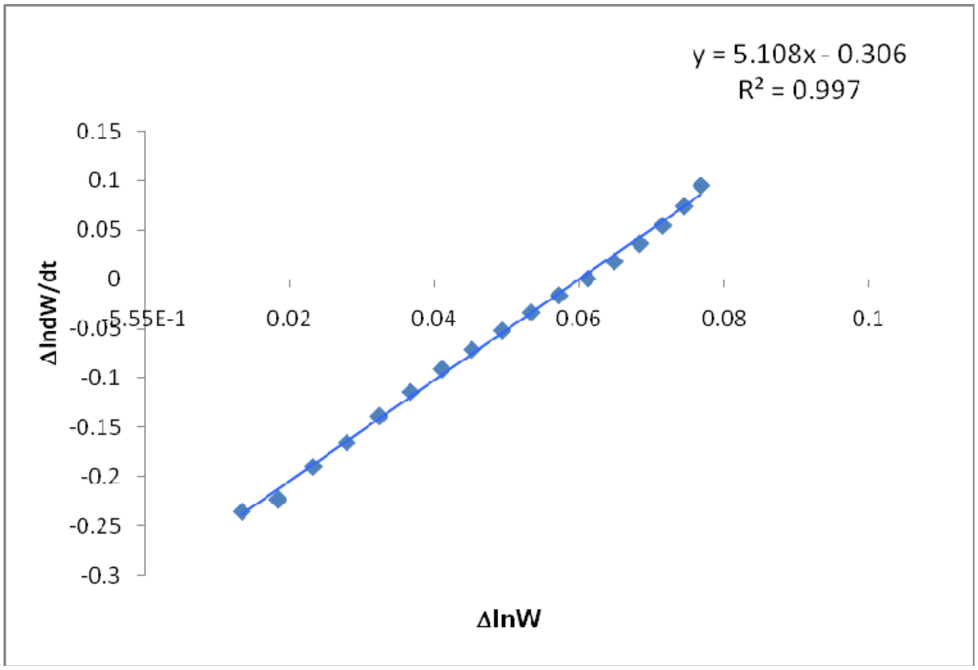

Fig.3.18: The Freeman-Anderson plots of EP-02 (step-1)

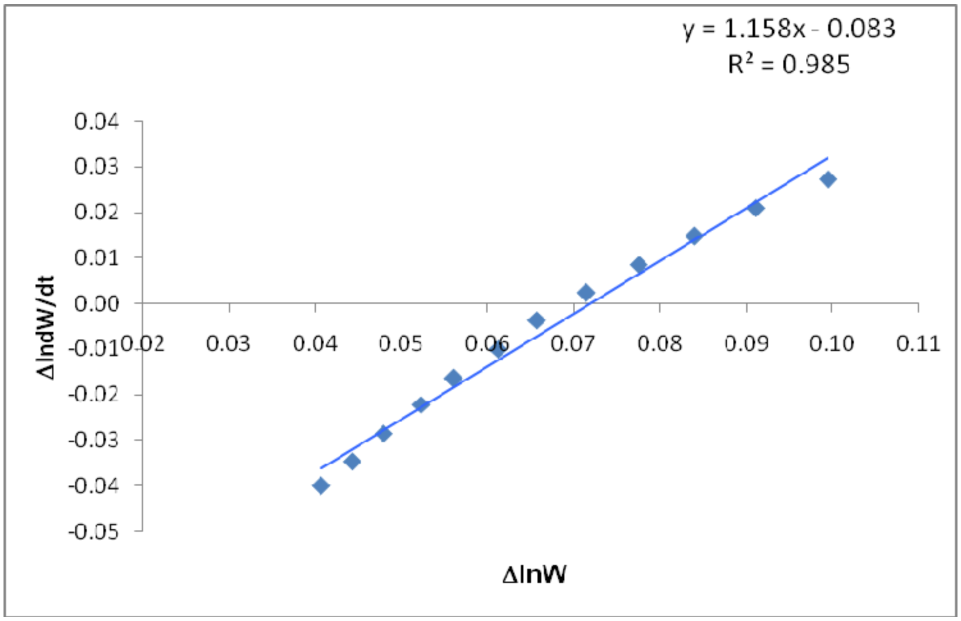

Fig.3.19: The Freeman-Anderson plots of EP-02 (step-2)

Table-3.12: Detail calculations for EP-03 according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	∆lnW	∆lndW/dt
Step : 01							
1.7	12.44	5.810	37.65	3.628	1.760	-0.062	0.105
1.69	14.72	6.453	35.37	3.566	1.865	-0.071	0.081
1.68	17.15	6.996	32.94	3.495	1.945	-0.081	0.059
1.67	19.70	7.418	30.39	3.414	2.004	-0.091	0.038
1.66	22.34	7.706	27.75	3.323	2.042	-0.102	0.019
1.65	25.04	7.850	25.06	3.221	2.061	-0.115	-0.001
1.64	27.75	7.846	22.34	3.106	2.060	-0.129	-0.020
1.63	30.46	7.694	19.63	2.977	2.040	-0.147	-0.039

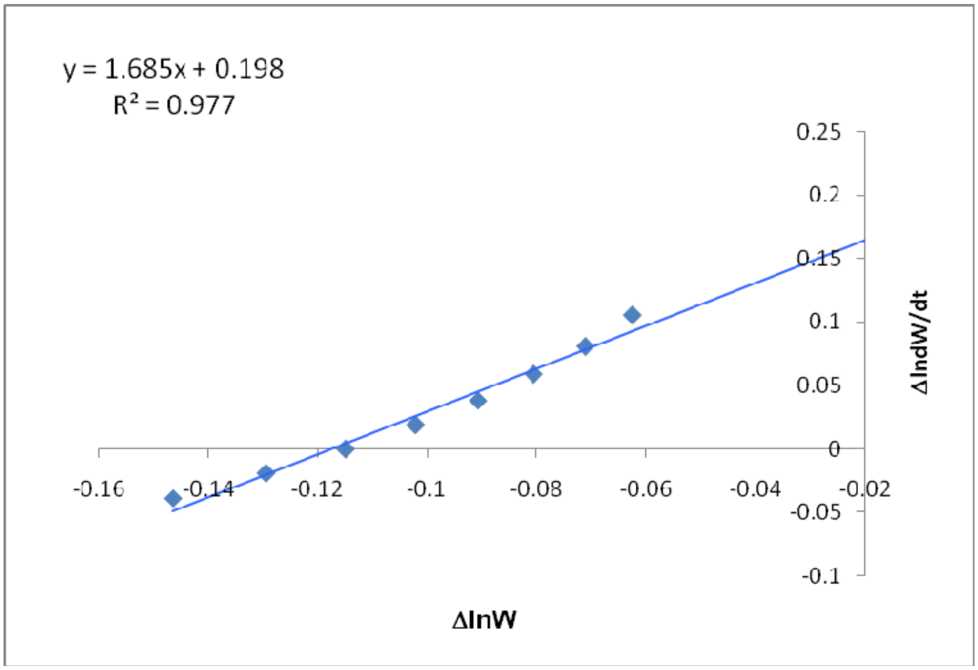

Fig.3.20: The Freeman-Anderson plots of EP-03 (step-1)

Table-3.13: Detail calculations for PU–I film according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
1.59	57.99	4.354	12.16	2.50	1.471	-0.133	-0.039
1.6	56.26	4.529	13.89	2.63	1.510	-0.120	-0.033
1.61	54.50	4.681	15.65	2.75	1.544	-0.109	-0.028
1.62	52.70	4.812	17.45	2.86	1.571	-0.099	-0.022
1.63	50.88	4.921	19.27	2.96	1.594	-0.091	-0.018
1.64	49.05	5.010	21.10	3.05	1.611	-0.084	-0.014
1.65	47.20	5.079	22.95	3.13	1.625	-0.077	-0.010
1.66	45.36	5.128	24.79	3.21	1.635	-0.072	-0.006
1.67	43.52	5.159	26.63	3.28	1.641	-0.066	-0.003
1.68	41.70	5.173	28.45	3.35	1.643	-0.062	0.001
1.69	39.89	5.169	30.26	3.41	1.643	-0.057	0.004
1.7	38.10	5.149	32.05	3.47	1.639	-0.053	0.007
1.71	36.34	5.114	33.81	3.52	1.632	-0.050	0.010
1.72	34.61	5.064	35.54	3.57	1.622	-0.046	0.013
1.73	32.92	4.999	37.23	3.62	1.609	-0.043	0.016
1.74	31.27	4.922	38.88	3.66	1.594	-0.040	0.018
1.75	29.67	4.832	40.48	3.70	1.575	-0.038	0.021
1.76	28.11	4.731	42.04	3.74	1.554	-0.035	0.024
1.77	26.60	4.618	43.55	3.77	1.530	-0.033	0.027

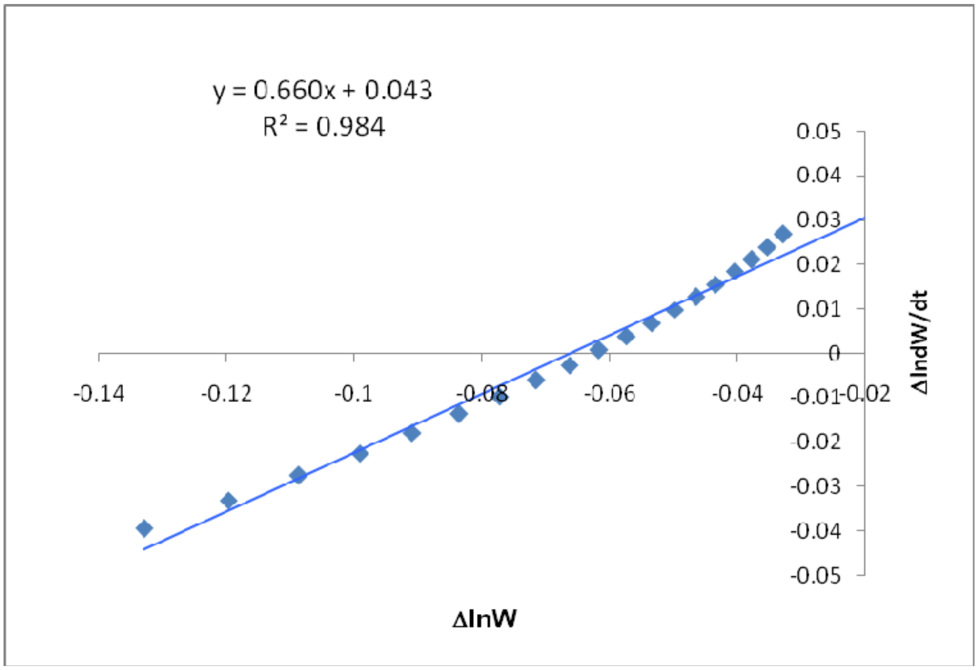

Fig.-3.21: The Freeman-Anderson plots of PU-I

Table-3.14: Detail calculations for PU–II film according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
Step-01							
1.72	34.66	2.764	5.19	1.647	1.017	-0.177	-0.039
1.73	33.65	2.873	6.20	1.824	1.055	-0.151	-0.031
1.74	32.65	2.963	7.20	1.975	1.086	-0.131	-0.024
1.75	31.64	3.036	8.21	2.105	1.111	-0.115	-0.019
1.76	30.63	3.093	9.22	2.221	1.129	-0.103	-0.013
1.77	29.63	3.135	10.22	2.324	1.143	-0.093	-0.009
1.78	28.64	3.162	11.21	2.417	1.151	-0.085	-0.005
1.79	27.65	3.177	12.20	2.502	1.156	-0.077	-0.001
1.8	26.66	3.179	13.19	2.579	1.157	-0.071	0.003
1.81	25.69	3.170	14.16	2.650	1.154	-0.066	0.006
1.82	24.73	3.151	15.12	2.716	1.148	-0.061	0.009

Table-3.15: Detail calculations for PU – II film according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
Step-02							
1.53	57.83	3.237	5.33	1.673	1.175	-0.237	-0.120
1.54	56.41	3.649	6.75	1.910	1.294	-0.204	-0.088
1.55	54.88	3.985	8.28	2.114	1.383	-0.177	-0.059
1.56	53.28	4.226	9.88	2.291	1.441	-0.154	-0.031
1.57	51.63	4.359	11.53	2.445	1.472	-0.135	-0.004
1.58	49.96	4.378	13.20	2.580	1.477	-0.119	0.022
1.59	48.30	4.282	14.86	2.699	1.455	-0.104	0.048
1.6	46.67	4.080	16.49	2.803	1.406	-0.090	0.075
1.61	45.12	3.786	18.04	2.893	1.331	-0.077	0.102
1.62	43.67	3.419	19.49	2.970	1.229	-0.065	0.128

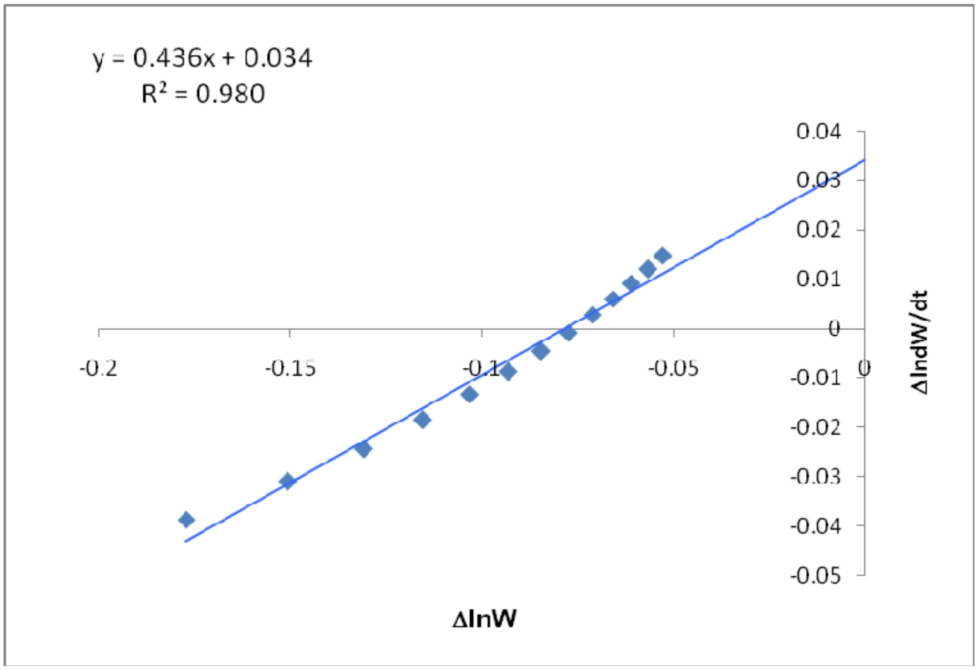

Fig.-3.22: The Freeman-Anderson plots of PU-II (step-1)

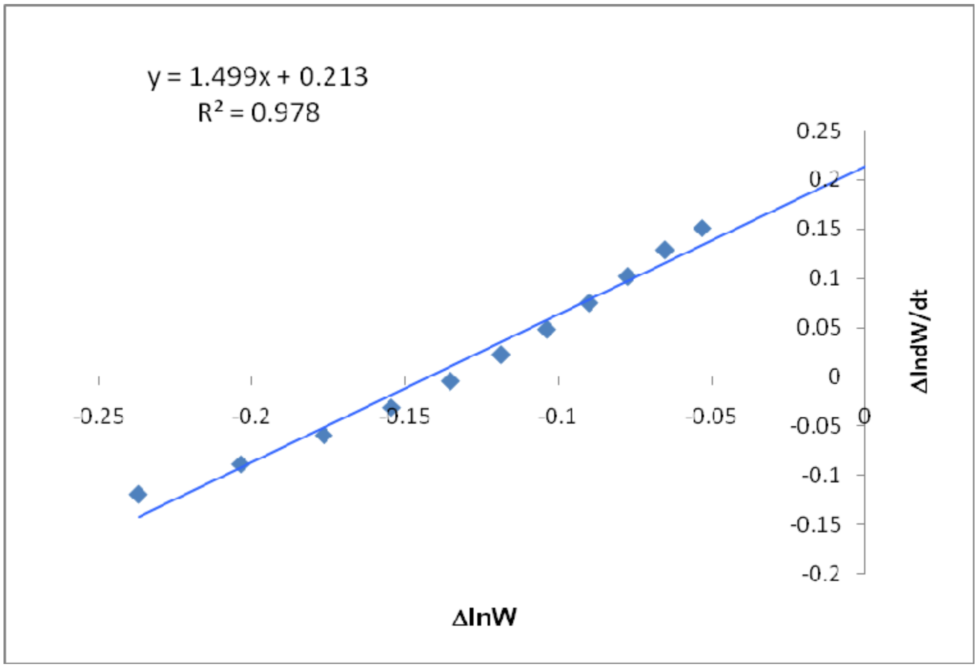

Fig.-3.23: The Freeman-Anderson plots of PU-II (step-2)

SECTION– 4.5: Gel permeation chromatography

The molecular weights of polymers can be determined by various methods such as chemical method, osmotic pressure measurements, light scattering, ultracentrifugation, viscometry, gel permeation chromatography (GPC), ebulliometry and cryoscopy. Except viscometry and gel permeation chromatography all other methods are absolute methods. GPC is also known as – Size Exclusion Chromatography (SEC) that separates analytes on the basis of size, is applied to polymers in particular.

When characterizing polymer, it is important to consider the Polydispersity Index (PDI) as well as molecular weight. Polymer can be characterized by a variety of defination for molecular weight including the number average molecular weight ($\overline{Mn}$), the weight average molecular weight ($\overline{Mw}$), the size average molecular weight ($\overline{Mz}$) or the viscosity average molecular weight ($\overline{Mv}$) [58, 59].

GPC method requires calibration by using standard samples of known molecular weights. Viscometry is empirically related with molecular weight. All these methods require solubility of the polymers and involve extrapolation to infinite dilution. For ideal behavior of polymer solutions, θ condition is essential.

Gel permeation chromatography (GPC) is a faster and efficient method for polymer fractionation and provides simultaneous determination of molecular weight distribution curve. It is based on size exclusion principle. In GPC column, the solute travels inside the column from top to the bottom. The solute distributes between stationary and mobile phases. In GPC, the solvent itself acts as both stationary as well as mobile phases. GPC column is filled with a gel material of known size.

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58. J. C. Moore, “Gel Permeation Chromatography. I: A new method for molecular weight distribution of polymers”, J. Polym. Sci., 2, 835-843, 1964.
59. B. Trathingg, “Determination of MWD and chemical composition of polymer by chromatographic technique”, Prog. Poym. Sci., 20, 615-650, 1995.

Usually styragel a cross-linked styrene divinyl benzene copolymer or glass beads having a large number of micro pores of uniform size are used. The beads are hard and incompressible and of different porosity (50 A° to 1000A°). When GPC column is filled with a suitable solvent, the solvent occupies both the void and pore volumes. The solvent phase occupying void volume acts as a mobile phase, while solvent occupying pore volume acts as a stationary phase.

The GPC operates on the principle that polymer molecules in solution separate according to their size and not chemical interaction or chemical retention. The separation is based on the difference in hydrodynamic volumes of polymer molecules of different molecular weights in their dissolved state. When dilute polymer solution is introduced in a solvent stream flowing through the column, the polymer solution along with the solvent starts streaming down the column.

The mobile phase around the beads contains polymer molecules, whereas the stationary phase does not contain polymer molecules. Because of concentration difference between mobile and stationary phases, the polymer molecules start diffusing into the stationary phase depending on their size and the pore-size distribution of the gel. Larger molecules can enter only to small extent or completely excluded. The smaller polymer molecule penetrates a larger fraction of the interior of the gel and the larger molecules excluded from entering the pores are washed down the column by the solvent. Thus, the highest molecular weight molecules elute out of the column first. The different molecules with different molecular weights elute according to their molecular size. The lowest molecular weight molecules spend maximum time in the column, while the highest molecular weight molecules spend minimum time in the column and those of intermediate molecular weights diffuse slowly between mobile and stationary phases. As the column is eluted further with a pure solvent, the mobile phase does not contain any molecule whereas the stationary phase contains some molecules. Due to concentration gradient, drives the molecules to diffuse into the mobile phase. During this diffusion in and out of the pore volume, the smallest molecular weight species are retained in the column for a longer time and hence elute last. The intermediate size molecules elute in between.

Molecular weights and molecular weight distribution of epoxy resins were determined by GPC Compact V 3.0 b-61 at SICART, Vallabh Vidhyanagar. The experimental details are as under:

Column : Shodex KD 804
Column material : Styragel
Solvent : DMF
Detector : RI-71
Sample concentration : 0.1g/dl
Flow rate : 1 ml/min.
Injection volume : 20μl

GPC chromatograms of EP-01 to EP-03 are presented in Figs.-3.24 to 3.26. Number Average ($\overline{M}n$), Number Average ($\overline{M}n$) and Poly Dispersity ($\frac{\overline{M}w}{\overline{M}n}$) data of resins are summerized in Table-3.16 from which it is observed that EP-01 and EP-03 posses almost same molecular weights and doubled than that of EP-02. Thus symmetric molecules are more reactive towards epoxidation reaction i.e. minimum steric hindrance.

Table-3.16 : GPC data of epoxy resins

Parameter	Epoxy Resin		
	EP-01	EP-02	EP-03
$\overline{M}n$	5150	2290	5400
$\overline{M}w$	7460	2570	7730
$\frac{\overline{M}w}{\overline{M}n}$	1.45	1.12	1.43

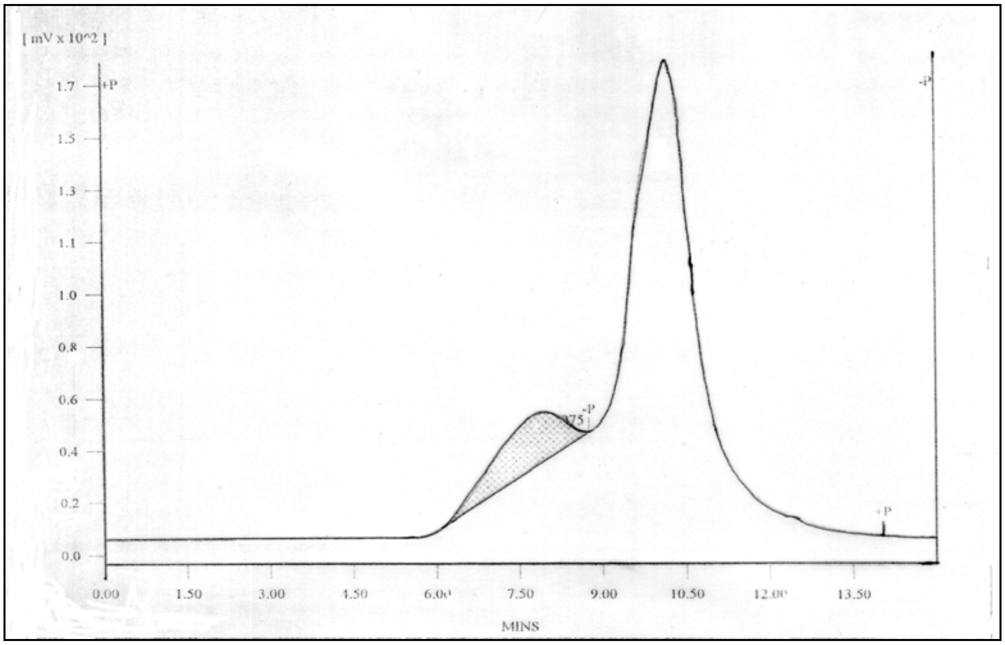

Fig.-3.24: Gel Permeation chromatogram of EP-01

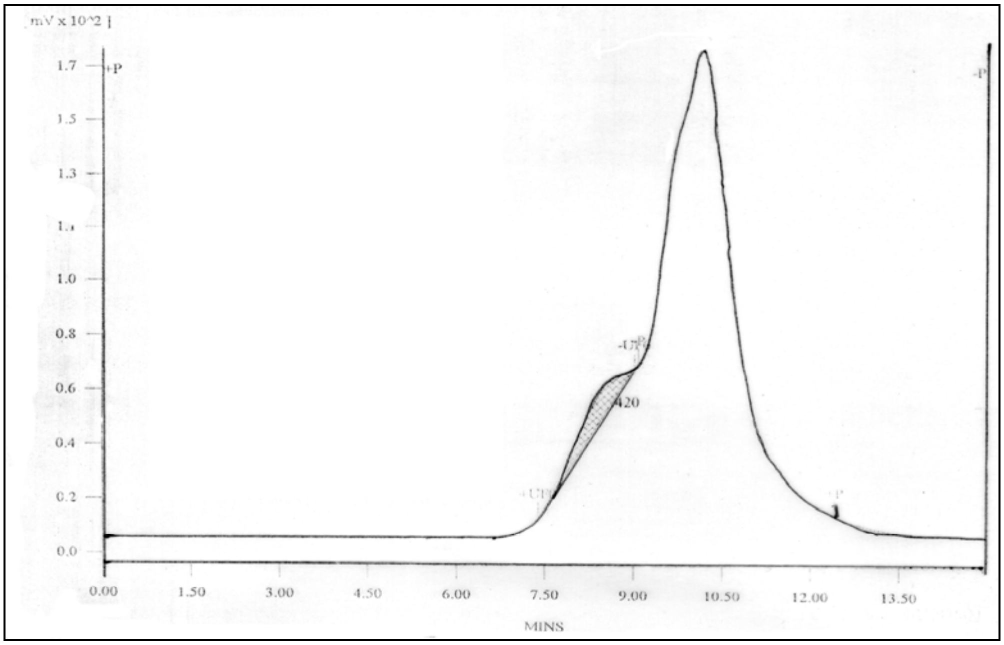

Fig.-3.25: Gel Permeation chromatogram of EP-02

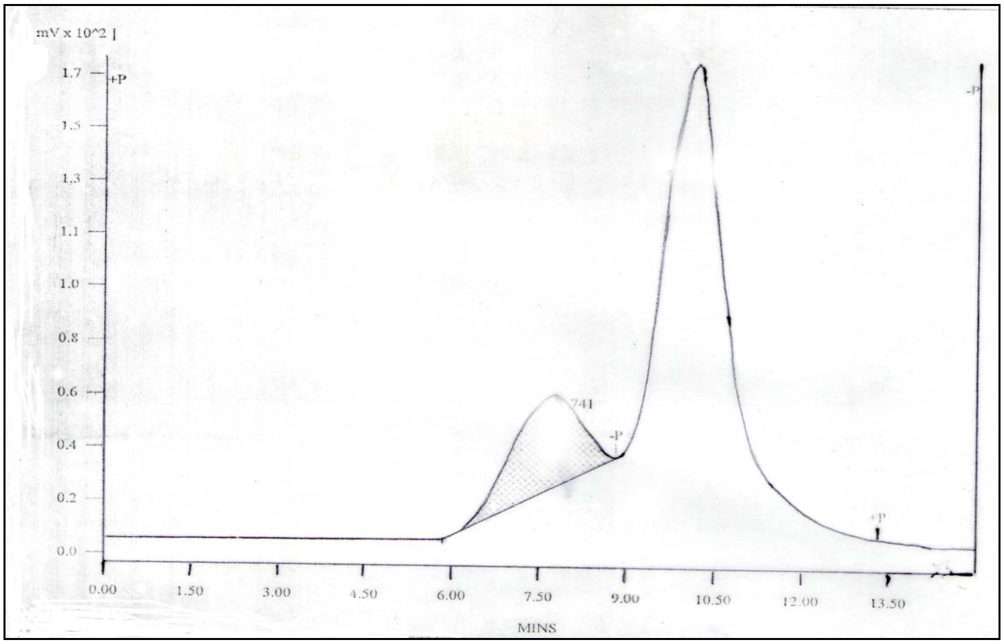

Fig.-3.26: Gel Permeation chromatogram of EP-03

SECTION-4.6 : 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 [60-61]. 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. [62] the density of the polymer may be expressed as:

$$\rho = \frac{KM}{N_A \sum \Delta Vi} \qquad \text{... 3.19}$$

where K is the packing coefficient, M is the molecular weight of the repeat unit of the polymer, $\Sigma\Delta Vi$ is the intrinsic volume of the polymer repeat unit and N_A is the Avogadro's number.

The values of $\Sigma\Delta Vi$ can be calculated from the knowledge of the volume increments ΔVi 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.

$$K = V_{int} / V_{true} = N_A \Sigma\, \Delta\, Vi / (M/\rho) \qquad \text{… 3.20}$$

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60. H. F. Mark, N. C. Gaylord and N. F. Bikales, “Encyclopedia of Polymer Science and Technology”, Vol.- 12, Willey Inter Science, New York, 1970.
61. C. Tanford, “Physical Chemistry of Macromolecules”, John Willey and Sons, Inc. New York, 1961.
62. G. L. Slonimskii, A. A. Askadskii and A. I. Kitaigorodkii, Polym. Sci. USSR, A-12(3), 556, 1970.

Slonimskii et. al [62] have calculated packing coefficient of seventy polymers of widely different chemical and physical structure for both addition and condensation polymers. They have reported the average value of K = 0.681 and 0.695 for both bulk and film samples, respectively. In addition to intrinsic volume of the repeat unit, the knowledge of packing coefficient K is also necessary for the calculation of the density of polymer.

Determination of density by floatation method

The densities of PU-I and PU-II 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 dropwise with shaking till the film remained suspended throughout and allowed to equilibrate at room temperature for 24h. The average of six measurements and standard deviation from mean value were determined for both the films.

The average of six measurements of densities of PU-I and PU-II are 1.0865±0.0012, and 1.0788±0.0012 g/cm^3, respectively. From density data, it is clear that PU-I possess slightly more density than PU-II and this is due to symmetry effect of the molecules. Density is an additive property and largely depends on molecular weight and polymer repeat unit structure. The side substituents cause packing of polymer molecules per unit volume. In case of crosslinked network structure crosslink density also play an important role on ultimate density of copolyurethanes.

