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**DEVELOPMENT OF *MESUA FERREA*  
L. SEED OIL BASED POLYURETHANE RESINS**

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF  
Doctor of Philosophy**

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*Dedicated to my*

*Beloved parents*

# ABSTRACT

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## BACKGROUND

Utilization of naturally renewable resources as the feed stocks for polymers is thriving all around in contemporary times. Vegetable oil is a renewable resource to be worth mentioned in this regard. These feed stocks are well accepted by the synthetic polymer chemists as well as industrialists due to assorted social, economical and environmental issues. Furthermore, there are many advantages of using vegetable oil as the feed stocks. Some of them to mention are (i) naturally renewable as can be grown wildy or agriculturally, (ii) environment friendly and biodegradable as they are obtained from natural resources, (iii) cost effective, (iv) available in large quantities, (v) reduced risk for handling, storage and transportation due to physical and chemical stability, (vi) aptitude to facile chemical modification, (vii) possibility of recycling etc.

The vast forest resources and farm lands yield varieties of oil bearing seeds. Among them, about 350 oil bearing crops have been identified so far. A few such vegetable oils have been explored for the development of different polymeric materials like alkyd, epoxy, polyesteramide, polyurethane etc. These polymers are largely used in different industrial applications such as paints, inks, binder for composites, adhesives etc. The vegetable oils successfully utilized so far are traditional oils like castor, linseed, soybean, sunflower, rapeseed, canola, corn, palm, tung, safflower, peanut, coconut, cottonseed etc. and non-traditional oils like rubber seed oil, kamala seed oil, mahua oil, karanja oil, neem oil, tobacco seed oil, *annona squamosa* oil, melon seed oil, jatropha seed oil etc. *Mesua ferrea* L. is a plant, locally known as Nahar, the seeds of which contain ca. 70% non-edible oil. This is a non-drying oil and the fatty acid content is consisting of 52.3% oleic and 22.3% linoleic acids as unsaturated fatty acids and 15.9% palmitic and 9.5% stearic acids as saturated fatty acids. It is available in different countries such as India, Srilanka, Bangladesh, Nepal, Indochina (Southeast Asia), Malay Peninsula etc.



Since its inception in the mid nineteen thirties, polyurethane is gaining vast popularity for its diversified applications in the fields of coatings, adhesives, leathers, elastomers, sealants, composites, biomaterials and many others. Polyurethane endows versatility from its block copolymeric character and the unique possibilities for tailor making their properties by varying the composition of hard and soft segments. Different vegetable oils such as castor, linseed, soybean, sunflower, argemone, corn, canola, palm, tobacco etc. have been investigated to synthesize different categories of polyurethanes successfully. The suitable fatty acid composition of *Mesua ferrea* L. seed oil indicates that it may be utilized for the synthesis of polyurethane resins along with other polymers.

### **SCOPES AND OBJECTIVES OF THE PRESENT INVESTIGATION**

From the literature survey, it has been found that many vegetable oils are widely used in place of petroleum based products as the raw materials in the production of many industrial products like binders for surface coatings including paints, varnishes, printing inks, soaps, cosmetics, pharmaceuticals, lubricants, emulsifiers, multipurpose additives, biodiesel, plasticizers etc. Although *Mesua ferrea* L. (Nahar) seed oil has tremendous potential as a renewable raw material but only a few reports have been found on its utilization in the fields of medicine and biodiesel. Further, there is no report on the use of this oil in the field of polymer, except polyester resins. Thus, it comes into sight that there is no study on this oil for development of polyurethane. Hence, the following questions may arise in this area.

- (i) Whether this oil can be utilized for the preparation of different types of polyurethane resins?
- (ii) Whether the performance characteristics of these polymers can be improved by any physical or chemical means?
- (iii) Whether these polymers can be used as a binder for surface coating, paint and composite materials?
- (iv) Whether these polymeric products are biodegradable or not? etc.

Under this background, the main objectives of the present investigation are as follows:

- (i) To synthesize, characterize and evaluate various properties of *Mesua ferrea* L. seed oil based polyurethane resins.

- (ii) To study the effect of NCO/OH ratio on the performance of the polyurethanes as surface coating materials.
- (ii) To improve the performance characteristics of these resins by blending with suitable commercially available resins.
- (iii) To study the performance characteristic of the blends as matrices for conventional composites and nanocomposites.
- (iv) To study the biodegradability of the virgin blends and their nanocomposites.
- (v) To use polyurethane blends as binders for the preparation of industrial paints.

## THE THESIS

**Chapter 1** deals with the general introduction of vegetable oils and their utilization for the production of polyurethanes. A brief review on polyurethanes with special emphasis on resins from vegetable oils, their importance, history, general techniques for preparation, characterization, properties and applications have been described in this chapter. This chapter also described the scopes and objectives along with the plan and methodology of the present investigation.

**Chapter 2** incorporates the synthesis, characterization and properties evaluation of two different types of *Mesua ferrea* L. seed oil based polyurethane (PU) resins, poly(urethane ester) (PUE) and poly(urethane amide) (PUA) with varying NCO/OH ratios using monoglyceride and fatty amide diol of the purified oil respectively. The synthesized resins have been characterized by measurement of physical properties like acid value, iodine value, saponification value, hydroxyl value, isocyanate value, drying time, viscosity etc. and FTIR and <sup>1</sup>HNMR spectroscopic studies as well as GPC analysis. The synthesized resins were cured under ambient conditions followed by post-curing at 120 °C for 2 h for both the cases. Various performance characteristics of the cured polyurethane films such as hardness, flexibility, gloss, adhesion, impact resistance and chemical resistance in different media were determined. Thermal stabilities were studied as a function of NCO/OH ratio by TGA technique, which indicates the increase of thermostability with the increase of NCO/OH ratio. The chapter concludes that *Mesua ferrea* L. seed oil based PUE and PUA resins can be utilized as surface coating materials and PUE resins are found to be more promising in this regard. Further, high

thermostability of the cured resins indicated their applicability under a range of climatic conditions.

**Chapter 3** reports the enhancement in performance characteristics of the PUE and PUA resins (NCO/OH ratio = 0.5) by blending with commercially available bisphenol-A based epoxy resin and with partially butylated melamine-formaldehyde (MF) resin at different weight ratios (PU:epoxy = 40:60, 50:50 and 60:40, whereas PU:MF = 85:15, 75:25 and 60:40). All the blends were prepared by solution blending technique using poly(amido amine) hardener [for epoxy modified PUE (EM) and PUA (EA) blends] or *p*-toluene sulfonic acid catalyst [for MF modified PUE (MM) and PUA (MA) blends] and xylene as the solvent under ambient conditions. Performance characteristics like tensile strength, impact resistance, adhesive strength, flexibility, hardness, elongation at break, swelling behavior and chemical resistance in different media as well as dielectric properties of the blends were studied. FTIR spectroscopic technique was used to study the crosslinking between polyurethane and epoxy/ MF resins, whereas scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) were used to study the morphology and thermostability of the blends respectively. The results showed good compatibility between the components of the blends and significant enhancement in blend properties including thermostability and chemical resistance. In the case of EM and EA blends, EM50 (PUE:epoxy = 50:50) and EA50 (PUA:epoxy = 50:50) exhibit the optimum film performance, whereas in the case of MM and MA blends, MM25 (PUE:MF = 75:25) and MA25 (PUA:MF = 75:25) exhibit the optimum film performance.

**Chapter 4** includes the studies on the preparation, characterization and evaluation of performance characteristics of the epoxy and MF modified *Mesua ferrea* L. seed oil based polyurethane composites reinforced with jute fiber and nanocomposites reinforced with bentonite nanoclay. Jute fiber reinforced composites were prepared by using epoxy and MF modified PUE and PUA resin blends through solution impregnation followed by curing at ca.130-140 °C under pressure of ca. 35-40 kg/cm<sup>2</sup> for ca. 2 h. Mechanical properties like tensile strength, flexural strength, elongation at break, hardness and density of all the composites were measured and compared. FTIR spectroscopy and SEM techniques were utilized to understand the

mode of interaction between the filler and the matrix of the fractured composite samples. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques were employed to analyze the thermal behavior of the composites. The study showed their high thermostability and high glass transition temperatures ( $T_g$ ). All the properties were found to be much better for epoxy modified polyurethane composites than MF modified ones.

The chapter also describes the preparation, characterization and evaluation of performance characteristics of the epoxy modified polyurethane nanocomposites with different weight % of clay loadings (1%, 2.5% and 5%). The nanocomposites were prepared by *ex-situ* solution technique under high mechanical shearing and ultrasonication under ambient conditions. The partially exfoliated nanocomposites were characterized by FTIR, XRD and SEM techniques. The chapter reports the nanocomposites to exhibit tremendous improvement in performance characteristics including barrier properties as compared to the pristine polymers. PUE nanocomposites were found to be better in all aspects than the PUA nanocomposites.

**Chapter 5** describes the biodegradation of the above mentioned *Mesua ferrea* L. seed oil based polyurethane blends and nanocomposites. The blends were studied for biodegradation with two techniques viz. microbial degradation (broth culture technique) and natural soil burial degradation. Microorganism attack after the soil burial biodegradation of 180 days was realized by the measurement of loss in weight and mechanical properties. In the broth culture technique, rate of increase in bacterial growth in polymer matrix was monitored via a visible spectrophotometer at the wavelength of 600 nm using McFarland turbidity as the standard. Biodegradation of the films was also evidenced by SEM, TGA and FTIR spectroscopic studies. The study showed that the chief mechanism behind biodegradation is the rupture of ester linkages. The study further depicts the EM50 to be more biodegradable than the MM25 blend.

One major finding of the work mentioned in this chapter is the higher extent of biodegradation of the polyurethane nanocomposites than the corresponding pristine polymers as reflected from the broth culture technique. The rate of biodegradation was found to be a little higher for the PUE cases than the PUA cases. The chapter also includes the cytotoxicity study of the blends and the nanocomposites by a simple anti-hemolytic test. All the nanocomposites showed overall non-cytotoxicity. Thus the

chapter concludes that *Mesua ferrea* L. seed oil based polyurethane blends as well as nanocomposites have incredible prospect to be utilized as biomaterials.

**Chapter 6** reports the application of *Mesua ferrea* L. seed oil based polyurethane blends with MF and epoxy resins as binder materials for industrial stoving paint. The preparation, characterization and properties of this stoving paint are described in this chapter. Maximum part of the work was carried out in a paint industry using their set up to establish the commercial viability of the resins. The results indicate that these resins could be used for low cost stoving deep color paints. Various parameters that reflect the performance characteristics of the test paints are found to be comparable with the standard industrial paint. Among the two test paints, the PUE/epoxy based one seems to be more effective in terms of performance characteristics than the PUE/MF based paint. The study reveals their perspectives for successful utilization as high performance stoving paints.

**Chapter 7** the last chapter of the thesis includes the concluding remarks, high lights of the findings and future scopes of the present investigation. The major achievements of the present investigation are as follows:

- i) A highly potential non-edible vegetable oil (*Mesua ferrea* L.) is utilized as value added polymeric product.
- ii) *Mesua ferrea* L. seed oil was successfully utilized for the first time to prepare industrially important polyurethane resins.
- iii) The blending technique with commercial epoxy or melamine-formaldehyde resin significantly improved the film properties especially thermal stability and chemical resistance of *Mesua ferrea* L. seed oil based polyurethane resins.
- iv) Fabrication of the resins into both conventional as well as nanocomposites caused tremendous improvement in performance characteristics.
- v) Biodegradability and cytotoxicity studies of the *Mesua ferrea* L. seed oil based resins and nanocomposites showed their potential to be applicable as biomaterials.
- vi) The *Mesua ferrea* L. seed oil based polyurethane resins were used for the first time to investigate the viability of commercial utilization as binders for industrial stoving paints.

## DECLARATION

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I do hereby declare that the thesis entitled "*Development of Mesua ferrea L. Seed Oil Based Polyurethane Resins*", submitted to the Department of Chemical Sciences, Tezpur University, is a record of original research work carried out by me. All sources of assistance have been assigned due acknowledgment. I also declare that neither this work as a whole nor a part of it has been submitted to any other University or Institute for any other degree, diploma or award.

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## CERTIFICATE

This is to certify that the thesis entitled "*Development of Mesua ferrea L. Seed Oil Based Polyurethane Resins*" submitted to the Tezpur University in the Department of Chemical Sciences under the School of Science & Technology, in partial fulfillment for the award of the Degree of Doctor of Philosophy in Science, is a record of research work carried out by Suvangshu Dutta under my personal supervision and guidance.

All helps received by him from various sources have been duly acknowledged.

No part of this thesis has been reproduced elsewhere for award of any other degree.

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## CERTIFICATE

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The committee recommends for the award of the degree of Doctor of Philosophy.

Principal Supervisor

External Examiner

Date:

Date:



## PREFACE

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The endangering petroleum based feedstocks are inclining the scientists to switch over to renewable starting materials like vegetable oil for developing various products including polymers. This can be envisioned as an avenue to counteract the vicious problems of emanation of green house gases, global warming, land filling and environmental denudation. Amongst the rich and diverse flora of India, many plants produce acceptable amount of vegetable oils. These oils are being utilized for production of myriad industrial polymers including polyurethanes.

North-eastern India abounds in *Mesua ferrea* L. (Nahar) plant, the seeds of which contain exceptionally high amount of oil. The co-occurrence of saturated and unsaturated fatty acid moieties in the oil leaves scope for the scientists to design varieties of polymers.

The focal objective of the present thesis is to probe into the possible utilization of this vegetable oil in the development of polyurethane resins. In this study, attempts have been made to prepare, characterize and evaluate the properties of polyurethane resins based on *Mesua ferrea* L. seed oil. Blending with commercially available resins, formation of green composites with natural fiber and nanocomposites with nanoclay led to improvement of the performance characteristics of the prepared resins as coating materials. Biodegradability and cytotoxicity assessment of the blends and nanocomposites revealed their potentiality as advance biomaterials. Finally, acceptable performance as binder for industrial stoving paints unmasked the industrial applicability of the prepared resin systems.

Date: 24/07/09

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## LIST OF SYMBOLS AND ABBREVIATIONS

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b.p.	boiling point
c.c.	cubic centimeter
cm	centimeter(s)
DBTDL	dibutyl tin dilaurate
deg C/ °C	degree centigrade
dia.	diameter
dL	decilitre(s)
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared
g	gram(s)
GPC	gel permeation chromatography
h	hour(s)
JF	jute fiber
K	Kelvin
kHz	kilo-hertz
kN	kilo-newton
L	litre(s)
lb	pound(s)
m	meter(s)
min	minute(s)
mL	mili liter(s)
mm	mili meter(s)
m.p.	melting point
$M_n$	number average molecular weight
$M_w$	weight average molecular weight
MF	melamine-formaldehyde
MPa	mega pascale
N	Newton

NC	nanoclay
NMR	nuclear magnetic resonance
nm	nano meter(s)
NVC	non-volatile content
OD	optical density
PEG	poly(ethylene glycol)
phr	parts per hundred
PP	polypropylene
ppm	parts per million
PTSA	<i>para</i> -toluene sulfonic acid
PUA	poly(urethane amide)
PUE	poly(urethane ester)
RBC	red blood cell
s	second(s)
SEM	scanning electron microscope
TDI	toluene diisocyanate
TEM	transmission electron microscopy
T <sub>g</sub>	glass transition temperature
TGA	thermogravimetric analysis
TMS	tetramethyl silane
UTM	universal testing machine
UV	ultraviolet
v	volume
w	weight
XRD	X-ray diffraction
μm	micro meter(s)
μM	micro molar(s)
μL	micro liter(s)
%	percentage
η <sub>inh</sub>	inherent viscosity
λ <sub>max</sub>	wavelength maximum
θ	scattering angle
ε <sub>0</sub>	permittivity of vacuum

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*Suvangshu Dutta*  
(Suvangshu Dutta)

# CHAPTER 1

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## General Introduction

### 1.1. Introduction

In the realm of material science, polyurethane has captured a unique niche of its own, instigating research in both industry and academic panorama in recent times. Following its inception in mid 1930s, its popularity has reached a pinnacle with colossal application oriented utilities in the domains of coatings, leathers, elastomers, sealants, composites, bio-medicals [1-6] and so on.

Polyurethane is a versatile multi-block copolymer and is often segmented consisting of soft (flexible polyether or polyester) and hard (rigid urethane) segment units in an alternate manner. The soft segment provides flexibility while hard segment provides dimensional stability to the polymer. Unlike 'A'-'B' or 'A'-'B'-'A' long block copolymers with segmental block 'A' and 'B', the blocks in segmented polyurethanes are usually very short [7]. The versatility is attributed to the unique possibilities for tailor making their properties by varying the composition of hard and soft segments [8]. The difference in hard to soft segment ratio i.e., incompatibility or thermodynamic differences in the segments [9-12], results in microphase separation to form domains. However, this incompatibility can be controlled by many factors such as the composition, structure and molecular mass of the hard and soft segments. A large number of reports are available on the effect of structures of hard and soft segments on physical, thermal and chemical properties of these polymeric materials [13-15]. The strength and high elasticity of polyurethanes are due to the hard domains stabilized by fascinating non-covalent interactions of hydrogen bonding between hard segments [16]. In the process, NH group in the urethane linkage acts as the proton donor, whereas the ether linkage (polyether polyurethanes) or carbonyl component of ester linkage

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\*Parts of this work is ready for communication

(polyester polyurethanes) as well as the carbonyl component of the urethane group acts as the proton acceptor [17-18]. Flexibility is another important unique feature of polyurethanes which arises from the presence of flexible ether linkages, ester linkages and long hydrocarbon polymer chains in the soft domains of their structure [11, 19-20].

The depletion of world oil pool, rising price of crude oil and increased environmental concerns are pressurizing the scientists for the use of renewable natural resources in different fields of applications as they are eco-friendly and cost effective materials. Vegetable oil is one such renewable resource possessing excellent properties for utilization in the production of different polymeric materials such as alkyd, epoxy, polyesteramide, polyurethane etc. in addition to many other applications [21-30]. The last decade has seen a growing interest in the use of the abundant and cheap vegetable oils for production of polymers, which are generally prepared from petrochemicals. The vast forest resources and farm lands yield varieties of oil-bearing seeds. Among them, about 350 oil bearing crops have been identified so far. Scientists and researchers are now using plant triglycerides as their feedstocks in the development of valuable polymeric resins and monomeric products such as polyesters [31-32], polyesteramides [33-37], epoxies [38-40], polyurethanes [41-50] and fatty amide monomers [51-52]. The traditional vegetable seed oils that have been utilized successfully to synthesize these resins are castor [53-57], linseed [40, 58-62], soybean [63-76], sunflower [77-79], tung [80], rapeseed [79, 81], canola [82-85], corn [85], palm [86-87], safflower [80,87], peanut [87], coconut [88], cottonseed [89] etc. In spite of these, some non-traditional oils are also used. They are rubber seed oil [90], kamala seed oil [91], mahua oil (*Madhumica Indica*) [92], karanja oil [93-94], neem oil [95], tobacco seed oil [96], annona squamosa oil [97], melon seed oil [98], African mahogany seed oil [99], jatropha seed oil [100] etc.

The emerging economies of India, Brazil and China due to the constant oscillating price of crude oil and limited success in finding vast crude oil reservoirs, the perception is growing among the mass that the end of the cheap oil era has arrived. The price of crude oil is more likely to increase than to decrease in the coming decades. Hence worldwide economic and scientific interest in vegetable oils as inexpensive and readily available renewable resource is growing incredibly in recent times. Besides the cost problem, the non-employment problem of the country can also be solved to certain extent by employing people in cultivation of naturally growing plants, collection of oil

seeds and extraction of the oil thereof. Utilization of vegetable oils may also conserve the energy required to convert the petrochemicals into the synthetic chemicals and also to conserve foreign exchange needed to pay for importing petroleum oil.

## **1.2. Background**

The basic polyurethane chemistry dates back to 1937. Otto Bayer developed the first polyurethane in the form of fiber in his laboratory at I.G. Farbenindustrie, Germany [101-103] in response to the competitive challenge arising from Wallace Carothers' work on polyamides (Nylon) at E.I. DuPont. The success of Carothers' work prompted Bayer to investigate similar materials not covered by DuPont patents. Initial research was primarily concerned with the reaction of aliphatic isocyanate with a diamine to form polyurea. Further research in the nineteen-forties emphasized the preparation of polyurethanes from the reaction of an aliphatic isocyanate with a glycol. The industrial scale production of polyurethanes was seriously affected by World War II (when polyurethanes were used in aircraft coating only). It is only after the availability of polyisocyanate (particularly the toluene diisocyanate) in 1952, Bayer developed different polyester-polyisocyanate systems in 1952-54. Thus these materials came into general use only in the 1950's as rigid foams, rubber, linear fibers (Lycra, spandex) and elastomers, to name a few [104]. Afterwards, polyurethanes are being manufactured continuously in a diversified manner and are used on industrial scale for myriad of applications that make polyurethane a resounding commercial success.

## **1.3. Polyurethane**

Polyurethane is an organic polymer formed by the reaction between three basic components: di-/ polyisocyanates, di-/ polyols and low molecular weight bifunctional chain extenders. The polymers are characterized by the presence of urethane group (-NHCOO) in their chains although some other functional groups like ester, amide, ether and urea may also present in the structure.