SECTION-4.7: Mechanical and electrical properties of copolyurethane films

The tensile strength, electric strength and volume resistivity of polymer films were determined according to standard test methods

Mechanical properties

Material properties associated with elastic and inelastic reactions to an applied force that is called mechanical properties. The mechanical properties of polymers are the foremost requirement for a designer. In recent years plastics have been increasingly used for mechanical applications principally as gears, spring and bearings. The usage of plastics for mechanical applications offers the advantages such as elimination of parts through design, elimination of finishing operations, simplified assembly, reduced maintenance, obviations of lubrications, weight savings, noise reduction and freedom from corrosion.

The mechanical properties of polymers can be divided into three types:

(1) Reversible mechanical properties
(2) Mechanical failure
(3) Complex mechanical properties

The tensile behavior of polymers is probably most fundamental mechanical property used in the evaluation of polymers. The tensile strength of a material is the ratio of the stress applied to the material at the rupture to its original cross-sectional area. This property is typically called the ultimate tensile strength i.e. the strength at break.

$$\text{Tensile strength (kg/cm}^2\text{)} = \frac{\text{Load at break (g) x 10}}{\text{Thickness in mm}} \qquad \text{…3.21}$$

Tensile strength (ASTM-D-638-IV) measurements were made on a Shimadzu Autograph AG-X Series at a speed of 0.05mm/min.

Choi et al. [63] 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.

Kozakiewicz et al. [64] 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 (Tg) of films.

PU-I and PU-II possess 9 and 7 MPa tensile strength, respectively indicating rigid and brittle nature of copolyurethane films. Introduction of soft segments in the polymer chains increases elasticity and decreases tensile strength. Increasing amount of hard segments usually increases intermolecular attraction and hence increases tensile strength.

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63. 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.
64. 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.

When the load is applied to the film, because of high flexibility of soft segment, load is thrown away to the rigid segment of copolyurethane and consequently stress is concentrated at the junction of rigid and soft segments resulting in rupture at low load. Thus, due to lack of coordination between soft and hard segments results non-uniform transfer of stress distribution and causes decrease of tensile strength. Mechanical properties of polymeric materials depend on many factors namely molecular structure and molecular weight, cross link density, nature of side substituents, test methods and method of preparation, temperature, humidity, etc.

Electrical properties

Till about the first few decades of the twentieth century, insulator items consisted primarily of glass, wood, paper, rubber, asphalt, mica, amber and related materials mostly of natural origin. The availability of a large spectrum of synthetic polymers has changed our option in this regard quite remarkably. Matter can be classified according to its specific conductivity into electrical insulators, semiconductors and conductors. Macromolecules with certain constitutional characteristics possess semiconductor properties. The majority of the commercially used polymers however are insulators. For common organic polymers, high resistivity of the order of 10^{12} to 10^{18} Ohm cm is typical and decrease on addition of conducting fillers. The electrical resistivity also depends on the frequency and voltage.

For electrical applications, the selection is required to be made on the basis of evaluation of electrical property parameters. The basic properties of dielectrics are dielectric constant or permittivity, dielectric breakdown voltage, dielectric strength, volume conductivity, volume resistivity, dielectric loss, power factor and surface resistance, etc. The choice of dielectric for each particular purpose is determined by the temperature and electric field frequency dependencies of these quantities.

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.

Volume resistivity

A good insulating material is one that offers a high electrical resistance under a variety of conditions. Volume resistivity of a material is the resistance between opposite faces of unit cube when the current flow is confined to the volume of rest specimen. This quantity is defined as the ratio of the potential gradient that is the electric field strength E, in a specimen to the current density J.

The volume resistivity ρ_v is proportional to the volume resistance R_v. the quantity that is reciprocal of ρ_v is known as the volume conductivity:

$\gamma_v = 1/\rho_v$ ... 3.22

In measuring R_v of a flat specimen, we determine the volume resistance of the specimen portion confined between the guarded and the unguarded electrode. In this case the calculated (effective) diameter d_m is equal to the arithmetic mean of d_1 and d_2:

$d_m = (d_1+d_2) / 2$

where, d_1 is the diameter of the guarded electrode, d_2 is the inner diameter of the ring shaped guarded electrode.

The resistance R_v of the flat specimen is expressed in the form:

$R_v = \rho_v . 4t / \pi (d_m)^2$ ... 3.23

Where d_m is the diameter of the electrode, and t is the thickness of the specimen.

If R is measured in Ohm.cm and t and d_m in meters the unit of measurements of ρ is the Ohm m.

$\rho_v = 0.785 R_v (d_m)^2 / t$ … 3.24

Dielectric breakdown voltage or dielectric strength

The working voltage applied to an electrical insulating material must be much lower than the voltage, which causes the material rupture. Electrical breakdown results from an electrical discharge through a material at a minimum voltage called breakdown or disruptive voltage V_{br}. In some cases voltages for lower than the breakdown voltage give rise to a surface discharge that does not penetrate deep into the bulk of a material.

This is a surface or creeping, breakdown occurring at a surface breakdown voltage. Breakdown voltage is dependent on the duration and the rate of voltage application, thickness of the test sample, frequency of the applied voltage, temperature, dimensions and geometry of the electrodes and also the nature of the prevailing environmental conditions

The basic characteristic of an electrical insulating material is its breakdown or dielectric strength E_{br} (also called electric strength) that is a minimum strength of the uniform electric field which causes dielectric breakdown.

The calculation of breakdown strength requires the measurement of the breakdown voltage of the material under test. The breakdown voltage (U_{br}) is proportional to the electric field strength (E_{br}) only if the field is uniform. Such a field exists between two electrodes, which have the shape of the bodies of revolution; the surface of these electrodes may be described by Rogovsky equations.

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

$$E_{br} = U_{br} / t \qquad \ldots\ 3.25$$

Where, t is the thickness of the material.

Thus, the determination of breakdown voltage allows calculation of dielectric strength with measure of the thickness of the specimen at the point of rupture. The dielectric strength is expressed in volts per mil (0.001 in) or volts per millimeters.

The voltage required to produce breakdown is dependent on many factors. The electric strength is influenced by various factors such as duration and rate of the voltage application, thickness of sample, frequency of the applied voltage, temperature, dimensions and geometry of the electrodes and nature of the prevailing environment.

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 give some relative indication of amount of insulating material that will be required to support a certain voltage level. Flexible plastics are characterized by high dielectric and mechanical strength in thin sections is useful as insulating tapes.

Dielectric constant

Dielectric constant ε' is defined as the ratio of capacitance C of a condenser filled with the dielectric to capacitance C_o of the same condenser with air as the dielectric:

$$\varepsilon' = C / C_o \qquad \ldots 3.26$$

The dielectric constant is measured in alternating field and depends on frequency and temperature. The mechanical analog of dielectric constant is the stiffness modulus. Most of the non polar polymers have dielectric constant of about 2-3. Introduction of polar and H-bonding considerably increases the dielectric constant of the polymer up to 10-12 and at the same time, introduction of polar groups increases the leakage current and the electrical energy is dissipated as heat. The dissipation factor tan δ is a measure of the hysteresis in charging and discharging a dielectric. It is related to the dielectric loss ε"

$$\text{Tan}\delta = \varepsilon'' / \varepsilon'$$

The use of polymers in engineering as dielectrics is becoming increasing by important choice of the dielectric for each concrete case depends on its dielectric and other physical properties over a wide range of temperatures and electric field frequencies. Investigation of dielectric properties is one of the most convenient and sensitive methods of studying polymer structures.

The change of resistivity with temperature and humidity may be great [65-68] and must be known when designing for operating conditions. Volume resistivity or conductivity determination are often used in checking the uniformity of insulating materials, either with regard to processing or to detect conductive impurities that affect the quality of the material and may not be readily detectable by other methods.

The volume resistivity (ASTM-D 257-2007) and electric strength (IEC 60243-pt-1-1998) measurements were done respectively on a high voltage tester (Automatic Electric- Mumbai) in air at 27°C and Hewlett Packard high resistance meter at 500 V DC after charging for 60 sec by using 25/75 mm brass electrodes.

The observed electrical strength and volume resistivity of PU-I and PU-II are 56 and 43 kv/mm; and 1.1×10^{15} and 3.7×10^{12} ohm.cm respectively. Both copolyurethane films possess excellent electrical strength. PU-I possesses 297 times more volume resistivity than of PU-II. Excellent electrical strength and volume resistivity of PU-I over PU-II is mainly due to more polar nature of PU-II. Electrical properties of polymer materials depends on many factors namely molecular structure and molecular weight, cross-link density, nature of side substituents, test methods and sample preparation, temperature, humidity, etc. Excellent electrical properties of copolyurethane films signify their importance in electrical and electronic industries as good insulating materials.

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65. H. L. Curtis, “Insulating Properties of Solid Dielectric”, Bulletin, National Institute of Standards and Technology, Vol. 11, 1915.
66. R. F. Field, “How humidity affects insulation, Part-I, D.C. phenomena”, General Radio Experimenter, Vol. 20, 1945.
67. R. F. Field, “The formation of ionized water films on dielectrics under condition of high humidity”, J. Appl. Phys., Vol.5, 1946.
68. O. M. Kazarnovasky, B. M. Tareev, I. O. Forsilova and L. I. Lyuimov, “Testing of electrical insulating materials”, Mir Publishers, Moscow, 1982.

SECTION-4.8: Chemical resistance study of copolyurethane films

Polymeric materials absorb moisture in humid atmosphere or when immersed in water. The extent of water absorption mainly depends on the presence of hydrophilic polar groups, void volume, additives, humidity and temperature. Hydrolytic stability of polymeric materials depends on the nature and molecular structure of polymers. The tendency of water absorption by polar groups present in polymers increases the dissociation and hydrolysis and hence introduces ionic impurities, which affect electrical and mechanical properties to a greater extent. Penetration of water in polymeric films may be transported through micro cracks. Absorbed water may induce irreversible changes like chemical degradation, cracking and de-bonding. Cracking and blistering cause high water absorption, while leaching of small molecules results in decrease in weight [69].

The chemical stability of a plastic is evaluated by change in the mass, linear dimensions and mechanical properties of material in the state of stress free state and also by the tendency to splitting in the stress-strain state after the samples has been exposed to reagents for a definite time [70-71].

Test specification such as procedure of conditioning a specimen for testing purpose, concentration of reagents, time and temperature of testing, apparatus and instrument should be described in more detail for chemical resistance.

The recommended reagents for testing chemical resistance of plastics are reported in Table-3.17.

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69. R. Bao and A. F. Yee, “Effect of temperature on moisture absorption in bismaleimides resin and its carbon fiber composites”, 43, 3987-3996, 2002.
70. S. J. Moravek, M. K. Hassan, D. J. Drake, T. R. Cooper, J. S. Wiggins, K. A. Mauritz and R. F. Storey, “Seawater degradable thermoplastic polyurethanes”, J. Appl. Polym. Sci., 115, 1873-1880, 2010.
71. T. Bremner, D. J. T. Hill, M. I. Killeen, J. H. Odonnell, P. J. Pomery, D. St. John and A. K. Whittaker, “Development of wear-resistant thermoplastic polyurethanes by blending with poly(dimethyl siloxane). II. A packing model”, J. Appl. Polym. Sci., 65, 939-950, 1997.

Table-3.17: Recommended reagents and their concentrations for chemical resistance

Reagent	Conc., %
Sulfuric acid (1.84 g/cc)	3,30,98
Nitric acid (1.42g/cc)	10,40,98
Hydrochloric acid (1.36g/cc)	10,35
Chromic acid	40
Acetic acid	5,100
Citric acid	10
Sodium hydroxide	1,10,60
Sodium chloride	3,10
Sodium hypochlorite	10
Sodium carbonate	2,20
Ammonium hydroxide	-
Hydrogen peroxide	3,30
Ethyl alcohol	50,96
Phenol	5

A brief description of each method is described below.

1. Chemical resistance by change in mass method

According to this method the change in the mass of a test specimen after exposure of a chosen reagent at temperature of 20, 40, 60 and 100°C is determined. The test duration is dependent on the time required for plastic specimen to attain sorption, equilibrium or to loose stability in the test medium. The specimens are weighed after 12, 24, 36, 48, 96 and 128h and then every seven days. The specimen that has passed the test may either loose or gain in mass. The chemical resistance of the material is determined by averaging the changing in mass of several specimens.

The test specimen for molded or extruded plastics is in the form of a disc (50mm in diameter and 3mm in thickness). The specimens are cut from laminated or sheet plastics, the end faces of the laminated specimens are coated with same binder as used in the production of material in questions. In case of rod samples, a length of rod should be 50mm and diameter should be < 50 mm

A reagent is taken in amount of 8 ml per cm^2 surface area of plastic sample free from extractable substance and it is 20 ml per cm^2 surface area of an extractable plastics sample.

After loading the specimen in the bath, the reagent is mixed or stirred at least once in a day. After every seven days specimens are removed from the reagents once at a time, washed, wiped, dry and weighed. A percentage increase or decrease in the mass of a specimen is determined according to Eqn. 3.27

$$\Delta M= [(M_2-M_1)/M_1] \times 100 \qquad \text{... 3.27}$$

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

2. Chemical resistance by change in linear dimensions

The method is based on change in linear dimensions of specimen after prolong exposure to a reagent. The form, size and nos. of specimens and the quantity of reagent must remain same as in the change in the mass method.

Before testing the thickness of central portion of the disc and two mutually perpendicular diameters of each specimen are measured after every seven days, the specimens are taken out from the bath, washed, wiped with a cloth and checked for the dimensions at the same place. A change in any of the linear dimensions in percent is determined according to following Eqn. 3.28

$$\Delta l = (l_2 - l_1/l_1) \times 100 \qquad \dots 3.28$$

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

3. Chemical resistance by change in mechanical properties

This method is based on the stability of mechanical properties of plastics under prolonged exposure to reagent. The form, dimensions and number of specimens for plastic materials are chosen in compliance with the standard. After exposure to a reagent, the specimens are washed, wiped and tested for one or two most important characteristics such as tensile strength, flexural strength, impact strength, hardness, %elongation at break and mechanical stress in bending that causes a deflection equal to 1.5 fold thicknesses of specimen. The relative change in mechanical properties may serve as a basis for dividing plastics into three groups as shown in Table-3.18.

Table–3.18: Stability characteristic of plastics on exposure to reagents

Type of plastics	Relative change in mechanical stability characteristics, %	
	Strength properties	Deformation
Thermoplastics	0-10 10.1-20 over 20	……………....Good …. .. Adequate …Poor
Thermosets	0-15 15.1-25 over 25	-……………....Good -……. Adequate -…Poor

In present investigation the hydrolytic stability of PU-I and PU-II films were determined by the change in weight method. For this purpose pre-weighed polymer films (dimension: 1cmx1cm, 0.28mm thickness) were immersed in pure water and 10% each of aqueous solutions of hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, potassium hydroxide and potassium chloride at room temperature at the interval of 24h. For this, the polymer films were taken out, washed, wiped, dried and weighed and reimmersed .The change in weight of film was evaluated according to equation 3.27. The percentage weight loss or gain after regular interval of 24h were determined and reported in Table-3.19 and 3.20 ; Figs. 3.27 and 3.28. Equilibrium water content and equilibrium time are reported in Tables 3.21 and 3.22, respectively for PU-I and PU-II.

Diffusivity

Various models have been proposed for water absorption in composites. It is well established that absorbed water in polymers and composites plays a significant role in mechanical behavior and long term durability. Assuming one-dimensional Fickian diffusion in composite, an attempt has been made to determine diffusivity (Dx) in different environments.

Diffusivity is assumed to depend only on temperature and independent of the moisture content as well as stress levels in composites. For one- dimensional water absorption in semi-infinite plate exposed on both sides to same environment, the amount of water absorbed is given by Eqn. 3.29

$$G=1-\frac{8}{\pi^2}\sum_{J=0}^{\infty}\frac{1}{(2j+1)^2}\exp\left[-\frac{(2j+1)^2\pi^2 D_x t}{h^2}\right] \qquad \ldots 3.29$$

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

The water content in the sample can be determined according to Eqn. 3.30

$$M=\frac{W_m-W_d}{W_d}X100 \qquad \ldots 3.30$$

Where M = % water absorbed, Wm = weight of moist sample and Wd = weight of dry sample.

The solution of diffusion equation in terms of % water absorption is given by eqn.3.31:

$$M=\frac{4M_m}{h}\sqrt{\frac{t}{\pi}}\sqrt{D_x} \qquad \ldots 3.31$$

Where Mm = equilibrium water content. Diffusivity in a given environment can be determined from the initial slope of the plot of %M against $\sqrt{t}$ according to Eqn. 3.32:

$$D_x=\pi\left(\frac{h}{4M_m}\right)^2(slope)^2 \qquad \ldots 3.32$$

Water absorption in polymeric composites is shown to be Fickian as well as non-Fickian in character [72-73]. The visco-elastic nature of polymers and cracks are responsible for non-Fickian diffusion. Water absorption in composites depend upon fraction of fibers, void volume, additives, humidity and temperature.

The % weight gain is probably due to hydrophilic polar groups (amino, urethane and ester groups), which undergo solvolysis as well as microcracks. Strong electrolytes used in the present work affect water structure and hence diffusivity. The observed effect of acids and alkalis on water absorption are HNO_3>HCl>H_2SO_4 and KOH>KCl>NaOH>Distilled water, respectively. Thus, nature of acids and alkalis has also affected water absorption.

From Table-3.21 and Fig.-27, It is observed that in distilled water, PU-I has very slow water absorption tendency and gained weight up to 120h and then remained constant (1.42%). In HCl solution it showed water absorption tendency up to 120h (4.17%). In H_2S0_4 solution it showed water absorption tendency up to 96h (2.91%) but in HNO_3 solution it showed weight gain tendency up to 168h and then remained constant (8.02%) and the film became yellowish after 6 days indicating nitration of aromatic rings. In KCl solution, water uptake is up to 96h and gained maximum weight (2.02%). In NaOH solution, it is up to 96h and then remained constant. The equilibrium weight gain in NaOH solution is 1.71. Similarly in KOH solution, it is up to 96h and then remained constant. The equilibrium weight gain in KOH solution is 2.14.

From Table-3.22 and Fig.-28, it is observed that in distilled water, PU-II has very low water absorption tendency and gained weight up to 144h and then remained constant (4.62%). In HCl solution it showed water absorption tendency up to 48h (16.55%). In H_2S0_4 solution it showed higher water absorption tendency within 24h (6.59%) but in HNO_3 solution weight gain tendency is up to 48h (22.8%).

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72. G. Pritchard and S. S. Speake, “The use of water absorption kinetic data to predict laminate property changes”, Composites, 18, 227-232, 1987.

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The film became dark-yellowish within a day and found brittle in H_2S0_4, HCl and HNO_3 solutions. In KCl solution, water uptake is up to 72h and gained maximum weight (0.65%). In NaOH solution, it is up to 144h and then remained constant. The equilibrium weight gain in NaOH solution is 9.28. Similarly in KOH solution, it is up to 96h and then remained constant. The equilibrium weight gain in KOH solution is 8.20.

Ether and urethane linkages are polar groups and contain lone pairs of electrons, which may form H-bonds with solvated water molecules. The presence of electrolytes affect the water structure and hence moisture uptake behavior of the polyurethanes. Thus, low water uptake tendency of PU-I is probably due to somewhat more hydrophobic character than that of PU-II. Upon comparing above mentioned results clearly indicates the profound stability and low water uptake tendency of PU-I signifying its superior importance as a coating and adhesive material though it containing PEG-600.Thus, PU-I film possess excellent resistance against water and 10% KCl solution. They have different moisture uptake and surface solvolysis tendency in acidic and alkaline conditions.

Table-3.19: Chemical resistance data of PU-I at 27°C.

Time, Hrs	Water	HCl	H_2SO_4	HNO_3	NaOH	KOH	KCl
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.28	1.39	1.09	1.78	0.73	0.43	0.51
48	0.57	2.31	1.82	3.39	1.22	0.85	1.01
72	0.85	3.24	2.55	4.99	1.47	1.28	1.52
96	1.13	3.70	2.91	6.42	1.71	1.71	2.02
120	1.42	4.17	2.91	7.31	1.71	2.14	2.02
144	1.42	4.17	2.91	7.84	1.71	2.14	2.02
168	1.42	4.17	2.91	8.02	1.71	2.14	2.02
192	1.42	4.17	2.91	8.02	1.71	2.14	2.02
216	1.42	4.17	2.91	8.02	1.71	2.14	2.02
240	1.42	4.17	2.91	8.02	1.71	2.14	2.02
264	1.42	4.17	2.91	8.02	1.71	2.14	2.02

Table-3.20: Chemical resistance data of PU-II at 27°C.

Time, Hrs	Water	HCl	H_2SO_4	HNO_3	NaOH	KOH	KCl
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	8.97	6.59	10.10	0.52	1.64	0.00
48	1.03	16.55		22.80	2.06	3.83	0.32
72	2.05				4.12	6.01	0.65
96	3.59				6.19	8.20	0.65
120	4.10				8.25	8.20	0.65
144	4.62				9.28	8.20	0.65
168	4.62				9.28	8.20	0.65

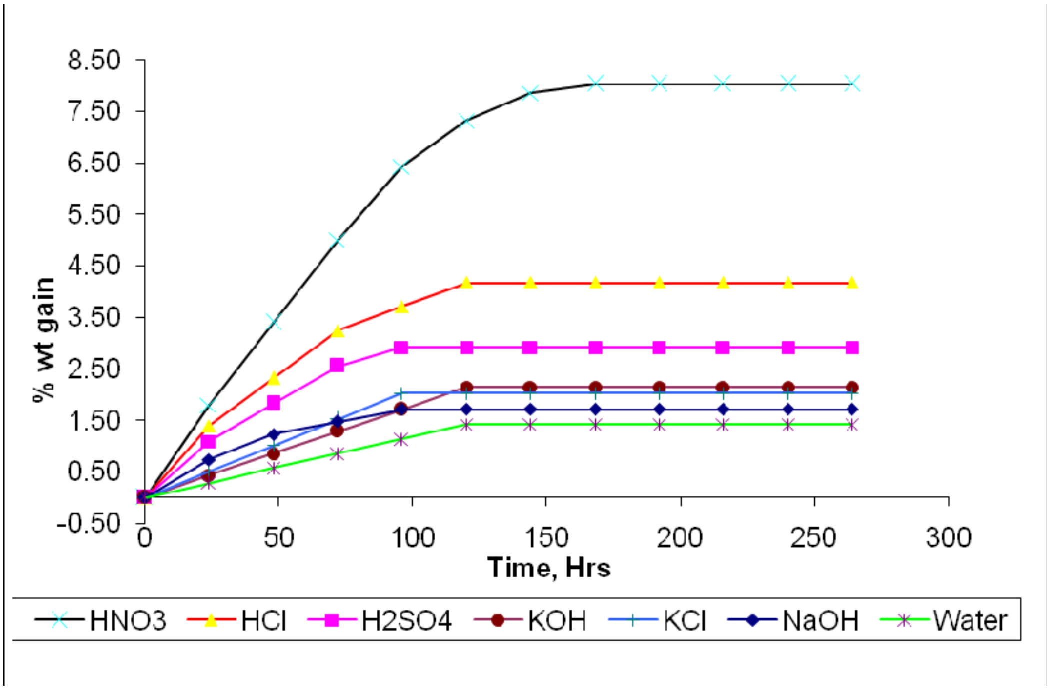

Fig.-3.27: % Wt gain against Time of PU-I in different (10%) solutions at 27°C

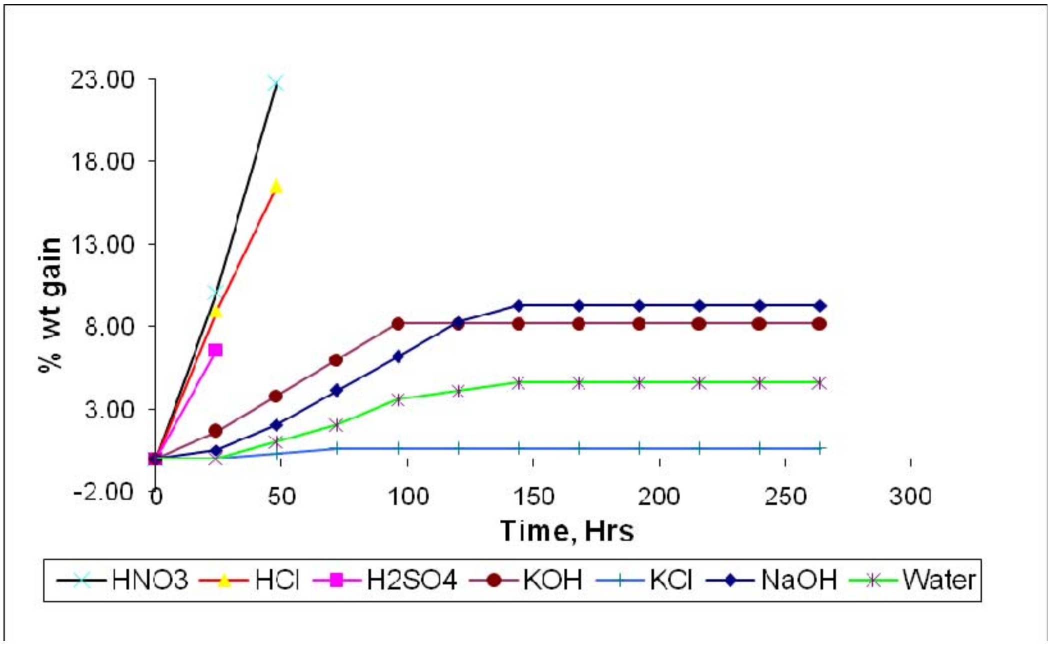

Fig.-3.28 : % Wt gain against Time of PU-I in different (10%) solutions at 27°C

Table-3.21: Diffusivity data of PU-I at 27°C

Solution	Equilibrium Time, h	% M at Equilibrium	Diffusivity
Water	120	1.42	1.22×10^{-13}
10 % HCl	120	4.17	8.85×10^{-14}
10 % H_2SO_4	96	2.91	1.21×10^{-13}
10 % HNO_3	168	8.02	8.79×10^{-14}
10 % NaOH	96	1.71	9.14×10^{-14}
10 % KOH	120	2.14	1.21×10^{-13}
10 % KCl	96	2.02	1.59×10^{-13}
Boiling Water	4	-0.55	4.27×10^{-12}

Table-3.22: Diffusivity data of PU-II at 27°C

Solution	Equilibrium Time, h	% M at Equilibrium	Diffusivity
Water	144	4.62	1.55×10^{-13}
10 % HCl	48	16.55	3.13×10^{-13}
10 % H_2SO_4	24	6.59	3.56×10^{-13}
10 % HNO_3	48	22.80	4.63×10^{-13}
10 % NaOH	144	9.28	1.54×10^{-13}
10 % KOH	96	8.20	1.62×10^{-13}
10 % KCl	72	0.65	4.69×10^{-13}
Boiling Water	4	9.47	2.29×10^{-13}

CHAPTER-4

CHAPTER-4: ULTRASONIC SPEED AND THERMODYNAMIC PARAMETERS OF EPOXY RESINS SOLUTIONS

This chapter describes the density, viscosity and ultrasonic speed measurements of epoxy resins (EP-01, EP-02 and EP-03) solutions in different solvents (chloroform, 1,4-dioxane and THF) at 35°C. Various thermodynamic parameters of these resin solutions are also determined and discussed in light of effect of structure, concentration and nature of solvents.

Ultrasonic technology is now a days employed in a wide range of applications such as medicine, biology, industry, material science, agriculture, oceanography, dentistry, consumer industry, sonochemistry research, etc. due to its non-destructive nature [1-8]

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2. T. J. Mason, Editor., "Sonochemistry: The Uses of Ultrasounds in Chemistry", Royal Soc. of Chem., 1990.
3. David R. Andrews, "Ultrasonics and Acoustics", Encyclopedia of Physical Science and Technology (3^{rd} Ed), 269-287, 2001.
4. M. Taghi, Zafarani-Moattar and N. Kheyrabi, "Volumetric, ultrasonic and transport properties of an aqueous solution of polyethylene glycol monomethyl ether at different temperatures", J. Chem. Eng., 55, 3976-3982, 2010.
5. M. Yasmin, K. P. Singh, S. Parveen, M. Gupta and J. P. Shukla, "Thermo acoustical excess properties of binary liquid mixtures / A comparative experimental and theoretical study", Acta Physica Polonica A, 115, 890-900, 2009.
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7. M. J. S. Lowe, "Ultrasonics", Encyclopedia of vibration, Elsevier Ltd, 1437-1441, 2001.
8. G. Chandrasekhar, P. Venkatesu and M. V. P. Rao, "Excess molar volumes and speed of sound of ethyl acetate and butyl acetate with 2-alkoxyethanols at 308.15 K", J. Chem. Eng. Data, 45, 590-597, 2000.

It is most useful in investigating various organic liquids, polymers and aqueous and non-aqueous electrolyte solutions. It provides a wealth of information about molecular interactions, the nature and strength of interactions. It offers a rapid nondestructive method for characterizing materials. The extensive uses of polymers in technology have promoted ultrasonic studies to understand the structures of polymers and furnish knowledge on solvophilic or solvophobic nature of polymers [9-11]. Applications in materials science include the determination of some properties of solids such as compressibility, specific heat ratios, elasticity [12], etc.

Ultrasound has also proved to be very useful for both soldering and welding. It is reported to improve the quality of homogenized milk. With the tracking of submarines, oceanographic applications include mapping of the sea bottom, discovering sunken ships and searching for schools of fish. Ultrasonic testing and evaluation techniques are widely used for obtaining information about micro structural and mechanical properties of metals and found wide applications in medical and biological fields [13].