### **1.3.1. Classes**

Like most of the polymers, polyurethanes can also be classified mainly into two categories viz. thermosetting (low molecular weight polymer easily flowable in the

intermediate state) and thermoplastic polyurethanes (relatively high molecular weight). The molecular weight is actually determined by the extent of chain extension and partial cross-linking (if any) that occur during the polymerization process. However, the thermoplastic polyurethane can be judiciously crosslinked to obtain thermosetting products. Again depending on the composition and nature of components, the presence and type of additional ingredients in the polymerization recipe, different classes of polyurethanes ranging from elastomers to solid foams including adhesive, resins, fiber etc. may be obtained.

#### 1.3.1.1. Elastomers

Polyurethane elastomers are a class of specialty polymeric materials with high reversible deformation and are characterized by high hardness, abrasion resistance, chemical resistance, excellent mechanical and elastic properties [11, 105]. The primary and essential requirements for a polyurethane elastomer are a flexible long chain oligomeric polyol of molecular weight ca. 2000-5000 g/mole, a diisocyanate and a low molecular weight chain extender [54] along with maintenance of NCO/OH ratio equal to one. There are three main classes of polyurethane elastomers namely, millable, castable and thermoplastic. Millable polyurethanes are a special type of synthetic rubber which finds interest in rubber industries because they can be mixed, extruded, calendered, compression or injection molded in the processing unit [54]. Thermoplastic polyurethanes are biphasic materials that exhibit performance characteristics like vulcanized rubber but processing characteristics like thermoplastic polymers [106]. Castable polyurethanes are obtained by mixing the polyol and the diisocyanate at elevated temperature for a short time in a pre-polymerization step. The chain extender is then added and mixed thoroughly and the resulting solution is poured into a mold.

#### 1.3.1.2. Foams

The major area of application of polyurethanes is in the foam sector [107]. The requirements for polyurethane foam are a low molecular weight polyol and an aromatic diisocyanate [105]. Polyurethane foams are formed by the reaction between moist polyol and isocyanate that produces gas bubbles of CO<sub>2</sub> in a liquid which is polymerizing followed by the growth and stabilization of those bubbles as the polymer

solidifies. Polyurethane foams are mainly classified as flexible and rigid foams. Flexible foams have molecular weight of ca. 3000-6000 g/mole and functionality of ca. 3. They possess light weight and high load bearing capabilities. The versatility of flexible polyurethane foams is reflected in their use in various products like mattress, bedding, furniture, automotive interiors, carpet and packaging. Rigid polyurethane foams are based on polyols of molecular weight below 1000 g/mole and functionality of ca. 3-6. Rigid polyurethane foams are utilized in energy efficient and versatile insulations in construction industry and in the global appliances industry [81].

#### 1.3.1.3. Resins

One significant class of polyurethanes is resin, which are largely employed for paints and coatings industry as binders. Polyurethane resins are low molecular weight highly functionalized polymers in their intermediate state and have been used for more than fifty years as surface coating materials. Polyurethane coatings are preferred for many applications because of their unique combination of performance and application properties with wide range of flexibility combined with toughness, hardness, high abrasion resistance, high chemical and solvent resistance, excellent electrical properties and low curing temperatures [108-109]. Being reactive coatings, their low molecular weight oligomers react to form polymeric networks on various substrates. Polyester polyol based polyurethanes are found to be suitable for highly durable coatings of high mechanical strength, chemical resistance and heat resistance, whereas polyether polyol based polyurethanes are suitable for flexible coating even under low temperature and high humid conditions and possess resistance to microorganism attack [105, 108]. Researchers have given their attention from conventional organic solvent based coatings to solvent free high solid polyurethane coatings (coatings with 70% or above solids) and waterborne polyurethane coatings in order to keep the environment clean and green [55]. However, because of their inherent difficulties, the present thesis has not given emphasis on this subject although it deals with polyurethane resins only.

#### 1.3.1.4. Adhesives and sealants

Polyurethane adhesives are as old as polyurethane itself whereas polyurethane sealants are known since 1965 and have developed a reputation for reliability and

performance owing to high shear and tensile strengths and hence are broadly used in many industries. This may be attributed to their capability of wetting the surface easily, forming H-bonds with various substrates, allowing themselves to permeate through porous substrates and forming covalent bonds with substrates containing active hydrogen atoms [105, 110-112]. The factors that affect the performance of polyurethane adhesives are the nature of the isocyanate (aromatic isocyanates are better than aliphatic ones), nature of the polyol (polyether polyols are poorer in performance than polyester polyols), amount of aromatic and aliphatic groups, type of the solvents used during casting and the crystallinity of the polyols [112].

#### 1.3.1.5. Fibers

The initial research on polyurethane was focused towards the preparation of fiber forming polymers [113]. Polyurethane fibers can be prepared from the diisocyanate with low molecular weight chain extender like ethylene glycol, hydrazine, hydroxyl amine etc. under nitrogen atmosphere at elevated temperature. The polymer is then spun into fibers. Polyurethane fibers, in most cases, are used as blends along with some other fibers for better performance. For example, a highly elastic fiber known as “two way tricol” is a blend of polyurethane fiber with nylon (or polyester fiber). Lately, elastic polyurethane fibers have been developed to obtain Elasthane (fibers containing polyurethane urea of aromatic diisocyanate) and Spandex (fibers composed of at least 85% urethane linkages in structure). They are based on low molecular weight diol or diamine chain extenders and diisocyanates [105].

#### 1.3.1.6. Ionomers

Polyurethanes containing ionic groups to certain extent at the backbone of the polymer are known as polyurethane ionomers. In general, polyurethanes with moderate to high ionic content are termed as polyurethane ionomers whereas polyurethanes with very high ionic content are called polyelectrolytes [110]. Further, depending on the nature of the ionic group, polyurethane ionomers can be classified as cationic, anionic and zwitterionic or ampholytic [114-115]. The application of polyurethane ionomers is growing rapidly, particularly in the biomedical field and in modern pharmaceuticals including their use as semi-permeable membranes.

### **1.3.2. Preparation**

#### 1.3.2.1. Materials

##### *1.3.2.1.1. Macroglycol*

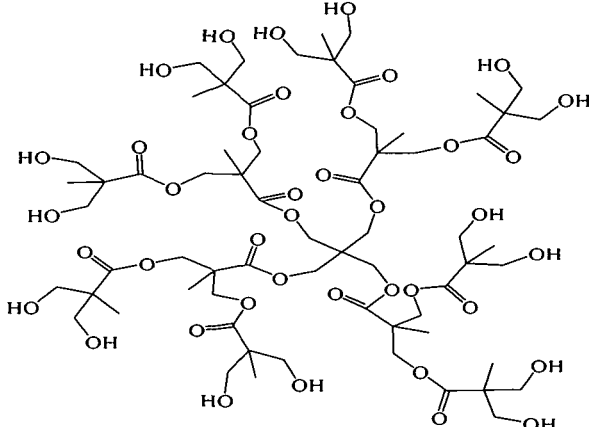
One major factor on which the properties of polyurethane depends is the nature and structure of the polyol component (macroglycol). The relatively high molecular weight (generally 400 to 5000 g/mole) diols/ polyols are used as macroglycol in polyurethane preparation [105]. These high molecular weight polyols result less numbers of urethane groups in the structure of polyurethane and hence these segments are highly flexible. Various macroglycols used for polyurethane synthesis as mentioned in Table 1.1 include polyesters, polyethers, polycarbonates, polyhydrocarbons, polycaprolactones, polyacrylics etc. [11, 105, 116-117].

Long chain macroglycols with low functionality generally results soft elastomeric polyurethanes, whereas short chain macroglycols with high functionality yields rigid crosslinked product [117]. Polyester polyols are the most common and are obtained by the condensation reaction of polycarboxylic acids or anhydrides with polyfunctional alcohols, while polyether polyols are prepared by the addition of ethylene or propylene oxide to a polyhydroxy compound in the presence of a catalyst. Polyether polyols may confer to the polymers with some specific properties such as metal chelation, hydrophilicity, crystallinity, surface activity etc. The polyester polyol based polyurethane is advantageous over the polyether based one in terms of performance characteristics related to strength, heat stability, adhesion and low cost. This is due to the presence of more polar linkages in the polyester. But at the same time the ester groups suffer easy hydrolysis, especially by alkali, to the carboxylic acid and alcohol. Further, *in-situ* formation of carboxylic acids catalyzes the hydrolysis of ester groups which causes an autocatalytic effect [118] and thereby deteriorates the mechanical properties. Some other specialty polyester polyols like polycarbonate and polycaprolactone possess much improved hydrolytic resistance. Aliphatic polyhydrocarbon polyol such as hydroxyl terminated polybutadiene (HTPB) is advantageous in many respects. These are resistant to acidic or basic hydrolysis, possess good adhesion and can be used where low polarity and good electrical insulation is required [119]. Acrylic polyols are prepared by free radical polymerization of hydroxyethyl acrylate or methacrylate with other acrylic precursors [117]. To



introduce rigidity and stiffness in the polymer, the polymer structure must be highly crosslinked which can be done by using polyhydroxyl polyols (triol or higher polyols). Trifunctional polyols leads to network formation instead of chain extension done by diols. This reduces flexibility of the polymer. Different types of macroglycols used in polyurethane preparation are listed in the Table 1.1.

Table 1.1 Commonly used macroglycols in polyurethane synthesis

Type of polyol	Structure	Ref.
Polyester	$\text{HO}-\text{R}-\left[ \text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R} \right]_n-\text{OH}$ <p>where R = hydrocarbon part that may contain ether linkages also</p>	11
Polyether (Polyalkylene oxide)	$\text{HO}-\left[ \left( \text{CH}_2 \right)_x-\overset{\text{R}}{\text{CH}}-\text{O} \right]_n-\text{H}$ <p>where, x = 1,3 for R = H and x = 1 only for R = Me and Et</p>	105, 116
Polycaprolactone	$\text{HO}-\left[ \left( \text{CH}_2 \right)_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{O} \right]_n-\left( \text{CH}_2 \right)_6-\left[ \text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\left( \text{CH}_2 \right)_5 \right]_n-\text{OH}$	11, 116
Polycarbonate	$\text{HO}-\left[ \left( \text{CH}_2 \right)_6-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O} \right]_n-\text{OH}$	11, 116
Polyhydrocarbon	$\text{HO}-\left[ \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \right]_n-\text{OH}$ <p>Hydroxy terminated polybutadiene glycol (HTPB)</p>	116
Polyacrylic	$\text{CH}_3-\left[ \underset{\text{COOR}}{\text{CH}}-\text{CH}_2-\underset{\text{COOCH}_2\text{CH}_2\text{OH}}{\text{CH}} \right]_n-\text{CH}_3$	117
Polyhydroxyl	$\begin{array}{c} \text{CH}_2\text{-ORO} \\   \\ (\text{CH-ORO})_x \\   \\ \text{CH}_2\text{-ORO} \end{array}$ <p>where x = 1 for triol and 6 for hexol</p>	105
Hyperbranched		117

Recently, highly branched and functionalized dendritic or hyperbranched polyols are attracting scientists for their beautiful architecture. Dendritic polymers have got high reputation over the last two decades due to their unique architectural features and the presence of large number of end groups. Due to their highly branched, compact and globular non-entangled structures, hyperbranched polymers possess low viscosity, high reactivity and good solubility, and are generally amorphous materials. Several grades of hyperbranched polyester polyols are now commercially available in the trade name of “Bolton™” (Table 1.1). Hyperbranched polyurethanes with hydroxyl or isocyanate end groups displayed better performances than their linear analogs [120].

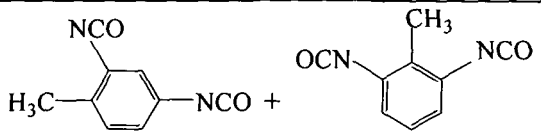
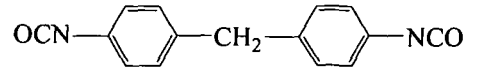
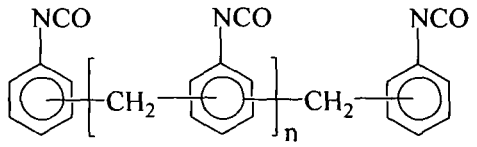
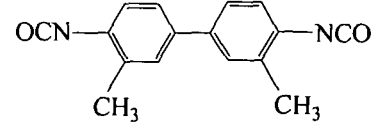
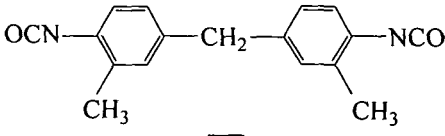
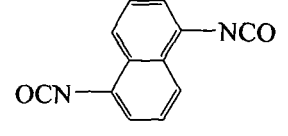
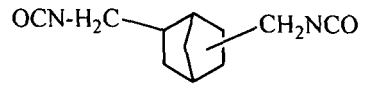
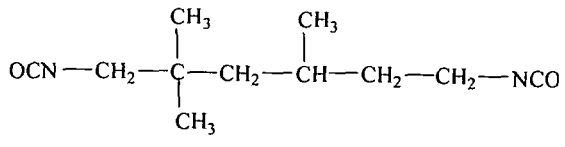
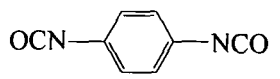
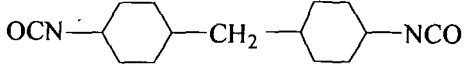
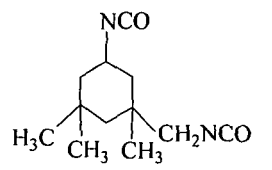
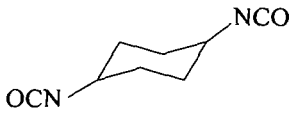
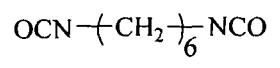
#### *1.3.2.1.2. Diisocyanate*

The properties of polyurethanes depend mostly upon the structure of the isocyanate component. Structure of the final product can be controlled by suitable selection of the isocyanate component. Isocyanates are prepared by phosgenation of an amine or an amine salt [109]. Polyisocyanates used for synthesizing polyurethanes are generally aromatic, aliphatic, cycloaliphatic or polycyclic in structure. The most commonly used diisocyanates are listed in Table 1.2.

Among these, the most common diisocyanates used in large scale are TDI and MDI [110, 121]. Toluene diisocyanate was the first commercially available isocyanate and is available as a mixture of 80% of 2,4- and 20% of 2,6-toluene diisocyanate isomers (Table 1.2), though they are also available as pure single isomers [109, 121]. Similarly, MDI has three isomers namely 4,4-, 2,4- and 2,2-diphenyl methane diisocyanate. However, only 4,4-isomer is used in commercial purposes [121] though in PMDI, all the isomers are present and is used in polyurethane preparation.

The reactivity of aromatic diisocyanates is higher than the cycloaliphatic or aliphatic diisocyanates. The rigidity of the polyurethane network and the enhancement of most of the properties are found to be in the order, aromatic diisocyanate > cycloaliphatic diisocyanate > aliphatic diisocyanate [122]. However, elongation at break and impact resistance are found to be in the opposite order. The oxidative and ultraviolet stabilities of aromatic diisocyanates and polymers made from them are somewhat low and they become yellow with time. This yellowing nature may be ascribed to the presence of aromatic or benzenoid structures, capable of undergoing

Table 1.2 Commonly used diisocyanates in polyurethane synthesis

Type of isocyanate	Trade Name	Structure	Ref.
Toluene diisocyanate	TDI		11
4,4-Diphenyl methane diisocyanate	MDI		11
Polymeric methylene diphenyl diisocyanate	PMDI		105
3,3- Bitoluene (or o-Toluidine) diisocyanate	TODI		11
3,3-Dimethyl diphenyl methane diisocyanate	DDI		105
Naphthalene diisocyanate	NDI		105
Norbornane diisocyanate	NBDI		2
2,2,4-Trimethyl hexamethylene diisocyanate	TMDI		11
p-Phenylene diisocyanate	PPDI		11
Dicyclohexyl methane diisocyanate	HMDI		11
Isophorone diisocyanate	IPDI		11
Cyclohexyl diisocyanate	CDI		11
Hexamethylene diisocyanate	HDI		11

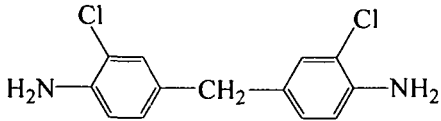


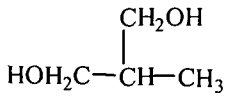
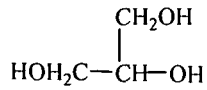
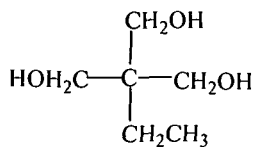
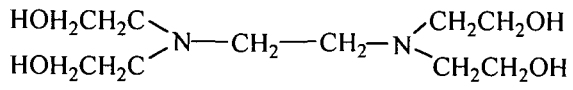
resonance, which tend to tarnish on exposure to light [116-117, 123]. Hence aliphatic and cycloaliphatic diisocyanates find wider use in elastomer and coating applications than their aromatic counterparts. HDI and HMDI are the two most common aliphatic diisocyanates used commercially. Further, cycloaliphatic diisocyanates based polyurethanes possess superior retention of hardness, modulus, resistance to water uptake and hydrolysis and thermal degradation compared to aromatic diisocyanate based polyurethanes. Cycloaliphatic diisocyanates like CDI and HMDI are comparatively more reactive and gives polyurethanes with high strength and thermal stability [11, 123]. Aromatic triisocyanate (e.g., Desmodur RF<sup>R</sup> and Desmodur CB 75N<sup>R</sup>) based polyurethanes exhibit even much improved properties [124-125]. This may be due to the greater density of aromatic triisocyanate based polyurethane as compared to the cycloaliphatic and aliphatic diisocyanates [124].

#### *1.3.2.1.3. Chain extender*

Chain extenders are active hydrogen containing difunctional compounds having low molecular weight (up to 300 g/mole). The primary role of a chain extender is to extend the length of the hard segment, and to increase the hydrogen bond density and the molecular weight of the polyurethane. Chain extenders may be categorized as diols, diamines and aminoalcohols and can be both aliphatic and aromatic. In general, aliphatic chain extenders offer comparatively softer material than aromatic chain extenders. The most commonly used chain extenders are mentioned in Table 1.3.

Diol chain extenders suffer from difficulties like limited solubility in polyol and often require organometallic catalysts to speed up the urethane reaction [105]. In contrast, amine chain extenders react rapidly and increase the interaction between substituted urea linkages giving rise to polymers crosslinked with biuret link which ultimately gives thermoset materials. Cyclic and aromatic chain extenders generally result materials with superior performance characteristics. Trifunctional and higher branched chain extenders like trimethylol propane, hyperbranched polyol etc. are also reported to be used as branching or cross-linking agents [116].

Table 1.3 Commonly used chain extenders in polyurethane synthesis

Name	Chemical Structure	Ref.
Ethylene glycol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	11, 116
1,4-Butanediol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$	11, 116
1,6-Hexanediol	$\text{HO}-\left(\text{CH}_2\right)_6-\text{OH}$	11, 116
Ethylene diamine	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	116
Ethanolamine	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$	11
4,4-Methylene bis(2-chloroaniline) (MOCA)		116
1,4-Dihydroxydiethyl benzene		123
1,4-Cyclohexane dimethanol		105
2-Methyl-1,3-propane diol		105
1,2,3-Propanetriol		105
Trimethylol propane		105
N,N,N,N-tetrakis (2-hydroxyethyl)ethyl diamine		105
Diethylene triamine	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	105

#### 1.3.2.1.4. Catalyst

Various catalysts used for the preparation of polyurethane at lower temperature at much faster rate as compared to the uncatalyzed reaction are given in Table 1.4. The catalysts can be classified into two broad categories namely, amine (basic) compounds and organometallic complex compounds. Followed by the pioneering work on catalysis of urethane reaction by Baker and Gaunt [126] and Baker and Bailey [127], tertiary

amine catalyst is still one of the most often used urethane catalysts [128]. Commonly used amine catalysts are triethylenediamine (TEDA) also known as 1,4-diazabicyclo [2.2.2] octane (DABCO), triethylamine (TEA), dimethylethanolamine (DMEA), dimethylcyclohexylamine (DMCHA) etc. [117]. The catalysis mechanism of tertiary amine catalysed urethane reaction, as suggested by Lenz [129], involves complexation of the amine with isocyanate groups followed by reaction of the complex with alcohol to produce polyurethane [117].

Table 1.4 Commonly used catalysts in polyurethane synthesis

Name	Trade Name	Chemical Structure	Ref.
Triethylenediamine	TEDA/ DABCO		117
Triethylamine	TEA/ TEN		117
Dimethylethanol-amine	DMEA		117
Dimethylcyclohexyl-amine	DMCHA		116
Tetravalent tin compounds	-	$R_nSnX_{(4-n)}$ Where R=alkyl, aryl etc. and X= halogen/ carboxylate group	117
Stannous octoate	-		117, 121
Dibutyltindilaurate	DBTDL		117, 121
Dibutyltin oxide	DBTO		117, 121

Organometallic compounds based on mercury, lead, tin, bismuth and zinc are also used to catalyze the urethane reaction [117, 121]. However, due to their toxicity and disposal problems, bismuth and zinc carboxylates have been used as alternatives since 1990's. Now-a-days, alkyl tin carboxylates, oxides and mercaptide oxides such as dibutyl tin dilaurate (DBTDL), dioctyltin mercaptide, stannous octoate, dibutyltin oxide

etc. are used successfully in all types of polyurethane applications (Table 1.4) [117, 121] among which, DBTDL is found to be the most widely used. The catalytic effect of the organometallic compounds is due to their complex forming capability with the isocyanates and polyols [130-131]. The catalysis mechanism involves interaction of the metal cation with isocyanate and hydroxyl groups followed by rearrangement of the resulting complex to yield the final urethane product [130-132].