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11. W. Bell and R. A. Pethrik, “Ultrasonic investigations of linear and star shaped polybutadiene polymers in solutions of cyclohexane, hexane and ethylbenzene”, Polymer, 23, 369-378, 1982.
12. J. J. Gilman, B. J. Cunningham and A. C. Holt, “Method for monitoring the mechanical state of a material”, Mater. Sci. and Engg., 39 A, 125-133, 1990.
13. H. J. Mueller, J. Lauterjung, F. R. Schilling, C. Lathe and G. Nover, **“**Symmetric and asymmetric interferometric method for ultrasonic compressional and shear wave velocity measurements in piston-cylinder and multi-anvil high-pressure apparatus**”,** Eur. J. Mineralogy, 14, 581-585, 2002.

Further, cleaning is the most common type of application of ultrasonic, which includes the removal of grease, dirt, rust and paint from metal, ceramic glass and crystal surfaces. Another area where ultrasonic is now a day being used, is to obtain the information about microstructures [14-15].

Sound velocity measurements on condensation polymers in protic or aprotic solvents are carried out by Parsania et al. [16-21] and investigated the influence of solvent, concentration, temperature and the nature of the substituents on the structure of polymers and molecular interactions in the solutions under investigations.

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14. I. I. Perepechko, V. A. Danilov and V. V. Nizhegorodov, "Ultrasonic velocity in epoxy resin at temperatures down to 4.2K ", Mechanics of Compos. Mater., 32, 316-320, 1996.
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16. D. R. Godhani, Y. V. Patel and P. H. Parsania, "Ultrasonic velocity and acoustical parameters of poly (4,4'-diphenyl phthalide diphenyl methane-4, 4'-disulfonate)-DMF solutions at 30, 35 and 40°C" J. Pure and Appl. Ultrason., 23, 58-62, 2001.
17. D. R. Godhani and P. H. Parsania, "Studies on acoustical properties of poly(4,4'-diphenylphthalide-diphenyl-4,4' disulfonate) at 30°C", J. Ind. Chem. Soc., 79, 620-623, 2002.
18. Y. V. Patel, D. R. Bhadja and P. H. Parsania "Ultrasonic study of poly (R, R', 4, 4'–cyclohexylidene diphenylene phosphorochloridate)-DMF solutions at different temperatures", J. Pure and Appl. Ultrason., 24, 47-53, 2002.
19. V. M. Kagathara and P. H. Parsania, "Studies on ultrasonic velocity and acoustical parameters of bromo epoxy resins of bisphenol-C solutions at different temperatures", Europ. Polym. J., 38, 607-610, 2002.

Solvents and chemicals used in the present investigation were purified according to reported methods [22]. Ultrasonic speed, density and velocity measurements of pure solvents: chloroform, THF and 1,4-dioxane and epoxy resins (EP-01, EP-02 and EP-03) solutions (0.5,1.0,1.5 and 2.0 wt %) were carried out at 35 °C, by using F-81 Ultrasonic Interferometer (2 MHz) (Mittal Enterprises, New Delhi), specific gravity bottle and Ubbelohde suspended level viscometer. Ultrasonic speed (U), density (ρ) and viscosity (η) measurements were accurate to ±0.1%, ±0.1 kgm^{-3} and ±0.01 mPas, respectively.

Density measurements

Densities of pure solvents and solutions were measured by means of specific gravity bottle at 35±0.1°C by determining the weights of distilled water, solvents and solutions. The density (ρ) was calculated according to Eqn. 4.1 with an accuracy of ± 0.1 kg/m^3.

$$\rho\ (g / cc) = \frac{Wt. of solvent / solution}{Wt. of water} \qquad \dots 4.1$$

Viscosity measurements

The method for determining the dynamic viscosity or coefficient of viscosity of liquids relies on Stoke's law.

In present investigation, suspended level viscometer developed by Ubbelohde was used. The viscometer was washed with chromic acid, distilled water, acetone and then dried at 50°C in an oven.

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20. B. G. Manwar, S. H. Kavthia and P. H. Parsania, "Ultrasonic velocity study of poly (R, R', 4, 4'-cyclohexylidene diphenylene toluene-2, 4-disulfonates) solutions at 30, 35 and 40°C", J. Pure and Appl. Ultrason., 26, 49-57, 2004.
21. B. D. Bhuva and P. H. Parsania, "Effect of temperature and solvents on ultrasonic velocity and allied acoustical parameters of epoxy oleate of 9, 9'-bis(4-hydroxy phenyl) anthrone-10 solutions", J. Sol. Chem., In Press.
22. E. S. Proskaur and A. Weisberger, "Techniques of Organic Solvents", New York, 1955.

Viscometer was suspended in a thermostat at 35±0.1°C and measured quantity of the distilled water / solvent / solution was placed into the viscometer reservoir by means of a pipette and thermally equilibrated for about 10 min. The flow time of liquid between two marks was measured by means of digital stopwatch with an accuracy of ±0.01sec.Three replicate measurements on each liquid were made and the arithmetic mean was considered for the purpose of calculations. Using the flow times (t) and known viscosity of standard (water) sample, the viscosities of solvents and solutions were determined according to Eqn. 4.2 :

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2} \qquad \ldots 4.2$$

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

Sound velocity measurements

Ultrasonic interferometer (F-81) (Mittal Enterprises, New Delhi) was used in the present investigation. The working of interferometer was tested by measuring the sound velocity of pure solvents: chloroform (CF), THF, 1,4-dioxane(DO) and comparing the results with literature data.

The measuring cell (2 MHz) with quartz crystal was filled with the solvent/solution and then micrometer with reflector plate was fixed. The circulation of water from the thermostat (at 35°C) was started and the experimental liquid in the cell is allowed to thermally equilibrate. The high frequency generator was switched on and the micrometer was rotated very slowly so as to obtain a maximum or minimum of the anode current. A number of maximum readings of anode current (n) were counted. The total distance (d) traveled by the micrometer for n=10 were recorded. The wave length (λ) was determined according to Eqn. 4. 3:

$$\lambda = \frac{2d}{n} \qquad \ldots 4.3$$

The ultrasonic speed (U) of solvents and solutions were calculated from the wave length (λ) and frequency (F) according to Eqn. 4.4:

$$U = \lambda . F \qquad ...4.4$$

Theoretical equations for acoustical parameters

1. Adiabatic compressibility

Adiabatic compressibility (κ_{α}) can be evaluated according to Newton and Laplace:

$$\kappa_{\alpha} = \frac{1}{U^2 \rho} \qquad \ldots 4.5$$

2. Specific acoustical impedance

$$Z = U\rho \qquad ... 4.6$$

3. Rao's molar sound function

Rao's molar sound function (R) can be evaluated by employing a method suggested by Bagchi et. al [23]

$$R = \frac{M}{\rho} U^{1/3} \qquad \ldots 4.7$$

The apparent molecular weight (M) of the solution can be calculated according to Eqn. 4.8:

$$M = M_1 W_1 + M_2 W_2 \qquad ... 4.8$$

Where, W_1 and W_2 are weight fractions of solvent and epoxy resin, respectively. M_1 and M_2 are the molecular weights of the solvent and epoxy resins respectively.

4. Van der Waals constant

Van der Waals constant (b) [24] can be calculated according to Eqn.4.9

$$b = \frac{M}{\rho}\left[1 - \left[\frac{RT}{MU^2}\right]\left[\sqrt{1 + \frac{MU^2}{3RT}} - 1\right]\right] \qquad ... 4.9$$

Where R (8.314 JK^{-1} mol^{-1}) is the gas constant and T (^{o}K) is the absolute temperature.

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[23] S. Bagchi, S. K. Nema and R. P. Singh, "Ultrasonic and viscometric investigation of ISRO polyol in various solvents and its compatibility with polypropylene glycol", Eur. Polym. J., 22, 851-857, 1989.

[24] P. Vigoureux, 'Ultrasonic', Chapman and Hall, Landon, 1952.

5. Internal pressure

Internal pressure (π) can be evaluated according to Suryanarayana and Kuppuswamy [25]:

$$\pi = bRT\left(\frac{K\eta}{U}\right)^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \quad \ldots \quad 4.10$$

Where R=8.3143 JK^{-1} mol^{-1} is the gas constant and b'=2, is the packing factor and K=4.28 X 10^{9} is a constant.

The internal pressure (π) depends on temperature, density, ultrasonic speed and specific heat at a constant pressure.

6. Classical absorption coefficient

The classical absorption coefficient $(\alpha/f^2)_{cl}$ has its origin in the viscosity of the medium and it is proposed by Subrahmanyam et al. [26]:

$$\left(\alpha/f^2\right)_{cl} = \frac{8\pi^2\eta}{3U^3\rho} \quad \ldots \quad 4.11$$

7. Viscous relaxation time

The resistance offered by viscous force in the flow of sound wave appears as a classical absorption associated with it is the viscous relaxation time (τ):

$$\tau = \frac{4\eta}{3\rho U^2} \quad \ldots \quad 4.12$$

8. Solvation number

The solvation number (S_n) can be evaluated according to Passynsky [27] method.

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25. C. V. Suryanarayana and J. Kuppuswamy, J. Acoust Soc. (India), 9(1), 4, 1954.
26. T. V. S. Subrahmanyam, A. Viswanadhasharma and K. Subbarao, J. Acoust. Soc. 7(1), 1, 1979.
27. Z. Passynsky, Acta Phys. Chem. USSR, 22, 317, 1943.

The number of grams of solvent connected in the apparent solvation of 1 g of solute assuming that the solvent molecules participating in the solvation are effectively incompressible due to strong localized electronic fields, is expressed as:

$$n = \left[1 - \frac{\kappa_s (100 - X)}{\kappa_{s1} X} \right] \qquad \ldots\ 4.13$$

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

The Solvation number (Sn) can be expressed as:

$$Sn = \frac{M_2}{M_1 \left(1 - \frac{\kappa_s}{\kappa_{s1}} \right) \left(\frac{100 - X}{X} \right)} \qquad \ldots\ 4.14$$

Where, M_1 and M_2 are the molecular weights of solvent and epoxy resin, respectively.

9. Apparent molar volume

Apparent molar volume [28] can be calculated according to Eqn.4.15:

$$\phi_{V2} = \frac{M}{\rho_1} \left[1 - \frac{(100)}{C} (\rho - \rho_1) \right] \qquad \ldots\ 4.15$$

Where, M is the molecular weight of epoxy resins and ρ_1 and ρ are the densities of solvent and epoxy resins, respectively.

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[28] P. R. Chowdhury, Indian J. Chem., 7, 692, 1969.

10. Apparent molar compressibility

Apparent molar compressibility [29] can be calculated according to Eqn. 4.16:

$$\phi\kappa_s = M_2\kappa_{s1}\left[\frac{100}{C}\left(\frac{\kappa_s}{\kappa_{s1}} - \frac{\rho}{\rho_1}\right) + \frac{1}{\rho_1}\right] \quad \ldots 4.16$$

Where C is the concentration in dl/g and κ_{s1} and κ_s are the adiabatic compressibility of solvent and epoxy resin solutions, respectively

11. Free volume

Free volume [30] can be calculated according to Eqn. 4.17:

$$V_f = \left[\frac{MU}{K\eta}\right]^{3/2} \quad \ldots 4.17$$

12. Inter molecular free path length

Inter molecular free path length (L_f) can be evaluated according to Eqn. 4.18, as proposed by Jacobson [31]:

$$L_f = K.(\kappa_a)^{1/2} \quad \ldots 4.18$$

Where, *K* = (93.875 + 0.375T) x 10^{-8} is a constant and temperature dependent.

In order to understand the effect of concentration, temperature, nature of solvents and nature of substituents of solute, various acoustical parameters were determined by using the experimental data on ρ, η and U of epoxy resins solutions at 35°C according to above mentioned standard relations.

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29. C. V. Surayanarayana and J. Kuppusami, J. Acoust. Soc. India, 4, 75, 1976.
30. S. Das, R. P. Singh and S. Maiti, "Ultrasonic velocities and Rao formulism in solution of polyesterimides", Polym-Bull., 2, 400-409, 1980.
31. B. Jacobson, Nature, 173, 772, 1954.

The concentration dependence acoustical parameters provide valuable information about strength of molecular interactions occurring in the solutions. Various acoustical parameters were fitted with concentration according to least square method to ascertain concentration dependence of molecular interactions occurring in solutions and hence solvophilic or solvophobic nature of epoxy resins under investigation.

High frequency (>1MHz, usually low intensity) waves are useful in providing information on relaxation phenomena such as segmental motion, conformational analysis, vibrational-translational energy interchange and polymer-solvent interactions, whereas low frequency waves provide information on both polymerization and depolymerization [32-36].

When a low intensity wave one without cavitation is passed through a liquid, there is attenuation, α, of the wave due to viscous and thermal losses

$$\frac{\alpha}{f^2} = \frac{2\pi^2}{\rho U^3}\left\{\frac{4\eta_s}{3} + \frac{(\gamma-1)K}{C_P}\right\} \quad \ldots\ldots 4.19$$

Where f = frequency, K = thermal conductivity, $\gamma = C_P/C_V$, C_P = molar heat capacity at constant pressure, η_s and ρ are viscosity and density of the medium and U = ultrasonic speed. For a given liquid at temperature T, all the parameters on the right hand side should be constant making (α/f^2) constant no matter what the frequency.

The total energy of a given system is not restricted solely to translational energy but is the sum of many components. For liquids conformational and structural energies must be taken into account. The coupling of the translational energy with other forms of energies leads to the absorption of sound in excess of that deduced by Eqn. 4.19 and no constancy of (α/f^2) with increasing frequency. The time lag between the excitation and de-excitation process is observed as an acoustic relaxation. This relaxation process is observed as either an increase in velocity with frequency or a decrease in the (α/f^2) with frequency.

32. K. Rajagopal and S. Chenthilnath, “Study on excess thermodynamic parameters and theoretical estimation of ultrasonic velocity using scaled particle theory in binary liquid mixtures of 2-methyl-2-propanol and nitriles at different temperatures”, Chinese J. Chem. Eng., 18, 804-816, 2010

33. Anil Kumar Nain, Dinesh Chand, Prakash Chandra, and Jata Dhari Pandey, “Excess internal pressures, excess free volumes and excess thermodynamic parameters of some non-aqueous binary mixtures from ultrasonic speed, density and viscosity data”, Phy. and Chem. Liq., 47, 195-209, 2009.

34. P. F. Pires, J. M. S. S. Esperança, and H. J. R. Guedes, “Ultrasonic speed of sound and derived thermodynamic properties of liquid 1,1,1,2,3,3,3-heptafluoropropane (HFC227ea) from 248K to 333K and pressures up to 65 MPa”, J. Chem. Eng. Data, 45, 496–501, 2000.

35. Joanna Krakowiak and Wacław Grzybkowski, “Apparent molar volume and compressibility of tetrabutylphosphonium bromide in various solvents”, J. Chem. Eng. Data, 55, 2624–2629, 2010.

36. João Carlos R. Reis, Ângela F. S. Santos and M.S. Isabel, “Chemical thermodynamics of ultrasound speed in solutions and liquid mixtures”, Chem Phys Chem, 11, 508-516, 2010.

The dependence of attenuation with temperature allows determination of ΔG*, ΔH, ΔV and ΔS associated with various conformational changes. There will be a perturbation of the equilibrium on the passage of an ultrasonic wave.

It is possible to obtain information on the rate constants for forward (k_f) and backward (k_b) reactions, the free energy barrier ΔG_b^* and the free energy difference ΔG.

$$A \underset{k_b}{\overset{k_f}{\leftrightarrows}} B$$

Assuming unimolecular reaction in ideal solution, relaxation frequency f_r can be correlated with the rate constants.

$$fr = \frac{1}{2\pi\tau} = \frac{k_f + k_b}{2\pi} \qquad \ldots\ 4.20$$

Where τ = relaxation time of the equilibrium.

For any reaction the rate constant k can be expressed in terms of the free energy of activation ΔG*.

$$fr = \frac{k_b T}{h}\, e^{-\frac{\Delta G_f *}{RT}}$$

$$= \frac{k_B T}{2\pi h}\left[e^{-\frac{\Delta G_f *}{RT}} + e^{-\frac{\Delta G_b *}{RT}}\right] \qquad \ldots.\ 4.21$$

Where k_B = Boltzmann constant and h = Planck’s constant.

Assuming that equilibrium lies well to the left then

$\Delta G_f^* \gg \Delta G_b^*$ *such that*

$$fr = \frac{k_b T}{2\pi h}\, e^{-\frac{\Delta G_b *}{RT}} \qquad \ldots\ 4.22$$

Since

$$\Delta G = \Delta H - T\Delta S \qquad \ldots\ 4.23$$

$$fr = \frac{k_b T}{2\pi h}\left(e^{-\frac{\Delta S_b *}{RT}}\right)\left(e^{-\frac{\Delta H_b *}{RT}}\right) \qquad \ldots 4.24$$

$$ln\frac{fr}{T} = ln\frac{k_B}{2\pi h} + \frac{\Delta S_b^*}{RT} - \frac{\Delta H_b^*}{RT} \qquad \ldots 4.25$$

From the plot of ln f_r/T against 1/T, ΔH_b^* and ΔS_b^* can be determined.

Results and Discussion

The ρ, η, and U data of pure solvents and resins solutions at 35°C are summarized in Tables-4.1 - 4.3, from which it is observed that they increased linearly with concentration (C) except ρ in chloroform system in which it decreased with C. The density is an additive property. The density of CF is greater than those of resins and hence density of solutions decreased with increasing C. The observed trends in ρ, η and U are CF > DO > THF; DO > CF > THF; DO > THF > CF, respectively. They are correlated with C and the least square equations along with regression co-efficient are summarized in Tables-4.4-4.6. A fairly good to excellent correlation between a given parameter and C is observed.

The variation of η and U with C is considerably more than that of ρ due to specific molecular interactions i.e. association, expansion, unfolding, etc. Molecular interactions depend on the strength of the repulsive forces acting amongst solvent and solute molecules and hence intermolecular motion is affected accordingly. Attractive forces result into molecular association (solvation), i.e. modification of the resin molecules. Molecular association leads to change in both apparent molecular volume as well as mass and hence density changes accordingly. Thus ρ, η and U are affected by molecular interaction under a set of experimental conditions. Van der Waals, H-bonding, dipolar and London types forces between solvent and solute molecules results in the aggregation of solvent molecules around solute molecules as a consequence of structural modification results. It is expected that EP-01 and EP-03 (symmetric molecules) have more structure forming tendency than EP-02 (asymmetric molecule). –OCH_3 group in EP-03 may hinder molecular association and as a result it has slightly less association tendency than EP-01.

In order to understand molecular interactions in the resins solutions, various thermodynamic parameters namely adiabatic compressibility (K_α), Van der Waals constant (b), intermolecular free path length (L_f), internal pressure (π) and viscous relaxation time (τ) have been determined by using ρ, η, and U data of resins solutions and are correlated with C. The least square equations and regression coefficients (R^2) are summarized in Tables- 4.4 to 4.6 from which it is clear that a good to excellent correlation between a particular parameter and C is observed.

The linear increase of b and τ ; and linear decrease of K_α and L_f (except EP-01: THF and EP-03: THF) and π with C indicate existence of strong molecular interactions in the solutions. Decrease of K_α, L_f, and π with increasing C is due to increase in cohesive forces (molecular interactions) and vice-versa.

Ultrasonic speed in the solutions depends on intermolecular free path length. When ultrasonic wave are indicated on the solution, the molecules get perturbed. Due to some elasticity of the medium, perturbed molecules regain their equilibrium positions. When a solute is added to a solvent, its molecules attract certain solvent molecules towards them. The phenomenon is known as compression and also as limiting compressibility. The aggregation of solvent molecules around solute molecules supports powerful solvent-solute interactions. Because of solvent-solute interactions, the modification of the structure of the solute takes to a considerable extent. Relaxation process causes dispersion of U in the system. Molecular interactions such as solvent-solute interaction, quantum mechanical dispersive forces and dielectric force may cause either contraction or expansion and as a consequence transport properties of the solutions alter with concentration and temperature.

Azomethine, methyl, ether, methoxy and hydroxyl groups are polar groups, which are responsible for molecular interactions (molecular association) i.e. solvent-solute interactions. The dipole-dipole intractions of the opposite type favor molecular association; while of the same type disrupt structure formed previously.

The Gibb's free energy of activation (ΔG^*) for viscous relaxation process can be determined according to Eyring rate process theory [37].

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\Delta G^* / RT}$$

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37. H. Eyring, "The activation complex in chemical reactions", J. Chem. Phys., 3, 107-15, 1935.

Where k is the Boltzamnn constant, h is the Planck's constant, R is the gas constant, and T is the temperature.

Observed τ is due to structural relaxation processes. The value of ΔG^* was calculated as a function of concentration at 35°C and are summarized in Table-4.7. From which it is observed that ΔG^* varied with C to a small extent in solvent system studied indicating condensation and absorption due to structural modification is fairly concentration independent and are characteristic physical properties of the solute only. Observed ΔG^* is a fairly similar in a given solvent for resins under investigation. It is strongly dependent on the nature of the solvent used. Thus, nature of the solvent and structure of the solute play a vital role in relaxation process.

Table-4.1: The density (ρ), viscosity (η), sound velocity (U) and pooled precision standard deviation (Sp) data of EP-01 solutions in three different solvents at 35°C temperature

Conc., %	Density ρ, kg/m^{-3}	Viscosity η, m Pa s	Ave. Dist. d. 10^3, m	Wave Length λ, 10^3, m	U ms^{-1} F=2MHz	Std. devi. mm(±)
EP-01 + CH at 35 °C						
0	1461.22	0.5588	2.346	0.4692	938.4	0.0011
0.5	1458.81	0.5777	2.3620	0.4724	910.8	0.0016
1.0	1458.98	0.5967	2.3920	0.4784	922.8	0.0022
1.5	1459.18	0.6175	2.4130	0.4826	931.2	0.0017
2.0	1459.35	0.6451	2.4360	0.4872	940.4	0.0021
EP-01 + DO at 35 °C						
0	1025.86	1.0702	3.2350	0.647	1294	0.0009
0.5	1026.12	1.1156	3.2540	0.6508	1301.6	0.0013
1.0	1027.31	1.1445	3.2660	0.6532	1306.4	0.0021
1.5	1027.59	1.1850	3.2770	0.6554	1310.8	0.0018
2.0	1028.09	1.2241	3.2880	0.6576	1315.2	0.0014
EP-01 + THF at 35 °C						
0	877.55	0.4519	3.072	0.6144	1228.8	0.0011
0.5	879.31	0.4805	3.089	0.6178	1227.2	0.0016
1.0	881.33	0.5038	3.081	0.6162	1224	0.0012
1.5	882.79	0.5260	3.073	0.6146	1220.8	0.0019
2.0	884.91	0.5494	3.065	0.613	1217.6	0.0014

Table-4.2: The density (ρ), viscosity (η), sound velocity (U) and pooled precision standard deviation (Sp) data of EP-02 solutions in three different solvents at 35°C temperature

Conc., %	Density ρ, kg/m^{-3}	Viscosity η, m Pa s	Ave. Dist. d. 10^3, m	Wave Length λ, 10^3, m	U ms^{-1} F=2MHz	Std. devi. mm(±)
EP-02 + CH at 35 °C						
0	1461.22	0.5588	2.346	0.4692	938.4	0.0011
0.5	1452.12	0.5749	2.354	0.4708	941.6	0.0014
1.0	1452.35	0.5871	2.364	0.4728	945.6	0.0023
1.5	1451.57	0.5976	2.375	0.475	950	0.0016
2.0	1450.28	0.6250	2.384	0.4768	953.6	0.0021
EP-02 + DO at 35 °C						
0	1025.86	1.0702	3.2350	0.647	1294	0.0009
0.5	1025.01	1.0578	3.229	0.6458	1296.4	0.0013
1.0	1026.70	1.0856	3.251	0.6502	1305.2	0.0015
1.5	1027.74	1.1143	3.272	0.6544	1313.6	0.0023
2.0	1028.87	1.1425	3.289	0.6578	1320.4	0.0010
EP-02 + THF at 35 °C						
0	877.55	0.4519	3.072	0.6144	1228.8	0.0011
0.5	879.06	0.4646	3.066	0.6132	1234	0.0014
1.0	880.49	0.4738	3.081	0.6162	1240	0.0020
1.5	881.85	0.4844	3.093	0.6186	1244.8	0.0017
2.0	882.61	0.4931	3.104	0.6208	1249.2	0.0025

Table-4.3: The density (ρ), viscosity (η), sound velocity (U) and pooled precision standard deviation (Sp) data of EP-03 solutions in three different solvent at 35°C temperature

Conc., %	Density ρ, kg/m^{-3}	Viscosity η, m Pa s	Ave. Dist. d. 10^3, m	Wave Length λ, 10^3, m	U ms^{-1} F=2MHz	Std. devi. mm(±)
EP-03 + CH at 35 °C						
0	1461.22	0.5588	2.346	0.4692	938.4	0.0011
0.5	1459.52	0.5761	2.376	0.4752	950.4	0.0013
1.0	1461.62	0.5958	2.386	0.4772	954.4	0.0021
1.5	1460.45	0.6161	2.395	0.479	958	0.0016
2.0	1458.50	0.6427	2.404	0.4808	961.6	0.0016
EP-03 + DO at 35 °C						
0	1025.86	1.0702	3.2350	0.647	1294	0.0009
0.5	1025.01	1.0822	3.222	0.6444	1288.8	0.0021
1.0	1026.70	1.1392	3.235	0.647	1294	0.0025
1.5	1027.74	1.1872	3.247	0.6494	1298.8	0.0018
2.0	1028.87	1.2319	3.258	0.6516	1303.2	0.0013
EP-03 + THF at 35 °C						
0	877.55	0.4519	3.072	0.6144	1228.8	0.0011
0.5	879.63	0.4708	3.064	0.6128	1225.6	0.0019
1.0	881.34	0.4924	3.057	0.6114	1222.8	0.0017
1.5	884.57	0.5007	3.049	0.6098	1219.6	0.0026
2.0	886.46	0.5253	3.040	0.608	1216	0.0023

Table-4.4: The correlation equations and regression coefficients of different epoxy solutions in chloroform solvent

Parameter	Correlation equation (regression coefficients), R^2		
	ER-1	ER-2	ER-3
ρ, $kg.m^{-3}$	$0.362C + 1458.6$ $R^2 = 0.999$	$-1.126C + 1452$ $R^2 = 0.842$	$-30.84C + 1486$ $R^2 = 0.585$
η, mPas	$0.044C + 0.553$ $R^2 = 0.992$	$0.031C + 0.556$ $R^2 = 0.952$	$0.044c + 0.552$ $R^2 = 0.994$
U ms^{-1}	$19.44C + 907.6$ $R^2 = 0.993$	$8.08C + 937.6$ $R^2 = 0.998$	$7.44C + 946.8$ $R^2 = 0.999$
Z, 10^6 $kg.m^{-2}.s^{-1}$	$0.028C + 1.324$ $R^2 = 0.994$	$0.01C + 1.362$ $R^2 = 0.991$	$0.009C + 1.383$ $R^2 = 0.947$
κ_{α}, 10^{-10} Pa^{-1}	$-0.332C + 8.310$ $R^2 = 0.991$	$-0.128C + 7.83$ $R^2 = 0.994$	$-0.112C + 7.633$ $R^2 = 0.986$
V_f, 10^{-7} m^3	$-0.120C + 3.060$ $R^2 = 0.947$	$-0.10C^2 + 0.158C + 3.07$ $R^2 = 0.947$	$-0.176C + 3.263$ $R^2 = 0.989$
R, 10^{-4} $m^{10/3}.s^{-1/3}.mol^{-1}$	$0.256C + 7.896$ $R^2 = 0.999$	$0.24C + 8.005$ $R^2 = 0.998$	$0.239C + 7.995$ $R^2 = 0.998$
b, 10^{-5} m^3	$0.197C + 8.025$ $R^2 = 0.999$	$0.213C + 8.049$ $R^2 = 0.999$	$0.220C + 8.003$ $R^2 = 0.997$
π, 10^8 Pa	$0.032C^2 - 0.089C + 4.076$ $R^2 = 0.997$	$0.04C^2 - 0.128C + 4.015$ $R^2 = 0.985$	$0.029C^3 - 0.098C^2 + 0.099C + 3.93$ $R^2 = 1$
L_f, 10^{-11} m	$-0.124C + 6.035$ $R^2 = 0.990$	$-0.048C + 5.86$ $R^2 = 0.96$	$-0.046C + 5.79$ $R^2 = 0.988$
τ ,10^{-13} s	$0.118C^2 – 0.095C + 6.304$ $R^2 = 0.999$	$0.16C^2 – 0.168C + 6.005$ $R^2 = 0.968$	$0.348C + 5.633$ $R^2 = 0.987$
$(a/f^2)_{cl}$, 10^{-14} s^2m^{-1}	$0.029C^2 - 0.058C + 1.374$ $R^2 = 0.994$	$-0.034C^2 - 0.047C + 1.264$ $R^2 = 0.958$	$0.017C^2 + 0.019C + 1.195$ $R^2 = 0.999$

Table-4.5: The correlation equations and regression coefficients of different epoxy solutions in DO solvent