#### 1.3.2.2. Techniques of preparation

Polyurethane is generally synthesized by rearrangement polymerization method. The polymer chains are formed as in addition polymerization but the kinetics resemble to condensation polymerization. The low molecular weight polyurethanes are advantageous in many applicational aspects particularly in coating industries [133]. The techniques for preparation of such polyurethanes are discussed here.

##### *1.3.2.2.1. One shot process*

One shot technique for the preparation of polyurethane is the easiest and generally offers a more random block copolymer [134] compared to other techniques. It is of three types viz. oxidative cured, moisture cured and heat cured methods.

The one shot oxidative cured technique is analogous to that used for alkyd manufacture and is characterized by the absence of free isocyanate groups. In this method, generally an unsaturated drying oil (soybean, safflower, tall etc.) is reacted (alcoholised) with a polyhydroxy compound such as pentaerythritol or glycerol. The intermediate containing free hydroxyl groups are then reacted with the diisocyanate to obtain the product. As the products, also known as urethane oils, contain no unreacted free isocyanate groups, they are free from moisture sensitivity. The curing of the product is accomplished by solvent evaporation and oxidation of the unsaturated oil in air like that of the conventional alkyds [117, 135]. The polyurethanes obtained by one shot moisture cured technique contain NCO terminated polyurethane prepolymer which on curing with atmospheric oxygen produces highly crosslinked networks [109, 136]. The mechanism behind the curing reaction involves interaction of water with isocyanate to generate primary amine which further reacts to produce urea linkage [117]. Moisture present on the surface completes the chemical reaction in such

polyurethanes and these materials adhere well to the damp surfaces. However, these types of polyurethanes suffer from a serious disadvantage of formation of by-products like biuret and allophanate which increases viscosity of the prepolymer and changes the onset of gelation point thereby reducing the storage stability [137-138]. On the other hand, in the one shot heat cured method, the free isocyanate groups are blocked by reacting them with compounds like phenol or low molecular weight monohydric alcohols like butanol. The isocyanate reactivity is restored by heating at ca. 150 °C or above. Thus the polyurethanes are cured by thermal release of blocking agent and subsequent chemical reactions of reactivated isocyanate groups with the high molecular weight polyols [109, 139]. The advantage of this type one shot technique is the elimination of handling problem as two reactive materials (including toxic isocyanates) can be stored in the same package.

#### *1.3.2.2.2. Two shot or prepolymer process*

The two shot process, more commonly known as the prepolymer method, of polyurethane synthesis is more common and offers less random and more block polymers (multiblock copolymer) [134]. The two shot methodology involves mixing of two separate packages to obtain the polyurethanes at the time of application. One package consists of relatively small molecules of isocyanate terminated prepolymer whereas the second package consists of a cross-linking agent or a chain extender (diamine or diol). The two shot methodology is generally of two types, two shot prepolymer catalyst and two shot prepolymer polyol methods [109, 117].

The prepolymer used in two shot prepolymer catalyst technique is of the same kind as the one used in one shot moisture cure technique. In addition, they are provided with a separate catalyst to accelerate the curing process [105]. Thus in this method, prepolymers containing free isocyanate groups comprise of one package, whereas the second package consists of small quantities of a suitable catalyst, accelerator or cross-linking agent that could contain polyol/ amine [117]. Therefore, the polyurethane obtained by this technique dries at a much faster rate as compared to the one obtained from one shot moisture cured technique [109]. On the other hand, in the two shot prepolymer polyol technique, the prepolymer used is of the same kind as that of the one shot heat cured technique. Thus in this method, isocyanate blocked prepolymers comprise of one package whereas the second package contains a solution of a polyol.



The final adduct (relatively lower molecular weight) [117] is obtained by mixing the two packages, if desired, heat can be applied to deblock the isocyanates [109].

To obtain high molecular weight thermoplastic and elastomeric polyurethanes generally similar type one shot and prepolymer techniques are used with proper maintenance of the NCO/OH ratio close to one.

Polyurethane formation is a highly exothermic process. The synthesis of polyurethanes is done in the laboratory by bulk or solution polymerization technique. Although bulk polymerization is used commercially in most of the cases, the solution polymerization technique is also used widely in laboratory. The most common solvents used for the purpose are dimethyl formamide (DMF), dimethyl acetamide (DMA), tetrahydrofuran (THF), dimethyl sulphoxide (DMSO), toluene and xylene.

### ***1.3.3. Characterization***

Polyurethanes are being characterized by the conventional analytical and spectroscopic techniques like other polymers. Standard techniques are used for determining different physical properties like viscosity, specific gravity, drying time, hydroxyl value, isocyanate value [109] etc. Structural confirmation, molecular weight determination, rheological behavior and thermal characterization are generally done by spectroscopic techniques like FTIR/ NMR, GPC analysis, rheometer / DMA studies and TGA/ DSC/ TMA respectively. Crystallinity and morphology in certain cases are characterized by X-ray diffractometer [140-144] and scanning electron microscopy [145-146] respectively.

#### **1.3.3.1. Analytical techniques**

Viscosity is an important physical property of any polymer to determine. The intrinsic viscosity of a polymer solution is usually given by Huggin's equation for very dilute solution. The relative viscosity and thus reduced viscosity of a polymer solution can be experimentally determined by recording the flow times of the polymer solution and the pure solvent in a capillary viscometer [147-148]. The specific gravity is a function of the molecular weight of the individual molecule and the way they packed. Specific gravity is determined according to the conventional liquid displacement method (Archimedes principle) [109]. Hydroxyl value of a polymer is a measure of the

hydroxyl content and is defined as the number of milligrams of KOH equivalent to the hydroxyl content of one gram of the polymer [109]. The isocyanate value helps to have an idea about free NCO groups present in the resin which may be determined by the standard method given by Campbell and Sorenson [149].

#### 1.3.3.2. Spectroscopic techniques

Fourier transform infrared (FTIR) spectroscopy is one of the most often used techniques to characterize polyurethanes. Presence of certain functional groups such as carbonyl, ester, hydroxyl, secondary amine (NH), isocyanate, cyanide, ether, double bond, aromatic moiety etc. can be determined by FTIR spectroscopic technique [140, 142-144]. The most important application of FTIR spectroscopy in the synthesis of polyurethanes is to monitor the progress of the reaction. This is done by observing gradual disappearance of the absorption peak of isocyanate group and sharpening of the broad peak of hydroxyl group which confirms the completion of the reaction. The isocyanate absorption peak is found to be present for polyurethane resins with NCO/OH ratio  $> 1$  indicating the presence of free isocyanate groups, whereas it is absent for polyurethane resins with NCO/OH ratio  $< 1$ . Curing of the resins as well as their blends and interpenetrating networks (IPN) with commercial resins by the formation of some new linkages are also characterized by FTIR technique [150-151].

Nuclear Magnetic Resonance (NMR) spectroscopy determines different types of chemically equivalent nuclei like  $^1\text{H}$  and  $^{13}\text{C}$ , present in the structure [140-141] and hence is employed largely to understand the actual structure of polyurethane along with its precursors (polyol, isocyanate).  $^1\text{H}$ NMR indicates different types of protons in functional groups such as hydroxyl, secondary amine, methyl, aromatic moiety etc. present in the structure of polyurethane. Similarly,  $^{13}\text{C}$ NMR is used to determine the presence of chemically different carbon atoms in aliphatic, aromatic, saturated, unsaturated hydrocarbons, esters, ethers, carbonyl groups etc. Further an idea can be generated regarding the degree of curing of the resin and hence the extent of the reaction by observing the resolution of the NMR spectrum [152].

The molecular weight and its distribution of polymers are generally determined by gel permeation chromatography (GPC) technique wherein macromolecules are separated according to their size in organic solvents [143, 145]. Thermal

characterization of polyurethanes is done by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. Besides determining thermostability of the polymers in different environments, TGA can be utilized to know the mode of degradation, kinetics of degradation, formation of char residue etc. [142-143]. DSC technique is widely used to know the phase change, phase separation (by observing two glass transition temperatures), chemical change that take place during degradation, cross-linking etc. [142-143]. Polyurethane formation may be monitored and cure kinetics of them can be studied by DSC technique [153]. DSC is also reported for the determination of optimum curing temperature or onset gel point of polyurethanes and their blends as well as composites [154-155].

The crystallinity of a material is due to the systematic or regular packing of the atom or molecules in three dimensions. This can be observed as intense (clear) Bragg diffraction peaks in WXR D patterns which are obtained by a X-ray diffractometer [145]. X-ray diffraction studies of polyurethanes indicate their amorphous/ crystalline nature [156-157]. Polyurethanes may have crystallinity to certain extent depending on the nature of the components though many of them are known to be amorphous.

Polyurethane is a multiphase polymer. The homogeneity of such materials can be observed by taking fracture micrographs by scanning electron microscopy (SEM) [146]. Observation of domains in certain regions of the micrograph indicates heterogeneity. Further, the morphology of the polyurethane composites and blends of polyurethanes with commercial resins are also investigated by SEM technique which indicate the dispensability and phase characteristic of different components present in the system. Furthermore, the morphology of polyurethane nanocomposites, obtained by introducing clay into polyurethane matrix, can be studied by SEM and more conveniently by transmission electron microscopy (TEM) technique [158-161]. Atomic Force Microscopy (AFM) is a widely used technique to examine surface or phase structure in polyurethanes and polyurethane/ clay nanocomposites [162-163] and hence can give a better understanding on the relationship between the structure and properties.

#### ***1.3.4. Properties***

Polyurethane is a unique class of material gaining vast popularity due to its diversified applications as they can be prepared from a large variety of polyols and diisocyanates [109]. A lot of studies have been done on the structure property

relationship, which is very useful to understand the expected properties of the polyurethanes. Such properties include physical, chemical, mechanical, rheological, electrical, biological, thermal etc.

#### *1.3.4.1. Physical*

The most important physical property to characterize polyurethanes is their viscosities. It is well known from Mark-Houwink-Sakurada equation, ( $[\eta] = KM_v^a$ ) that the viscosity average molecular weight ( $M_v$ ) increases with the increase of intrinsic viscosity ( $\eta$ ). Polyurethane resins possess lower viscosities and hence exhibit lower molecular weight than the thermoplastic or elastomeric polyurethanes [105].

The solubility of polyurethane becomes complicated due to increase in solution viscosity as the molecular weight increases. Linear polyurethanes are soluble in most polar organic solvents, whereas crosslinked polyurethanes are swellable only. The greater the cross-linking density, the lower is the degree of swelling. Polyurethane possesses low specific gravity possibly due to its amorphous nature indicating irregular packing. The specific gravity values are found to be slightly higher for polyurethanes containing heavy elements. It also increases with increase in NCO/OH ratio which may be due to increase in rigid aromatic moiety in the structure and due to increase in cross-linking by H-bonding and other molecular interactions [105].

#### *1.3.4.2. Mechanical and rheological*

Mechanical and rheological properties of a polymer depend upon a number of factors such as chain entanglement, coiling, cross-linking density, intermolecular and intramolecular attractive forces, molecular weight and its distribution etc. Higher the molecular weight, higher is the chain entanglement and coiling and better are the mechanical properties [88]. The presence of flexible hydrocarbon chains, ether linkage and ester linkage along with amorphous nature make polyurethanes very much flexible. The high strength properties of polyurethanes may be attributed to the same reason. Increase in cross-linking density results in the formation of a three dimensional dense network which causes increase in hardness also. Thus measurement of impact resistance is a unique method to ascertain both flexibility as well as hardness at the

same time. Presence of polar ester group, free hydroxyl and isocyanate group makes the adhesion property of the resinous polyurethane remarkably high.

The rheological behavior is the flow behavior which is complex in nature for polyurethane resins. Viscosity is found to be decreased with the increase of temperature as generally expected from Andrade equation [164]. Thixotropy is a time dependent fluid behavior in which the viscosity decreases with the time of shearing and the viscosity nears to its original value when shearing ceases [165-166]. Thixotropy is important as it prevents setting and sagging and cause easy application which improves film appearance. Polyurethane shows thixotropic behavior due to the presence of weak intermolecular interactions like H-bonding in it. It is also seen that certain polyurethanes are used as high solid coatings by reducing solvent amount [164].

#### 1.3.4.3. Chemical

The chemical resistance of a polymer depends upon a number of factors such as temperature, physical state of the polymer, degree of cross-linking, chemical linkages present in the chain, diffusion through polymer network and the environmental conditions [105]. Polyurethane is polar in nature and involves H-bonding. Thus it is highly resistant to hydrocarbon fuel and oil and are also resistant to ozone and oxidative ageing. Polyurethanes, particularly the polyester based ones, suffer ester hydrolysis and possess weak hydrolytic stability [107]. However, such stability can be improved by using hydrocarbon, polycaprolactone, polyether or polycarbonate based polyols [117].

#### 1.3.4.4. Thermal

Thermal property of a polymer is of great importance as it determines the stability in actual field under different thermal conditions. Polyurethanes have been known to be thermally unstable materials [167-168] due to the presence of labile urethane groups which decomposes by three mechanisms giving isocyanate, alcohol, primary amine, secondary amine, alkene and carbon dioxide as degradation products [169]. The thermal stability of polyurethane is governed by the polymerization depolymerization equilibria of the functional groups [105]. Some polyurethane are known to be flame retardant materials. Polyurethanes prepared from phosphorous or halogen containing polyols fall into this category. Polyurethanes may also be made

flame retardant by using additives such as phosphate esters, halogenated phosphates or hydrocarbons with high carbon to hydrogen ratio [105] etc.

#### 1.3.4.5. Electrical

The efficiency of a polymeric material as a dielectric to be used as insulators in microelectronic industry can be understood in terms of the parameters like dielectric constant, dielectric strength, resistivity, loss factor etc. A polymer is said to possess excellent dielectric properties when there is a very low conductivity to avoid current leak, a low dielectric constant to minimize capacitive coupling effects, and a low loss factor to reduce electrical loss [170]. Polyurethanes are polar molecules and have considerable flexibility that allows their polar groups to orient producing high dielectric constants [105]. Presence of any rigidity in the network prevents such orientation decreasing dielectric constant. This phenomenon is also dependent on frequency and temperature variation and hence polyurethanes possess variable dielectric constant.

#### 1.3.4.6. Biological

Assessment of the ultimate biodegradability of a polymeric product is of great significance from environmental viewpoints to reduce global environmental pollution [171]. To be applicable for short life time as in packaging materials or in controlled release of drugs, a polymer must be biodegradable whereas for engineering applications with long service, the polymer must be non-biodegradable. The ester linkages present in polyurethanes are susceptible to attack by bacterial or fungal activity in real field conditions after disposal [172]. Biodegradation occurs by hydrolytic attack via evolution of CO<sub>2</sub>. For most of the polyurethanes, the initial rate of biodegradation is high and then remains constant with time. However for long term application purposes, the biostability of polyurethanes can be increased by using polyether polyols and sometimes by adding biocides and biostats [105].

#### 1.3.4.7. Damping and shape memory

Damping properties of polyurethanes have been reported for a broad range of temperature and frequencies [173]. High damping intensities are observed due to the

presence of ester groups in the polymer chains. Increase in cross-linking reduces the damping intensities by restricting the polymer segmental motions. Broad damping regions can be observed for segmental inhomogeneity when the polymer is combined with two or more structurally dissimilar polymers to form blends or IPN's with phase separated morphology [173]. Such materials are therefore expected to be efficient damping materials and can be utilized for sound and vibrational applications.

Shape memory properties of a polymer indicate its ability to remember a specific shape on demand even after severe deformation. Polyurethanes are good shape memory polymers [174-175]. They exhibit mechanical behavior that fixes the deformation of the polymer at room temperature and recover the deformation as elastomers at high temperatures. The shape memory properties of polyurethanes depend upon a number of factors such as conjugation present in the chain, curing temperatures, physical or chemical cross-links present in the polymer etc. [176].

### ***1.3.5. Applications***

Since their discovery over seventy years ago, polyurethane chemistry has been developed and adapted to make the diverse range of products available today. Polyurethane contributes more than 5% of total world consumption of plastics. A recent report states that world consumption of polyurethanes in 2005 was 8.8 million tons. North America is dominating the market by producing 3.7 million tons, whereas China is producing 2.9 million tons of polyurethanes [107]. Although the greatest consumption of urethane products is still in the foam sector, the trend of polyurethane applications is increasing in the field of surface coatings, medical, composites and even in microelectronics. Besides various outstanding properties, the most important characteristic of polyurethanes that makes it extremely versatile in diversified applications is their tailor made nature which can be done by proper variation (choice) of the hard and soft segments.

Polyurethanes have found numerous applications in the high performance coatings for the automotive, appliance and wood industries [177] as they exhibit a wide range of mechanical properties, excellent abrasion resistance, hardness, flexibility, chemical and corrosion resistance. Most of the polyurethane paints available in the market are based on aliphatic isocyanates and polyester or acrylic polyols due to their

excellent weatherability. Polyester polyurethanes are known to be utilized in electrically insulating lacquer coating materials [108]. The experimental results and literature data on physico-mechanical and insulating properties of polyurethanes make it clear that it has the capacity to act as anticorrosive coatings in many applications [178]. For example, polyurethane coatings have been utilized successfully for the last fifteen years in oil and gas pipelines and in large steel reservoirs of oil and fat products in Ukraine [179]. Examples of polyurethane coatings used in anticorrosive protection of underground pipelines are Copon Hycote 165 Varplex (Poland), Protegol UR Coating 32-55 (Germany), Ambercoat 2000 (Poland and Canada), Acothane TU (Great Britain) etc. and also in steel reservoirs are based on UR698 and AU699 (Ukraine), Hardtop AS (Norway) [178-179] etc.

Polyurethane adhesives and sealants are widely used in packaging, footwear, furniture assembly and automotive industry. Thermosetting polyurethane adhesives have higher thermal and chemical resistance as compared to the thermoplastics. Water or solvent carried polyurethane adhesives are preferred for large laminating areas such as fabrics or plastics [105]. One component polyurethane adhesives are used in laminated films for packaging while two component polyurethane adhesives are used as structural adhesives in solvent free applications for bonding plastic automotive parts. Among other applications, the fiber polyurethanes in combination with other fibers are widely used in stretchable clothing like swimsuits, leotards, foundation garments, hosiery etc. The newest and most advanced sports shoes and clothes are made from the polyurethane based spandex fibers [110]. Polyurethanes are also the preferred liner materials under landfills to prevent seepage contamination.

The application of polyurethanes in the medical field is limitless and has occupied an enviable and irreplaceable position [116]. Polyurethanes play a vital role in medicine at all scales from the construction of surgical instruments and medical implants to microscale encapsulation devices. Polyurethanes have the potential to be used for both permanent medical implants and in systems where degradation is required such as scaffolds for tissue regeneration. Among the various polymers used in medical sector, polyurethane is often the material of choice where complex mechanical and biocompatibility problem occurs. The requirements for a polymer to be used in various cardiovascular devices, depend on the intended duration of use, method of application and on function. Polyurethane is found to be suitable for cardiovascular devices used



for heart transplant patients awaiting a suitable donor. Such devices include the ventricular assist devices, total artificial hearts, blood conduits etc. Polyurethane has been used as a coating material in cardiac pacemaker lids and for breast implants. Polyurethane intra-aortic balloon devices are used in open heart surgery. Polyurethane is often used for gastric balloons, for catheters and other general purpose tubing. The polymer is also used for wound dressings (Tegaderm™) because of its good barrier properties and oxygen permeability, particularly in the treatment of difficult healing problem caused by burns and tissue adhesives [180]. Lycra<sup>R</sup>, a thermoplastic polyurethane elastomer is widely used in clothing related to surgical apparels to improve shape retention. A commercial poly(ether urethane) namely Elasthane™ and a similar material namely Pellethane<sup>R</sup> are largely used as implantable devices. Other commercial polyurethanes utilized in the medical field for different applications include Cardiothane, Biomer™, BioSpan<sup>R</sup>, Corvita<sup>R</sup>, Thoratec<sup>R</sup>, Pulse-Tec<sup>R</sup>, Mitrathane™ etc. Cardiothane is silicone based polyurethane used in intra-aortic balloons. Biomer™ is a poly(ether urethaneurea) and its alternative BioSpan<sup>R</sup> is used in a range of applications. The Corvita<sup>R</sup> is a vascular prosthesis made of poly(carbonate urethane) that offers compliant and low stress fibrous structure. The Thoratec<sup>R</sup> prosthesis is a poly(ether urethane) which offers less space for tissue ingrowth [116, 181]. Besides such numerous applications in medical sector, future developments are likely to come from tissue engineering with composite and biodegradable polyurethanes.

Polyurethane is attractive due to its structural versatility as a binder for composite materials both in macro and nano scale. The existing composites are the ones reinforced with traditional reinforcing materials such as glass fibers, talc, carbon or graphite, steel and mica [182]. However, natural fiber reinforced composite materials are now emerging as realistic alternatives to the existing traditional composites due to several environmental concerns [183-184]. Polyurethane composites are widely used in the areas like aerospace, military, construction, electrical and electronics, medicine, transportation etc. [182-185]. Polyurethane nanocomposites are now well known due to tremendous improvement in mechanical, thermal and gas barrier properties arising from the huge surface area of the nano-fillers that increases the interfacial interaction between the filler and polymer [186-187]. A lot of polyurethane nanocomposites have been developed by using different categories of polyurethanes and nano-fillers for various applications [186-188].