Parameter	Correlation equation (regression coefficients), R^2		
	ER-1	ER-2	ER-3
ρ, $kg.m^{-3}$	1.252C + 1025 R^2 = 0.913	2.28C + 1027 R^2 = 0.998	2.524C + 1023 R^2 = 0.912
η, mPas	0.098C+ 1.016 R^2 = 0.966	0.056C+ 1.03 R^2 = 1	0.099C + 1.035 R^2 = 0.997
U ms^{-1}	9.04C + 1297 R^2 = 0.999	16.08C+ 1284 R^2 = 0.996	9.6C + 1284 R^2 = 0.998
Z, 10^6 $kg.m^{-2}.s^{-1}$	0.01C + 1.331 R^2 = 0.979	0.019C + 1.319 R^2 = 0.996	0.013C + 1.315 R^2 = 0.994
κ_α, 10^{-10} Pa^{-1}	-0.092C+ 5.795 R^2 = 0.998	-0.154C + 5.899 R^2 = 0.995	-0.100C + 5.921 R^2 = 0.997
V_f, 10^{-7} m^3	-0.018C+ 1.237 R^2 = 0.981	0.018C + 1.301 R^2 = 0.985	-0.051C + 1.283 R^2 = 0.955
R, 10^{-4} $m^{10/3}.s^{-1/3}.mol^{-1}$	0.496C + 9.366 R^2 = 1	0.500C + 9.315 R^2 = 1	0.506C + 9.351 R^2 = 1
b, 10^{-5} m^3	0.430C + 8.456 R^2 = 1	0.418C + 8.440 R^2 = 1	0.437C + 8.473 R^2 = 1
π, 10^8 Pa	-0.144C + 5.273 R^2 = 0.992	-0.176C + 5.186 R^2 = 0.999	-0.092C + 5.199 R^2 = 0.980
L_f, 10^{-11} m	-0.036C + 5.039 R^2 = 0.997	-0.054C + 5.745 R^2 = 0.991	-0.04C+ 5.09 R^2 = 1
τ ,10^{-13} , s	0.423C+ 8.317 R^2 = 0.988	0.205C + 8.110 R^2 = 0.997	0.614C + 8.192 R^2 = 0.995
$(a/f^2)_{cl}$, 10^{-14} s^2m^{-1}	0.054C+ 1.265 R^2 = 0.987	0.015C + 1.246 R^2 = 0.969	0.083C + 1.259 R^2 = 0.995

Table-4.6: The correlation equations and regression coefficients of different epoxy solutions in THF solvent

Parameter	Correlation equation (regression coefficients), R^2		
	ER-1	ER-2	ER-3
ρ, $kg.m^{-3}$	3.66C+ 877.5 $R^2 = 0.996$	2.402C + 878 $R^2 = 0.982$	4.75C + 877 $R^2 = 0.985$
η, mPas	0.045C + 0.458 $R^2 = 0.999$	0.019C + 0.455 $R^2 = 0.996$	0.034C + 0.454 $R^2 = 0.970$
U ms^{-1}	-6C + 1230 $R^2 = 1$	10.08C + 1229 $R^2 = 0.994$	-6.4C + 1229 $R^2 = 0.996$
Z, 10^6 $kg.m^{-2}.s^{-1}$	-0.002C+ 1.08 $R^2 = 1$	0.012C+ 1.079 $R^2 = 0.985$	0.001C +1.076 $R^2 = 1$
κ_α, 10^{-10} Pa^{-1}	0.048C + 7.525 $R^2 = 0.993$	-0.140C + 7.534 $R^2 = 0.992$	0.039C + 7.547 $R^2 = 0.973$
V_f, 10^{-7} m^3	-0.112C + 3.04 $R^2 = 0.992$	0.186C + 3.077 $R^2 = 0.998$	- 0.01C + 3.079 $R^2 = 0.934$
R, 10^{-4} $m^{10/3}.s^{-1/3}.mol^{-1}$	0.596C + 8.82 $R^2 = 0.998$	0.672C + 8.795 $R^2 = 1$	0.621C+ 8.814 $R^2 = 0.999$
b, 10^{-5} m^3	0.577C + 8.082 $R^2 = 0.999$	0.593C + 8.073 $R^2 = 1$	0.590C + 8.088 $R^2 = 0.999$
π, 10^8 Pa	-0.038C + 1.266 $R^2 = 0.998$	-0.235C + 3.993 $R^2 = 0.999$	-0.165C + 3.995 $R^2 = 0.971$
L_f, 10^{-11} m	0.02C + 5.74 $R^2 = 1$	-0.068C + 5.085 $R^2 = 0.996$	0.02C + 5.75 $R^2 = 1$
τ ,10^{-13} , s	0.492C + 4.595 $R^2 = 0.999$	0.1C + 4.573 $R^2 = 0.994$	0.373C + 4.570 $R^2 = 0.970$
$(a/f^2)_{cl}$, 10^{-14} s^2m^{-1}	0.084C + 0.735 $R^2 = 0.999$	0.01C + 0.733 $R^2 = 0.979$	0.065C + 0.732 $R^2 = 0.972$

Table-4.7: ΔG* data of EP-01, EP-02 and EP-03

Conc., %	ΔG*, kJ mol^{-1}		
	CF	1,4-Dioxane	THF
	ESDSB-1		
0.5	3.58	4.29	2.86
1	3.53	4.34	2.98
1.5	3.57	4.41	3.10
2	3.63	4.46	3.22
	Avg. = 3.56	Avg. = 4.37	Avg. = 3.04
	78.4C x 3465 R^2 = 0.937	115C x 4230 R^2 = 0.990	238.3C x 2740 R^2 = 0.999
	ESDSB-2		
0.5	3.38	4.19	2.74
1	3.41	4.22	2.77
1.5	3.47	4.25	2.80
2	3.53	4.29	2.82
	Avg. = 3.45	Avg. = 4.24	Avg. = 2.78
	103.6C x 3317 R^2 = 0.986	62C x 4158 R^2 = 0.996	53.73C x 2714 R^2 = 0.994
	ESDSB-3		
0.5	3.33	4.27	2.81
1	3.38	4.38	2.93
1.5	3.45	4.46	2.97
2	3.54	4.53	3.11
	Avg. = 3.43	Avg. = 4.41	Avg. = 2.96
	144.4C x 3245 R^2 = 0.990	172C x 4192 R^2 = 0.993	186.9C x 2721 R^2 = 0.972

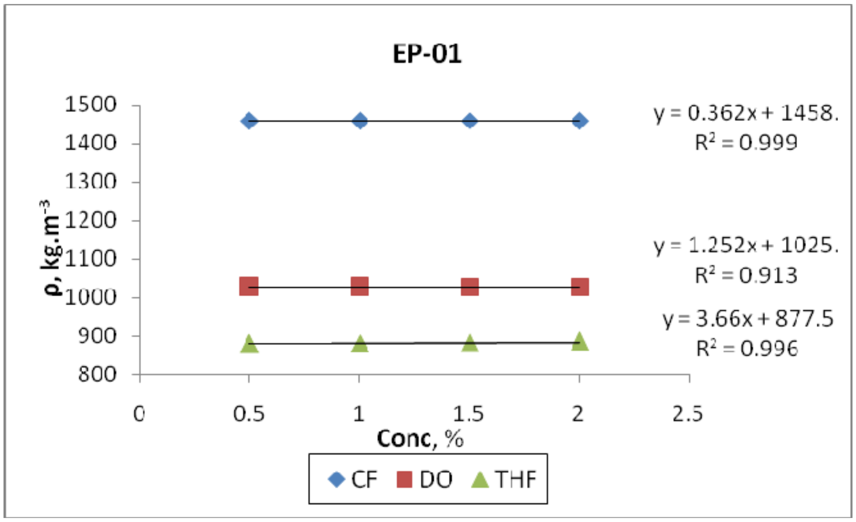


Fig. 4.1: The plots of ρ against C for EP-01 at 35°C.

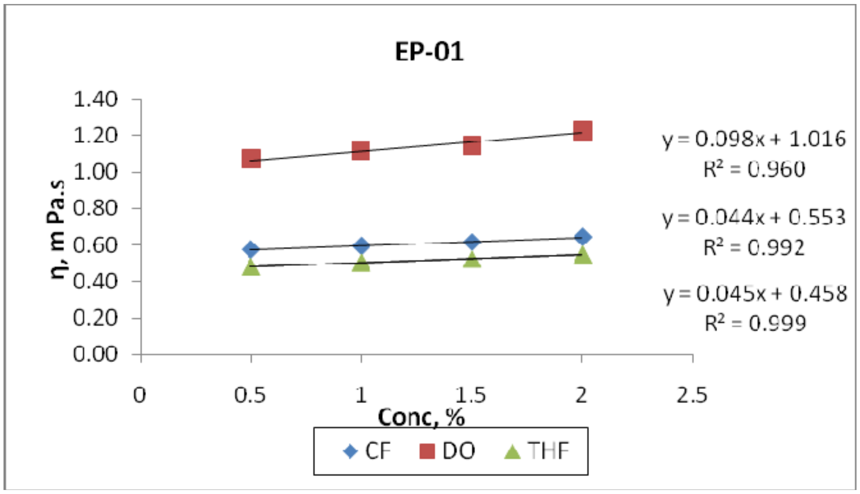


Fig.4.2: The plots of η against C for EP-01 at 35°C.

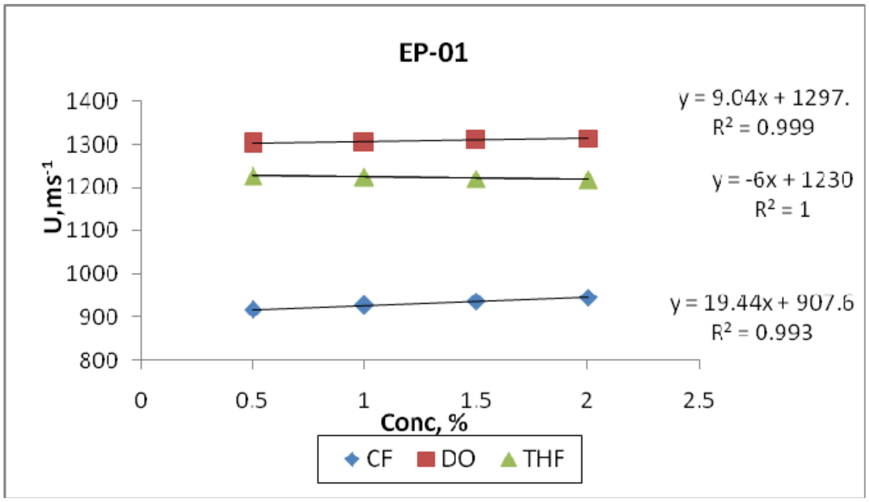


Fig. 4.3: The plots of U against C for EP-01 at 35°C.

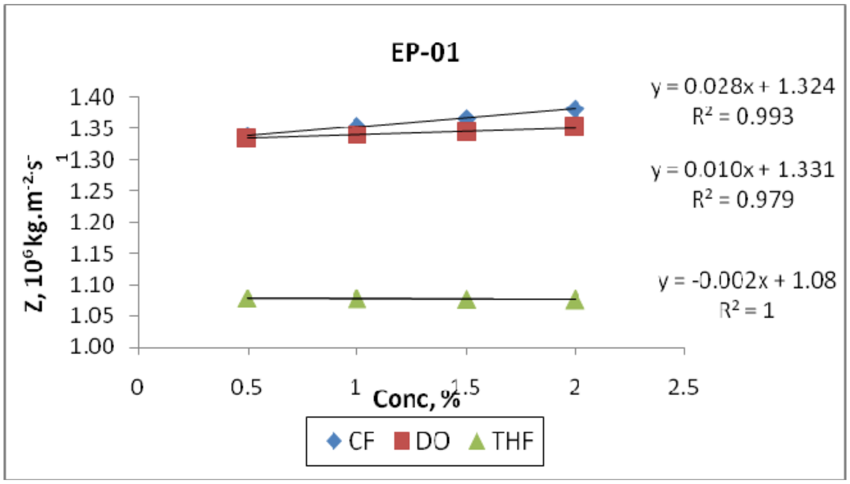


Fig. 4.4: The plots of Z against C for EP-01 at 35°C.

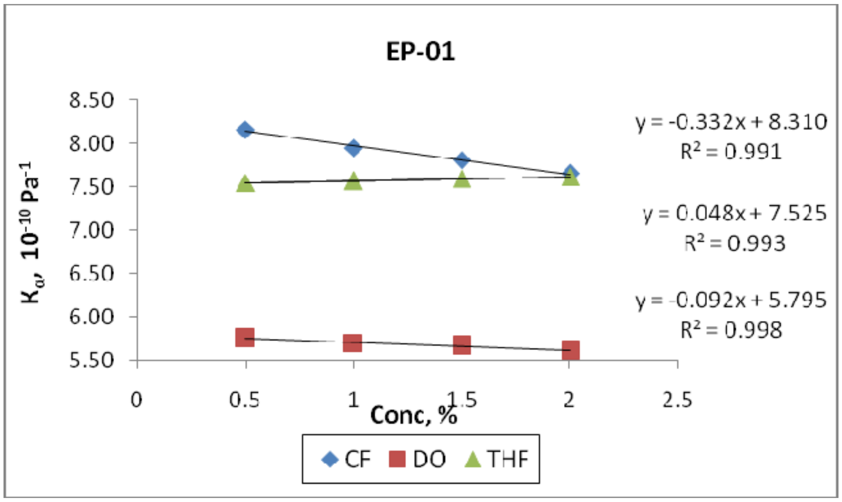


Fig. 4.5: The plots of κ_α against C for EP-01 at 35°C.

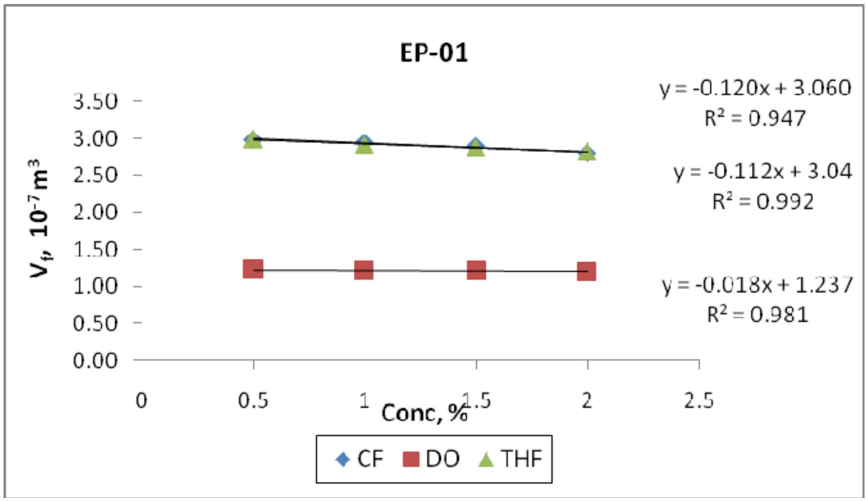


Fig. 4.6: The plots of V_f against C for EP-01 at 35°C.

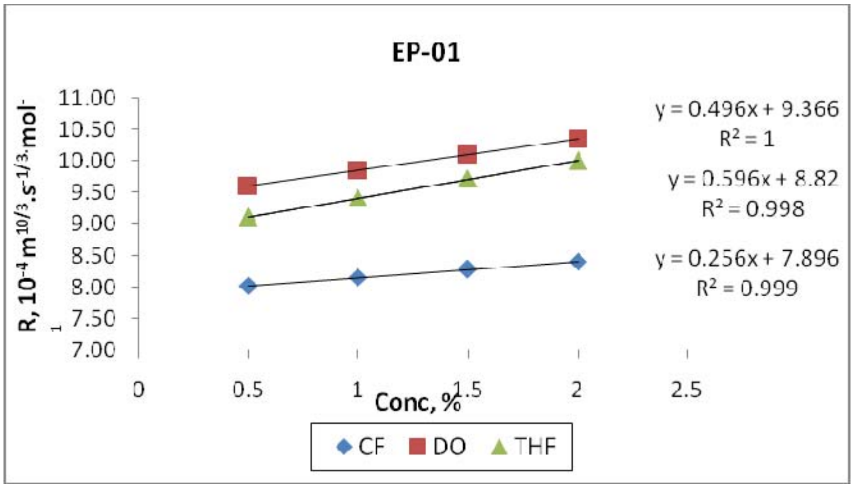


Fig. 4.7: The plots R against C for EP-01 at 35°C.

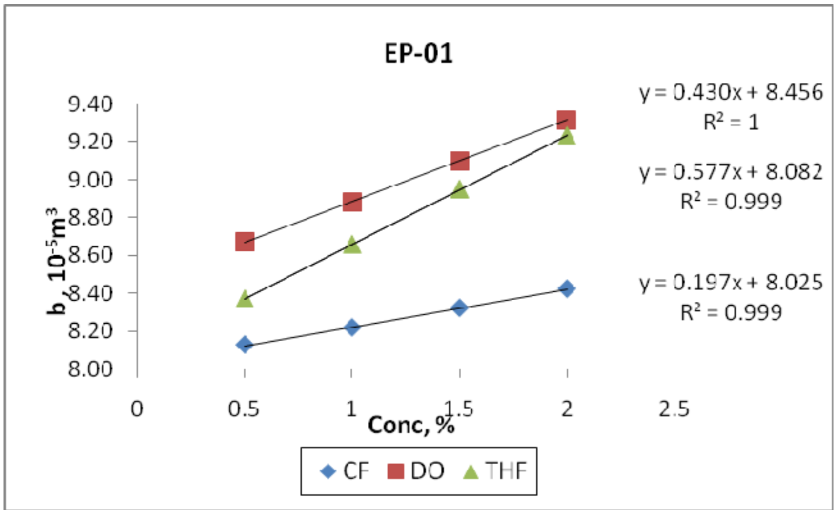


Fig. 4.8: The plots of b against C for EP-01 at 35°C.

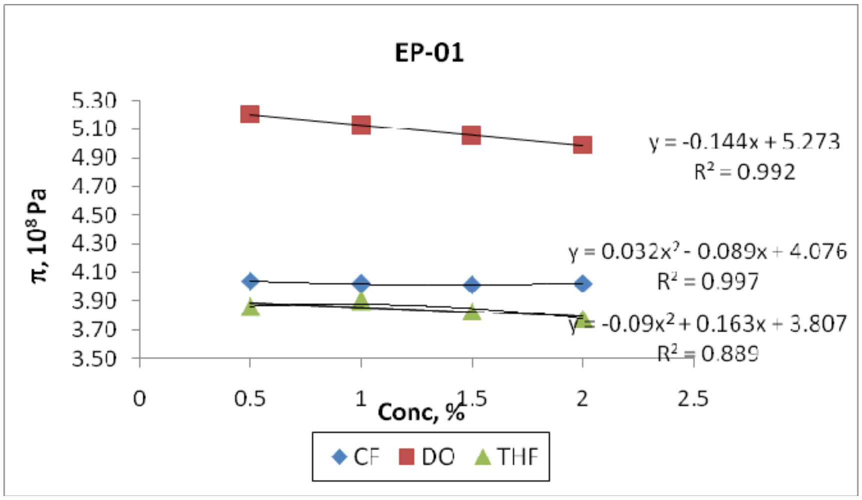


Fig. 4.09: The plots of π against C for EP-01 at 35°C.

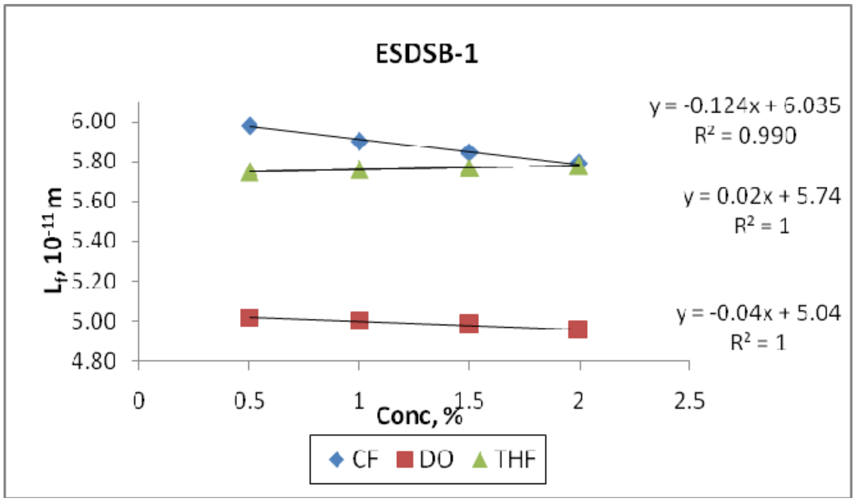


Fig. 4.10: The plots of L_f against C for EP-01 at 35°C.

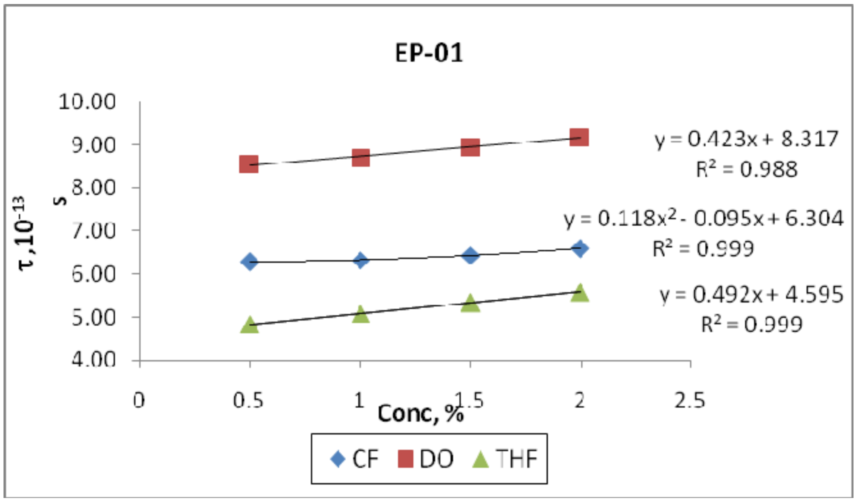


Fig. 4.11: The plots of τ against C for EP-01 at 35°C.

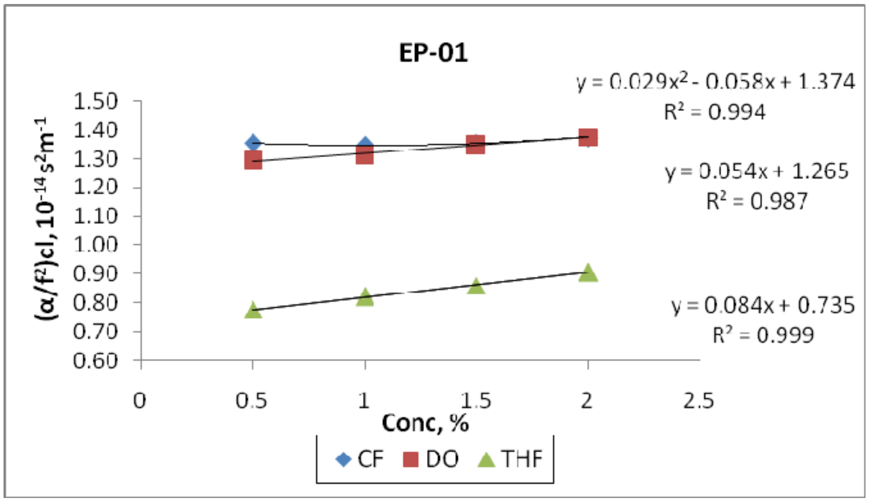


Fig. 4.12: The plots of $(\alpha/f^2)_{cl,}$ against C for EP-01 at 35°C.

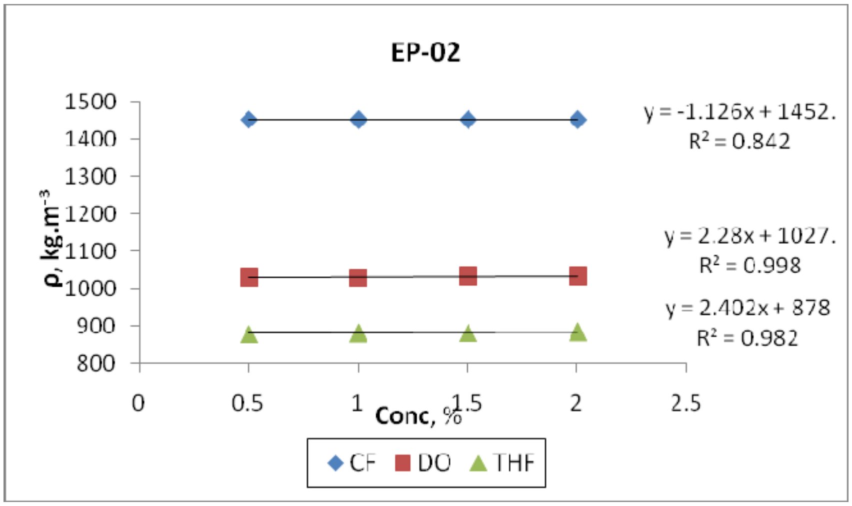


Fig. 4.13: The plots of ρ against C for EP-02 at 35°C.

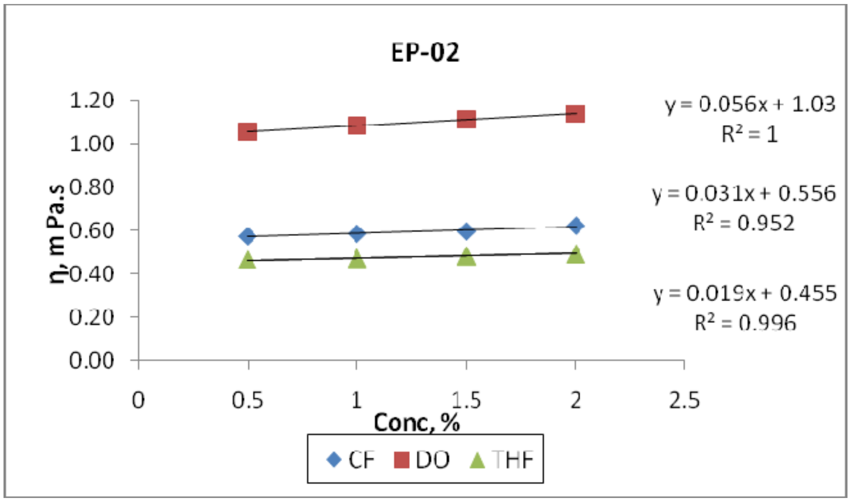


Fig. 4.14: The plots of η against C for EP-02 at 35°C.

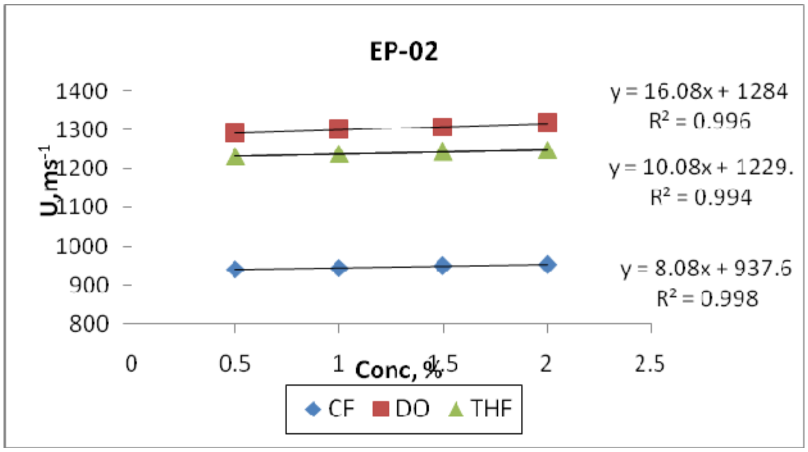


Fig. 4.15: The plots of U against C for EP-02 at 35°C.

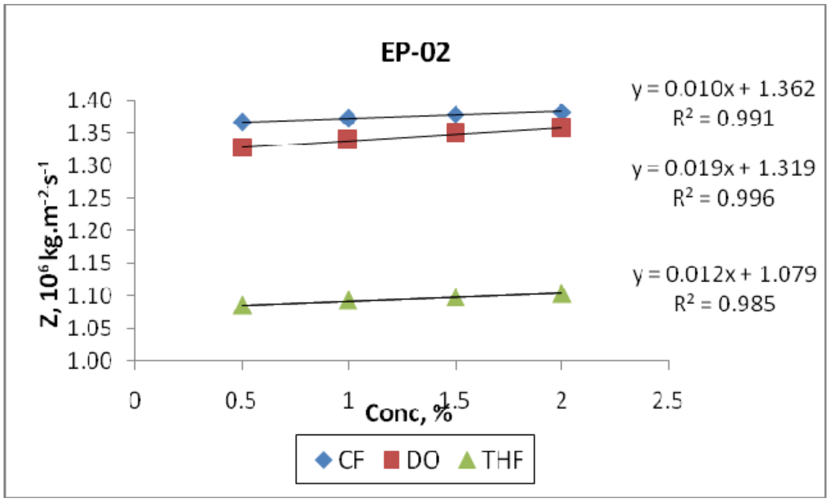


Fig. 4.16: The plots of Z against C for EP-02 at 35°C.

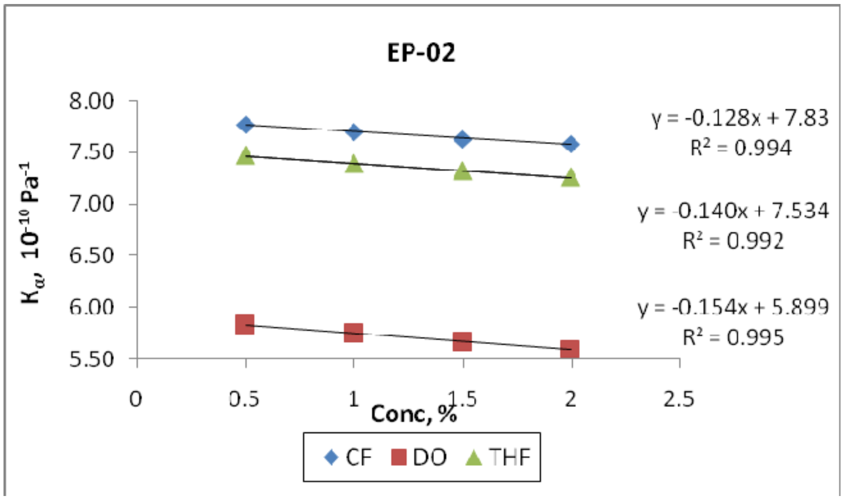


Fig. 4.17: The plots of κ_α against C for EP-02 at 35°C.