## **1.4. A short review on vegetable oil based polyurethanes**

### ***Introduction***

The depletion of petroleum reserves, the increase of demand for petroleum products, the threat of global warming and stringent environmental rules and regulations are inclining the society to make renewable resources indispensable in recent times. There is a growing urgency of novel and innovative technologies to be developed to produce products from such renewable resources that can unhook worldwide dependence on fossil fuel and at the same time can reduce the emission of CO<sub>2</sub> as well as other green house gases. Various renewable resources introduced into the act are biomass or plant derived resources like starch, cellulose and lignin, lipids (triacylglycerols, phospholipids, sterols etc.), proteins, sea resources, vegetable oils and other agricultural components. Among them, vegetable oil is of considerable importance as they possess some remarkable advantages. Some of them to mention are easy availability in large quantities with varieties of structure and compositions, less toxicity (as they do not develop VOC), easy handling and overall environmental benignness [21-24]. This results in a steady growth in the use of vegetable oils in paint and coating industries as well as in other non-food value added products of current and potential uses like shampoos, soaps, lubricants, emulsifiers, cosmetics, plasticizers, biodiesels, pharmaceuticals etc. [25-30]. Vegetable oil has also been utilized to develop different polymeric materials including polyurethanes as discussed in the introduction section. Different vegetable oils such as castor, linseed, soybean, sunflower, argemone, corn, canola, palm, tobacco etc. have been explored to synthesise different categories of polyurethanes successfully [53-96].

### ***Historical background***

The potential of vegetable oil for edible and industrial purposes was first demonstrated by J.G. Kane, known as the father of vegetable oils [189]. In 1925, Kienle and Hovey synthesized a series of polyester resins from vegetable oils for surface coating applications which was the beginning of vegetable oil based resins [88]. The concept for the development of vegetable oil based polyols for manufacturing polyurethanes was built in early nineteen-fifties initially from castor oil [190-191]. However, vegetable oil based polyurethanes started garnishing attention beginning

around the late nineteenth century as a consequence of the rising costs of petroleum feedstocks and the desire for having environment friendly green products [103]. Development of a wide variety of vegetable oil based polyurethanes has been reported in literature in almost steady ascending order of publications [53-96]. This is reflected in the increasing number of publications as confirmed from scopus search (Figure 1.1).

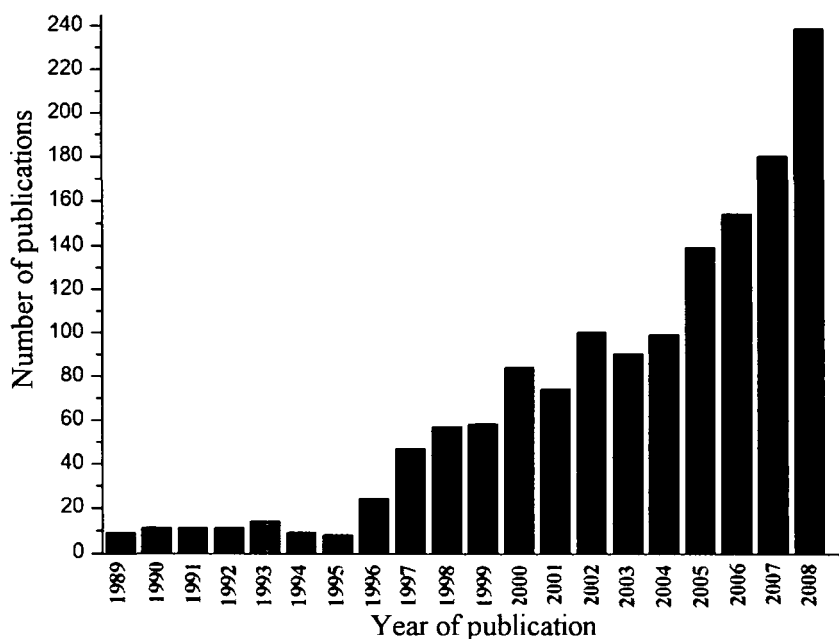


Figure 1.1 Scientific publications as a function of publication year searched by scopus

### ***Preparation of vegetable oil-based polyurethane***

The versatility of polyurethanes becomes more encompassed when they are synthesized from naturally renewable vegetable oils. Various seed oils as mentioned earlier [53-96] have successfully been utilized to synthesize polyurethane resins. The salient features of vegetable oil based polyurethanes that make it versatile are as follows,

- (i) The resource of one of the raw materials is naturally renewable and is available in large quantities.
- (ii) The cost involved in the raw materials and processing are relatively low as compared to the synthetic polyurethanes.
- (iii) They are soluble in low cost industrially used solvents.
- (iv) They are mostly environment friendly and are biodegradable.

(v) They exhibit excellent properties such as flexibility, mechanical strength, abrasion resistance, toughness, adhesion, chemical and corrosion resistance etc. which make them comparable with conventional petrochemical polyurethanes in many cases.

(vi) Due to the hydrophobic nature of triglyceride moiety, vegetable oil based polyurethanes have excellent chemical and physical properties such as enhanced hydrolytic and thermal stability.

(vii) The most important feature of polyurethanes is their structures and properties which can be tailor made by proper choice of the raw materials to meet the highly diversified demands of modern technological applications.

The preparation techniques mentioned in the general section are also employed to obtain vegetable oil based polyurethanes. The components viz. diisocyanate, chain extender and catalyst required for synthesizing such polyurethanes are exactly same as mentioned earlier, except the component vegetable oil or its derivative in the polyol section. Hence, only the details of vegetable oils are presented here.

### *Vegetable oils*

Vegetable oils or plant oils differ from mineral oils (petroleum fractions, obtained from mines) in terms of stability. Mineral oils are more stable than vegetable oils as the latter has a high degree of unsaturation. Unlike volatile essential oils found in the stems, leaves, flowers, fruits etc. of plants, vegetable oils (another category of plant oils) are non-volatile. They are commonly known as fixed oils because of their fixed composition and boiling point. Chemically, vegetable oils are generally triglycerides or triacylglycerols (esters of glycerol) with long chain fatty acids (Figure 1.2). The fatty acid content per molecule of triglyceride oil [192] is 94-96% of the total weight. Since there are a number of different fatty acids that occur in vegetable oils, a great many different triglycerides are encountered in nature. Arachidic, lauric, palmitic,

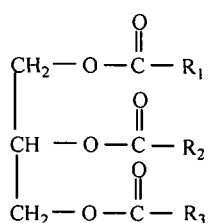


Figure 1.2 Structure of triglyceride (where R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> represent the hydrocarbon parts of different fatty acids).

stearic etc. as saturated and oleic, linoleic, ricinoleic, linolenic etc. as unsaturated fatty acids are generally found in different triglycerides. Besides these fatty acids, some others like myristic, behenic, capric, caproic, eleostearic, erucic, licanic, isanic, caprylic etc. are also found to be present to certain extent in some vegetable oils. These fatty acids contain some special functionalities like ketonic, hydroxyl, epoxy, triene etc. in addition to the regular carboxylic, saturated or unsaturated moieties. The structures of some such important fatty acids along with their physical properties like density, boiling point (b.p.) and melting point (m.p.) are shown in Table 1.5 [88, 121, 193]. Depending on the fatty acid distribution, different vegetable oils possess different physical and chemical properties (Table 1.6). However, the fatty acid profile of vegetable oils is fixed and acts as its “finger print”. Thus the fatty acid composition of the vegetable oils (Table 1.6) can be used to distinguish the vegetable oils from one another.

Along with these triglycerides the other constituents of a vegetable oil, of course in little amounts, are phospholipids, hydrocarbons, some fat soluble vitamins, tocopherols, tocotrienols, sterols, stanols and fatty acyl esters [109, 194]. The properties of different vegetable oils depend upon the characteristics of the triglycerides of which they are mixtures and upon the proportions of these triglycerides to one another.

Vegetable oils may be of various types (Scheme 1.1) depending upon certain factors. Three such important factors are film forming ability, edibility (or toxicity) and yellowing tendency (linolenic acid content). The film forming ability of a vegetable oil depends on its unsaturation content determined by measurement of iodine value. In general oils with iodine value greater than 150 may be termed as drying oils (linseed, tung), in between 120-150 may be termed as semi-drying (sunflower, soybean, rubber seed) and those having under 120 are called non-drying oils (castor, palm, canola, peanut) (Table 1.7). For non-conjugated oils, however, the drying rates are more closely related to the average number of methylene groups adjacent to two double bonds per oil molecule ( $f_n$ ) instead of their iodine values. An oil with  $f_n$  value  $> 2.2$  is said to be a drying oil, whereas oil with  $f_n$  value less than 2.2 is semi-drying. This method cannot be used to classify conjugated systems, though this method is superior and more reliable than the conventional iodine value method [195]. Non-conjugated oils can also be categorized on the basis of their drying index values defined as,

$$\text{Drying index} = \% \text{ linoleic acid} + 2 \times (\% \text{ linolenic acid})$$

Table 1.5 Chemical structure and physical properties of some fatty acids present in vegetable oils [88, 121]

Fatty Acid	Structure	Density (g/c.c.) at 25 °C	m.p. (°C)	b.p. (°C)
Arachidic		0.8240	74-76	328
Behenic		0.822	75-80	306
Capric		0.888	31-32	269
Caproic		0.92	-3	202
Caprylic		0.910	16-17	237
Eleostearic		-	-	-
Erucic		-	-	-
Eicosenoic		-	25-32	-
Gadoleic		-	-	-
Heptadecan- -oic		0.853	59-61	227
Heptadecen- -oic		-	-	-
Isanic		-	-	-
Lauric		0.880	44-46	299
Licanic		-	-	-
Lignoceric		-	74-78	306
Linoleic		0.9	-5	229
Linolenic		0.914	-11	230-232
Myristic		0.862	58.8	250
Nervonic		0.918	42-44	398
Oleic		0.895	13-14	360
Palmitic		0.853	63-64	351
Palmitoleic		-	33	162
Ricinoleic		0.94	5.5	245
Stearic		0.83- 0.94	66-70	365-370
Vernolic*		-	-	-

\* Reference has been taken from [193]

Table 1.6 Fatty acid composition of some important vegetable oils

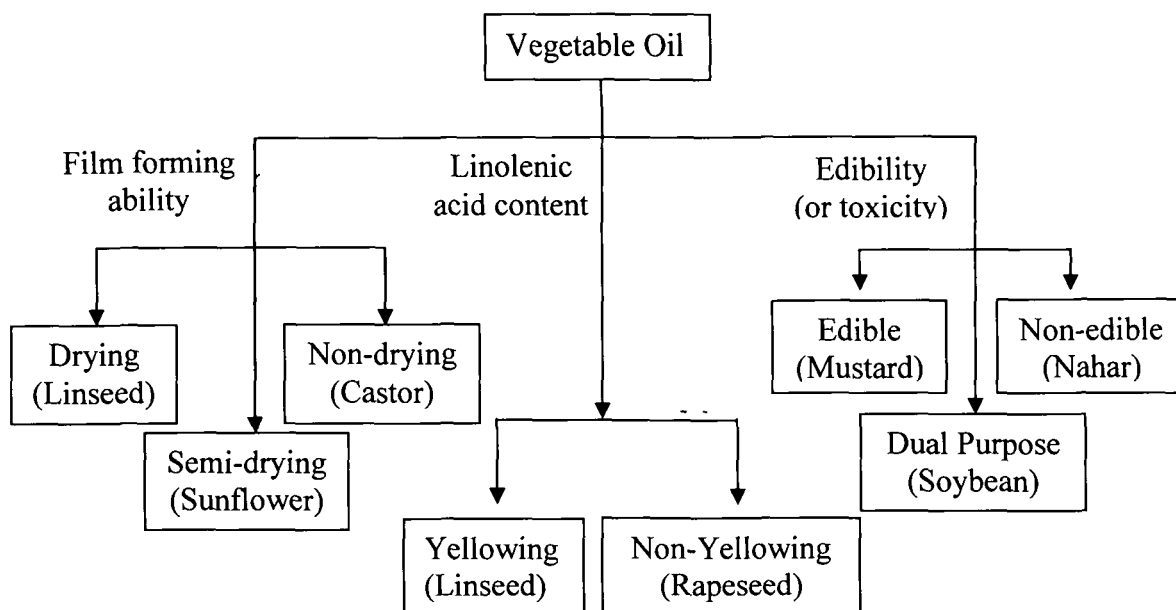
Vegetable Oil	Fatty Acids (in approximate %)						Worldwide Production*	Ref.
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Others		
Castor	2.0	1.0	7.0	3.0	-	87 (ricinoleic)	0.44	77, 85
Soybean	11	4.0	23	53	7.0	2.0	31.88	77, 85
Linseed	6.0	4.0	22	16	52	-	0.63	77, 85
Canola	4.0	2.0	61	21	9.0	2.0 (Eicosenoic), 1 (Others)	-	77, 107
Corn	10.9	2.0	25.4	59.6	1.2	0.9 (Others)	2.02	67, 85
Sunflower	7.0	4.5	18.7	67.5	0.8	0.7 (Behenic), 0.4 (Arachidic), 0.4 (Others)	9.49	85, 107
Sunflower (high oleic)	3.7	5.4	81.3	9.0	-	0.4 (Arachidic), 0.2 (Others)	-	85, 107
Safflower	6.8	2.3	12	77.7	0.4	0.3 (Arachidic), 0.5 (Others)	-	107
Safflower (high oleic)	3.6	5.2	81.5	7.3	0.1	1.2 (Behenic), 0.4 (Arachidic), 0.7 (Others)	-	107
Cottonseed	21.6	2.6	18.6	54.4	0.7	0.7 (Myristic), 0.6 (Palmitoleic), 0.8 (Others)	3.92	67, 85
Rapeseed	3.8	1.2	18.5	14.5	11.0	41.1 (Erucic), 6.6 (Eicosenoic), 1.0 (Lignoceric), 0.7 (Arachidic), 1.6 (Others)	13.05	85
Coconut	9.1	2.8	6.8	1.9	0.1	47.1 (Lauric), 32.2 (Others)	3.33	85
Palm	44.4	4.1	39.3	10	0.4	1.0 (Myristic), 0.8 (Others)	28.13	77, 85
Olive	9.0	2.7	80.3	6.3	0.7	0.6 (Palmitoleic), 0.4 (Arachidic)	2.81	77, 85
Peanut	11.1	2.4	46.7	32	-	2.9 (Behenic), 1.6 (Eicosenoic), 1.5 (Lignoceric), 1.8 (Others)	4.81	85
Tung	-	4.0	8.0	4.0	-	84 ( $\alpha$ -elaeostearic)	-	67

\*Data in million metric tons (2004 figures)

Table 1.7 Analytical parameters of some traditional vegetable oils

Vegetable oil	Scientific name	Family	Hydroxyl value (mg KOH/g)	Saponification value (mg KOH/g)	Iodine value (g I <sub>2</sub> /100 g)	Specific gravity (25 °C)	Ref.
Castor	<i>Ricinus communis</i>	Euphorbiaceae	160-168	175-185	81-91	0.958-0.969	77, 80, 107
Linseed	<i>Linum usitatissimum</i>	Linaceae	306-307	192-195	173-201	0.931-0.936	77, 80
Soybean	<i>Glycine max</i>	Papilionaceae	231-232	192-193	123-139	0.923-0.939	80, 107
Canola	<i>Brassica napus</i>	Brassicaceae	205-210	188-198	100-115	0.916-0.921	107, 121
Corn	<i>Zea mays</i>	Poaceae	226-227	188-193	118-128	0.914-0.921	121
Coconut	<i>Cocos nucifera</i>	Arecaceae	-	248-265	7-12	0.908-0.921	121
Sunflower	<i>Helianthus annus</i>	Asteraceae	237-238	185-194	125-140	0.916-0.923	121
Safflower	<i>Carthamus tinctorius</i>	Asteraceae	-	135-190	140-150	0.922-0.930	107, 121
Palm	<i>Elaeis guineensis</i>	Arecaceae	216-225	193-205	50-55	0.890-0.893	77, 107
Peanut	<i>Arachis hypogaea</i>	Papilionaceae	-	190-196	84-100	0.912-0.920	107, 121





Scheme 1.1 Classification of vegetable oil

Oils are said to be drying when drying index is greater than 70 [196]. Industrially, vegetable oils are classified as yellowing or non-yellowing depending on the linolenic acid content of the oil. Generally, the drying oils are yellowing and semi-drying and non-drying oils are non-yellowing. Based on edibility (which depends on odor, taste and toxicity), vegetable oils may be edible e.g. cotton seed, peanut, olive, mustard, corn etc. and non-edible (industrial) e.g. castor, tung, oiticica etc. Some are used for dual purpose such as sunflower, safflower, rapeseed, soybean [109] etc.

#### *Extraction and purification of vegetable oils*

There are generally four methods in literature used for oil extraction. These are mechanical pressing, solvent extraction, enzymatic process and high pressure CO<sub>2</sub> extraction processes [197-199]. In the mechanical pressing method, the pretreated seeds are subjected to either a hydraulic press or a screw press to squeeze out the oil from the protein meal of the seeds. In solvent extraction technique, the oil is isolated by using a soxhlet apparatus, where the pretreated seeds are immersed in a suitable solvent system for a considerable period at 60-80 °C and then the oil is separated by distillation. However, the process involves loss of solvent. In the enzyme driven process, the pretreated seeds are boiled in water and mixed with a suitable enzyme viz. cellulase, α-amylase, protease etc. which digest the solid material from the seed. The oil is then extracted by liquid-liquid centrifugal method. Finally in the high pressure CO<sub>2</sub> method,

the pretreated seeds are mixed with CO<sub>2</sub> under high pressure, which dissolves the oil. Then the pressure is released which makes liquid CO<sub>2</sub> gaseous and hence the oil gets separated. The yields of the last two methods viz., enzymatic and high pressure CO<sub>2</sub> method are quite high and hence are adopted largely in commercial scale. In order to avoid the hydrolysis of the oil to free fatty acids by moisture present in the atmosphere, the extracted oil is kept at low temperature. Again, care should be taken during storage and handling to minimize the chances of contamination by oxygen. The best way to keep the oil without losing quality and stability is under nitrogenous atmosphere [200].

The crude oil obtained after extraction generally contains certain impurities consisting of phosphatides, gums, resins, free fatty acids and coloured substances. Before utilization of the vegetable oils for industrial and edible purposes, they should be refined in order to remove the impurities. Dirts can be removed by settling or by simple filtration technique [88]. Gums are removed by degumming which exploits the affinity of phosphatides towards water by converting them to hydrated gums via. treatment with water, salt solution, acid etc. As a result, gums coagulate and are separated by a centrifugal separator [200].

The alkali refining technique is a complete refining process which removes free fatty acid contents and causes effective color removal without excessive saponification of the oil and without loss of oil by emulsification [88,109]. In this technique, a caustic soda solution is used in sufficient quantity to neutralize the free fatty acids. The quantity of caustic soda required depends upon the type of oil, the impurities present and the final color required [109]. Sometimes, acid refining technique is also used although color removal in the process is not suitable as in alkali refining technique. In this process, the cold oil is stirred with concentrated sulphuric acid solution. On settling, the impurities are drawn off and the oil is washed to make free from mineral acids. As a finishing step of the refining process, bleaching should be done for partial or complete removal of color [109, 201]. Bleaching can be done either by chemical or by physical means. The chemical method is disadvantageous as the oil suffers oxidation during the process. However, in the physical method, the oil is heated with an adsorbent such as fullers earth, activated carbon, silica, bentonite etc. in the absence of oxygen. The process is generally carried out at about 110 °C with 0.2-2.5% solution of the adsorbent for a duration of ca. 30-60 min [109, 200, 202].

### Processes for preparation of polyols from vegetable oils

Polyols of industrial importance require low viscosity and high hydroxyl content. Preparation of polyols from vegetable oils has been the subject of many studies [41-50, 85, 107]. Vegetable oil based polyols are generally oligomers with a wide distribution of molecular weight and a considerable degree of branching. They are multifunctional starting materials with mostly heterogeneous triglyceride structures that attract chemists to design polymers for different applications. This has been found in literature to be accomplished either by direct polymerization or by functionalization of the oil through double bond reactions such as epoxidation, hydroformylation and metathesis or through ester bond breaking reactions to get the polyols.

Castor oil is a natural polyol (Figure 1.3) consisting of glyceryl esters of ca. 90% with ricinoleic acid and ca. 10% with oleic, linoleic and other fatty acids (Table 1.6) [77, 80, 85]. Castor oil is approximately 70% trifunctional and 30% difunctional (average hydroxyl functionality = 2.7 eqv). It was the castor oil which was first utilized to prepare vegetable oil based polyurethane way back in nineteen fifties. In the initial stage, Metz et al. found that a temperature of 50 °C was desired for the urethane reaction as a better control of the reaction [191]. However, due to trifunctionality,

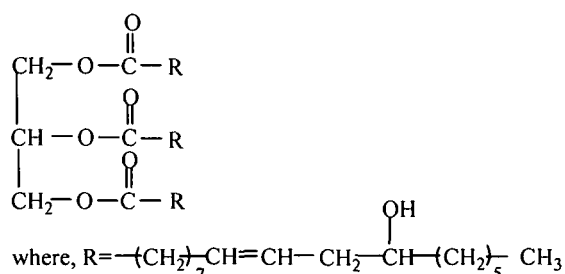


Figure 1.3 Typical structure of a castor oil triglyceride

castor oil polyol is highly reactive towards diisocyanates creating difficulties in controlling the reaction. Hence, different workers devised different methods to achieve the control by converting the trifunctional part of castor oil into difunctional moieties. Yeganeh et al. did it by the reaction of castor oil with phenyl isocyanate at 100 °C for 2 h [54]. According to another report, castor oil was treated with calculated amount of maleic anhydride at 40 °C followed by heating the system to 75 °C for 4-5 h to obtain the acid ended modified castor oil (MCO) [203]. Similarly, castor oil can be catalytically dehydrated to obtain dehydrated castor oil (DCO) [204]. Somani and Kansara isolated ricinoleic acid from castor oil and treated it with ethylene glycol,

diethylene glycol and triethylene glycol at 230 °C to obtain a series of difunctional polyester polyols [3].