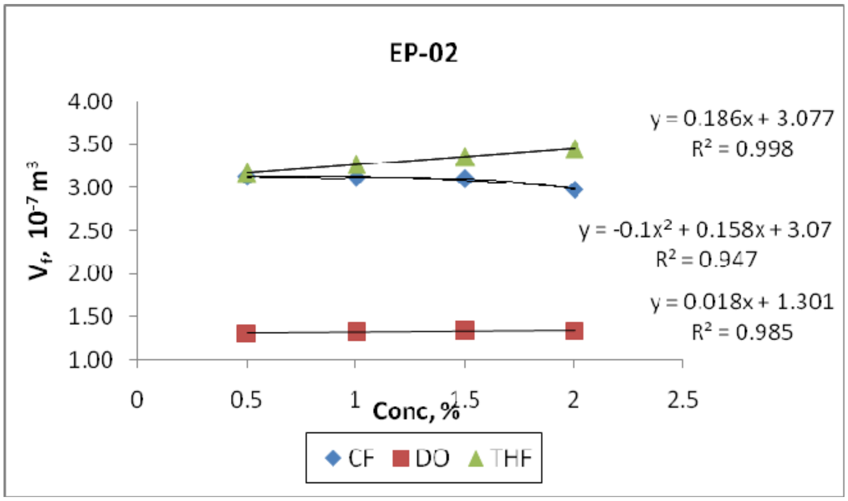


Fig. 4.18: The plots of V_f against C for EP-02 at 35°C.

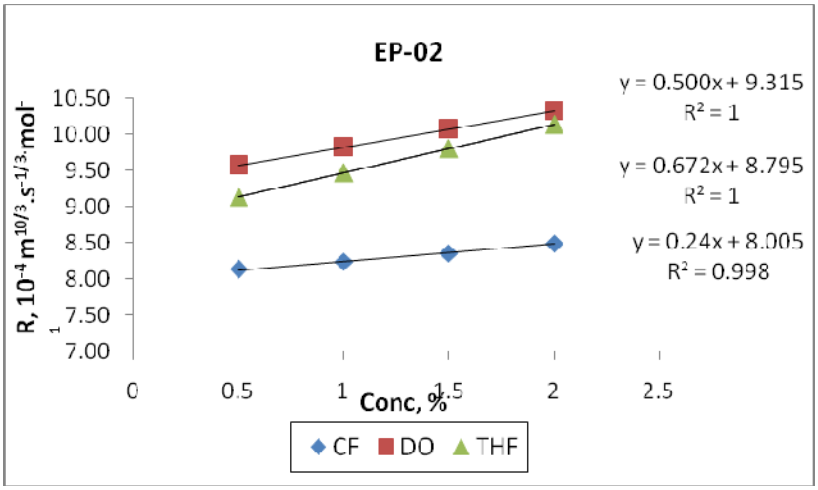


Fig. 4.19: The plots of R against C for EP-02 at 35°C.

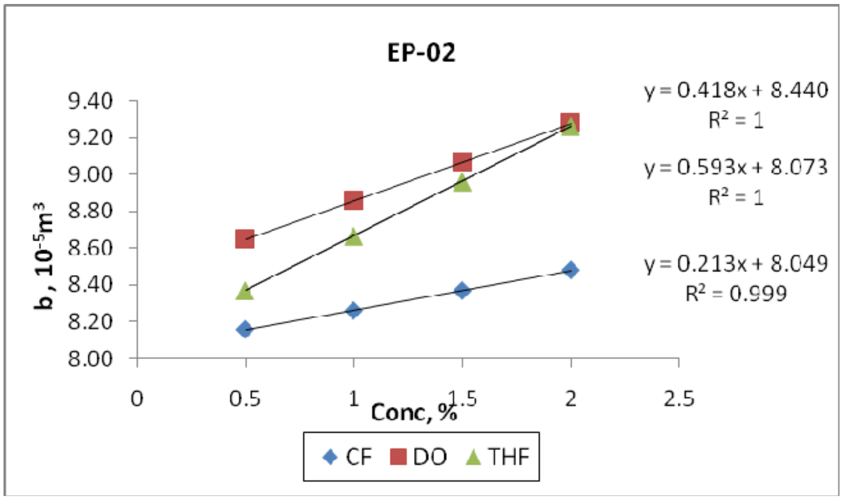


Fig. 4.20: The plots of b against C for EP-02 at 35°C.

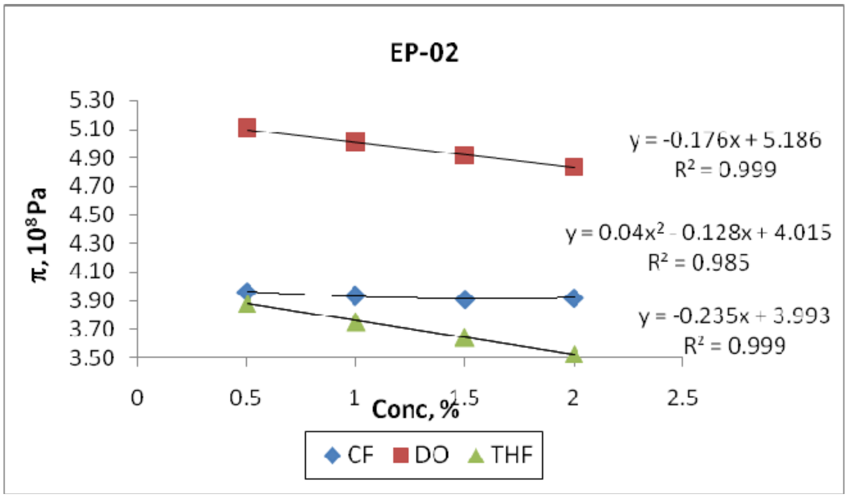


Fig. 4.21: The plots of π against C for EP-02 at 35°C.

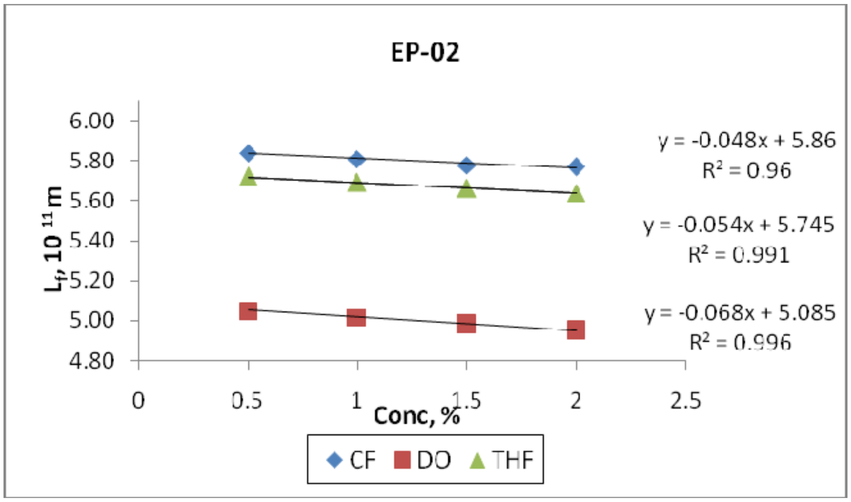


Fig. 4.22: The plots of L_f against C for EP-02 at 35°C.

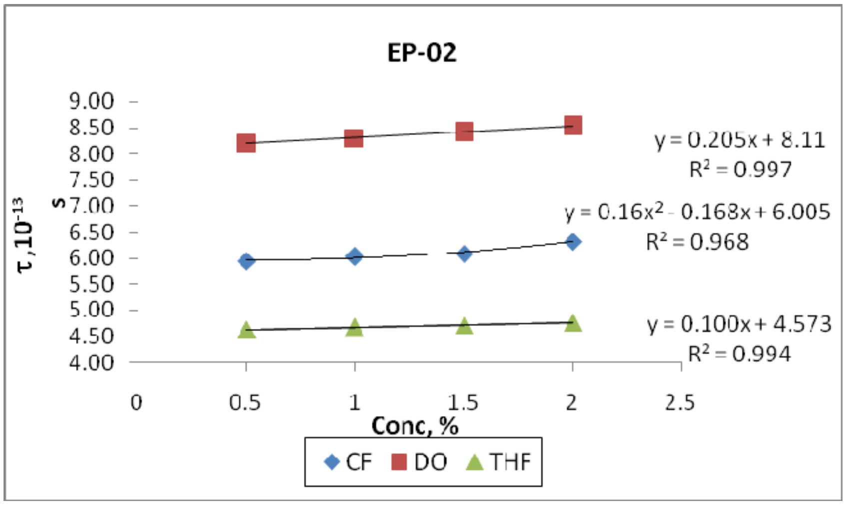


Fig. 4.23: The plots of τ against C for EP-02 at 35°C.

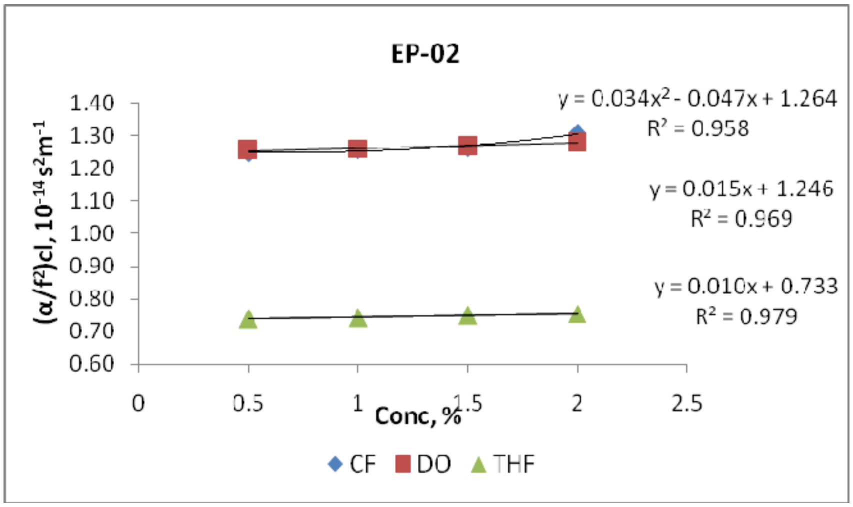


Fig. 4. 24: The plots of $(\alpha/f^2)_{cl}$, against C for EP-02 at 35°C.

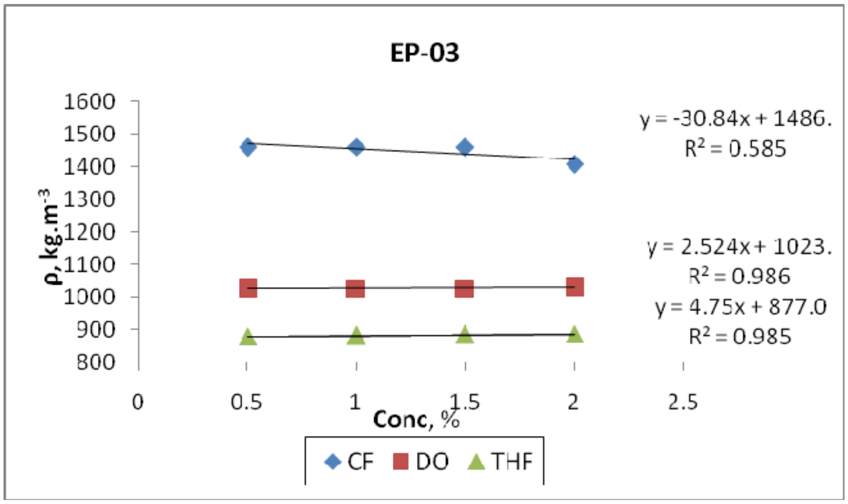


Fig. 4.25: The plots of ρ against C for EP-03 at 35°C.

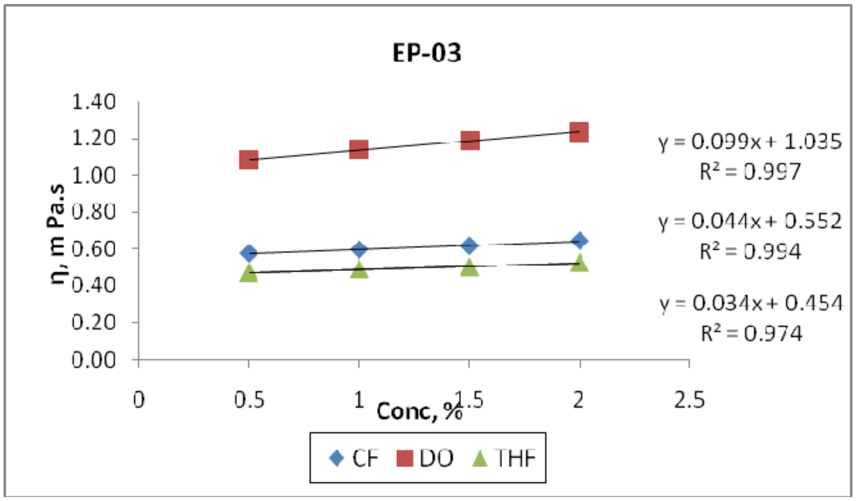


Fig. 4.26: The plots of η against C for EP-03 at 35°C.

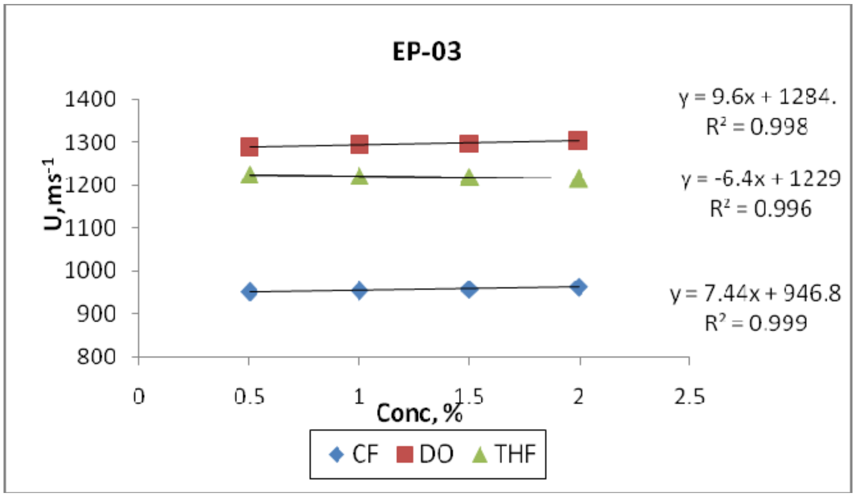


Fig. 4.27: The plots of U against C for EP-03 at 35°C.

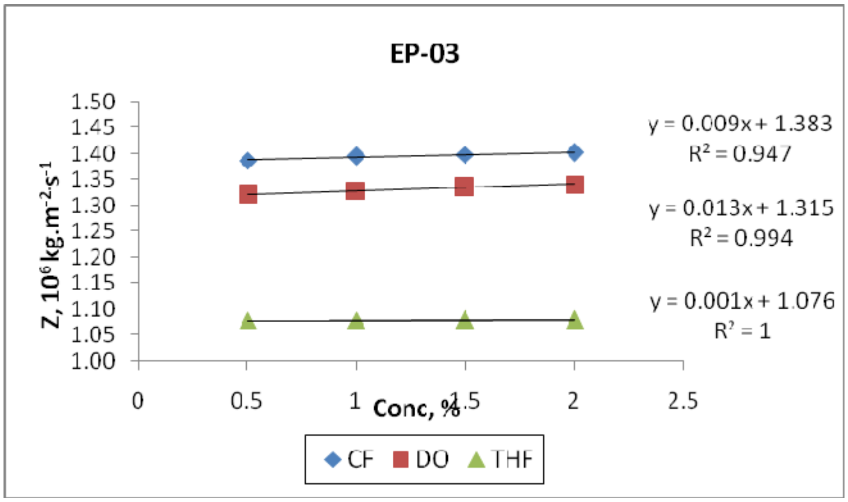


Fig. 4.28: The plots Z against C for EP-03 at 35°C.

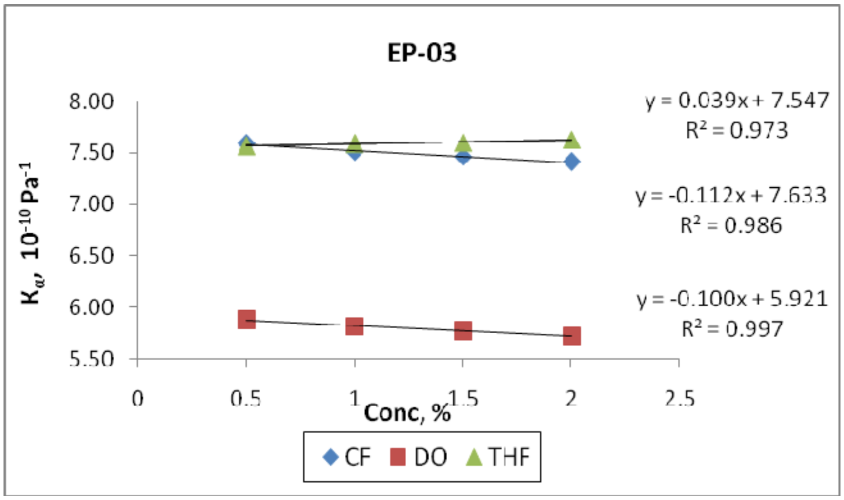


Fig. 4.29: The plots of κ_α against C for EP-03 at 35°C.

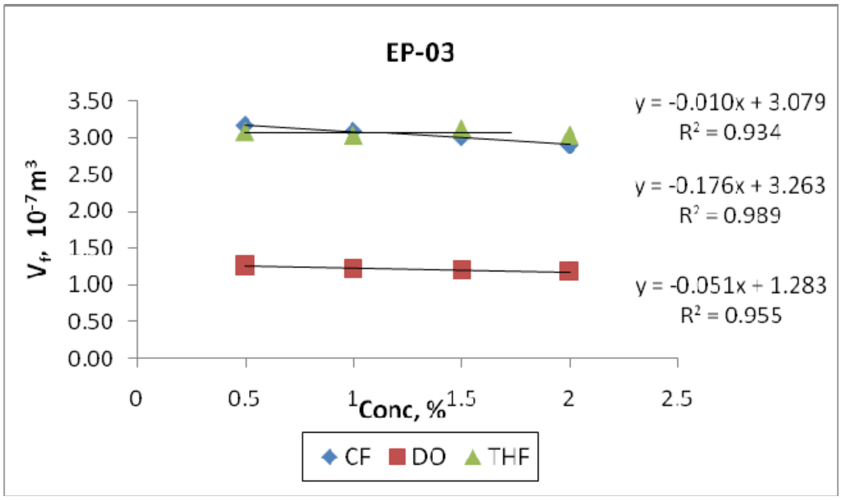


Fig. 4.30: The plots of V_f against C for EP-03 at 35°C.

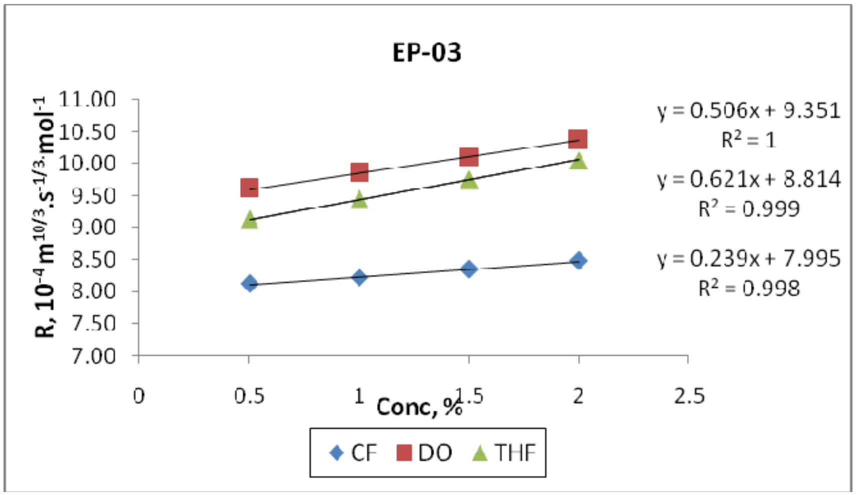


Fig. 4.31: The plots of R against C for EP-03 at 35°C.

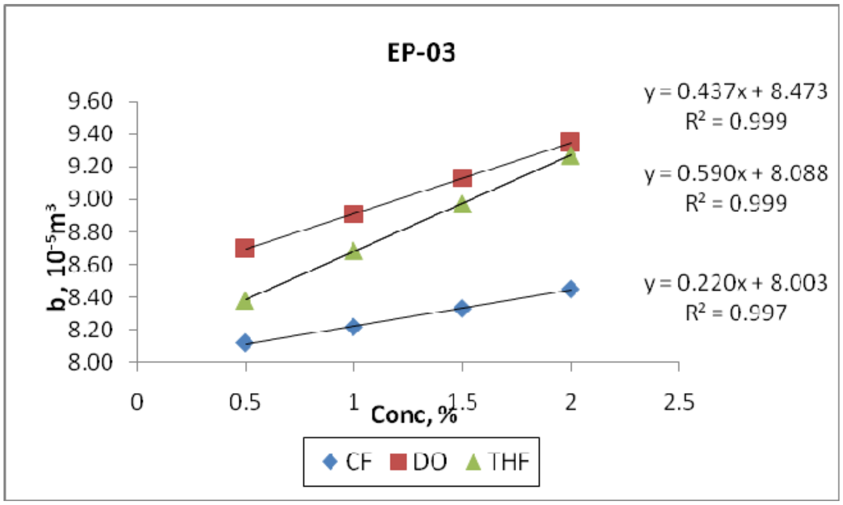


Fig. 4.32: The plots of b against C for EP-03 at 35°C.

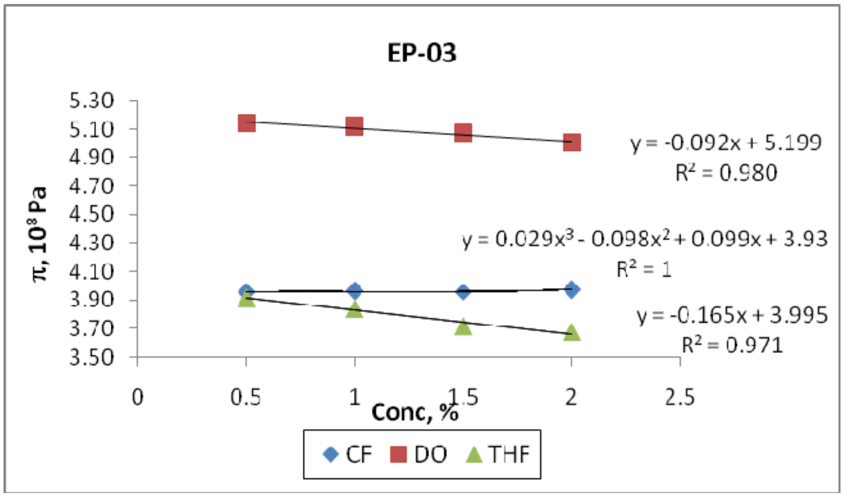


Fig. 4.33: The plots of π against C for EP-03 at 35°C.

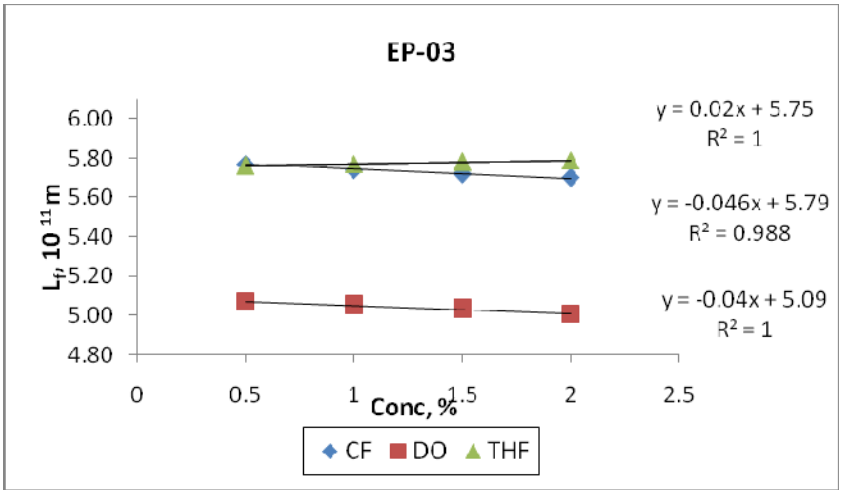


Fig. 4.34: The plots of L_f against C for EP-03 at 35°C.

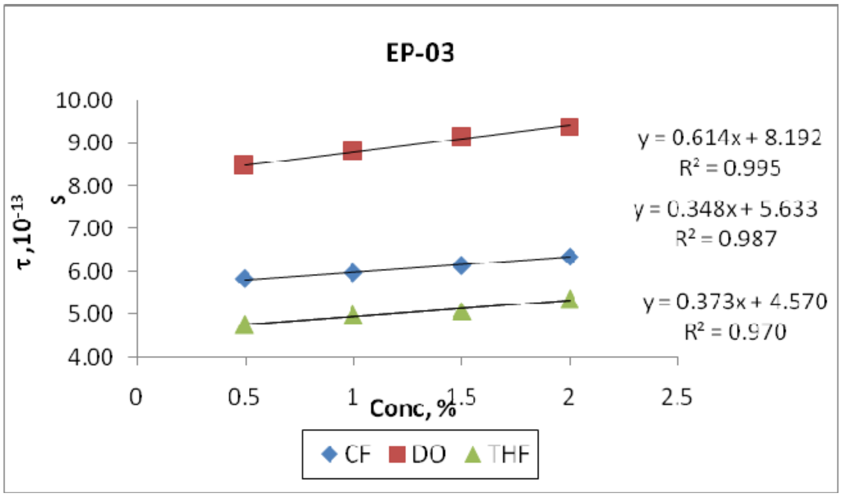


Fig. 4.35: The plots of τ against C for EP-03 at 35°C.

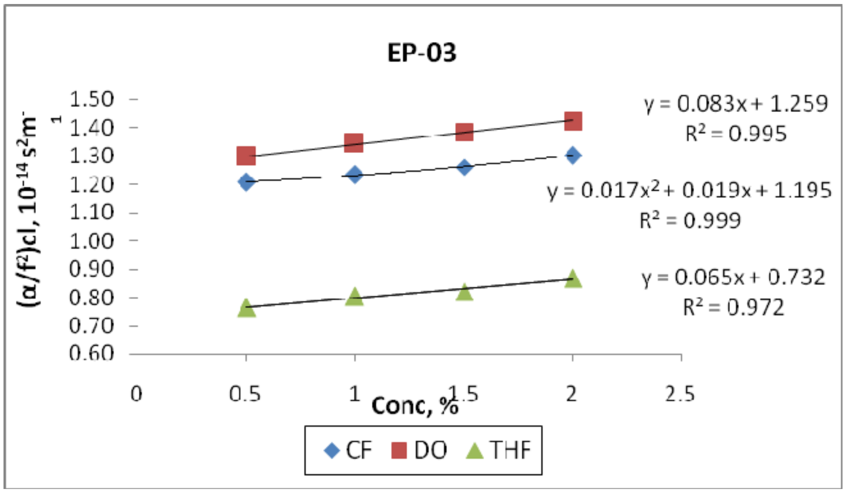


Fig. 4.36: The plots of $(\alpha/f^2)_{cl,}$ against C for EP-03 at 35°C.

CHAPTER-5

CHAPTER-5: SYNTHESIS AND CHARACTERIZATION OF POLYESTER POLYOLS; SYNTHESIS OF POLYURETHANE COMPOSITES AND THEIR PHYSICO-CHEMICAL CHARACTERIZATION

This chapter of the thesis describes the synthesis and characterization of polyester polyols, synthesis of polyurethane composites and their physico-chemical characterization. This part is further subdivided into five sections.

SECTION – 1: General Introduction
SECTION – 2: Synthesis of Polyester Polyols
SECTION – 3: Characterization of Polyester Polyols
SECTION – 4: Synthesis of Composites
SECTION – 5: Physico-Chemical Characterization of Composites

SECTION – 1: General Introduction

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

Composite - 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, aluminum, timber, etc. Now a days composite [1-4] 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 interior applications composites are used in the manufacturing of the shower enclosures, trays, bath, sinks, troughs and spas. Cast composites products are widely used for the production of vanity units, bench tops and basins. Owing to their good combination of properties [5-7], 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.

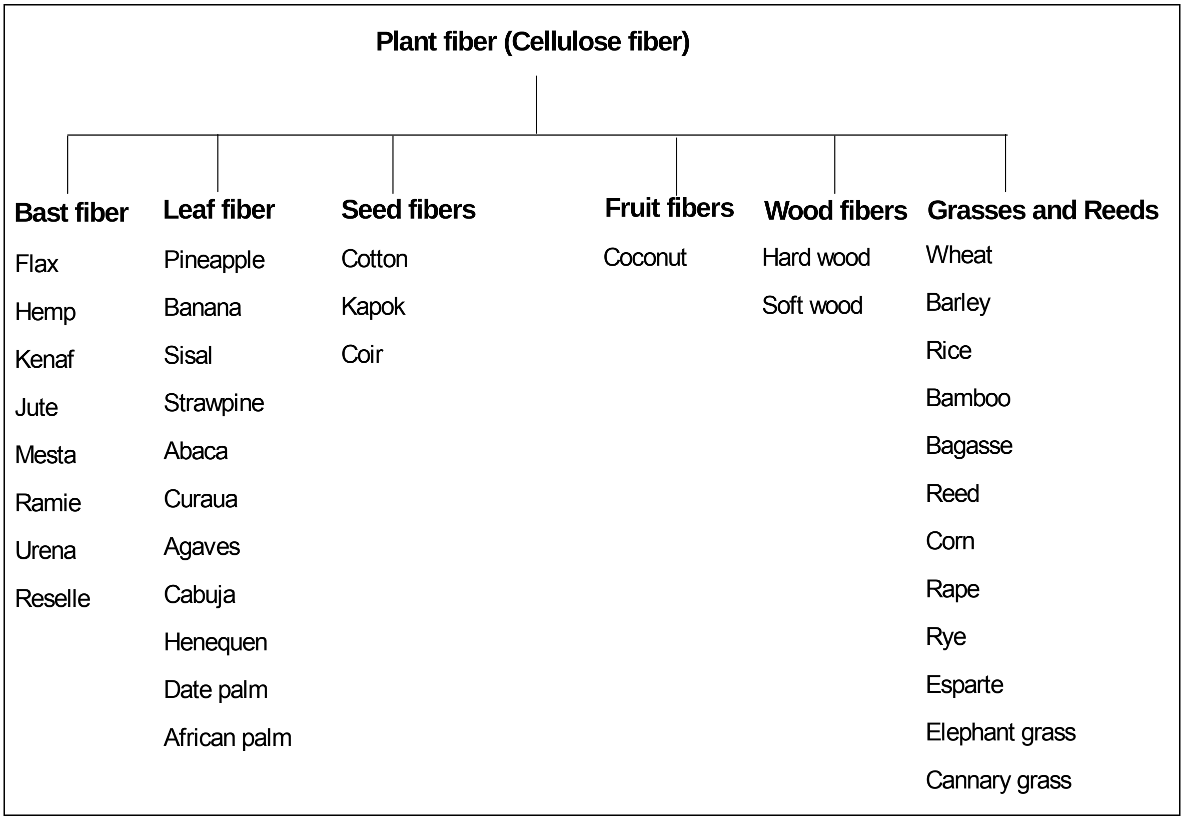
Reinforcing fibers

The base of the composite is fibers. It is often called reinforcing materials. A strength of composite is mainly depends upon the nature of reinforcing fibers [8-9]. 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.

1. M. S. Sobhy and M. T. Tammam, "The influence of fiber length and concentration on the physical properties of wheat husk fibers rubber composites", Inter. J. Polym. Sci., 2010.
2. Myrtha Karina, Holia Onggo and Anung Syampurwadi, "Physical and mechanical properties of natural fibers filled polypropylene composites and its recycle", J. Biological Sci., 7, 393-396, 2007.
3. Turgay Ozdemir and Fatih Mengeloglu, "Some properties of composite panels made from wood flour and recycled polyethylene", Int. J. Mol. Sci., 9, 2559–2569, 2008.
4. Byoung-Ho Lee, Hee-Soo Kim, Sena Lee, Hyun-Joong Kim , John R. Dorgan, "Bio-composites of kenaf fibers in polylactide: Role of improved interfacial adhesion in the carding process", Compo. Sci. and Techno., 69, 2573–2579, 2009.
5. Z. Yaakob, A. Min Min, M. N. Satheesh Kumar, S. S. K. Kamarudin, M. M. Hilmi and H. M. Khairul Zaman, "Oleic acid-based polyurethane and its biocomposites with oil palm trunk fiber dust", J. Thermoplas. Compo. Mater., 23, 447-458, 2010.
6. E. I. Maafi, Lan Tighzert and Fouad Malek,"Elaboration and characterization of composites of castor oil-based polyurethane and fibers from alfa stems", J. Appl. Polym. Sci., 118, 902-909, 2010.
7. U. Ude, A. K. Ariffin, K. Sopian, A. Arifin and C. H. Azhari, "The impact damage response of plain woven natural silk/epoxy laminated composite plates", Intern. J. Engg., Sci. and Techn., 2 , 128-140, 2010.
8. Zhi-Hong Donga, Li Zhanga, Yu-Bao Lia, Gang Zhouab and Soo-Whon Leeb, "A guided bone regeneration membrane composed of hydroxyapatite and polyurethane", J. Ceramic Proc. Research, 9, 478-481, 2008.
9. F. O. Aramide, I. O. Oladele, and D. O. Folorunso, "Evaluation of the effect of fiber volume fraction on the mechanical properties of a polymer matrix composite" Leonardo Electro. J. Practices and Technol., 14, 134-141, 2009

The fibers like glass, aramid, kevlar, carbon, spectra (PE-fibers) etc are popular for load bearing applications. The glass fiber is most popular due to low price and suitable for engineering applications. Where cost is no factor, one can use strong fibers like kevlar, aramid, carbon and spectra fibers. The other cheap option for composite application is natural fibers in its raw form, originated directly from nature. Natural fibers have been used as reinforcement in composite materials since the beginning of our civilization, when grass, straw and animal hair were used to reinforce mud bricks also known as adobe. Recent years have seen a growing interest in the development of natural fiber reinforced composites in terms of both industrial applications and fundamental research. The natural fibers are incorporated in to a matrix material such as thermosetting plastics, thermoplastics or rubber. The significant weight savings and the ease of low cost of the raw constituent materials make these composites an attractive alternative material to glass and carbon. The most commonly used natural fibers are shown in the Chart-1 and their properties are shown in Table-5.1



Plant fiber (Cellulose fiber)

Bast fiber	Leaf fiber	Seed fibers	Fruit fibers	Wood fibers	Grasses and Reeds
Flax	Pineapple	Cotton	Coconut	Hard wood	Wheat
Hemp	Banana	Kapok		Soft wood	Barley
Kenaf	Sisal	Coir			Rice
Jute	Strawpine				Bamboo
Mesta	Abaca				Bagasse
Ramie	Curaua				Reed
Urena	Agaves				Corn
Reselle	Cabuja				Rape
	Henequen				Rye
	Date palm				Esparte
	African palm				Elephant grass
					Cannary grass

Chart-1. Classification of natural fibers

Table-5.1: Properties of selected natural fibers

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

The advantages of natural fibers over the synthetic fibers are:

- Low cost
- Light weight, low density
- Easy availability
- Enhanced energy recovery and biodegradability
- High strength to weight ratio
- High specific strength
- Reduced tool wear and safer handling
- Reduced dermal and respiratory irritation
- Easy surface modification

Amongst all the natural fibers jute fibers have received considerable attention for its diversified used as a potential reinforcement in the production of the polymer composites [10-13].

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10. Suvangshu Dutta, Niranjan Karak, and Sasidhar Baruah,” Jute-fiber-reinforced polyurethane green composites based on mesua ferrea L.seed oil”, J. Appl.Polym.Sci., 115, 843-850, 2010.
11. R. G. Schmidt and C. E. Frazier, “Network characterization of phenol-formaldehyde thermosetting wood adhesive”, Adhesion and Adhesives, 18, 139 -146, 1998.
12. J. Gassan and V. S. Gutowski, “Effects of corona discharge and UV treatment on the properties of jute-fibre epoxy composites”, Compos. Sci. and Technol. 60, 2857-2863, 2000.
13. M. S. Sreekala, M. G. Kumaran, S. Joseph and M. Jacob, “Oil palm fiber reinforced phenol formaldehyde composites: Influence of fibre surface modifications on the mechanical performance”, J. Appl. Compos. Mater., 7, 295-329, 2000.

Jute is an attractive natural fiber for the reinforcement because of its low cost, renewable nature and much lower energy requirement for processing. Jute fiber contains high proportion of stiff natural cellulose. Rated fibers of jute have three principle chemical constituents, namely α- cellulose, hemicellulose and lignin. In addition, they contain minor constituents such as fats and waxes, minerals, nitrogenous matter and trace of pigments like β-carotene and xanthophylls. Several studies of fiber composition and morphology have found that cellulose content and micro fibril angle tend to control the mechanical properties of the cellulosic fibers. The specific mechanical properties of the composites are comparable to those of the glass fiber reinforced plastics (GRP). Comparison of mechanical properties of E-glass with jute is listed in Table-5.2. Various items such as school buildings, food grain silos, wood substitutes, low cost housing units, roofing, pipes [14], etc. have been fabricated from the jute fiber reinforced composites.

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14. M. A. Semsarzadesh, “Fiber matrix interactions in jute reinforced polyester resin”, Polym. Compos., 7, 23-25, 1986.

Table-5.2: Mechanical properties of E-Glass and Jute

Properties	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 (GN/m^2)	28.8	42.7

Hybrid composites are the materials made by combining two or more different types of fibers in a common matrix. They offer a range of properties that cannot be obtained with a single kind of reinforcement. By careful selection of reinforcing fibers, the material cost can be reduced substantially [15].

Low cost hybrid composites are produced by the use of biomass or agro waste in combination with jute. In India rice husk (RH) and wheat husk (WH) are the biomass materials, which are byproducts from the crops. Considerable work has been carried out on the utilization of biomass for particle board, medium density board, pulp and composites [16]. The incentives of utilizing agro waste in the fabrication of composites are greater deformability, low density, less abrasiveness to equipments, low cost, etc.

Matrices

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

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15. S. V. Joshi, L. T. Drzal, A. K. Mohanty and S. Arora, “Are natural fiber composites environmentally superior to glass fiber reinforced composites?”, Compos. Part-A, 35, 371-376, 2004.
16. A. Khalil, H. Ismail, M. N. Ahmed, A. Ariffrin and K. Hassan, “The effect of various anhydride modifications on mechanical properties and water absorption of oil palm empty fruit bunches reinforced polyester composites” Polym. Int., 50, 396-413, 2001.

Unsaturated polyester resin is being used in combination with glass woven cloth for composite fabrication, but restricts their use due to high shrinkage when cured, more moisture absorption, lower impact strength and low chemical resistance.

Another specialized matrix system is polyurethane, which possesses three dimensional network structures. The unique feature of polyurethane is that it can be tailor made to fit the application requires. Today, polyurethanes are finding a growing interest for the applications as composites virtually in all the sectors especially in the automotive market because of their flexibility, excellent adhesion, high cohesive strength, excellent hardness, impact resistance, high scratch and abrasion resistance and excellent chemical resistance [17].

Another low cost system is vinyl ester resin derived from esterification of diepoxide with acrylic and methacrylic acids results in vinyl ester epoxy resin that is curable with vinyl monomers like styrene and divinyl benzene by free radical mechanism. Such a low cost system is advantageous over unsaturated polyester resin due to low shrinkage, low moisture absorption and good chemical resistance.

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

Mechanical properties of FRP v/s other conventional material are shown in Table- 5.3.

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17. J. P. L. Dwanisa, A. K. Mohanty, M. Misra, M. Kazemizadeh and L. T. Drzal, “Novel soy oil based polyurethane composites: Fabrication and dynamic mechanical properties evolution”, J. Mater. Sci., 39, 1887-1890, 2004.

Table-5.3: Mechanical properties of FRP Vs other conventional 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
Izod impact strength (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. (^{0}C)	120	170	55	600	600	160

SECTION – 2: Synthesis of Polyester Polyols

Surplus vegetable oils represent attractive renewable resources for the production of useful chemicals. Fatty acids derived from vegetable oils and they are value added materials for synthesizing polyols. Some commonly used fatty acids are shown in Table-5.4.

Syntheses of epoxy polyester polyols of ER-1/ER-3 with some unsaturated fatty acids

To a 250ml three necked round bottomed flask, equipped with a condenser, thermometer and a mechanical stirrer, were placed into a thermostat bath and added 0.001mol ER-1/ER-3, 0.002mol fatty acids and 50ml 1,4-dioxane containing 2ml triethylamine as a catalyst. The reaction mass was brought to reflux and stirrered 3-3.5h so that desired acid values were achieved (<30 mg KOH/g of resin). Solid resins were isolated from cold water, filtered, washed well with water and dried in an oven at 50°C. The yields were 83-86%. Epoxy polyester polyols are soluble in common organic solvents like chloroform, THF, DMF, DMSO, etc.

Table-5.4: Some commonly used fatty acids

Fatty acid	Nature	IUPAC name	Formula	Molecular weight
Oleic acid	mono unsaturated, omega-9 fatty acid	cis, 9-octadecenoic acid	$C_{18}H_{34}O_2$	282.96
Recinoleic acid	unsaturated, omega-9 fatty acid	12-Hydroxy 9-cis octadecenoic acid	$C_{18}H_{34}O_3$	298.46
Linoleic acid	poly unsaturated, omega-9 fatty acid	9,12,15 – octadecatrienoic acid	$C_{18}H_{32}O_2$	280.45

Table-5.5: Different epoxy polyester polyols

Name	Epoxy Resin	Unsaturated fatty acids
UPER-1	ER-1	Recinoleic acid
UPER-2	ER-1	Oleic acid
UPER-3	ER-1	Linoleic acid
UPER-4	ER-3	Recinoleic acid
UPER-5	ER-3	Oleic acid
UPER-6	ER-3	Linoleic acid

SECTION – 3: Characterization of Epoxy Polyester Polyols

[A] Acid value

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

Acid values of epoxy polyester polyols were determined by ASTM method and are reported in Table-5.6.

Epoxy polyester was exactly weighed (0.5 to 1g) in a small capsule and placed carefully into a 250 ml RBF and to it 50 ml of acetone was added. The flask was swirled for some time and heated gently for some time to dissolve sample completely. The solution was cooled and titrated with standard 0.1 N methanolic KOH by using phenolphthalein as an indicator. Similar procedure was repeated for blank titration under similar condition. The average of three measurements was used to determine the acid value according to following relationship [18].

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

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

Similarly acid values of the other epoxy polyesters were determined and are summarized in Table-5.6.

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18. ASTM-D-1639-Rev. 90, “Standard test method for acid value of organic coating material”

Table-5.6: Experimental details, acid and hydroxyl values of epoxy polyesters

Polyols	Weight in gm		Time, h	Acid value, mg KOH/g	Hydroxyl value, Mg KOH/g
	Epoxy resin, g	Fatty acid, g			
UPER-1	12.2	5.86	3.5	17	1117
UPER-2	12.2	5.66	3.5	21	1098
UPER-3	12.2	5.61	3.5	16	1115
UPER-4	10.60	5.86	3	8	1187
UPER-5	10.60	5.66	3	11	1143
UPER-6	10.60	5.61	3.5	11	1196

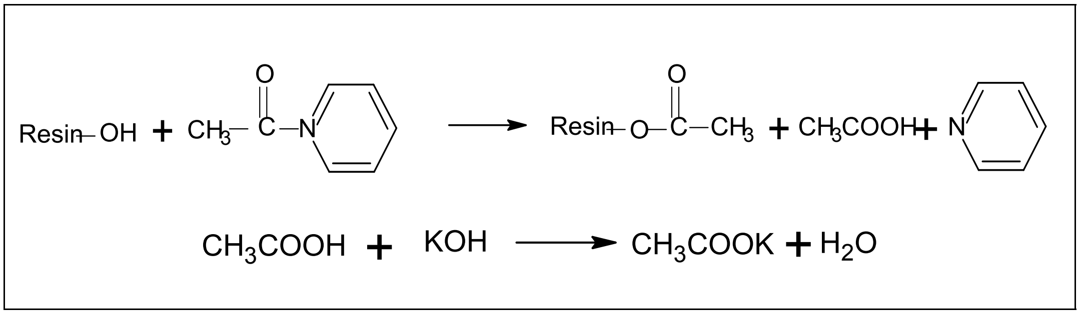
[B] Hydroxyl value

Hydroxyl value is a measure of free hydroxyl groups present in the polyester polyols (epoxy esters) and it is expressed as number of milligrams of potassium hydroxide equivalent to the quantity of acetic acid that binds with 1 g of hydroxyl containing substances.

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

Hydroxyl values of epoxy polysters are summarized in Table-5.6. Low acid values and high hydroxyl values confirmed formation of epoxy polyesters.

General reaction scheme as under:



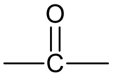
$$CH_3COOH + KOH \longrightarrow CH_3COOK + H_2O$$

Epoxy polyester was exactly weighed (1- 2 g) in to a small capsule and placed carefully in to a 250 ml RBF and to it 20 ml of acetylating mixture (1 volume of acetic anhydride and 3 volume of pyridine) was added. The flask was swirled for some time and heated gently to dissolve sample completely and then refluxed for 30 to 50 min., cooled to room temperature and 50 ml cold water was added slowly down to the condenser. Titrated the free acetic acid with standard 1N NaOH using phenolphthalein (10-15 drops) as an indicator. The procedure was repeated for blank titration under similar condition. The average of three measurements was used to determine the hydroxyl value of given sample according to following relationship [19].

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

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

[C] IR Spectra

IR (KBr pellets) of epoxy polyesters were scanned over the frequency range from 4000-400 cm^{-1} and are presented in Figs.-5.1 to 5.6. Characteristic absorption frequencies of epoxy polyesters are 3441-3420 –OH$_{str}$., 1740-1716  $-\overset{O}{\overset{\|}{C}}-$ $_{str}$., and 1253-1246 -C-O-C$_{str}$., besides normal modes of vibrations of alicyclic, aliphatic and aromatic groups confirming formation of epoxy polyesters.

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19. ASTM–D 1957-86 (2001), “Standard test method for hydroxyl value of fatty oils and acids”.

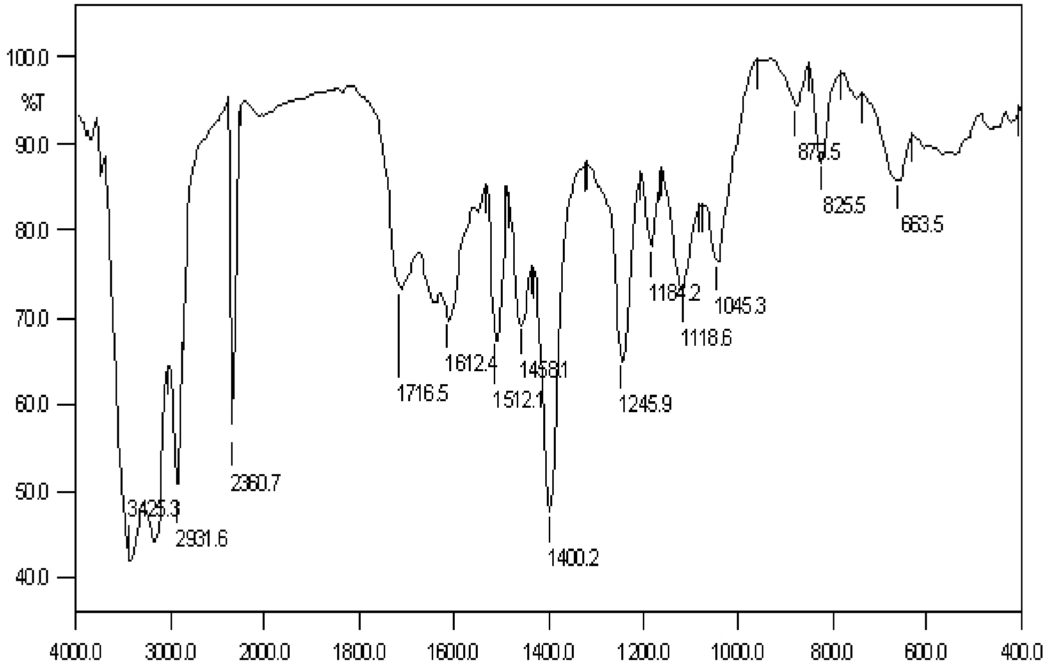


Fig. 5.1: IR spectrum of UPER-1

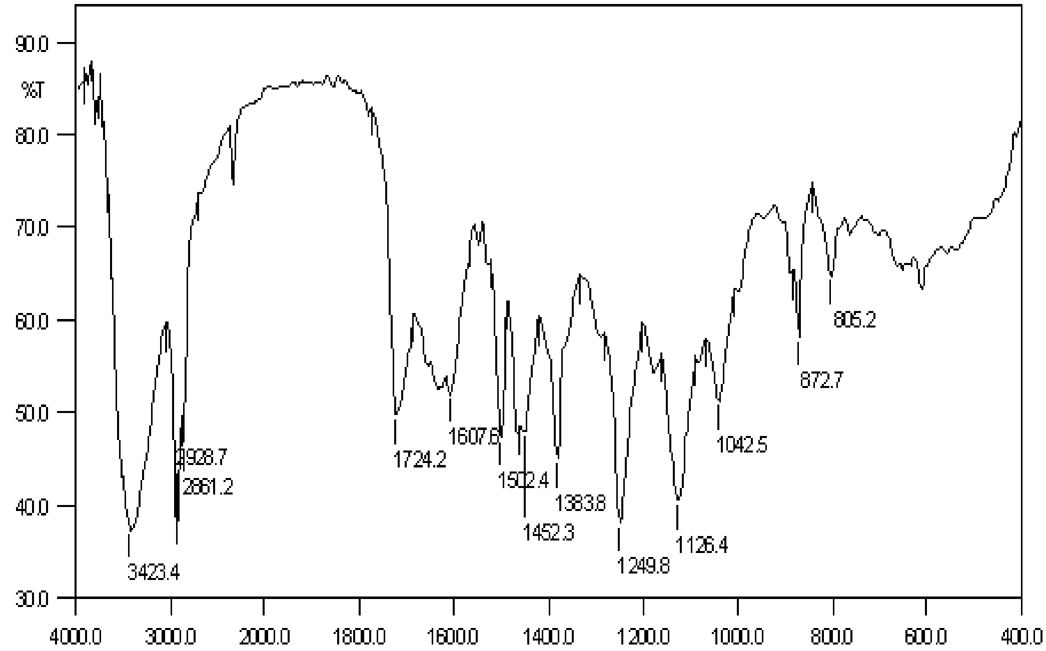


Fig. 5.2: IR spectrum of UPER-2

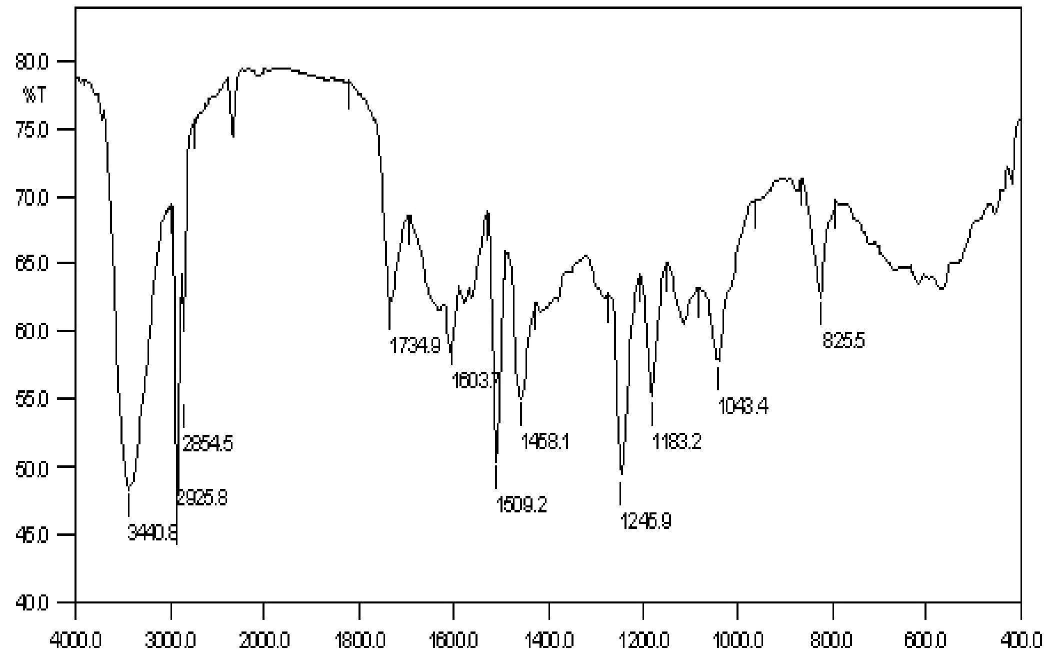


Fig. 5.3: IR spectrum of UPER-3

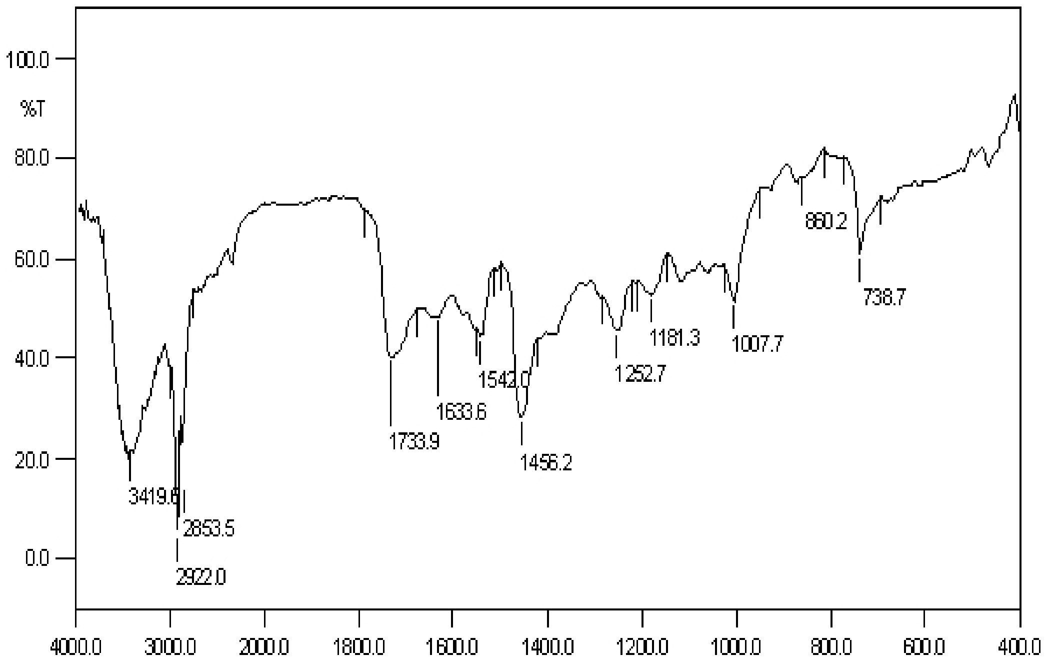


Fig. 5.4: IR spectrum of UPER-4

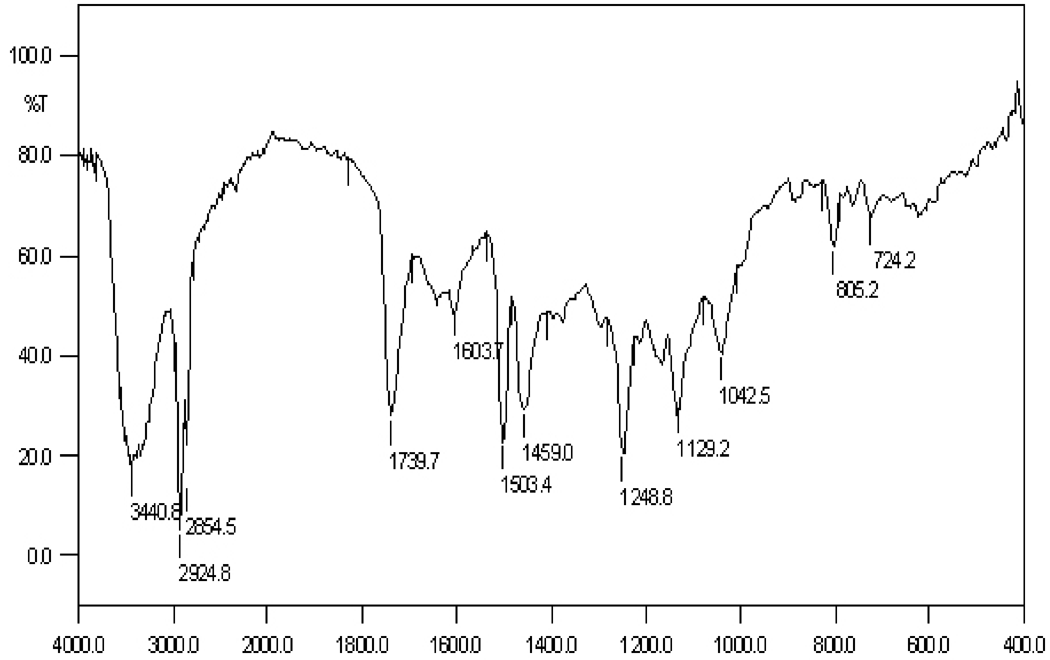


Fig. 5.5: IR spectrum of UPER-5

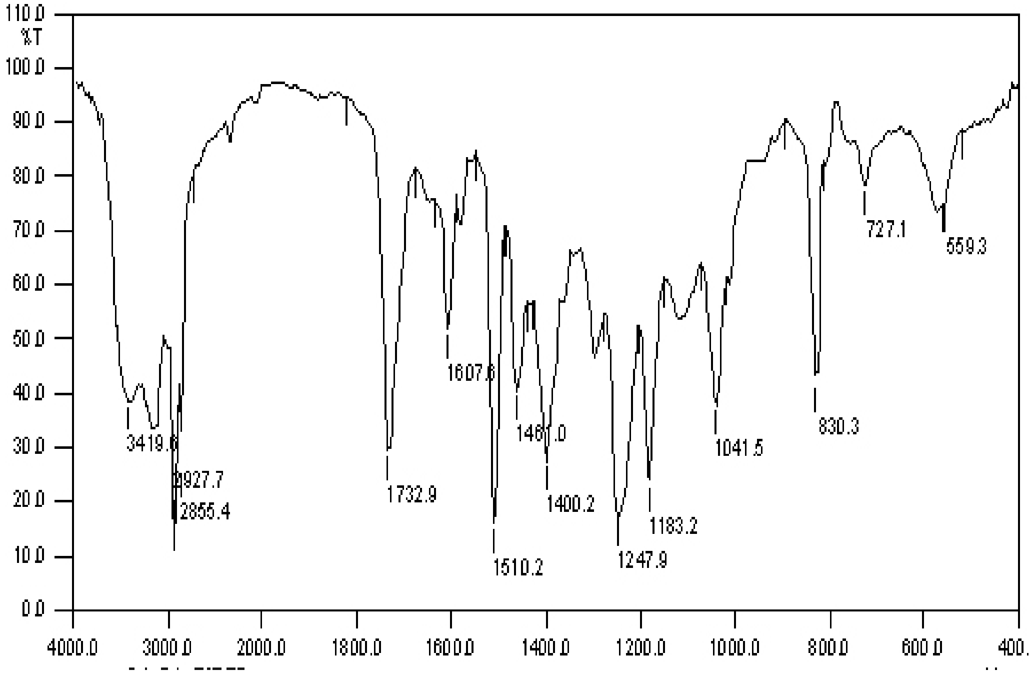
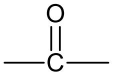


Fig. 5.6: IR spectrum of UPER-6

Table-5.7: The characteristic IR absorption frequencies of UPER-1-1 to UPER-6

Epoxy polyesters	Absorption frequencies, cm^{-1}			
	-OH $_{str}$.	$-CH_2$ $_{asym.\ str}$.	 $-\overset{O}{\overset{\|}{C}}-$ Str.	-C-O-C $_{Str.}$
(expected)	3550-3400	2930-2920	1740	1260-1200
UPER-1	3425.3	2931.6	1716.5	1245.9
UPER-2	3423.4	2928	1724.2	1249.8
UPER-3	3440.8	2925.8	1734.9	1245.9
UPER-4	3419.6	2922.0	1733.9	1252.7
UPER-5	3440.8	2924.8	1739.7	1248.8
UPER-6	3419.6	2927.7	1732.9	1247.9

SECTION – 4: Synthesis of Composites.