Vegetable oils generally offer two major reactive sites for their conversion into polyols. These are the double bonds present in the unsaturated fatty acids and the ester groups linking the fatty acid to the glycerol moiety. Polyols can be prepared by direct oxidation of the double bonds present in the vegetable oils containing sufficient unsaturation (linseed, safflower, soybean, tobacco etc.). However, control of oxidation is a difficult task as it gives a number of side oxidation products such as peroxides, aldehydes, ketones, carboxyls and other low molecular weight species produced by chain scission. Moreover, presence of high unsaturation in such polyols makes the product susceptible to oxidations resulting change in color and property with time.

The problems of oxidation can be overcome by epoxidation reaction which introduces epoxy groups exactly at the position of double bonds. Epoxidation of soybean, rapeseed, linseed, olive, corn, safflower, karanja, melon seed and cottonseed is carried out on an industrial scale [39-40, 93, 205]. Epoxidation is reported to be carried out by using four procedures (i) epoxidation with peracids like peracetic acid or perbenzoic acid in presence of acid catalyst [39, 42], (ii) epoxidation with organic and inorganic peroxides including transition metal catalysts [206], (iii) epoxidation with halohydrins using hypohalous acids (HOX) and their salts [207] and (iv) epoxidation with molecular oxygen [207]. The epoxy group, often called oxirane ring, is highly reactive and undergoes ring opening reactions with nucleophilic reagents. They are readily cleaved by alcoholysis in the presence of alcohols/ thiols, hydrolysis in the presence of acid catalysts and by hydrogenation [40, 107] to generate the polyols. Petrovic and his group reported the oxirane ring cleavage by HCl or HBr to obtain halogenated polyols [48, 68]. The polyols obtained by ring opening reaction with alcohols are liquid whereas the polyols obtained by hydrolysis with HCl or HBr and hydrogenation are solid at room temperature. Recently, Guo and coworkers synthesized soybean polyols by ring opening of the corresponding epoxides with water in the presence of phosphoric acid [208]. Besides catalyzing the ring opening hydrolysis, phosphoric acid chemically combines and becomes a part of the polyol and confers some special properties to the end product [208]. The reactivity of these polyols having secondary hydroxyl groups is however low as compared to petrochemical based polyols due to shielding by the long fatty acid chains. Petrovic et al. suggested improvement in

reactivity by converting secondary hydroxyl groups into primary via., ethoxylation with ethylene oxide at 35-45 °C in the presence of a superacid (HBF<sub>4</sub>) as catalyst [209].

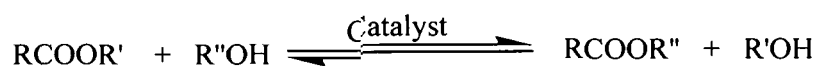
Hydroformylation, also known as the oxo synthesis, is a Fischer Tropsch reaction which involves the conversion of alkenes to aldehydes. Petrovic et al. suggested hydroformylation route to obtain polyols with primary hydroxyl groups by reacting triglycerides with carbon monoxide and hydrogen followed by conversion of resulting aldehyde groups to hydroxyls by hydrogenation [66, 107]. The conversion to polyaldehydes are carried out in the presence of either rhodium or cobalt as catalyst. In a recent report on hydroformylation of soybean oil, Guo et al. showed that an hydroxyl functionality of 4.1 is obtained (more than 95% conversion) if the reaction is rhodium catalyzed, whereas an hydroxyl functionality of 2.7 is obtained (about 65% conversion) if the reaction is cobalt catalyzed [66, 210]. Moreover, hydroformylation with rhodium does not cause oligomerisation but cobalt allows this possibility probably due to transesterification at higher temperatures.

Epoxidation and ring opening gives polyols with secondary hydroxyl groups whereas hydroformylation gives primary hydroxyl groups located generally within the fatty acid chains. But, polyols having terminal hydroxyl groups can be obtained by ozonolysis route in which the less costly and easily produced reagent ozone is used to oxidatively cleave the double bonds [211] present in the unsaturated vegetable oils.

Followed by the pioneering work of Pryde's group in 1960's, soybean oil was first subjected to ozonolysis to prepare aldehyde oils [212-213]. Recently, Petrovic et al. [214] utilized ozonolysis reaction followed by reduction by hydrogenation to develop a triol from triolein, soybean oil and canola oil which is then treated with diisocyanates to obtain the polyurethanes. Graiver et al. synthesized low viscosity polyols by ozonolysis using glycols as esterification agents [215].

All the processes epoxidation/ hydroxylation, hydroformylation/ hydrogenation and ozonolysis/ hydrogenation for polyol synthesis are restricted only to the vegetable oils containing unsaturated fatty acids. Furthermore, undesirable aldehyde and epoxy groups are sometimes found in the polyols and also a large number of reactants are utilized which increases the possibility of many side products. Purification of polyols by removal of byproducts makes the process more tedious and costlier. In addition, risks are associated in the handling (use) of reactants like hydrogen, carbon monoxide, peroxy acids, ozone etc.

Some progress has been realized in developing polyols by a transesterification technique. Transesterification is an important class of organic equilibrium exchange reaction wherein an ester is transformed into another via interchange of the alkoxy moiety (Scheme 1.2). In the transesterification of vegetable oils, the triglyceride (oil) is reacted with an alcohol and hence is often called alcoholysis. The process is catalysed by acids, bases and enzymes [216].



Scheme 1.2 General scheme for transesterification reaction

Alcoholysis with polyfunctional alcohols like glycerol gives rise to partial glycerides i.e., a mixture of monoglycerides and diglycerides. The extent of alcoholysis can be realized by observing solubility of the resulting glyceride in methanol. In reality, alcoholysis gives a mixture of monoglyceride (51%), diglyceride (40%), unreacted triglyceride (4%) and free glycerol (5%) [217]. This glycerolysis reaction was performed by Roy et al. on a number of vegetable oils and the study showed that the yield of the monoglyceride depends on the solubility of glycerol in the oil and not on the fatty acid composition of the oil [218]. The reaction can be carried out with or without catalyst, but the later requires very high temperature conditions which may cause darkening of the oil and increase in viscosity. The catalysts used are either acids or bases, the base like metal oxides, metal hydroxides and metal salts are far better catalysts than any acid [219]. The commercially used ones are oxides or alkoxides of lead, lithium, cadmium, zinc, tin etc. [219-220]. The alcoholysis route is generally applied for drying oils to obtain the monoglycerides.

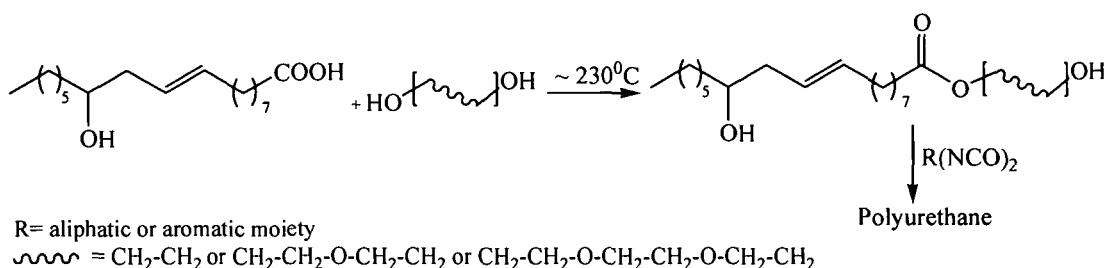
Transesterification or alcoholysis with a monohydric alcohol like methanol produces a mixture of fatty acid methyl esters and a molecule of glycerol [109, 216] in the presence of acid (sulphonic and sulphuric acids), base (sodium and potassium methoxide) or an enzyme catalyst. The glycerol thus produced is separated by solvent extraction technique. Several aspects including the type of catalyst, alcohol/ vegetable oil molar ratio, temperature and free fatty acid content have influence on the progress of the reaction [216]. In 2009, Koc et al. proposed an ultrasonic measurement method for monitoring the glycerol settling which could be useful for evaluating the effect of parameters like amount of catalyst, mixing time and temperature on transesterification reactions [73]. The transesterification is done with high excess of a diol in the presence

of organic bases [36]. Yadav et al. reported the preparation of a diol linseed fatty amide (DLFA) via aminolysis of linseed oil directly with diethanolamine and NaOCH<sub>3</sub> as catalyst [33, 51]. Transesterification of different vegetable oils with glycerol, trimethylol propane and ethylene glycols [221] were reported among which trimethylol propane gives the best results if the reaction can be carried out at 120 °C in presence of *p*-toluene sulphonic acid as the catalyst. In a recent literature, Perin et al. suggested transesterification of castor oil with methanol or ethanol by microwave irradiation for 30 min at 60 °C for 3 h [222]. Further, the reaction is found to be accelerated (3 min) under basic conditions (Al<sub>2</sub>O<sub>3</sub>/ 50% KOH) [222].

Lately, emphasis has been given on the development of vegetable oil based hyperbranched polyols. Petrovic et al. prepared two soybean oil based hyperbranched polyols as prepolymers starting from hydrogenated epoxidized soybean oil and from hydroformylated polyol reacting them with HMDI or adipoyl dichloride [107].

#### *Polyurethane preparation*

Natural polyols like castor oil (generally trifunctional) may directly be treated with diisocyanates to obtain polyurethanes though it is difficult to control reactivity of the reactants. However, the difunctional castor oil can be polymerized with diisocyanates in the presence of suitable chain extenders and catalysts to produce polyurethanes in a more controlled manner (Scheme 1.3) [3].

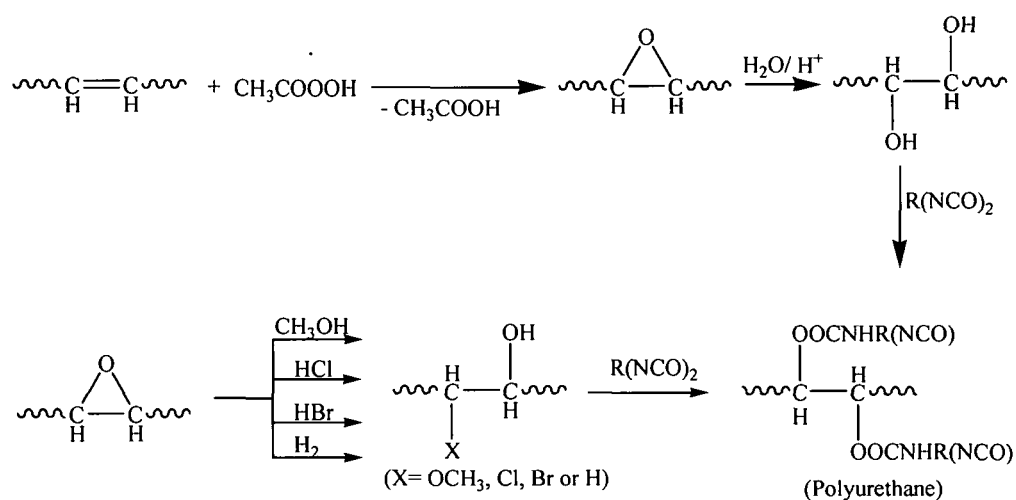


Scheme 1.3 Preparation of castor oil based polyurethane

The MCO or DCO as obtained by Bao et al. was treated with a polyether glycol at 120 °C followed by addition of IPDI and DBTDL [203]. To obtain a series of aqueous polyurethanes, butane diol and dimethylol propionic acids (DMPA) were added and the mixture was heated to 70 °C for 2 h to afford a NCO-terminated prepolymer which forms salts with triethylamine to form a water soluble polymer. The

reaction mixture was dispersed in water and a chain extender, ethylene diamine was added. Two aqueous polyurethanes, namely MCPU and DCPU were finally obtained from MCO and DCO respectively [203]. Qipeng et al. utilized a mixture of castor oil and hydroxyether of bisphenol-A (HBA) as the polyol to react with TDI in the presence of DBTDL catalyst at 35 °C and prepared a series of polyurethanes by keeping in air circulating oven for 48 h [223]. Some other hydroxylated fatty acid containing vegetable oils are dimorphothecca oil, lesquerella oil and lesquerelladensipila oil [221].

Natural polyols obtained from the epoxidation route are treated with diisocyanates in the presence of a suitable chain extender and catalyst to give polyurethanes (Scheme 1.4) [42, 68]. For example, Javni et al. reported the preparation of polyurethanes by epoxidation route, as mentioned in the earlier section, from olive, peanut, canola, corn, soybean, safflower, and sunflower oil via conventional epoxidation followed by treatment of the polyols with modified diphenylmethane diisocyanate [224]. Guo et al. reported the preparation of cast polyurethane resins by the treatment of soy polyols, obtained by methanolysis of epoxidised soybean oil with isocyanates at 50 °C [225]. Again, Ahmad et al. synthesized polyurethane resin from epoxidised linseed oil with TDI using xylene as the solvent [42].

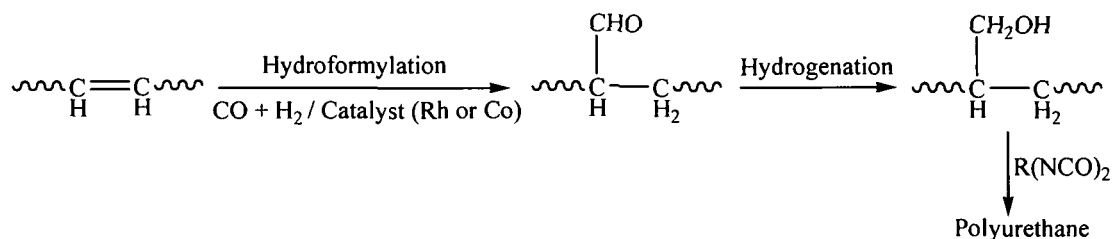


Scheme 1.4 Preparation of vegetable oil based polyurethane by epoxidation route

Polyols obtained by hydroformylation of vegetable oils have primary hydroxyl group and one extra methylene group and hence are more reactive as compared to the secondary hydroxyl groups of epoxidised polyols. Therefore, polyurethanes are

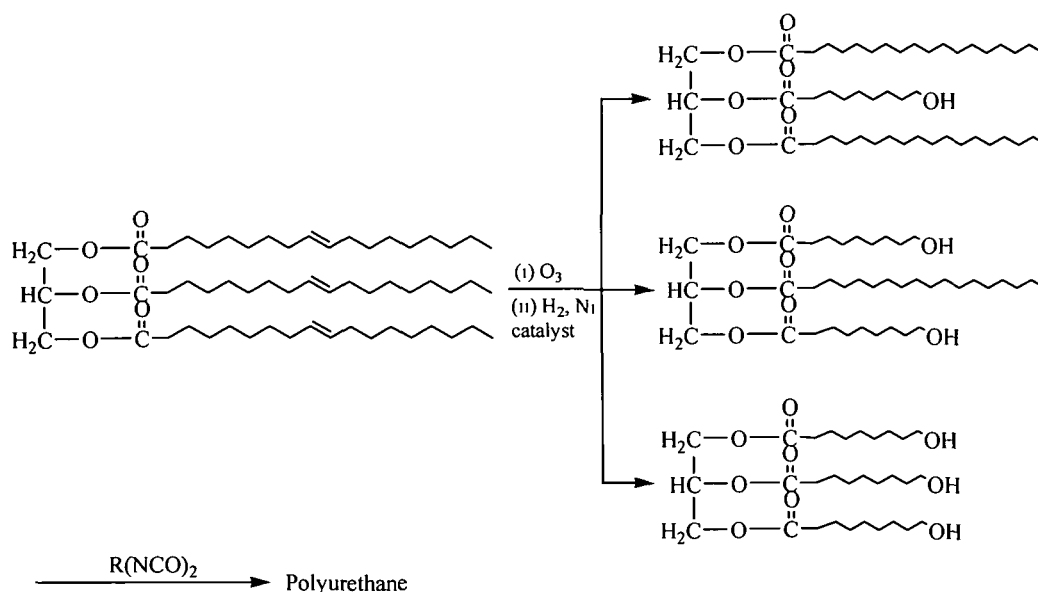


prepared in high yields by utilizing polyols obtained via. hydroformylation route (Scheme 1.5) [66, 107, 225].



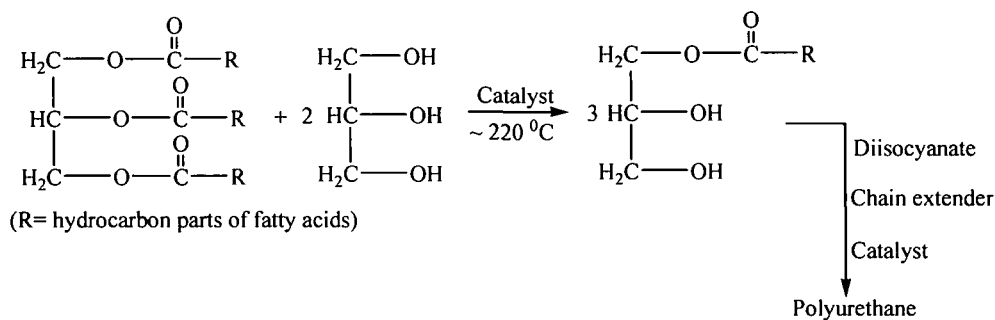
Scheme 1.5 Preparation of vegetable oil based polyurethane by hydroformylation route

In the synthesis of polyurethanes from epoxidised and hydroformylated vegetable oils, the reaction of the hydroxyl group in the middle of the chain leaves parts of the chain dangling which may affect the properties of the final product. However, dangling chains are absent in the polyols made by ozonolysis route and hence can be used suitably to synthesize polyurethanes (Scheme 1.6) [107, 214].



Scheme 1.6 Preparation of vegetable oil based polyurethane by ozonolysis route

The monoglycerides/ partial glycerides obtained via. alcoholysis route are reacted with diisocyanates to synthesize polyurethanes (Scheme 1.7) [226]. In a recent report, polyurethanes containing vinyl double bonds were prepared by treating partial glycerides (mono and di) obtained from linseed oil with methyl vinyl isocyanate (MVI) in the presence of DBTDL catalyst in toluene as solvent at 65 °C [227].



Scheme 1.7 Preparation of vegetable oil based polyurethane by alcoholysis route

Vegetable oil such as linseed oil can directly be aminolyzed to obtain DLFA (a polyol) as described earlier which is treated with TDI at room temperature in a one shot technique to obtain the polyurethane using minimum amount of xylene as solvent and without any chain extender or catalyst [33]. The reaction was stopped after reaching the desired hydroxyl value and the solvent was removed through rotary vacuum evaporator to obtain the poly(urethane fatty amide) resin.

Athawale et al. carried out chemoenzymatic synthesis of polyurethanes by ‘inesterification’ of castor and linseed oil at ambient temperature using lipase as a catalyst followed by treatment of the ‘inesterified’ product with TDI [228]. They also carried out a two step chemoenzymatic synthesis of low molecular weight polyurethanes for surface coating applications. In the first step, partial esters were prepared here by transesterification of soybean and linseed oils with n-butanol in the presence of lipozyme (a lipase) as the catalyst. The partial esters were then reacted with different diisocyanates to obtain a series of polyurethanes [229]. In another attempt, Yeganeh and Shamekhi synthesized polyhydroxy compounds by transesterification reaction between different compositions of castor oil and glycolized PET. They reacted the polyhydroxy compounds with diisocyanates to obtain polyurethane network for novel insulating coating applications [230]. Hyperbranched polyurethanes have been prepared from soybean oil modified hyperbranched polyol, obtained via. epoxidation and hydroformylation route. Castor oil based hyperbranched polyurethanes are reported to be synthesized by using castor oil as the B<sub>3</sub> monomer in an A<sub>2</sub>+B<sub>3</sub> approach. The A<sub>2</sub> monomer, NCO terminated prepolymer was obtained by reacting MDI with caprolactone diol. The urethane reaction was carried out at ca. 110 °C in the presence of 1,4-butane diol as the chain extender [231] for 2-3 h.

## ***Characterization***

Vegetable oil based polyurethanes are characterized by the same conventional analytical and spectroscopic techniques as discussed in the earlier sections (Sections 1.3.3.1 and 1.3.3.2). In addition, other physical properties like acid value, saponification value, iodine value etc. [122] are also sometimes required to be determined by using appropriate standard techniques.

### *Analytical techniques*

The drying ability of a vegetable oil based polyurethane resin can be imagined by determining its iodine value as iodine value indicates the degree of unsaturation present in the resin. Similarly, determination of physical properties like viscosity, acid value, saponification value, hydroxyl value and isocyanate value helps to have an idea about the processibility conditions, free COOH groups, chain length (molecular weight), free OH groups and free NCO groups present in the resin. Acid values of the polyols should be low. Because, high acid content may delay the reaction time of polyurethane synthesis by undesirably consuming isocyanates to form unstable anhydrides [105, 232]. The viscosities are found to be increased with increase in NCO/OH ratio. This is due to the increase in its molar mass, molecular interaction as well as the degree of hydrogen bonding with increase in isocyanate content.

### *Spectroscopic techniques*

The most important application of FTIR spectroscopy in characterizing polyurethane is to monitor the diminution of the NCO absorption peak at ca.  $2273\text{ cm}^{-1}$  during the polymerization process. This ensures the completion of the urethane reaction. Another striking feature observed in most of the vegetable oil based polyurethanes is the doublet like nature of the carbonyl absorption peak in the range ca.  $1700\text{-}1740\text{ cm}^{-1}$ . This is due to the involvement of the NH group in intramolecular hydrogen bonding with the carbonyl group of the hard segment and the oxygen of ether or carbonyl group of the soft segment [233-234]. The component of the doublet lying in the lower wavenumber region (ca.  $1700\text{ cm}^{-1}$  or even lower) is due to hydrogen bonded carbonyl group. This effect is found to be increased with increase in NCO/OH ratio. A similar doublet like peak may also be expected for the NH group [233-234]. But

unfortunately this is not observed as the region concerned overlaps with the broad OH absorption peak. The intensity ratio of the hydrogen bonded to the non-hydrogen bonded carbonyl groups ( $A_{\text{H-bonded CO}}/A_{\text{CO}}$ ) may give a clear idea about the extent of hydrogen bonding. For example, in a comparative study between canola and soybean oil based polyurethanes, the  $A_{\text{H-bonded CO}}/A_{\text{CO}}$  value was found to be higher for canola oil [82]. The lower extent of hydrogen bonding in soybean oil based polyurethane was then suggested to be due to a steric hindrance caused by the large amount of dangling chains present which prevents the formation of hydrogen bonds [82]. The broad absorption peak observed at ca. 3300-3500  $\text{cm}^{-1}$  due to OH stretching is found to be sharpening with increase in NCO/OH ratio. Among the other FTIR absorption peaks, the NH deformation (ca. 1500-1550 $\text{cm}^{-1}$ ), C-H stretching vibration of the alkane chain (ca. 2850-2950  $\text{cm}^{-1}$ , intense doublet peak), C=C stretching ( $\sim$ 1630-1660  $\text{cm}^{-1}$ ), =C-H bending (ca. 900 and 1010  $\text{cm}^{-1}$ ) etc. are important to be mentioned. Moreover, curing of the polymer can be studied by looking for the absence of band at ca. 770-815  $\text{cm}^{-1}$  (unsaturation) [96] and red shift of urethane and ester carbonyl group band.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy is also used to characterize vegetable oil based polyurethane resins. For example a castor oil based polyurethane may be characterized by observing  $^1\text{H}$  NMR peaks ( $\delta = 0.77$ - $0.79$  ppm for terminal methyl, 1.18-1.52 ppm for central methylene groups, 1.93 ppm for allylic methylene, 2.2-2.4 ppm for methylene at the adjacent position of carbonyl group, 3.1 ppm for methylene group attached to urethane nitrogen, 4.1 ppm for methane group bearing urethane oxygen atom, 4.20-4.30 ppm for glycerol methylene, 5.10 ppm for glycerol methane, 5.2-5.5 ppm for alkene moiety, 7.0 ppm for urethane NH group and aromatic protons) [140-141]. Other vegetable oil based polyurethanes are characterized in the same manner with slight shifts in the peaks depending on the nature and structure of the vegetable oil. In addition, some more peaks may be observed corresponding to protons adjacent to some special functionalities present in the fatty acid moiety. High resolution NMR spectroscopy can be used to study the extent of hydrogen bonding. As NH groups of polyurethane are known to form H-bonds, several NH peaks are observed at  $\delta$  greater than 7.5 ppm in the  $^1\text{H}$  NMR spectra. The relative amounts and the half widths of each NH peak remain the same upto a temperature of 80  $^{\circ}\text{C}$ . However, the chemical shifts of the NH peaks tend to change towards lower frequencies at higher temperatures. The percentage of NH groups forming H-bonds with carbonyl groups of

the hard segments is found to be greater than 45% [235]. The study shows the H-bonding between the hard segments to be very strong. The conformation of the hard segments has been studied by two dimensional nuclear overhauser effect spectroscopy (2D NOESY) and it has been found that hard segments are aligned in an orderly fashion [235]. NMR spectroscopy can also be used to study the curing mechanism and hence the extent of the reaction by observing the resolution of the spectra [152].

In addition to the determination of molecular weight and the distribution of molecular weight by GPC analysis, the technique can be used in calculating number of repeating units i.e., extent of polymerization [88]. GPC is also reported to be used in monitoring monoglyceride or diglyceride formation from vegetable oils during the alcoholysis route of polyurethane synthesis. Observation of two peaks in the chromatographs indicates two polymeric moieties which may be useful in characterizing polyurethane blends [236]. Most of the vegetable oil based polyurethane resins synthesized for surface coating applications are found to possess weight average molecular weight in the range of ca. 2000-3600 g/mole [96] whereas it is ca. 25,000-40,000 g/mole for polyurethane elastomers [54].

Thermal characterization of vegetable oil based polyurethane is done by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques in a similar manner as for general polyurethanes. Most of the vegetable oil based polyurethanes with NCO/OH ratio equal to one show three step degradation in TGA corresponding to the decomposition of urethane bonds, ester or amide bonds, and hydrocarbon chains respectively [33, 51]. Different types of transitions and relaxations related to the structure and morphology are generally analysed by DMA (DMTA) method (variation of storage modulus and loss tangent with temperature). Typical DMA behaviour of vegetable oil based polyurethanes show a very broad transition from glassy to rubbery state at room temperature which indicates a wider distribution of cross-linking density and lower homogeneity in the network [107]. For most of the common thermoset polymers, the storage modulus is found to be independent of temperature in the glassy region which is not observed in the case of vegetable oil based polymers. The factors responsible for such broad glass transition are formation of triglyceride rich regions and the plasticizing effect of the long fatty acid chains [237].

In a study Petrovic et al. suggested that among different methods for glass transition temperature ( $T_g$ ) determination, both DSC and TMA do not show always a

clear transition [85].  $T_g$  values obtained from DMA and DEA are frequency dependent and temperature control is not as good as in DSC. However, TMA gives very close values to those of DSC.  $T_g$ , as determined by DSC is found to be around 77 °C for highly crosslinked linseed oil based polyurethane, 30 °C for soybean, corn, sunflower and canola oil and around 24 °C for mid-oleic sunflower oil-based polyurethanes [85]. DSC has also been reported to be used to monitor the urethane reaction under non-isothermal conditions at different heating rates [153].

Polyurethane is a semi-crystalline (amorphous) polymeric material. The crystallinity observed to a certain extent, as observed in DSC traces and WXR patterns, may be due to the presence of hard segments [203]. However, this is overshadowed by the presence of long aliphatic hydrocarbon chains in the vegetable oil moiety and hydrogen bonding in the structure. Thus vegetable oil based polyurethanes exhibit overall amorphous character even at higher NCO/OH ratios [203, 238].

As polyurethane is a block copolymer with phase separated hard and soft segments, the morphology can be studied by SEM technique. Various vegetable oil based polyurethanes have been characterized by SEM and is found to be biphasic or monophasic. Zawadski et al. explained the reason as coexistence of hard segment rich regions and their partial dispersion in the matrix. Wrinkling observed in certain cases may be ascribed to the evaporation of solvents during curing and the particles seen in some other cases may be attributed to the gel fraction that might have dissolved and deposited during solvent evaporation [239]. Blends, composites and IPN's of vegetable oil polyurethanes are checked for dispersability and compatibility of different components present in the system by this technique [240-241]. TEM and AFM is a widely used to investigate surface or phase structure in polyurethanes and polyurethane/ clay nanocomposites to understand structure property relationship [188].

### ***Properties***

The properties of vegetable oil based polyol and polyurethanes depend on the unsaturation content along with other specific functionalities like hydroxyl, epoxy, ketonic etc. present in the fatty acid chains. Such properties include physical, chemical, mechanical, rheological, electrical, biological, thermal etc. Most of the polyurethanes from vegetable oils are crosslinked products and the properties of such products depend on the nature and structure as well as on the cross-linking density of the network.

### *Physical*

Vegetable oil based polyurethanes are soluble in aliphatic hydrocarbon solvents in addition to the solvents where general polyurethanes are soluble. This is due to the presence of long non-polar hydrocarbon chains. However with decrease in oil length, mixtures of aliphatic and aromatic solvents are required. Resins with oil length below 50 are found to be soluble in aromatic solvents [242].

In a study of polyurethanes prepared from halogenated and non-halogenated soybean oil polyols [68] obtained by ring opening of epoxidised soybean oil by HCl, HBr, methanol and hydrogen, various properties were evaluated and compared. The density was found to be decreasing in the order brominated polyurethanes (1.26 g/c.c.) > chlorinated polyurethanes (1.15 g/c.c.) > methoxylated polyurethanes (1.11 g/c.c.) > hydrogenated polyurethanes (1.09 g/c.c.). The values are found to be increased with the increase of NCO/OH ratio which may be due to increase in rigid aromatic moiety in the structure and due to increase in cross-linking by hydrogen bonding and other molecular interactions [68, 107]. The molecular weight of the polyols obtained by ozonolysis route is about 40% lower than that of obtained by the epoxidation or hydroformylation route resulting in low viscosity [107]. The viscosity is however dependent on the type of polyurethane. For example, resinous polyurethanes synthesized for surface coating applications generally possess low viscosities.

### *Mechanical and rheological*

The most striking feature about vegetable oil based polyurethanes is their low (ambient) temperature curing. With increase in NCO/OH ratio, the drying time decreases due to increase in cross-linking reactions. The flexibility and adhesive strength is also found to be increased in the same order. According to a report, the adhesive strength of castor oil polyurethane adhesive is ten times greater than the commercially available wood adhesives [243]. This may be due to the presence of two types of crosslinks: covalent chemical crosslinks and physical crosslinks like intermolecular hydrogen bonds between urethane groups of different molecules [14, 244] which causes coiling.

In the comparative study between polyurethanes prepared from HCl, HBr, CH<sub>3</sub>OH and H<sub>2</sub> opened epoxidized soybean polyols, it has been shown that H<sub>2</sub>

(hydrogenation) produces softer polyurethanes than the other three ring openers [107]. Tensile strengths for HCl, HBr and CH<sub>3</sub>OH opened polyurethanes are in the range of up to ca. 40 MPa and elongation at break below 10%, whereas hydrogenation based polyurethanes possess lower tensile strength but higher elongation at break. The tensile strength and hardness are found to be increased on increasing the NCO/OH ratio. The imperfection due to dangling chain ends decreases as the NCO/OH ratio increases and hence the properties are also improved [68]. Polyurethanes obtained via hydroformylation route possess lower mechanical properties owing to their low T<sub>g</sub>'s. Hydroformylated polyols with high hydroxyl numbers are suitable for rigid applications only. However, they can be modified with reduced functionalities by blocking some OH groups by esterification in order to be applicable for flexible applications [72].

The linseed oil based polyurethanes obtained via epoxidation route offers the best physico-mechanical and anticorrosive properties with 10% loading of TDI [42]. These polyurethanes were transparent, amorphous and single phase polymers [224]. Mortley et al. suggested a four-fold increase in modulus and tensile strength for castor oil based polyurethanes cured by thermal radiation. They proposed that formation of radicals initiated by radiation allows unreacted OH and NCO groups of the castor oil based polyurethanes to react and cause intermolecular cross-linking which results in improvement of the physico-mechanical properties [245]. Naraine et al. prepared elastomeric polyurethanes from polyols obtained via ozonolysis route (low hydroxyl value of 152 mg KOH/g) from canola seed oil with HMDI. The product possesses low mechanical strength and low elongation, probably due to the imperfect networks [82]. Polyurethanes obtained by chemoenzymatic synthesis via interesterification of castor and linseed oil was found to show significant improvement in hardness, adhesion, impact and chemical resistance [228]. Polyurethanes prepared via transesterification of soybean and linseed oils with n-butanol in the presence of lipozyme (a lipase) also possess such improved properties, particularly the MDI based polyurethanes [229].

The rheological behavior is the flow behavior which is complex in nature for polyurethane resins. Vegetable oil with aromatic isocyanate based polyurethane solutions exhibit non-Newtonian behavior, whereas polyurethane solutions based on other isocyanates exhibit nearly Newtonian behavior at moderate to high shear rate [164]. This is because of the presence of aromatic ring which makes the polymer chain rigid that increases viscosity of the polymer solution at high shear rates. Viscosity is



found to be decreased with increase in temperature [164]. Again, polyurethane shows thixotropic behavior due to the presence of weak intermolecular interactions like hydrogen bonding in it. From the flow properties, it can be concluded that certain polyurethanes can be used as high solid coatings by reducing solvent amount [164].

### *Chemical*

Most of the vegetable oil based polyurethanes exhibit low chemical resistance as they are susceptible to hydrolysis due to the presence of ester bonds. In addition, the urethane linkages may also hydrolyze under highly humid conditions giving an amine and CO<sub>2</sub> [116]. However, such deteriorations are resisted significantly by shielding of the ester groups by non-polar hydrocarbon chains and aromatic rings adjacent to the ester/ urethane groups. The hydrophobic character of hydrocarbon chains limits the water diffusion through the polymer network and hence slows down the hydrolysis process. Steric factors may also contribute to hydrolytic stability [246]. Many attempts have been made to modify polyurethanes by grafting with different acrylic monomers on the double bonds of polyol for improving the curing rate, durability and chemical resistance.

### *Thermal*

Vegetable oil based polyurethanes generally show thermograms with three step degradations. Sometimes a slight initial weight loss may occur at ca. 120-150 °C corresponding to loss of entrapped volatiles. The first step associated with the weight loss from 180- 230 °C, the second with weight loss at more than 350 °C and the third with maximum amount of weight loss at more than 500 °C. The first step is due to the degradation of the urethane bonds. It is reported that the decomposition of urethane bond occurred between 180 and 230 °C depending on the type of substituents on the diisocyanate and polyol. The second and third decomposition steps correspond to decomposition of ester, amide and hydrocarbon chains respectively. However, two step degradations are also observed in certain cases. For example, castor oil based millable polyurethane elastomers show two step degradations at 270 °C and at 380 °C [54].

Javni et al. showed that initial degradation of oil based polyurethanes occurred at a faster rate than the synthetic poly(propylene oxide) (PPO) based polyurethanes,

though at higher temperatures, PPO based polyurethanes displayed quicker loss. However, the situation is just reverse in oxygen atmosphere (air). Thus, vegetable oil based polyurethanes exhibit better oxidative thermal stability as compared to the standard PPO based one [224]. In a comparative study between polyurethanes prepared from halogenated and non-halogenated soybean oil polyols, Petrovic et al. showed that polyurethanes from non-halogenated polyols have higher thermal stability than the halogenated one [107]. The Tg's obtained by them were 70-80 °C for the polyurethanes based on HBr, HCl and CH<sub>3</sub>OH opened polyol and below 40 °C for the polyurethanes based on H<sub>2</sub> opened polyol [107]. A linear increase in Tg of the polymers has also been observed with the NCO/OH ratio increase from 0.4 to 1.05 [68]. Polyurethanes based on modified MDI and polyols obtained via. epoxidation of olive, peanut, canola, corn, soybean, safflower, and sunflower oil possess Tg's ranging from 7-87 °C and is found to be dependent almost linearly on hydroxyl number. In a study of soybean and canola oil based polyurethanes, the Tg of Canola oil based polyurethane is reported to be higher for the same NCO/OH ratio [233]. The relatively poor properties of soybean oil based polyurethanes is due to the higher amount of dangling chains present which results in significantly higher steric hindrance to further cross-linking [233].

Petrovic et al. reacted ozonolysed polyol with pure MDI to give polyurethane with excellent properties (53 °C of Tg, 51 MPa of tensile strength, 25% of elongation at break) all of which are much greater as compared to the polyurethanes obtained by epoxidation or hydroformylation route [107]. Incorporation of boron into naturally occurring castor polyol gives polyurethanes that may be safely employed upto 220 °C, as reported by Akram et al. [247]. The most interesting feature of silicon based vegetable oil modified polyurethanes is the appearance of melting endotherms of variable enthalpy and position and a downward shift in the Tg. They are found to be thermally stable over 250 °C due to the enhancement of the stability of the char [6, 248]. In another attempt, Koprululu et al. carried out homopolymerisation and copolymerization of the vinylated polyurethanes with styrene via. free radical polymerization to increase the thermal resistance of the material [227].

### *Electrical*

Polyurethanes are polar molecules but they have electrical insulating characteristics. In a study [249], it has been shown that castor and soybean oil based

polyurethane casting compounds exhibit considerably higher permittivity, higher  $\tan\delta$  (loss factor), lower dielectric strength and higher surface and volume resistivity as compared to conventional epoxy compounds under similar conditions. Krishna et al. studied [250] the variation of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) of a castor oil based polyurethane as a function of frequency and temperature. The study showed that dielectric constant decreases with increase in frequency whereas loss peak is observed indicating dielectric loss increases to certain extent and then decreases. Again, dielectric constant is found to be increased with the increase of temperature until a constant value is obtained at high temperature. Dielectric loss value passes through a maximum as the temperature has increased [250]. Such dielectric behavior can be attributed to the Maxwell Wagner Sillar interfacial polarization due to block copolymeric nature of polyurethanes [250-251]. The electrical encapsulation of many active agents by vegetable oil (non-polar) based polyurethanes are easy to process as they possess lower viscosity than the conventional epoxy, polyester or polyurethane resins. Furthermore, polyurethanes can be catalyzed to speed up such encapsulation even at below room temperatures [249].

### *Biological*

Vegetable oil based polyurethanes are biodegradable due to the natural origin of the vegetable oil component and hence are environment friendly. In real field conditions after disposal, such polyurethanes degrade by the evolution of  $\text{CO}_2$  resulting from bacterial or fungal attack [172] on certain functional groups (such as ester) present in the network. For most of the polyurethanes, the rate of evolution of  $\text{CO}_2$  is initially high during biodegradation and then remains almost constant followed by gradual decrease with time. The initial high rate is probably due to the presence of some low molecular weight fractions that degrades quickly. It has also been found from a study [172] that the degradation decreases with increase in polyol functionality. In this study, linseed oil based polyurethane was found to be less biodegradable than the soybean oil based polyurethane [172].

### *Damping and shape memory*

Damping properties of vegetable oil based polyurethanes have been reported for a broad range of temperature and frequencies [173]. High damping intensities are observed due to the presence of ester groups in the polymer chains. Increase in cross-linking reduces the damping intensities by restricting the polymer segmental motion. Broad damping regions can be observed for segmental in-homogeneity when the polymer is combined physically or chemically with two or more structurally dissimilar polymers to form blends or IPN's with phase separated morphology [173]. Such materials are therefore expected to be efficient damping materials and can be utilized for sound and vibrational applications. Polyurethanes are now also known to be good shape memory polymers [173-175]. The shape memory properties of vegetable oil based polyurethanes depend upon a number of factors such as conjugation present in the vegetable oil, curing temperature, physical or chemical cross-links present in the polymer etc. [176]. However convenient understanding about the shape memory behavior of vegetable oil based polyurethanes is yet to be explored.

### ***Applications***

The efforts of both industrialized and developing countries to use and cultivate vegetable oils for both food and non-food applications have led to a high growth in the production of vegetable oils worldwide. Among the various industrial applications, manufacturing of raw materials for polyurethanes is now widespread. Vegetable oil based polyurethanes can be used as a direct replacement of petrochemical polyol based polyurethanes in various fields like foams, binders for coatings and composites, adhesives and sealants. For example, the market potential for soy polyols in urethane market is estimated to be more than 800 million pounds per year in US [252].

Vegetable oil based polyurethanes containing two or more urethane groups per molecule possess great potential as surface coating materials. Being reactive, their low molecular weight oligomers react to form polymeric network on substrates like metal, plastic, wood, cloth, paper, leather [253] etc. Further, they may be used as rheological modifiers in other solvent based coatings to control the flow properties [254].

Kansara and co-workers found castor oil based polyurethanes to have 10 times more lap shear strength as compared to the commercially available wood adhesives.

Castor oil based polyurethanes are reported to be largely used as adhesives in medical and other fields [243]. For example, castor oil based polyurethane adhesive was used efficiently in the production of 12 beams of Glulam. Castor oil based polyurethane is also reported to be biocompatible and has been used successfully as a material for artificial bone [255]. Polyurethanes based on castor oil modified polyol and PEG chain extender with tunable biodegradable properties has been reported to be utilized in biomedical implants and tissue engineering [256]. These polyurethanes showed non-toxic behavior and good cytocompatibility on interaction with fibroblast cells [256]. Transparent polymeric membranes can be prepared from vegetable oil based polyurethanes as shown in many literatures for wound dressing applications [192]. It has been shown that the film properties, mechanical properties and gas permeabilities depend on the amount and type of diisocyanates used. Aliphatic polyurethanes excel over aromatic counterparts as the former has high flexibility and light stability. A series of castor oil based aliphatic polyurethanes have been developed and different characteristics were evaluated for long term biomedical applications [257].

Soybean oil based poly(esteramide urethane) has been suggested for biomedical applications after filling with boron, because it exhibited anti-microbial properties [77]. Due to its thermal stability, castor oil based polyurethanes have been successfully blended with conductive polymers [258]. Yeganeh et al. synthesized green polyurethane coatings from castor oil based amide/ ester/ ether polyols and recycled poly(ethylene terephthalate) and showed their potential as high performance metal insulator coatings [259]. Polyurethanes with higher silicon content are interesting bio-based materials for applications that require fire resistance [248].