This section of the thesis describes the fabrication of polyurethane-jute composites. Woven jute fibers (Brown jute, Corchous Capsularis) were purchased from local market. TDI (Toluene-2,4-diisocynate : Toluene-2,6-diisocynate; 80:20) was supplied by Gujarat Narmada Valley Fertilizers Limited, Bharuch and used as received.

In order to prepare jute-polyurethane composites, polyurethane matrix material was 60% of woven jute fabric. Thus to a 250ml beaker UPER-1 / UPER-4 (39 / 38.3 g) was dissolve in 75ml chloroform. To this solution (11.7/11.5g) toluene diisocyanate in 25ml chloroform was added dropwise with stirring at room temperature for 5min.

The resultant prepolyurethane solution was applied to 15cm x 15cm jute fabric with the help of smooth brush by hand lay up technique. The prepregs were allowed to dry in the sunlight for about 5 min. Eight such prepregs were stacked one over the other and pressed between the two preheated stainless steel plates under the hydraulic pressure of 30.4MPa at room temperature / 150°C for 8h under heating and 4h at room temperature using silicone spray as a mold releasing agent. Hereafter composites are designated as Compo-A and Compo-B respectively.

SECTION–5: Physico-Chemical Characterization of Composites

[A] Thermal analysis

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 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 evolution 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 [20]. 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.

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

Suresh et al. [21] 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 [22]. 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 and aliphatic amines were used as curatives for epoxy and methyl isobutyl ketone peroxide 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.

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21. 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.
22. 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.

DSC and TG of thermograms of composites were scanned respectively on a Shimadzu DSC-60 and Perkin Elmer TGA Model No. Pyris-1 at 10°C/min. heating rate in an N_2 atmosphere.

DSC thermograms of Compo-A and Compo-B are presented in Figs. 5.12 and 5.13, respectively. Endotherm transition at 75°C (Compo-A) and 93°C (Compo-B) is due to glass transition and it is further confirmed by weight loss in corresponding TG curve (Fig.-5.14).

From Fig. 5.14 and Table-5.8, it is evident that Compo-A followed two steps degradation, while Compo-B followed three steps degradation. Compo-A and Compo-B are thermally stable upto 210 and 245°C respectively. Energy of activation is from 82 to 160 $KJ.mol^{-1}$. Compo-A and Compo-B having 3.1 and 21.1 % residue at 550°C which proves that Compo-B has more complex structure. Degradation reaction is a complex reaction and involves a variety of reaction such as branching, rearrangement, crosslinking, etc. Urethane, ether and azomethine linkages are weak points in the epoxy polyester urethanes. Selective cleavage takes place, such weak linkages with evolution of carbon dioxide and ammonia with the formation of free radicals. These radicals further undergo recombination and degrade at elevated temperatures.

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.

$$\Delta \ln dW/dt = n \, \Delta \ln W - (E_a/R) \, \Delta (1/T) \quad .....5.1$$

$$A = E_a\beta / RT^2 \; e^{E_a/RT} \quad .....5.2$$

$$\Delta S^* = R \ln (Ah/kT) \quad .....5.3$$

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. The detail calculations according to Eqn 5.3

Detail calculation for Compo-A and Compo-B according to Anderson-Freeman method are mentioned in Table- 5.10 to 5.14. The plots of Δ lnW against Δ ln dW/dt are shown in Fig. 5.7 to 5.11.

Table-5.8: TG data of Compo-A and Compo-B

Parameters	Composite name	
	Compo-A	Compo-B
IDT,^{o}C	210 355	245 345 480
Decomposition range, ^{0}C	210-320 355-490	245-310 345-480 480-600
T_{max}, ^{0}C	280 435	275 435 545
% Wt.loss	23.4 32.3	14.9 19.8 25.2
% Residue at 550^{0}C	3.1	21.1
E_a, kJ mol^{-1}	131.4 158.8	107.3 82.3 159.6
n	1.5 2.2	0.92 1.0 1.3
A,s^{-1}	8.86×10^{-6} 6.52×10^{-6}	7.33×10^{-6} 3.34×10^{-6} 4.89×10^{-6}
ΔS^* JK^{-1} mol^{-1}	-347 -351	-348 -358 -355
R^{2}	0.964 0.959	0.971 0.980 0.970

Table-5.9: DSC data of Compo-A and Compo-B

Name	Type	Peak temp, ° C	Heat of Transition, ΔH, J/g^{-1}	ΔH, kJmol^{-1}
Compo-A	Endothermic	75	-0.45	-0.14×10^{-3}
Compo-B	Endothermic	93	-6.61	-2.06×10^{-3}

Table-5.10: Detail calculations for Compo-A according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	∆lnW	∆lndW/dt
Step -01							
1.69	37.71	1.123	0.239	-1.430	0.116	-0.822	-0.235
1.70	37.41	1.421	0.544	-0.609	0.351	-0.623	-0.195
1.71	36.94	1.728	1.015	0.015	0.547	-0.473	-0.163
1.72	36.32	2.033	1.629	0.488	0.710	-0.373	-0.135
1.73	35.59	2.328	2.365	0.861	0.845	-0.303	-0.112
1.74	34.75	2.604	3.202	1.164	0.957	-0.253	-0.092
1.75	33.83	2.854	4.122	1.416	1.049	-0.214	-0.074
1.76	32.84	3.073	5.106	1.630	1.123	-0.184	-0.058
1.77	31.81	3.255	6.137	1.814	1.180	-0.160	-0.043
1.78	30.75	3.398	7.200	1.974	1.223	-0.140	-0.029
1.79	29.67	3.497	8.280	2.114	1.252	-0.123	-0.016
1.80	28.59	3.552	9.364	2.237	1.267	-0.109	-0.003
1.81	27.51	3.561	10.439	2.346	1.270	-0.096	0.010
1.82	26.46	3.526	11.494	2.442	1.260	-0.085	0.023
1.83	25.43	3.447	12.519	2.527	1.238	-0.076	0.035
1.84	24.45	3.328	13.504	2.603	1.202	-0.067	0.048
1.85	23.51	3.171	14.443	2.670	1.154	-0.060	0.061
1.86	22.62	2.983	15.329	2.730	1.093	-0.053	0.075
1.87	21.79	2.768	16.155	2.782	1.018	-0.046	0.089
1.88	21.03	2.533	16.918	2.828	0.929	-0.040	0.102
1.89	20.34	2.286	17.615	2.869	0.827	-0.035	0.115
1.90	19.71	2.037	18.243	2.904	0.712	-0.030	0.126
1.91	19.15	1.795	18.801	2.934	0.585	-0.026	0.133
1.92	18.66	1.571	19.290	2.960	0.452	-0.022	0.131
1.93	18.24	1.378	19.711	2.981	0.321	-0.018	0.115
1.94	17.88	1.229	20.066	2.999	0.206	-0.015	0.077
1.95	17.59	1.138	20.359	3.014	0.129	-0.012	0.016
1.96	17.36	1.120	20.595	3.025	0.113	-0.009	-0.062
1.97	17.17	1.192	20.779	3.034	0.175	3.034	0.175

Table-5.11: Detail calculations for Compo-A according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
Step -02							
1.32	72.35	2.736	1.291	0.255	1.007	-0.793	0.000
1.33	70.79	2.737	2.854	1.049	1.007	-0.457	-0.016
1.34	69.13	2.780	4.507	1.506	1.023	-0.323	-0.026
1.35	67.42	2.853	6.224	1.828	1.048	-0.249	-0.030
1.36	65.66	2.940	7.980	2.077	1.078	-0.201	-0.030
1.37	63.89	3.029	9.753	2.278	1.108	-0.167	-0.026
1.38	62.12	3.110	11.523	2.444	1.134	-0.141	-0.020
1.39	60.37	3.173	13.271	2.586	1.155	-0.121	-0.012
1.4	58.66	3.213	14.981	2.707	1.167	-0.105	-0.003
1.41	57.00	3.222	16.637	2.812	1.170	-0.091	0.008
1.42	55.41	3.197	18.228	2.903	1.162	-0.080	0.019
1.43	53.90	3.135	19.742	2.983	1.143	-0.070	0.032
1.44	52.47	3.037	21.170	3.053	1.111	-0.061	0.045
1.45	51.13	2.902	22.506	3.114	1.065	-0.054	0.060
1.46	49.90	2.733	23.743	3.167	1.005	-0.047	0.075
1.47	48.76	2.534	24.880	3.214	0.930	-0.041	0.092
1.48	47.73	2.312	25.914	3.255	0.838	-0.035	0.109
1.49	46.79	2.073	26.846	3.290	0.729	-0.031	0.126
1.5	45.96	1.828	27.678	3.321	0.603	-0.026	0.142
1.51	45.22	1.585	28.416	3.347	0.461	-0.023	0.154
1.52	44.58	1.358	29.065	3.370	0.306	-0.019	0.156
1.53	44.01	1.162	29.633	3.389	0.150	-0.017	0.140
1.54	43.51	1.010	30.131	3.406	0.010	-0.014	0.092
1.55	43.07	0.922	30.570	3.420	-0.081	-0.013	0.008
1.56	42.67	0.915	30.965	3.433	-0.089	-0.012	-0.099
1.57	42.31	1.010	31.331	3.445	0.010	-0.011	-0.197
1.58	41.95	1.230	31.687	3.456	0.207	3.456	0.207

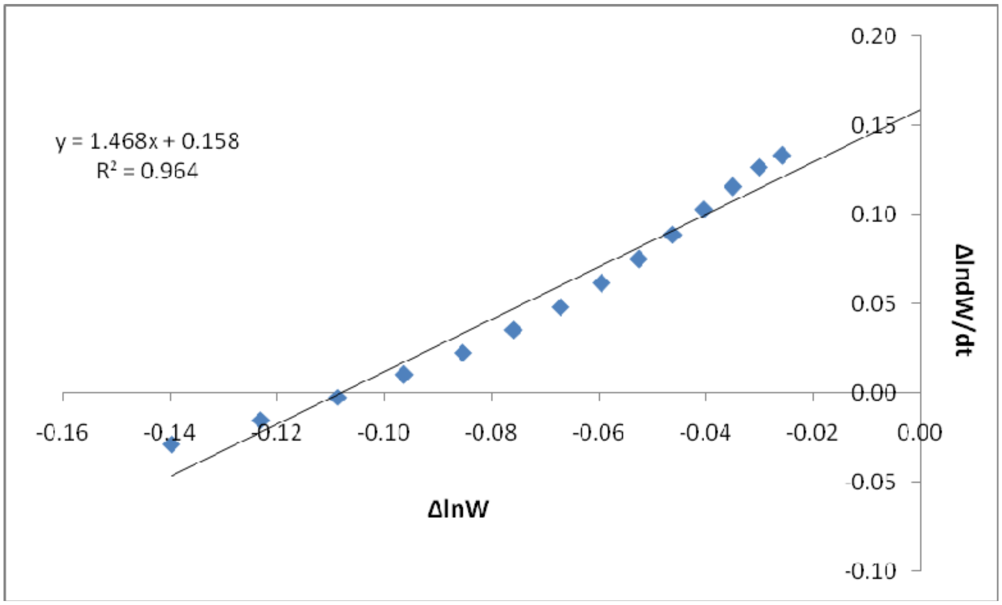

Fig.5.7: The Freeman-Anderson plots of Compo-A (step-1)

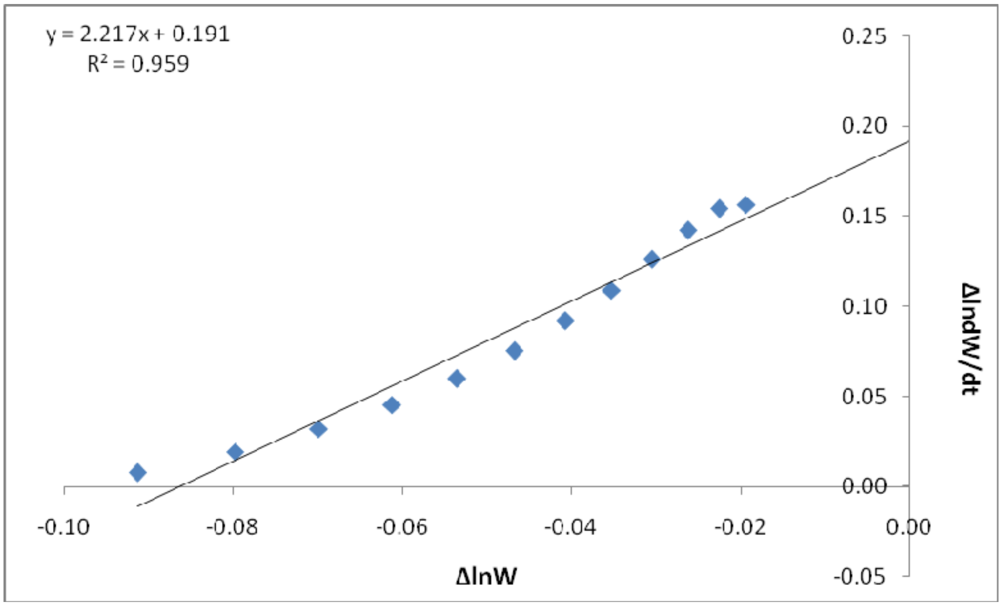

Fig.5.8: The Freeman-Anderson plots of Compo-A (step-2)

Table-5.12: Detail calculations for Compo-B according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
Step -01							
1.74	40.37	1.789	1.49	0.400	0.582	-0.206	-0.104
1.75	40.03	1.986	1.83	0.606	0.686	-0.265	-0.107
1.76	39.47	2.209	2.39	0.871	0.793	-0.264	-0.097
1.77	38.75	2.435	3.11	1.134	0.890	-0.239	-0.082
1.78	37.91	2.645	3.95	1.373	0.973	-0.209	-0.065
1.79	36.99	2.821	4.87	1.583	1.037	-0.180	-0.045
1.80	36.03	2.952	5.83	1.763	1.083	-0.155	-0.026
1.81	35.06	3.030	6.80	1.918	1.108	-0.132	-0.006
1.82	34.09	3.048	7.77	2.050	1.115	-0.113	0.014
1.83	33.17	3.007	8.69	2.163	1.101	-0.096	0.033
1.84	32.29	2.909	9.57	2.259	1.068	-0.082	0.052
1.85	31.47	2.761	10.39	2.341	1.016	-0.069	0.071
1.86	30.73	2.572	11.13	2.410	0.945	-0.059	0.088
1.87	30.05	2.356	11.81	2.469	0.857	-0.050	0.100
1.88	29.44	2.132	12.42	2.519	0.757	-0.043	0.105
1.89	28.89	1.920	12.97	2.563	0.652	-0.038	0.095
1.90	28.39	1.746	13.47	2.601	0.557	-0.035	0.064
1.91	27.91	1.638	13.95	2.635	0.494	-0.033	0.005
1.92	27.44	1.630	14.42	2.668	0.488	-0.033	-0.075
1.93	26.95	1.757	14.91	2.702	0.563	2.702	0.563

Table-5.13: Detail calculations for Compo-B according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
Step -02							
1.34	63.92	1.561	0.956	-0.044	0.445	-0.735	-0.041
1.35	62.89	1.626	1.995	0.690	0.486	-0.413	-0.035
1.36	61.87	1.684	3.014	1.103	0.521	-0.286	-0.029
1.37	60.87	1.734	4.014	1.390	0.550	-0.218	-0.023
1.38	59.89	1.774	4.993	1.608	0.573	-0.175	-0.017
1.39	58.93	1.804	5.950	1.783	0.590	-0.146	-0.011
1.40	58.00	1.824	6.884	1.929	0.601	-0.124	-0.005
1.41	57.09	1.832	7.794	2.053	0.606	-0.108	0.001
1.42	56.20	1.830	8.680	2.161	0.604	-0.094	0.007
1.43	55.34	1.817	9.539	2.255	0.597	-0.084	0.013
1.44	54.51	1.792	10.372	2.339	0.584	-0.075	0.020
1.45	53.70	1.758	11.177	2.414	0.564	-0.067	0.026
1.46	52.93	1.713	11.953	2.481	0.538	-0.061	0.032
1.47	52.18	1.659	12.700	2.542	0.506	-0.055	0.038
1.48	51.46	1.597	13.416	2.596	0.468	-0.050	0.044
1.49	50.78	1.527	14.101	2.646	0.424	-0.045	0.050
1.50	50.13	1.452	14.754	2.691	0.373	-0.041	0.056
1.51	49.51	1.373	15.373	2.733	0.317	-0.037	0.062
1.52	48.92	1.290	15.959	2.770	0.255	-0.034	0.067
1.53	48.37	1.207	16.510	2.804	0.188	-0.031	0.071
1.54	47.85	1.125	17.025	2.835	0.118	-0.028	0.073
1.55	47.38	1.046	17.505	2.862	0.045	-0.025	0.073
1.56	46.93	0.973	17.947	2.887	-0.028	-0.022	0.069
1.57	46.53	0.908	18.351	2.910	-0.097	-0.020	0.061
1.58	46.16	0.854	18.717	2.929	-0.158	-0.017	0.048
1.59	45.84	0.814	19.044	2.947	-0.206	-0.015	0.029

Table-5.14: Detail calculations for Compo-B according to Anderson-Freeman method

1/T, 10^3	% wt Loss	dW/dt	Active Wt.	lnW	ln(dW/dt)	ΔlnW	ΔlndW/dt
Step -03							
1.15	89.65	1.820	0.429	-0.847	0.599	-1.439	-0.050
1.16	88.27	1.914	1.809	0.593	0.649	-0.620	-0.077
1.17	86.72	2.066	3.364	1.213	0.726	-0.405	-0.082
1.18	85.03	2.243	5.046	1.619	0.808	-0.300	-0.074
1.19	83.27	2.416	6.811	1.918	0.882	-0.235	-0.058
1.20	81.46	2.560	8.617	2.154	0.940	-0.191	-0.038
1.21	79.65	2.659	10.430	2.345	0.978	-0.158	-0.015
1.22	77.86	2.700	12.216	2.503	0.993	-0.133	0.008
1.23	76.13	2.677	13.949	2.635	0.985	-0.112	0.033
1.24	74.48	2.590	15.604	2.748	0.952	-0.095	0.059
1.25	72.92	2.442	17.162	2.843	0.893	-0.081	0.084
1.26	71.47	2.245	18.606	2.924	0.809	-0.069	0.108
1.27	70.15	2.015	19.927	2.992	0.701	-0.058	0.128
1.28	68.96	1.773	21.115	3.050	0.573	-0.049	0.136
1.29	67.91	1.547	22.169	3.099	0.436	-0.041	0.122
1.30	66.99	1.370	23.088	3.139	0.315	-0.034	0.068
1.31	66.20	1.280	23.878	3.173	0.247	-0.028	-0.032
1.32	65.53	1.321	24.547	3.201	0.278	3.201	0.278

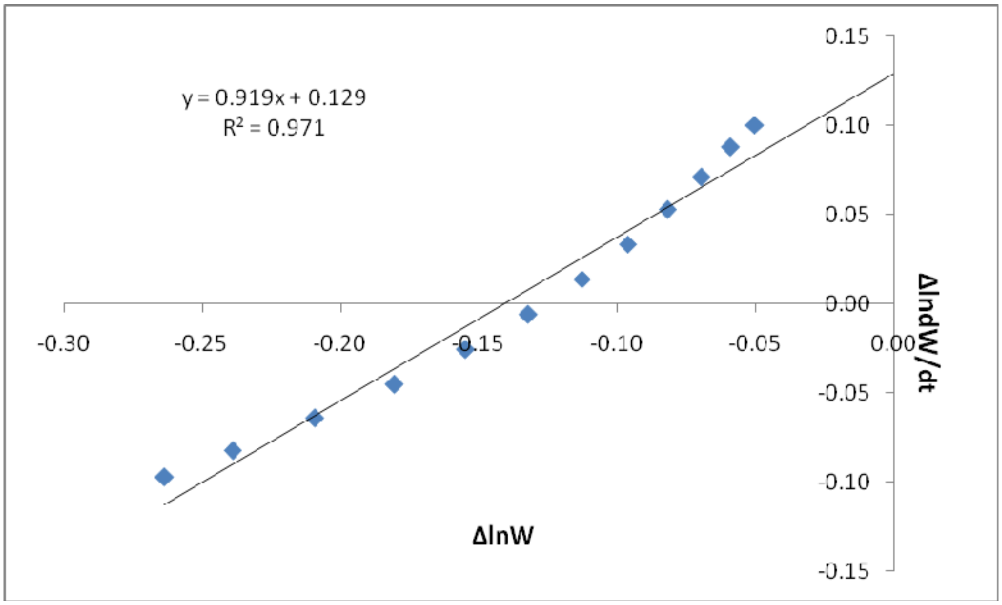

Fig.5.9: The Freeman-Anderson plots of Compo-B (step-1)

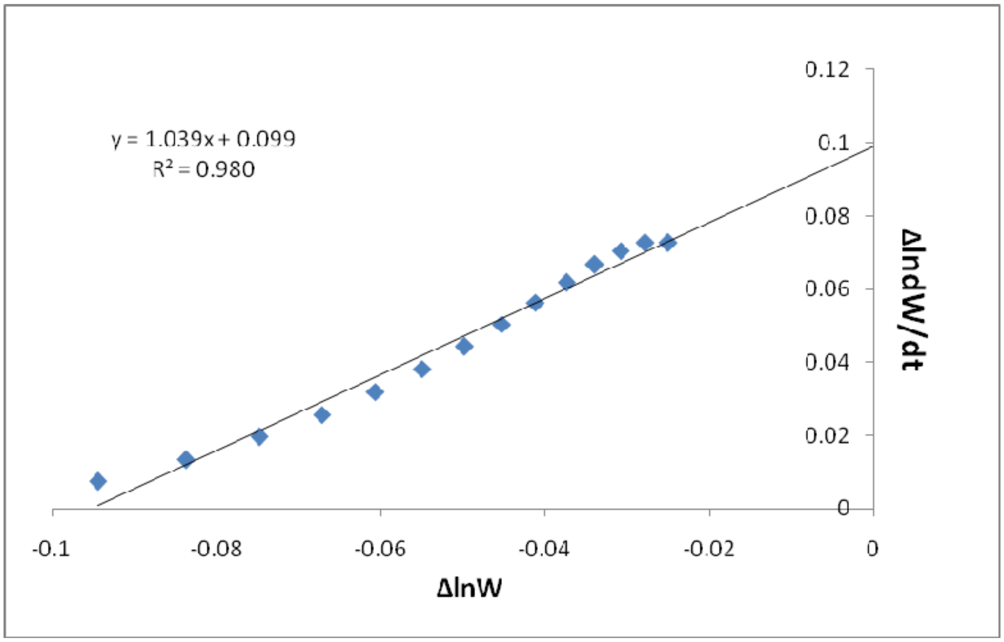

Fig.5.10: The Freeman-Anderson plots of Compo-B (step-2)

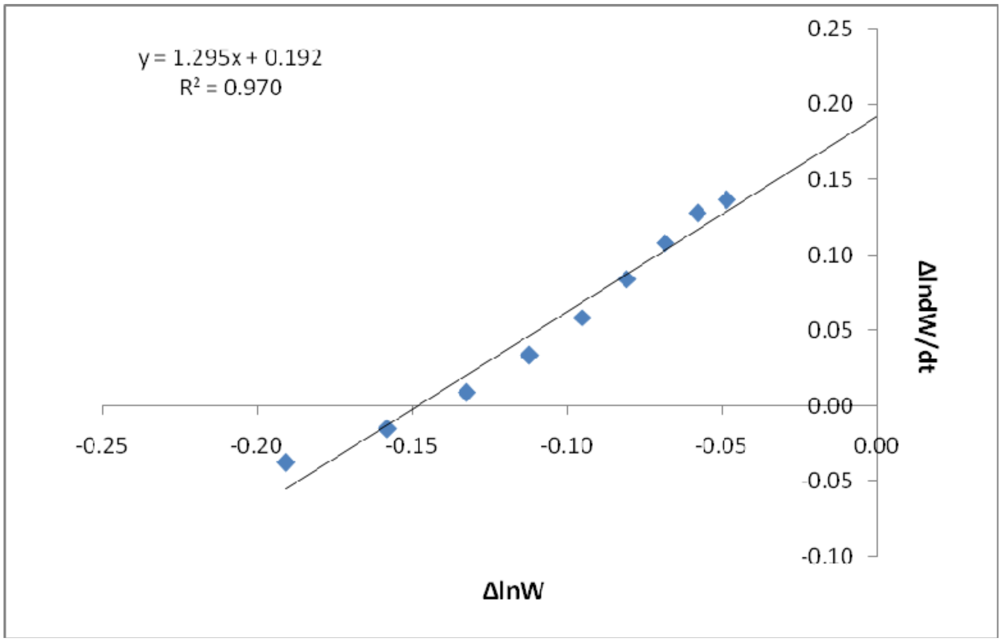

Fig.5.11: The Freeman-Anderson plots of Compo-B (step-3)

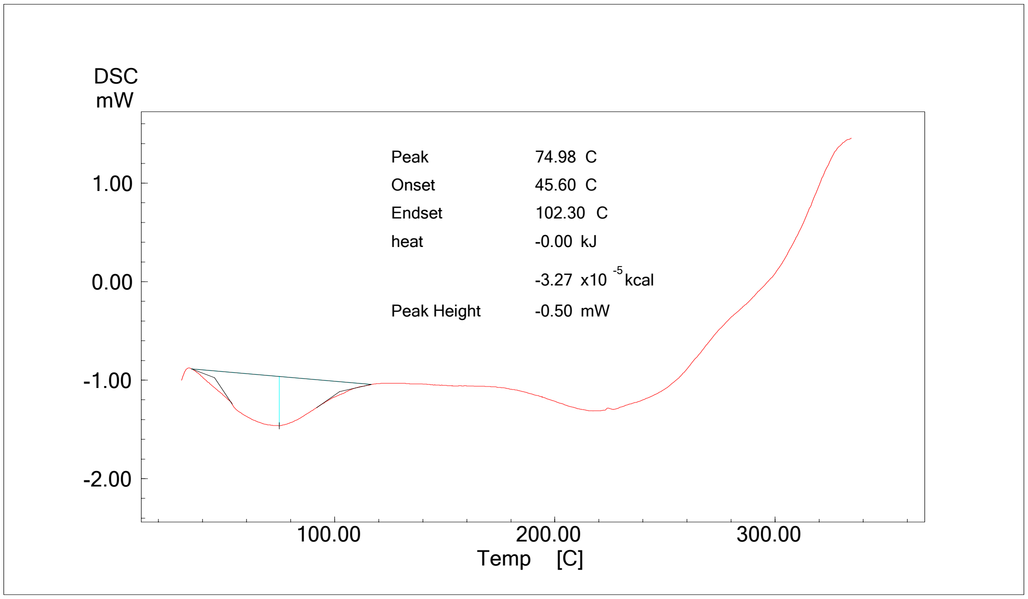

Fig. 5.12: DSC thermogram of Compo-A at the heating rate of 10°C/min in an N_2 atmosphere

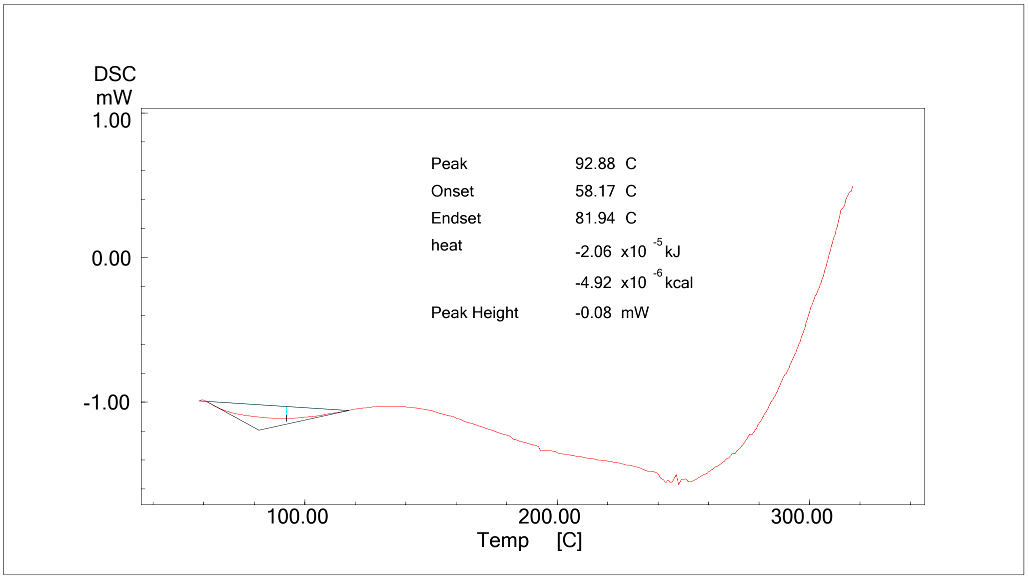

Fig. 5.13: DSC thermogram of Compo-B at the heating rate of 10°C/min in an N_2 atmosphere

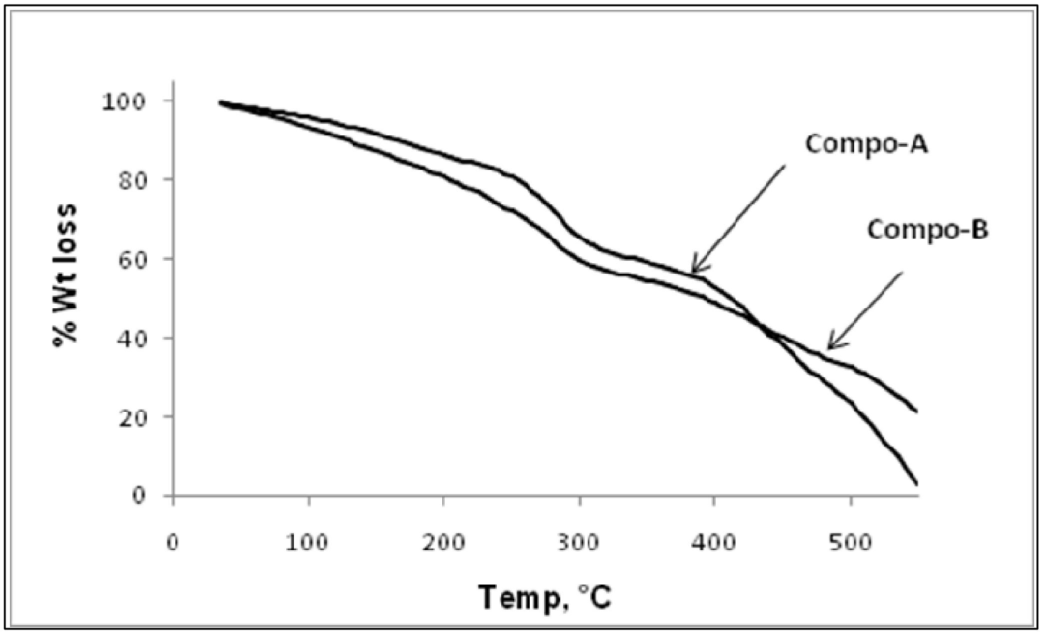

Fig.-5.14: TG thermograms of Compo-A and Compo-B at the heating rate of 10°C/min in an N_2 atmosphere

Mechanical properties

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

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

Various mechanical properties of composites depend upon type of reinforcing fiber, type of curing mechanism and density of curing, fiber-matrix adhesion, time and temperature of cure, molecular weight of polymer, fiber strength, modulus, fiber length and orientation, compatibilizers and impact modifiers, fiber content, presence of soft and hard segments, fiber loading etc.