Vegetable oil based polyurethane-graphite composite materials can be utilized for electrodes as detectors in electrochemical analysis [260]. For example, thin films of castor oil based polyurethane composite with ferroelectric ceramics like lead zirconate titanate and BaTiO<sub>3</sub> ceramic powder obtained by spin coating technique are used as suitable piezo as well as pyroelectric sensors [261]. Castor oil based polyurethane composite with 60% graphite content is used in the quantitative determination of hydroquinone in photographic developers [260]. Due to the reproducibility and accuracy of the method, there is a scope for many such applications in near future using this type of sensor. In another attempt, aluminium and graphite powder dispersed castor oil based polyurethanes were prepared with TDI followed by *in-situ* polymerization of

vinyl monomer to give powdered composite materials. These materials can be utilized as conductive coatings, adhesives for electrical industries and junction boxes, panels and as floor tiles where electrostatic charges are of great concern [262].

Preparation of polyurethane nanoparticles has also been reported from castor oil based polyol by miniemulsion polymerization technique [159]. The polyurethane particle size as measured by Zanetti Ramos through dynamic light scattering technique was found to be ca. 200 to 300 nm. Vegetable oil based polyurethanes also exhibit great potential to be used as shape memory polymers [231, 263].

### **1.5. Scope and objectives of the present investigation**

From the main features of the foregoing discussion, it has been found that many vegetable oils are widely used in place of petroleum based products as the raw materials in the production of many important industrial products like surface coatings including paints, varnishes etc. printing inks, soaps, cosmetics, pharmaceuticals, lubricants, emulsifiers, multipurpose additives, biodiesel, plasticizers etc. Again, vegetable oils are environment friendly as they are biodegradable and obtained from nature. Vast varieties of widely grown plants and herbs are available in India. Seeds of many plants contain oils which are viable alternatives of petroleum resources for many applications. *Mesua ferrea* L. (Nahar) is a plant that produces high oil containing seeds. It is available in different countries such as Srilanka, Bangladesh, Nepal, Indochina (Southeast Asia), Malay Peninsula etc. [189] in addition to India. The oil content of Nahar seeds is exceptionally high (70-75%) and it possesses both saturated and unsaturated fatty acids [264]. Also there are a few reports on the utilization of this oil in the fields of medicine and biodiesel [264-265]. However, there is no report on the utilization of this oil in the field of polymer, except for some polyester resins from our laboratory. Thus, it come into sight that there is no study on the utilization of this oil for development of polyurethane. Hence, the following questions may arise in this area.

- (i) Whether this oil can be utilized for the preparation of polyurethane?
- (ii) Whether this polymer can be used as a binder for surface coating, paint and composite materials?
- (iii) Whether the performance characteristics of this polymer can be improved by any physical or chemical means?
- (iv) Whether these polymeric products are biodegradable or not?

Under this background, the main objectives of the present investigation are as follows:

- (i) To synthesize, characterize and evaluate various properties of *Mesua ferrea* L. seed oil modified polyurethane resins.
- (ii) To study the effect of NCO/OH ratio on the performance of the polyurethanes as surface coating materials.
- (iii) To improve the performance characteristics of those resins by blending with commercially available resins and through nanocomposites formation.
- (iv) To use a *Mesua ferrea* L. seed oil modified polyester resin for the preparation of an industrial paint.

#### **1.6. Plan of work**

To fulfill the above objectives, the following plans of work have been adopted.

- (i) A state of art literature survey will be conducted in the area of vegetable oil based polyurethanes.
- (ii) Locally collected seeds will be utilized for isolation of oil followed by purification by the conventional methods.
- (iii) The purified oil will be utilized for preparation of polyurethane resins with varying NCO/OH ratios.
- (iv) The prepared resins will be characterized by different analytical and spectroscopic techniques.
- (v) The characterized polyurethanes will be used to study their performance as surface coating materials.
- (vi) The polyurethane resins will be blended with other commercial resins and will be utilized as surface coating materials.
- (v) Biodegradability of these blends will be studied.
- (vi) The resins will be utilized for the preparation of industrial paints.
- (vii) The resins will also be utilized as matrices for conventional composite and nanocomposites.

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## CHAPTER 2

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### Synthesis, characterization and property evaluation of *Mesua ferrea* L. seed oil based poly(urethane ester) and poly(urethane amide) resins

#### 2.1. Introduction

Bio and semi-bio polymers derived from renewable feedstocks have all the potentiality to replace the petroleum based polymers in near future because of their greener and sustainable nature. Vegetable oil is one such renewable resource and has the potential to confer competent properties to the material. The several advantages of using vegetable oil have been discussed in the earlier chapter. A number of both traditional and non-traditional vegetable oils are being utilized for the development of various polymers [1-8]. Different parts of India, particularly the North-eastern region have a great potential for the production of a variety of wildy grown plants and herbs. One such non-traditional plant namely *Mesua ferrea* L., locally known as “Nahar” plant, has remarkable potential in this regard as the seeds contain ca. 70% of non-edible oil [9]. This is a non-drying oil and the fatty acid content is consisting of 52.3% oleic and 22.3% linoleic acids as unsaturated fatty acids and 15.9% palmitic and 9.5% stearic acids as saturated fatty acids [9]. There are reports on exploitation of this oil in the fields of medicine, biodiesel and polyesters [10-11]. But this oil has yet not been introduced for the preparation of polyurethane.

Polyurethane is a multipurpose polymeric material, first synthesized by Otto Bayer and coworkers, way back in 1937 [12]. Polyurethane endows versatility from its block copolymeric character that results in incompatibility between hard and soft segments, which results phase segregation into separate domains [13]. According to

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\*Parts of this work have been published in (i) *Prog Org Coat*, **2005**, 53, 147.

(ii) *Polym Int*, **2006**, 55, 49.

different studies, better properties have been achieved when the microphase segregation between soft and hard segment is significant. The properties of polyurethanes, however, can be manipulated as desired by judicious variation of its chemical constitution or structure. A large number of reports are available in literature on the effect of the structure of hard and soft segments on physical, thermal and chemical properties of these polymeric materials [14-15]. Such investigations of structure-property relationship in polyurethanes have gained importance and made them widely applicable in various industrial and medical sectors like foams, elastomers, fibers, composites, adhesives, paints etc. [16-18].

Polyurethane resins are low molecular weight polymers (1000-5000 g/mole) with high functionality [19] in their intermediate state and have been used for more than fifty years as surface coating materials. As polyurethanes exhibit better abrasion resistance, toughness, chemical resistance, mechanical strength and low curing temperature as compared to polyester or poly(ester amide), thus they have been found extensive applications in high performance coatings for the automotive appliance and wood industries [20]. Being reactive coatings, their low molecular weight oligomers react to form polymeric networks on various substrates. The seed oils such as castor, linseed, soybean, sunflower, corn, canola, palm, tobacco etc. [21-27] have successfully been utilized to synthesize polyurethane resins. Most of these polyurethanes are based on either polyester polyols to impart rigidity or polyether polyols to impart flexibility. But there is a lack of reports on the synthesis of vegetable oil based polyurethanes from amide polyols even though it may offer better performance due to the presence of amide bonds instead of ether or ester linkages.

Transesterification of vegetable oils in the presence of acid, base or enzyme catalyst is now well known [28-30]. It is an organic equilibrium exchange reaction where the triglyceride ester is transformed into another ester through interchange of the alkoxy moiety. Transesterification (also called alcoholysis or glycerolysis) of vegetable oils with glycerol or amidolysis with diethanol amine have been reported to develop polyols [30-32]. But there is no report on utilization of vegetable oil based amidolyzed polyol (fatty amide diol) in the synthesis of polyurethane resins. Again, as *Mesua ferrea* L. seed oil is yet to be explored for developing polyurethane resins, so this chapter reports on synthesis of two types of polyurethane resins with different NCO/OH ratios from *Mesua ferrea* L. seed oil by using monoglyceride and fatty amide

diol. Characterization and properties evaluation of the synthesized resins have also been investigated.

## 2.2. Experimental

### 2.2.1. Materials

The *Mesua ferrea* L. (Nahar) seeds used in the present investigation were collected from Jorhat, Assam, India. The seeds were obtained from the plant, which is a large tree with a conical crown and is about 3-15 m in height. It is found in different parts of India [33-34] such as North-east region, West Bengal, Karnataka, Kerala etc. along with other countries like Srilanka, Bangladesh, Nepal, Indochina (Southeast Asia), Malay Peninsula etc. The oil is a slightly viscous liquid having brown color and a characteristic smell. The tree bears flowers between April and July, and fruits between October and November. The average yield of seeds per tree is around 10-15 kg per annum. The oil utilized for the present investigation was extracted from the dried powder of seeds by solvent soaking technique using n-hexane (Merck, India) as the solvent. The oil was purified by degumming with water followed by alkali refining technique using 0.01% aqueous NaOH solution and then washed with distilled water and dried under vacuum [35].

Glycerol (Figure 2.1) was obtained from Merck, India with density 1.26 g/mL, maximum sulphated ash 0.005% and minimum assay 99%. Other impurities present are glycerol tributyrate 0.05%, chloride 0.0001%, sulphate 0.0005% and heavy metals 0.0002%. In organic synthesis, glycerol is used as a prochiral building block. Besides pharmaceutical and medical applications, glycerol is generally used in the production of hydrogen gas, citric acid, propylene glycol, acrolein, ethanol, epichlorohydrin for epoxy synthesis etc. Herein, glycerol was used as a triol (alcoholizing reagent) for converting triglyceride into monoglyceride. It was used after drying under vacuum.

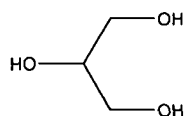


Figure 2.1 Structure of glycerol (1,2,3-propane triol)

Lead mono-oxide (PbO) was obtained from Loba Chemie, India with minimum assay 99% and maximum limit of impurities chloride 0.02%, copper 0.005% and iron 0.01%. It is used in lead paints, lead-acid batteries, vulcanization of rubber and as

catalysts in many organic condensation reactions. Herein, it was used as a catalyst for transesterification reaction of triglyceride with glycerol. It was utilized as received.

Diethyl ether was obtained from Merck, India. It has formula weight ( $F_w$ ) 74.12 g/mole, purity  $\geq 98\%$  and density 0.713-0.716 g/c.c. at 20 °C. Impurities present are water 0.2%, aldehydes and ketones 0.02% and ethanol 0.5%. It is a common laboratory solvent and was used after distillation.

Anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was obtained from Merck, India. It has molecular weight ( $M_w$ ) 142.04 g/mole and purity 99% with chloride (0.01%), nitrate (0.01%), potassium (0.01%) and iron (0.01%) as impurities. It is widely used in the laboratory as an inert drying agent for removing traces of water from organic solutions. It was used as received.

Diethanolamine (Figure 2.2) was obtained from Merck, India. The compound has melting point (m.p.) 25-28 °C, minimum assay 98.0%, water 0.5% and molecular weight ( $M_w$ ) 105.14 g/mole. Diethanolamine is prepared in the laboratory by the reaction of ethylene oxide with aqueous ammonia. It was used after drying under vacuum.

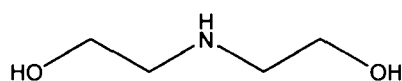


Figure 2.2 Structure of diethanol amine

Magnesium turning (Mg-turning) was purchased from SRL, India. It has atomic weight ( $A_w$ ) 24.31 g/mole and purity 99.8% with maximum 0.05% iron as impurity. It was purified by thorough washing with dilute HCl followed by washing with distilled water. The process is repeated for several times until the turning became shining. Finally it was washed with acetone and dried under vacuum at 45 °C for 4-5 h. The dried turnings were used immediately.

Hydrochloric acid was obtained from Merck, India and was used as received. It has formula weight ( $F_w$ ) 36.46 g/mole, purity  $\geq 35\%$  and density 1.16-1.18 g/c.c. at 20 °C and has strength of 11.6N.

Methanol ( $\text{CH}_3\text{OH}$ ) obtained from Merck, India has formula weight ( $F_w$ ) 58.0 g/mole, purity  $\geq 99.5\%$ , density 0.971 g/c.c. and boiling point (b.p.) 56-57 °C. It is generally used as an antifreeze, solvent, fuel, transesterification reagent for biodiesel production and also as denaturant for ethanol. Here it was used as a solvent, as a

reagent to prepare sodium methoxide ( $\text{NaOCH}_3$ ) and also as a transesterification reagent.

Sodium metal (Na) was obtained from Merck, Germany. It has atomic weight ( $A_w$ ) 22.9 g/mole and purity 98.8% with chloride (0.01%), silica (0.002%), calcium (0.1%) and iron (0.01%) as impurities. It was kept in paraffin oil and used as received after cutting into small pieces to prepare sodium methoxide.

Sodium hydroxide (NaOH) is the principal strong base used in chemical industry. It was obtained from Merck, India and was used as received. It has molecular weight ( $M_w$ ) 40.0 g/mole and purity > 97% with  $\text{Na}_2\text{CO}_3$  (1.0%), potassium (0.02%), chloride (0.005%), heavy metals (0.05%) and  $\text{NH}_4\text{OH}$  (0.02%) as the impurities.

Xylene from Merck, India was used as a solvent after distillation under reduced pressure. It has formula weight ( $F_w$ ) 106.17 g/mole, purity  $\geq 98.0\%$ , density 0.86 g/c.c. at 20 °C and boiling point (b.p.) 137-143 °C.

Poly(ethylene glycol) (PEG) (Figure 2.3) was obtained from Merck, India. It is used in polymer industry, preservation of objects, gas chromatography, microbiology etc. Herein, it was used as a chain extending diol during polyurethane synthesis. The material has density 1.124-1.126 g/c.c. at 20 °C, hydroxyl number 535-590 mg KOH/g and number average molecular weight ( $M_n$ ) ca. 200.

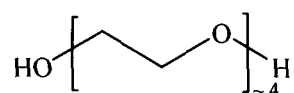


Figure 2.3 Structure of poly(ethylene glycol)

Toluene diisocyanate (TDI) (Figure 2.4) was obtained from Aldrich Chemie, Germany. It has formula weight ( $F_w$ ) 174.16 g/mole, composition of 80% 2,4-isomer and 20% 2,6-isomer, density 1.214 g/c.c., melting point (m.p.) 21.8 °C and boiling point (b.p.) 251 °C. Pure TDI can be synthesized in the laboratory in a multistep process. Dinitrotoluene obtained by nitration of toluene is treated with hydrogen and a catalyst to form toluene diamine (TDA) which is distilled to produce m-TDA. It is then reacted with phosgene to form a crude TDI mixture which is then distilled to produce an 80:20 mixture of 2,4-TDI and 2,6-TDI. In the present work, TDI was used as received as a reagent for polyurethane synthesis.

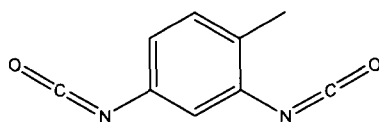


Figure 2.4 Structure of toluene diisocyanate

Dibutyl tin dilaurate (DBTDL) (Figure 2.5) was also obtained from Aldrich Chemie, Germany and has formula weight (Fw) 631.56 g/mole, purity 95% and density 1.066 g/c.c. It is used as an organotin compound in organic synthesis. Here, it was used as a catalyst without further purification.

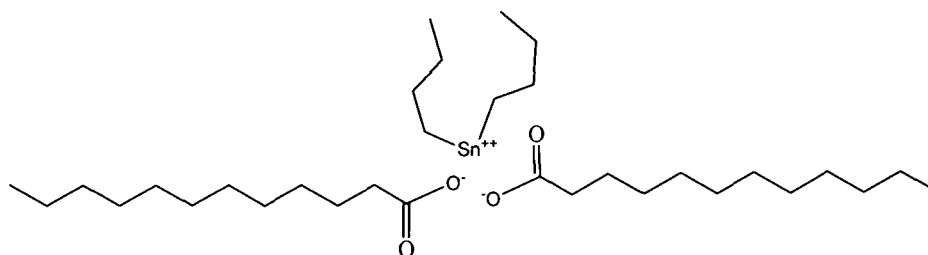


Figure 2.5 Structure of dibutyl tin dilaurate

Molecular sieve of 4A type has been purchased from Merck, India. Its equilibrium capacity for water at 30 °C and 75% relative air humidity is  $\geq 20\%$  and bulk density is 650-700 g/L. They often consist of aluminosilicate minerals, clays, zeolites, active carbons etc. having open structures through which small molecules can diffuse. It was used as received to trap trace amount of moisture present in solvents.

Sodium chloride (NaCl) and ethanol (C<sub>2</sub>H<sub>5</sub>OH) were obtained from Merck, India and were used as received for chemical resistance study.

Acetone (CH<sub>3</sub>COCH<sub>3</sub>) was obtained from SRL, India. It has purity  $\geq 99.8\%$  with water  $\leq 0.2\%$  and boiling point (b.p.) 64-65 °C. It was used as a common solvent, as received.

### 2.2.2. Instruments and methods

Viscosity of the polymer solutions (0.5 g/dL in xylene) was measured by an Ubbelohde capillary viscometer (suspended-level viscometer) at (27±0.1) °C. The molecular weights of the resins were determined by GPC analysis (Waters, USA, Model 515) using THF as the solvent. The density of the polymers was determined by pycnometer at room temperature (ca. 27 °C) by the conventional liquid displacement method (Archimedis principle) [29]. The chemical resistance tests were performed in

different chemical media as per the ASTM D 543-67 standard procedure [36] by taking dried resin coated glass plates in 250 mL beakers containing 150 mL of the individual chemical medium for 10 days. The chemical resistance was determined by making observations of visual changes in the films and calculation of the percent weight loss.

FTIR spectra of the resins and the intermediates were recorded in a FTIR spectrophotometer (Impact-410, Nicolet, USA) using KBr pellet. <sup>1</sup>H NMR spectra were recorded in a Varian 400 MHz NMR spectrometer (Australia) using CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. Thermal analysis (TGA) of the cured resins was carried out by using a Perkin Elmer (Boston, USA) Pyris-1 thermal analyzer with the N<sub>2</sub> flow rate of 20 mL min<sup>-1</sup> and heating rate of 10 °C min<sup>-1</sup>.

The other physical properties of the resins such as acid value, iodine value, saponification value, hydroxyl value, isocyanate value and drying time were determined by earlier reported standard methods [29]. Thickness of the cured films was determined by the Pentest, coating thickness gauge (Sheen Instrument Ltd., Model 1117, UK). The coating performance of the cured films was evaluated by the determination of various mechanical properties. The pencil hardness of the cured films was measured using pencils of different grades ranging from 6B to 6H (ASTM D 3363-00) [37]. Impact resistance was determined by falling weight (ball) method (standard ASTM D 1037). The flexibility was determined by bending test of tin plates by examining any crack or damage in the substrate by bending around a cylindrical mandrel [38]. The adhesion performance of the coated films on mild steel plate was tested by using the commercial cello tape as per the cross-cut tape test method (ASTM D 3359-97) [39] and by using the “Lap shear adhesion method” [40] with plywood as the substrate. The lap shear test was carried out with the help of a UTM machine (Zwick Z010, Germany) at jaw separation speed of 50 mm/min. Gloss characteristics of the cured films were evaluated [41] using a glossmeter (Minigloss meter, Sheen, UK) over dried resin coated mild steel plates at an angle of incidence of 60°.

#### 2.2.2.1. Synthesis of poly(urethane ester) (PUE) resin from *Mesua ferrea* L. seed oil

##### 2.2.2.1.1. Preparation of monoglyceride of the oil

A three neck round bottom flask equipped with a mechanical stirrer, a thermometer and a nitrogen gas inlet was charged with 15.0 g (0.017 mole) of *Mesua*

*ferrea* L. (Nahar) seed oil, 3.14 g (0.034 mole) of glycerol and 0.05 weight % (with respect to the oil) lead mono-oxide (catalyst) with continuous stirring. Then the reaction mixture was heated up to  $(240\pm 5)$  °C for 30-40 min until the monoglyceride was formed, confirmed by solubility in methanol (monoglyceride: methanol=1:3 v/v) at ambient temperature.

#### 2.2.2.1.2. Preparation of poly(urethane ester) (PUE) resin

An amount of 10.0 g (0.028 mole) of monoglyceride was taken along with 2.8 g (0.014 mole) of PEG as chain extender and 0.05 weight % DBTDL as the catalyst (with respect to the total diol content) in a three neck round bottom flask fitted with a mechanical stirrer, a nitrogen inlet and a dropping funnel. Then 100 mL of xylene was added into the mixture to facilitate proper mixing. TDI was then added (as per the requirement to maintain the NCO/OH ratio, Table 2.1) through the dropping funnel in a drop wise manner over a period of 15 min with constant vigorous mechanical stirring. The reaction was continued at 40-50 °C until the solution became viscous. The resins were obtained as 30-40 weight % solid content in xylene with yield of greater than 90%.

#### 2.2.2.2. Synthesis of poly(urethane amide) (PUA) resin from *Mesua ferrea* L. seed oil

##### 2.2.2.2.1. Preparation of super dry methanol

Super dry methanol was used for the preparation of sodium methoxide, which was obtained as follows. An amount of about 3 g of purified dry Mg-turnings was taken in a 1000 mL single neck round bottom flask. The flask was fitted with a reflux condenser along with a guard tube containing anhydrous calcium chloride. A pinch of iodine was added into it and heated for 2-3 min. About 50 mL of distilled methanol was added into the above mixture. The mixture was refluxed until the color of the iodine disappeared. Then about 600 mL of distilled methanol was added in the flask and it was refluxed until the color of the solution became milky white due to the formation of  $Mg(OH)_2$ . The solution was then distilled and the distillate obtained (super dry methanol) was kept in an amber bottle using 4A type molecular sieves.