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

Gassan et al. [23] have fabricated the flex fiber reinforced polyurethane composites and determined their mechanical properties. Flax fibers coated with two types and various amounts of silicones. Coating conditions have been found to affect strongly the composites properties. The effect of these two types and different amounts of silicone on the impact toughness, flexural strength and modulus, dynamic modulus and loss-energy and notch sensitivity is determined.

Carvalho et al. [24] have evaluated the tensile and impact behavior of jute fabrics-polyester composites as a function of the fabric style (knitted or weaved cloths), fiber weight fraction, and direction of the applied load. The tensile properties of plain-weave-fabric-reinforced composites (PWF) were higher than those of plain weft knit cloth composites (WKT) and were dependent on fiber content and test direction. The properties of the WKT, however, were independent of these variables. The results obtained indicate that the orthogonal fiber alignment of weaved cloths favors anisotropy, while the interconnected loops in knit fabrics favors isotropy. The results also indicated weak fiber-matrix interactions in both fabrics and a better fabric impregnation for the plain weave fabric if compared with that of the knit fabric. The impact strengths of both composites were higher than that of the matrix and were shown to increase with fiber content. WKT-reinforced composites showed better impact absorption capacity than PWF composites.

Sastra et al. [25] have determined the tensile properties of arenga pinnata fiber as a natural fiber and epoxy resin as a matrix. For this the arenga pinnata fibers were mixed with epoxy resin at the various fiber weight percentages of 10%, 15%, and 20% arenga pinnata fiber and with different fiber orientations such as long random, chopped random and woven roving. Results from the tensile tests of arenga pinnata fiber reinforced epoxy composite were that the 10 wt% woven roving arenga pinnata fiber showed the highest value for maximum tensile properties.

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23. J. Gassan, T. Dietz and A. K. Bledzki, “Effect of silicone interphase on the mechanical properties of flax-polyurethane composites” Compos Interfaces, 7, 103 -115, 2000.
24. L. H. de Carvalho, J. M. F. Cavalcante, J. R. M. d’Almeida, “Comparison of the mechanical behavior of plain weave and plain weft knit jute fabric-polyester-reinforced composites”, Polym. Plast. Technol. Eng. 45, 791-797, 2006.
25. H. Y. Sastra, J. P. Siregar, S. M. Sapuan and M. M. Hamdan, “Tensile properties of arenga pinnata fiber-reinforced epoxy composites”, Polym. Plast. Technol. Eng., 45, 149-155, 2006.

The tensile strength and Young's modulus values for 10 wt.% of woven roving arenga pinnata fiber composite are 51.725 MPa and 1255.825 MPa, respectively. The results above indicated that the woven roving arenga pinnata fiber has a better bonding between its fiber and matrix compared to long random arenga pinnata fiber and chopped random arenga pinnata fiber. Scanning electron microscopy (SEM) tests were also carried out after tensile tests to observe the interface of fiber and matrix adhesion.

Wang et al. [26] have fabricated waterborne polyurethane (WPU) composites and have studied the effect of crosslinking agent on the different properties. Waterborne PU (WPU) and casein (1: 1 by weight) were blended at 90°C for 30 min, and then were crosslinked by adding 1-10 wt % ethane diol to prepare a series of sheets. The results indicated that crosslinked blend sheets exhibited a certain degree of miscibility, and exhibited much higher tensile strength and water resistivity than did the WPU, casein, and the uncross linked blend from WPU and casein. When the ethane diol content was 2 wt %, the tensile strength and elongation at break of crosslinked sheets achieved 19.5 MPa and 148% in the dry state, and 5.0 MPa and 175% in the wet state, respectively. A 2 wt % content of ethane diol played an important role in the enhancement of mechanical properties, thermal stability, and water resistivity of the blends of WPU and casein.

Cao et al. [27] have fabricated waterborne polyurethane (WPU)/starch (ST) with different contents (10-90 wt %) composites and studied the effect of different starch content on the various properties of the composites. The results indicated that tensile strength of composite materials not only depended on the starch content, but also related to the microstructure of WPU.

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26. N. Wang, Y. Lu, Y. Du and L. Zhang, “Properties of crosslinked casein/waterborne polyurethane composites”, J. Appl Polym Sci., 91, 332-338, 2004.
27. X. Cao, J. Huang, G. Yang, Y. Wang and L. Zhang, “Structure-properties relationship of starch/waterborne polyurethane composites”, J. Appl Polym Sci., 90, 3325-3332, 2003.

The sample WPU2 (1.75 of NCO/OH molar ratio) exhibited hard-segment order, but WPU1 (1.25 of NCO/OH molar ratio) had no hard-segment order. The blend material from 80 wt % WPU1 and 20 wt % starch exhibited better tensile strength (27 MPa), elongation at break (949%), and toughness than others.

Fujii et al. [28] have fabricated bamboo reinforced polypropylene composites for ecological purposes (Eco-composites) and have studied their basic mechanical properties. The steam explosion technique was applied to extract bamboo fibers from raw bamboo trees. The experimental results showed that the bamboo fibers (bundles) had a sufficient specific strength, which is equivalent to that of conventional glass fibers. The tensile strength and modulus of PP based composites using steam-exploded fibers increased about 15 and 30%, respectively, due to well impregnation and the reduction of the number of voids, compared to the composite using fibers that were mechanically extracted. The steam explosion technique was an effective method to extract bamboo fibers for reinforcing thermoplastics.

The tensile strength (IS: 11298-Pt-2-87) and flexural strength (ASTM D-790-2003) measurements were made on a Shimadzu Autograph AG-X Series at a speed of 0.05mm/minute.

Compo-A (3.8mm thick) and Compo-B (4.1mm thick) possess 32.9 and 38.7 MPa tensile strengths; 20 and 50.9 MPa flexural strengths respectively. From these data it is observed that Compo-B posses better tensile strength and flexural strength. Fairly good tensile and flexural strengths of composites signify their importance for low load bearing applications.

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28. T. Fujii, Y. Yamamoto and K. Okubo, “Development of bamboo-based polymer composites and their mechanical properties”, Compos. Part-A: Appl. Sci. and Mfg., 35, 377-383, 2004.

Electrical Properties

Electric strength (IEC-60243-Pt-1-1998) and volume resistivity (ASTM D-257-2007) measurements were made on a high voltage tester (Automatic Electric-Mumbai) in air at 27°C by using 25/75mm brass electrodes and a Hewlett Packard high resistance meter at 500 V DC after charging for 60 sec, respectively.

Compo-A (3.8mm thick) and Compo-B (4.1mm thick) showed respectively 1.3 and 1.9 kV/mm electric strength; and 7.6 x 10^9 and 2.2 x 10^{11} ohm.cm volume resistivity. Compo-B showed better electric and volume resistivity. From volume resistivity data it is observed that Compo-B is much more polar than Compo-A.

Fairly good electric properties are due to presence of polar groups in epoxy polyester polyurethanes.

SECTION-3: Chemical Resistance Study of Composites

The unique combinations of properties found in polymers have made it possible to use them in almost all areas of applications. Tailoring of polymer molecules to specifically achieve the required performance properties has further widened the scope of their applications. The performance and life span of polymeric materials depend on various factors, their molecular characteristics being the controlling one; exposure of polymers to different environmental conditions impairs their useful properties.

The highest consumption area of the plastic material is in packaging. This is mainly due to the superiority of plastic material over the other materials in terms of inertness and stability to contacting chemicals like water, oxidizing agents, oils, lubricants, industrial solvents and food stuffs. The selection of particular plastic materials for specific industrial applications has to be based on the chemical environment to which they will be exposed.

The interaction of chemicals with plastics can take place in different ways, affecting adversely their useful properties at varying rates and at varying degrees. The mechanisms involved can be chemical reaction, solvation, absorption, plasticization and stress cracking. The strength of chemical bonds, the degree of crystallinity, branching and polarity are the deciding factors for the chemical resistance of polymers. Rise in temperature increases the rate of chemical interaction.

Somani et al. [29] have studied the equilibrium swelling of polyurethanes (PU) in various solvents in order to calculate their solubility parameters. The kinetics of swelling and sorption were also been studied in 1,4-dioxane at 30°C. The PU was synthesized by reacting a novel polyol (castor oil derivative and epoxy based resin) 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.

Ajithkumar et al. [30] 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°C. 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. A number of standard chemical resistance tests have been developed which include tests for moisture and water absorption, effects of immersion in chemicals, stain resistance and stress cracking.

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29. 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.
30. 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.

Most of these tests involve measurement of change in weight, dimensions and appearance and mechanical properties before and after the exposure to chemical reagents. Exposure time, temperature, concentration and reactivity of the reagents are the important factors for the tests.

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

(1) Chemical resistance by change in mass method

(2) Chemical resistance by change in linear dimensions

(3) Chemical resistance by change in mechanical properties

Various models have been proposed for water absorption in composites. It is well established that absorbed water in polymers and composites plays a significant role in mechanical behavior and long term durability. Assuming one-dimensional Fickian diffusion in composite, an attempt has been made to determine diffusivity (Dx) in different environments. Diffusivity is assumed to depend only on temperature and independent of the moisture content as well as stress levels in composites. For one- dimensional water absorption in semi-infinite plate exposed on both sides to same environment, the amount of water absorbed is given by Eqn.5.4:

$$G = 1 - \frac{8}{\pi^2} \sum_{J=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left[-\frac{(2j+1)^2 \pi^2 D_x t}{h^2} \right] \qquad \ldots 5.4$$

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

The water content in the sample at time t can be determined according to Eqn.5.5:

$$\% M_t = \frac{W_m - W_d}{W_d} \times 100 \qquad \ldots 5.5$$

Where M_t = % water absorbed at time t, W_m = weight of moist sample and W_d = weight of dry sample. The solution of diffusion equation in terms of % water absorption is given by eqn.5.6:

$$M = \frac{4M_m}{h} \sqrt{\frac{t}{\pi}} \sqrt{D_x} \qquad \ldots 5.6$$

Where M_m = equilibrium water content. Diffusivity in a given environment can be determined from the initial slope of the plot of %M against $\sqrt{t}$ according to Eqn. 5.7:

$$D_x = \pi \left(\frac{h}{4M_m} \right)^2 (slope)^2 \qquad \ldots 5.7$$

In present case assuming unidimensional Fickian diffusion, water absorption in composites was carried in pure water, 10% HCl and 10% NaCl at room temperature by a change in mass method. 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, reweighed and reimmersed in the solutions. The process was carried out till equilibrium was established.

The plots % weight gains with the passage of time (t1/2) in different environment at 27°C are presented in Figs.-5.15-5.17. Equilibrium water content and equilibrium time are reported in Table-5.15.

Water uptake behavior of both the composites is HCl > water > NaCl. High water uptake tendency in acidic environment is due to solvation effect via H-bond formation. The lone pair of electrons is responsible for solvation effect in the composites.

Diffusivity in composites was determined from initial slopes and also reported in Table-5.15 by using Eqn.5.7. Diffusivity behavior is practically almost same in both the samples. Comparatively low diffusivity in acidic environment is due to strong solvation effect environment. High diffusivity in saline environment is due to structure breaking tendency of sodium chloride.

Water penetration in composite is conducted mainly by diffusion mechanism. The penetration of water in composites also occurs through capillary flow along the fiber/matrix interface followed by diffusion from the interface into the bulk resin and transported by 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.

Water absorption in boiling water

Water absorption in composites mainly depends on temperature and it is independent on water content. The effect of boiling water on water absorption in Compo-A and Compo-B with time is summarized in Table-5.15 and Fig.-5.16, from which it is evident that equilibrium reached after 7h in both composites. Observed equilibrium water content in Compo-A and Compo-B was 12.7 and 22.6 % respectively. Thus equilibrium time is reduced 24 and 20.6 times in Compo-A and Compo-B respectively without damaging composites.

Table-5.15: Water uptake and diffusivity data of Compo-A and Compo-B at 27°C

Properties	Water	10% HCl	10%NaCl
	Compo-A		
Equilibrium time, h	168	192	120
Equilibrium water content,%	10.8	20.2	9.1
Diffusivity D_x,10^{-12} ,m^2/s	0.23	0.17	0.29
	Compo-B		
Equilibrium time, h	144	216	168
Equilibrium water content,%	16.7	22.1	14.3
Diffusivity D_x,10^{-12} ,m^2/s	0.26	0.17	0.32

Table-5.16: The effect of boiling water on water absorption in composites with time

Time (h)	% Weight change	
	Compo-A	Compo-B
0	0	0
1	2.2	7.3
2	4.9	14.4
3	7.8	17.5
4	10	19.5
5	12.1	21.2
6	12.6	22.2
7	12.7	22.6
8	12.71	22.6

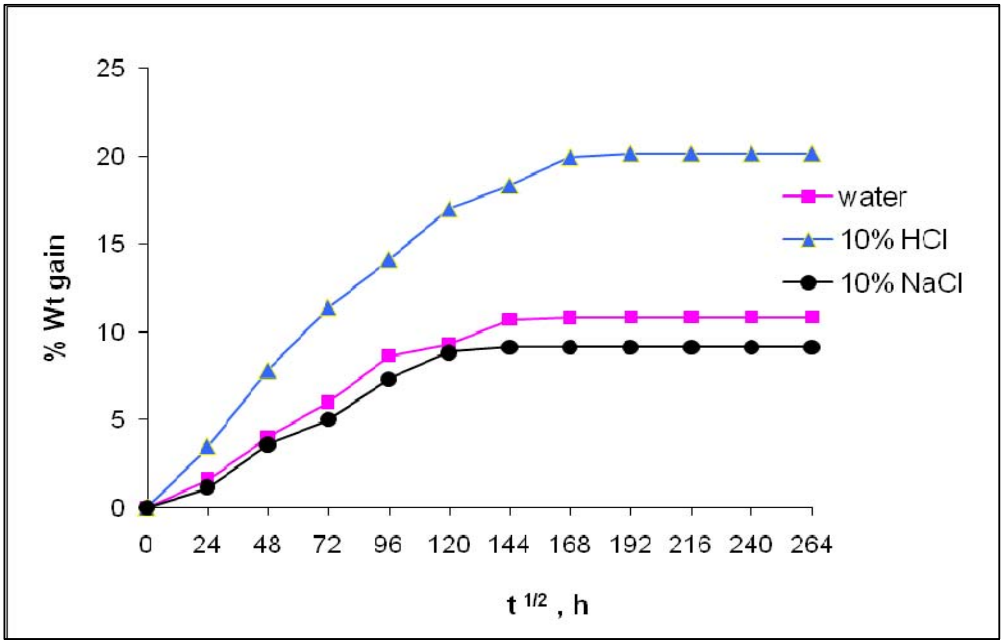

Fig.- 5.15 : The plots of % weight gain against $t^{1/2}$ for Compo-A in different environments at 27^0C

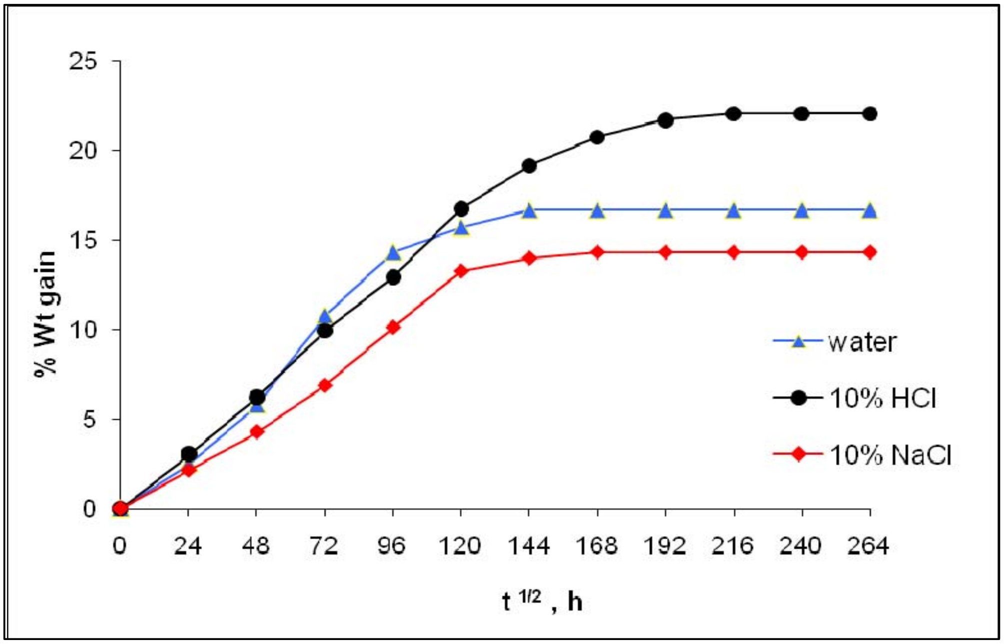

Fig.- 5.16 : The plots of % weight gain against $t^{1/2}$ for Compo-B in different environments at 27^0C

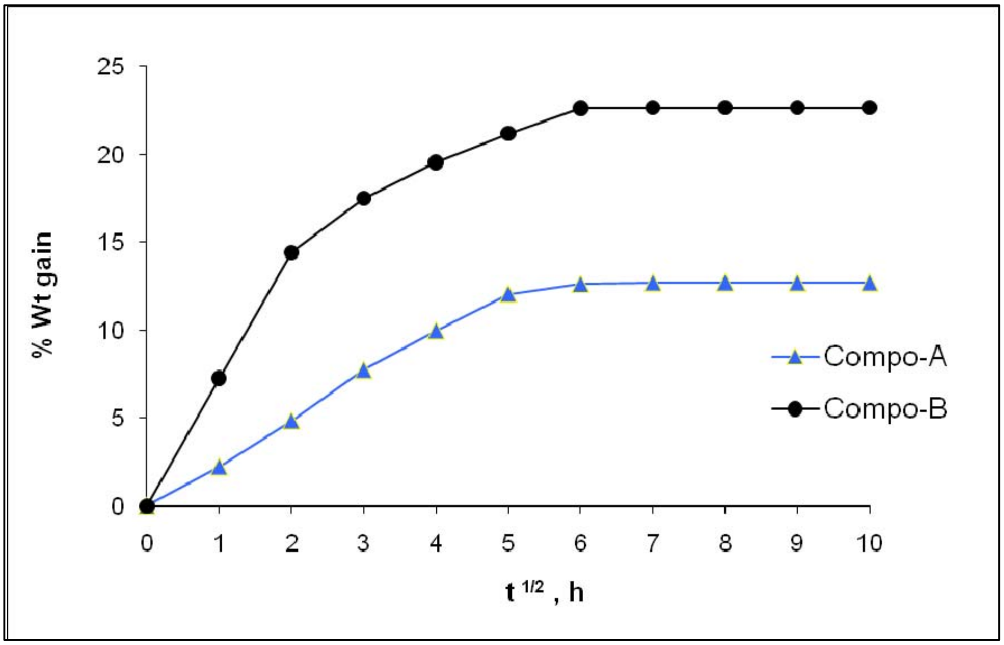

Fig.- 5.17 : The plots of % weight gain against time $t^{1/2}$ for Compo-A and Compo-B in boiling water.

CHAPTER-6

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

CHAPTER-1

This chapter of the thesis describes upto date literature survey on cardo diamines, Schiff bases, epoxy resins, epoxy polyester polyols, polyurethane resins, properties and applications of natural /synthetic fibers and composites in diverse field.

CHAPTER-2

This chapter deals with the synthesis and characterization of cardo diamine [1,1'-bis (4-amino phenyl) cyclohexane and 1,1'-bis (3-methyl-4-amino phenyl) cyclohexane] and Schiff bases (SB-01 to SB-06). The characterizations were done by IR spectral data.

CHAPTER-3

This chapter describes the synthesis of epoxy resins (EP-01, EP-02 and EP-03), their characterization by IR, ^{1}HNMR spectral data, GPC, epoxy equivalent, DSC and TGA data. Epoxy equivalent of epoxy resins for EP-01, EP-02 and EP-03 are 1220; 680 and 1060 respectively. DSC and TG thermograms were scanned at the heating rate of 10°C/min in an N_2 atmosphere. EP-01and EP-02 followed two step degradation while EP-03 followed single step degradation. They are found to be thermally stable upto about 250°C.

This chapter also describes the synthesis of copolyurethanes. Yellowish to brown films were obtained by using 0.0005M EP-01/EP-03, 0.0005M PEG-600 and 0.0045M TDI. These films were characterized by IR spectral data. The density of the films was determined by a floatation method at 27°C by using CCl_4-n-hexane system. The observed density of PU-I is 1.0865 $\pm$ 0.0012 g/cm^3 and PU-II is 1.0788 $\pm$ 0.0012 g/cm^3. Low tensile strength of PU-I (9 MPa) and PU-II (7 MPa) indicate rigid and brittle nature of copolyurethanes. Electric resistivity and volume resistivity of PU-I and PU-II are 56 and 43 kv/mm; 1.1x10^{-15} and 3.7x10^{-12} ohm.cm respectively. DSC thermograms show broad endothermic transition for PU-I (91°C) and for PU-II (95°C) is due to glass transition temperature. From TG thermograms, it is clear that PU-I followed single step decomposition while PU-II followed two step decomposition. PU-I (215°C) is slightly more thermally stable than that of PU-II (205°C).

Water uptake study of PU-I and PU-II films were tested against various reagents (distilled water, 10 % each aqueous solution of HCl, H_2SO_4, HNO_3, NaOH, KOH, KCl) at 27°C by change in weight method. Water uptake is high in acidic environments and minimum in distilled water. Ester and urethane linkages are polar groups, which form H-bonding with reagents solution and hence increase in weight gain. Thus, copolyurethane films have good hydrolytic stability against water, saline, alkaline and acidic environments without any damage (except acidic environment for PU-II). The observed water absorption order for PU-I is HNO_3 (8.02) > HCl (4.17) > H_2SO_4 (2.91) > KOH (2.14) > KCl (2.02) > NaOH (1.71) > distilled water (1.42) and for PU-II is NaOH (9.28) > KOH (8.20) > distilled water (4.62) > KCl (0.65).

CHAPTER-4

This chapter describes the acoustical and thermodynamic properties of EP-01, EP-02 and EP-03 solutions in three different solvents at 35°C. Various thermodynamic parameters such as density (ρ), viscosity (η) and ultrasonic speed (U), specific acoustical impedance (Z), adiabatic compressibility (K_α), Rao's molar sound function (R), van der Waals constant (b), internal pressure (π), free volume (V_f), intermolecular free path length (L_f), classical absorption coefficient (($(\alpha/f^2)_{Cl}$), and viscous relaxation time (τ were determined and discuss in light of effect of solvent, concentration and length of polymer. The observed trends in ρ, η and U are CF > DO > THF; DO > CF > THF; DO > THF > CF, respectively in EP-01, EP-02 and EP-03 solutions. The ρ, η, and U increased linearly with concentration (C) except ρ in chloroform system in which it decreased with C. The density is an additive property. The density of CF is greater then those of resins and hence density of solutions decreased with increasing C. The linear increase of b and τ ; linear decrease of K_α and L_f (except EP-01 : THF and EP-03 : THF) and π (except CF it is nonlinear) with C indicate existence of strong molecular interactions in the solutions. Decrease of K_α , L_f, π with increasing C due to increase in cohesive forces (molecular interactions) and vice-versa.

Azomethine, methyl, ether, methoxy and hydroxyl groups are polar groups, which are responsible for molecular interactions (molecular association) i.e. solvent-solute interactions. The dipole-dipole interactions of the opposite type favor molecular association; while of the same type disrupt structure formed previously.

Gibb's free energy of activation is found to be practically concentration independent but it is dependent on the nature of the resins and solvents used.

CHAPTER-5

This chapter of the thesis elaborates the fabrication, mechanical, electrical and chemical resistance studies of the composites (Compo-A and Compo-B). Jute composites were prepared by hand lay up technique under 30.4 MPa pressure and 150°C for 8h. DSC thermograms show endothermic peak at 75°C (Compo-A) and 93°C (Compo-B) due to glass transition. Compo-A followed two step degradation while Compo-B followed three step degradation. Compo-A and compo-B are found thermally stable upto 210 and 245°C respectively. Tensile strength and flexural strength of Compo-A and Compo-B are 32.9; 38.7 and 20; 50.9 respectively which signify their importance for low load bearing applications. Electric resistivity and volume resitivity of Compo-A and Compo-B are 1.3; 1.9 and $7.6x10^9$; $2.2x10^{11}$ respectively. Fairly good electrical properties are due to presence of polar groups in epoxy polyester polyurethanes.

Water absorption in composites was carried in distilled water, 10% HCl and 10% NaCl at 27°C by change in mass method. The observed water absorption order for Compo-A is HCl (20.2) > Water (10.8) > NaCl (9.1) and for Compo-B is HCl (22.1) > Water (16.7) > NaCl (14.3). High water uptake tendency in acidic environment is due to salvation effect via. H-bonding formation. Diffusion behavior is practically almost same in both the samples. Comparatively low diffusivity in acidic environment is due to strong salvation effect. High diffusivity in saline environment is due to structure breaking tendency of sodium chloride.

ACHIEVEMENTS

LIST OF PAPERS PUBLISHED/ACCEPTED/COMMUNICATED

---

1. U. G. Pathak, J. V. Patel and P.H. Parasina, “Synthesis, spectral and thermal srudy of novel epoxy resins based on cardo symmetric double Schiff bases”, Polym. Plast. Techno. Engg.
2. U. G. Pathak, J. V. Patel and P.H. Parasina, “Ultrasonic speed and thermodynamic parameters of novel epoxy resins solutions based on cardo symmetric double Schiff bases” J. Soln. Chem.
3. U. G. Pathak, J. V. Patel and P.H. Parasina, “Synthesis and physico-chemical study of copolyurethanes derived from epoxy resins of cardo symmetric double Schiff bases” J. Appl. Polym. Sci.

CONFERENCES/WORKSHOP/SEMINAR/SYMPOSIUM PARTICIPATED AND PAPER PRESENTED

1. National Seminar on Emerging Trends in Polymer Science and Technology (Poly-2009), Saurashtra University, Rajkot (October 08-10, 2009).(One paper and one oral presentation)
2. National Seminar on Emerging Trends in Chemical Science Research, Sardar Patel University, V.V. Nagar (January 20-21, 2009)
3. XXII Gujarat Science Congress, Bhavnagar University, Bhavnagar (March 9, 2008).