#### 2.2.2.2.2. Preparation of sodium methoxide

In a completely dried 100 mL three neck round bottom flask fitted with a water condenser and a nitrogen inlet, about 50 mL 'super dry' methanol was charged. The reaction flask was placed in an ice-water bath to maintain the temperature of the reaction at 0-5 °C. About 10 g of small pieces of pure and dry sodium metal was added in parts very slowly with vigorous stirring. After completion of addition, the reaction mixture was refluxed for 2 h. Finally, the excess methanol was removed by vacuum distillation. Sodium methoxide thus obtained was in the form of white powder, which was stored in a desiccator for further use.

#### 2.2.2.2.3. Preparation of methyl ester of the oil

25 g of the purified *Mesua ferrea* L. seed oil and 50 mL of super dry methanol were taken along with 0.5 weight % sodium methoxide (with respect to the oil) in a 250 mL round bottom flask under the nitrogen atmosphere. The solution was refluxed for 3 h and kept overnight. The excess methanol was removed by distillation and the methyl ester was extracted by solvent extraction (liquid-liquid extraction) technique using petroleum ether as the solvent (b.p. 60-80) °C and washed with 15% aqueous NaCl solution. The moist methyl ester thus obtained was dried over anhydrous sodium sulfate for overnight. The methyl ester was then made free from ether by distillation. The product obtained was in quantitative yield.

#### 2.2.2.2.4. Preparation of diethanol amide (DEANO) from the methyl ester of the oil

3.45 g diethanol amine and 0.5 weight % sodium methoxide (with respect to the ester) were charged into a three necked round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and a dropping funnel. The contents were heated to (110-115) °C with constant mechanical stirring under the nitrogen atmosphere. Then an amount of 8.42 g of methyl esters of the oil taken in the dropping funnel was added into the reaction mixture drop wise over a period of 1 h. The heating was continued for another 3 h with constant stirring. Then the reaction mixture was cooled to room temperature, dissolved in petroleum ether, washed with 15% aqueous NaCl solution and dried over anhydrous sodium sulfate for overnight. The petroleum ether was removed by

distillation to obtain the N,N'-bis(2-hydroxyethyl) Nahar oil amide (fatty amide diol or diethanol amide of the fatty acids, DEANO). The yield was around 80%.

#### 2.2.2.2.5. Preparation of poly(urethane amide) (PUA) resin

2.5 g (0.00687 mole) of DEANO was taken along with 0.87 g (0.00435 mole) of PEG as chain extender and 0.05 weight % DBTDL as the catalyst (with respect to the total diol content) in a three neck round bottom flask fitted with a mechanical stirrer, a nitrogen inlet and a dropping funnel. Then 25 mL of xylene was added into the mixture to facilitate proper mixing. TDI was then added (as per the requirement to maintain the NCO/OH ratio, Table 2.1) through the dropping funnel in a drop wise manner over a period of 15 min with constant vigorous mechanical stirring. The reaction was continued at 40-50 °C until the solution became viscous. The resins were obtained as 30-40 weight % solid content in xylene with yield of ca. 90-92%.

Table 2.1 Composition of PUE and PUA resins

Resin Code*	NCO/OH ratio (mole)	Diol** (mole)	PEG (mole)	TDI (moles)
PUE0.8/PUA0.8	1:0.8	1.0	0.5	1.20
PUE1.0/PUA1.0	1:1.0	1.0	0.5	1.50
PUE1.25/PUA1.25	1:1.25	1.0	0.5	1.87
PUE1.5/PUA1.5	1:1.5	1.0	0.5	2.25
PUE2.0/PUA2.0	1:2.0	1.0	0.5	3.00

\*indicates the NCO/OH ratio in the resins

\*\*indicates monoglyceride for PUE and DEANO for PUA resins

#### 2.2.2.3. Curing of PUE and PUA resins

The homogenous solutions of PUE or PUA resins with 30-40 weight % solid content in xylene were coated at ambient temperature on commercially available mild steel strips (150 mm X 100 mm X 1.44 mm) for gloss, pencil hardness and impact resistance measurements, tin plates (150 mm X 50 mm X 0.19 mm) for bending and adhesion tests, and glass plates (75 mm X 25 mm X 1.75 mm) for chemical resistance

test. The plates were then allowed to dry completely and the drying times were noted. Thickness of the resulting coatings was found to be in the range of 25-35  $\mu\text{m}$ .

## **2.3. Results and discussion**

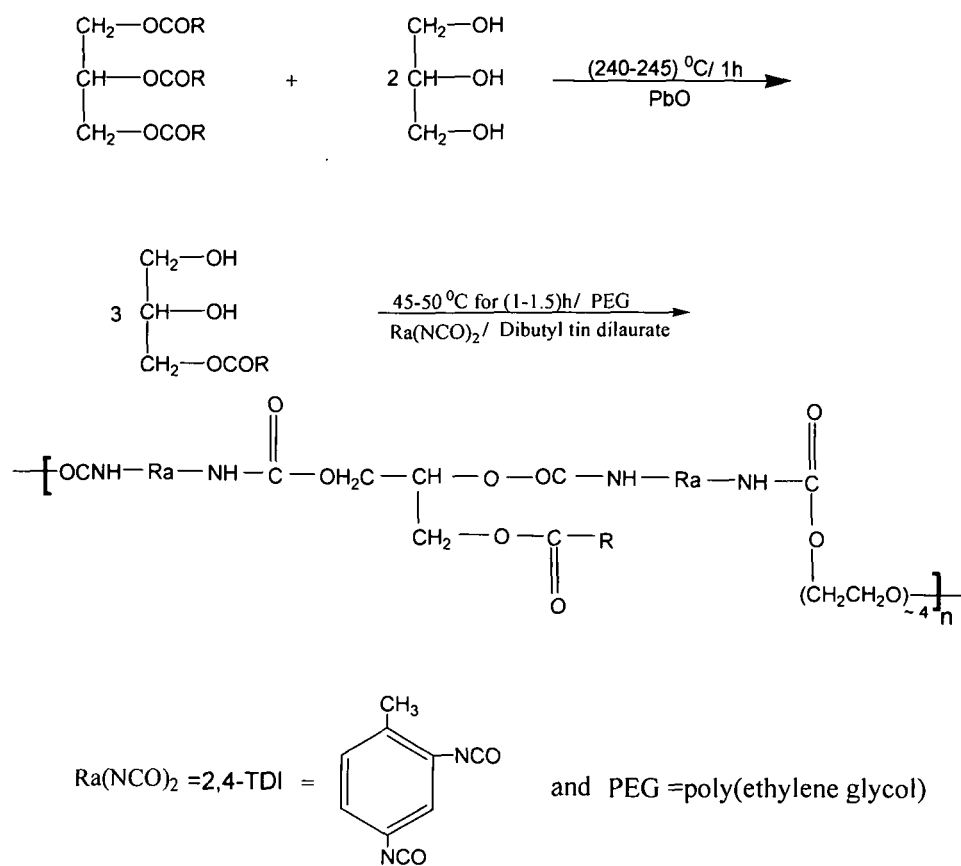
### **2.3.1. Synthesis**

As the urethane reaction is very much sensitive to moisture, the product can be obtained by solution polymerization technique without gel formation only under highly restricted (controlled) conditions. The resins PUE and PUA were synthesized (with different NCO/OH ratios from 0.8 to 2.0) by using varying compositions of the monoglyceride and DEANO respectively with TDI and PEG in the presence of DBTDL catalyst at 40-50  $^{\circ}\text{C}$  for specified time periods. Even though in most of the reports [42], azeotropic technique (aided with Dean Stark apparatus) was used but in our technique, it has been found that the resin was formed very easily by lesser time with good yields of greater than 90% in all the cases. The resins were obtained as 30-40 weight % solid content in xylene.

Urethane linkages in PUE resins were formed by reaction of the isocyanate groups with the hydroxyl groups of the monoglyceride and PEG (Scheme 2.1), whereas the PUA resins were formed by the reaction of isocyanate groups with the hydroxyl groups of the DEANO and PEG (Scheme 2.2). Formation of the monoglyceride, methyl ester, DEANO and the resins were confirmed by the determination of viscosity, hydroxyl values, isocyanate values etc. (Table 2.3) and also by spectroscopic studies.

### **2.3.2. Characterization**

The intermediates like monoglyceride, methyl ester of the fatty acids and oil fatty amide (DEANO), as well as the synthesized PUE and PUA resins with different NCO/OH ratios were characterized by determination of physical properties like acid, saponification, iodine, hydroxyl, isocyanate, dilute solution inherent viscosity etc. values and spectroscopic techniques such as FTIR and  $^1\text{H}$ NMR [43-46] and GPC analysis.



(R= Hydrocarbon parts of Palmitic, Stearic, Oleic and Linoleic acids)

Scheme 2.1 Synthesis of PUE resin

### 2.3.2.1. PUE resin and its intermediates

The important absorption bands in the FTIR spectrum of monoglyceride of *Mesua ferrea* L. seed oil appeared at ca. 3316-3332  $\text{cm}^{-1}$  (OH stretching frequency), ca. 1735  $\text{cm}^{-1}$  (C=O stretching frequency of ester), ca. 1651  $\text{cm}^{-1}$  (C=C stretching frequency of fatty acid), ca. 2852-2921  $\text{cm}^{-1}$  (C-H stretching frequency of fatty acid chain). For PUE resins (Figure 2.6), the bands appeared at ca. 3300-3330  $\text{cm}^{-1}$  (strong OH stretching frequency overlapped with NH stretching frequency of urethane linkage), ca. 2273  $\text{cm}^{-1}$  (NCO stretching frequency for resins with NCO/OH greater than one), ca. 1720  $\text{cm}^{-1}$  (C=O stretching frequency of ester carbonyl), 1601  $\text{cm}^{-1}$  (C=C stretching frequency of fatty acid), ca. 1530-1545  $\text{cm}^{-1}$  (C-N stretching frequency combined with NH out of plane bending frequency), ca. 1070  $\text{cm}^{-1}$  (C-O stretching frequency of ester) and ca. 767  $\text{cm}^{-1}$  (aromatic moiety of TDI). Disappearance of the NCO band (for the resins with NCO/OH  $\leq$  1), sharpening of the broad OH band,



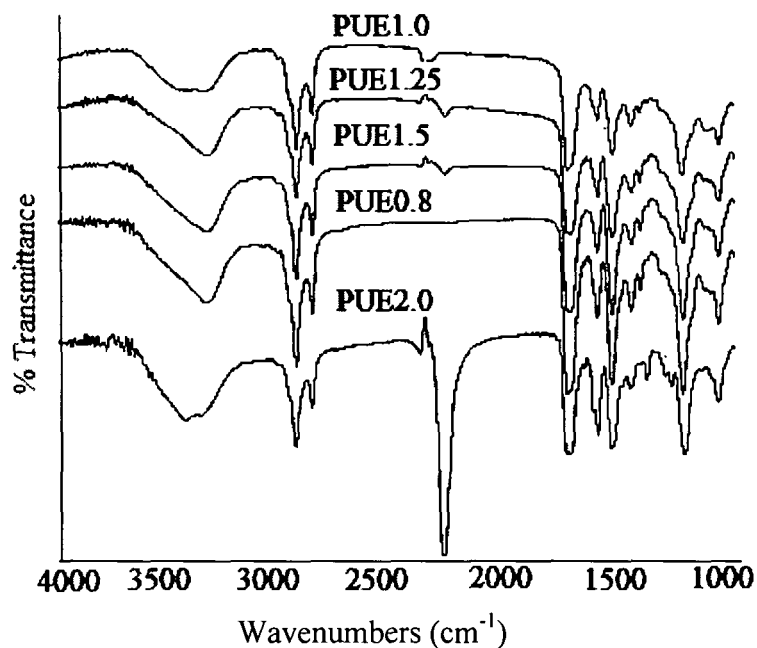


Figure 2.6 FTIR spectra of PUE resins

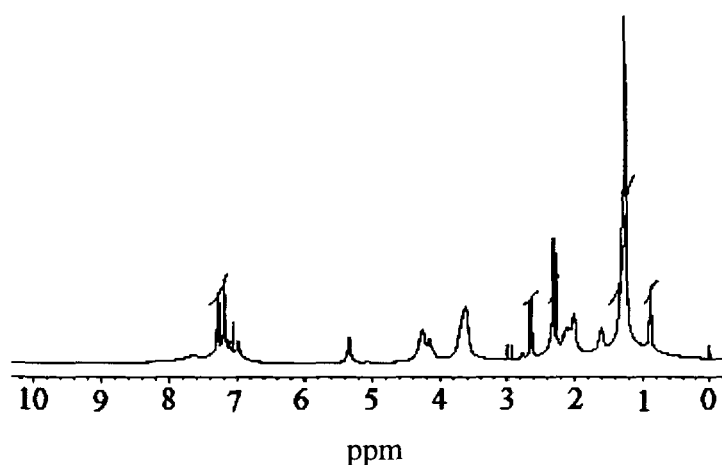


Figure 2.7 <sup>1</sup>H NMR spectra of PUE resin

### 2.3.2.2. PUA resin and its intermediates

The important bands in FTIR spectrum of methyl ester of the fatty acid appeared at ca.  $1772\text{ cm}^{-1}$  (C=O stretching frequency of ester), ca.  $1617\text{ cm}^{-1}$  (C=C stretching frequency of fatty acid), DEANO appeared at ca.  $3380\text{ cm}^{-1}$  (OH stretching frequency), ca.  $1739\text{ cm}^{-1}$  (C=O stretching frequency of amide carbonyl), ca.  $1621\text{ cm}^{-1}$  (C=C stretching frequency of amide carbonyl), ca.  $2853\text{-}2923\text{ cm}^{-1}$  (C-H stretching frequency of fatty acid chain) [Figure 2.8 (a)]. The bands for PUA resins [Figure 2.8

(b)] appeared at ca.  $3300\text{ cm}^{-1}$  (strong OH stretching frequency overlapped with NH stretching frequency), ca.  $2273\text{ cm}^{-1}$  (NCO stretching frequency for resins with NCO/OH > 1), ca.  $1712\text{ cm}^{-1}$  (C=O stretching frequency of amide carbonyl),  $1603\text{ cm}^{-1}$  (C=C stretching frequency of fatty acid), ca.  $1530\text{-}1545\text{ cm}^{-1}$  (C-N stretching frequency combined with NH out of plane bending frequency), ca.  $1041\text{ cm}^{-1}$  (C-O stretching frequency of ester) and ca.  $744\text{-}767\text{ cm}^{-1}$  (aromatic moiety of TDI). These peaks in FTIR spectra clearly indicated the formation of urethane linkage [21, 43-44, 46].

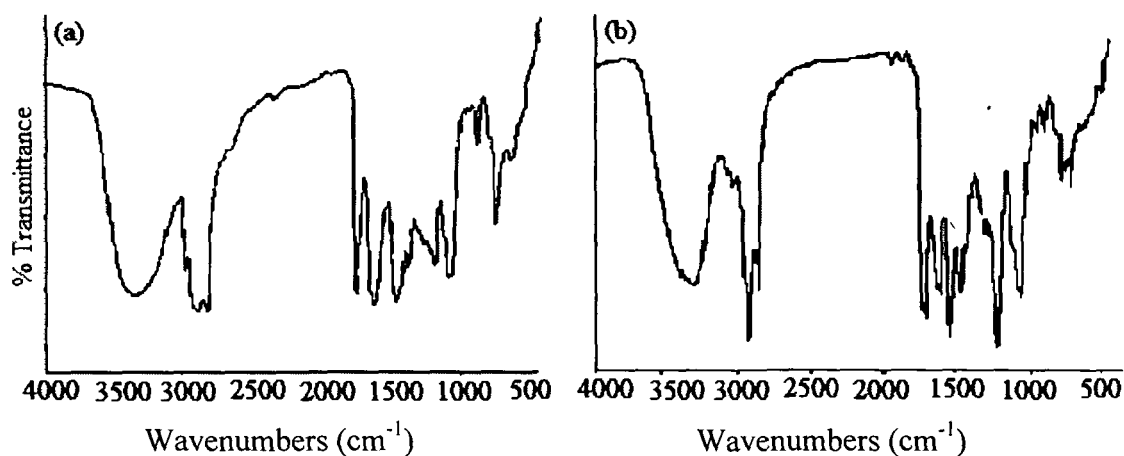


Figure 2.8 FTIR spectra of (a) DEANO and (b) PUA resin

This was further supported by  $^1\text{H}$ NMR studies (Figures 2.9 and 2.10). The peaks appearing at  $\delta = 0.80\text{-}0.88\text{ ppm}$  are due to the terminal methyl group of the fatty acid chains and  $\delta = 1.52\text{-}1.6\text{ ppm}$  are due to the protons of  $\text{CH}_2$  group attached next to the above terminal methyl group. The peaks at  $\delta = 1.18\text{-}1.30\text{ ppm}$  account for the protons of internal  $\text{CH}_2$  groups present in the fatty acid chains. The peaks for protons of unsaturated carbons appeared at  $\delta = 5.2\text{-}5.3\text{ ppm}$ . The  $\text{CH}_2$  protons attached with the double bonds were found at  $\delta = 1.9\text{-}2.0\text{ ppm}$ , whereas the protons for  $\text{CH}_2$  adjacent to amide carbonyl was observed at  $\delta = 2.2\text{-}2.3\text{ ppm}$  for all the intermediates i.e., methyl ester and DEANO (Figure 2.9) and the PUA resin (Figure 2.10).

The peak for the protons of methoxy group of methyl ester derivative appears at  $\delta = 4.1\text{-}4.3\text{ ppm}$ . The peaks at  $\delta = 3.4\text{-}3.5\text{ ppm}$  and  $\delta = 3.6\text{ ppm}$  were found for  $\text{CH}_2$  protons of amide derivatives attached directly with tertiary nitrogen and OH group respectively. The aromatic protons as well as the NH proton of the urethane linkage of the resins appeared at  $\delta = 6.8\text{-}7.2\text{ ppm}$ , whereas the  $\text{CH}_3$  protons of TDI moiety

appeared at  $\delta = 2.8$  ppm [21, 43, 45-46]. The resin formation was confirmed by the dilute solution viscosity measurement.

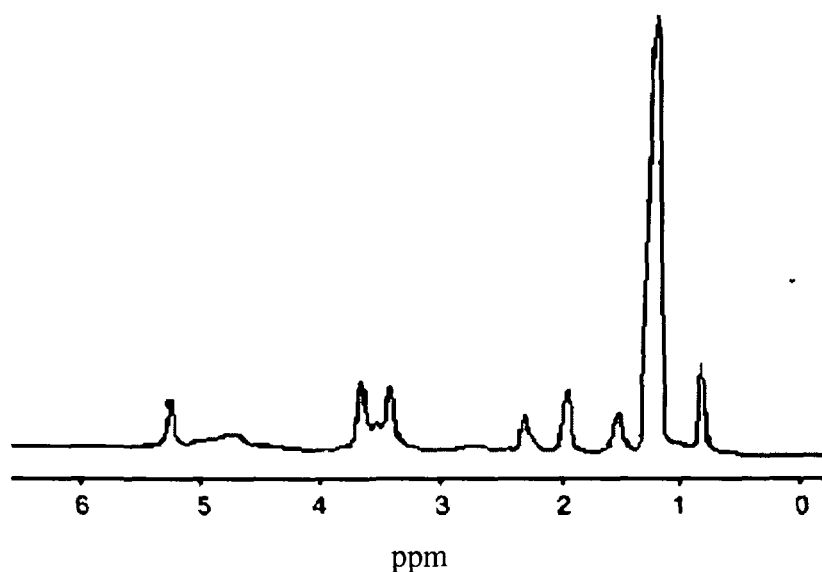


Figure 2.9 <sup>1</sup>H NMR spectra of DEANO

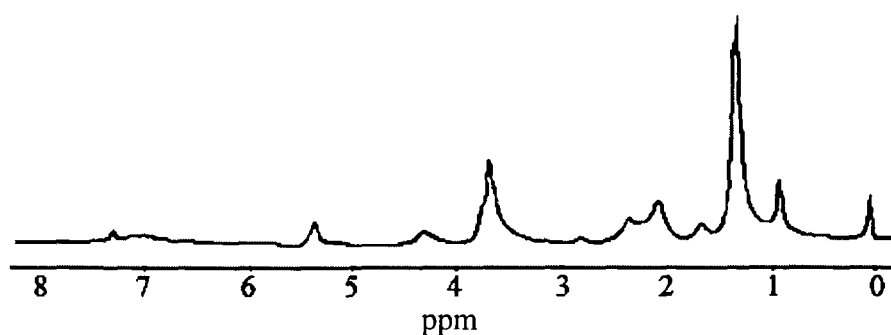


Figure 2.10 <sup>1</sup>H NMR spectra of PUA resin

### 2.3.2.3. GPC analysis of the PUE and PUA resins

The GPC chromatograms for PUE and PUA resins are shown in Figures 2.11 and 2.12 respectively. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity index (PDI) for the polymers are given in Table 2.2. This low average molecular weight and relatively low PDI confer low viscosity to the polymer which will help in obtaining easily flowable coating.



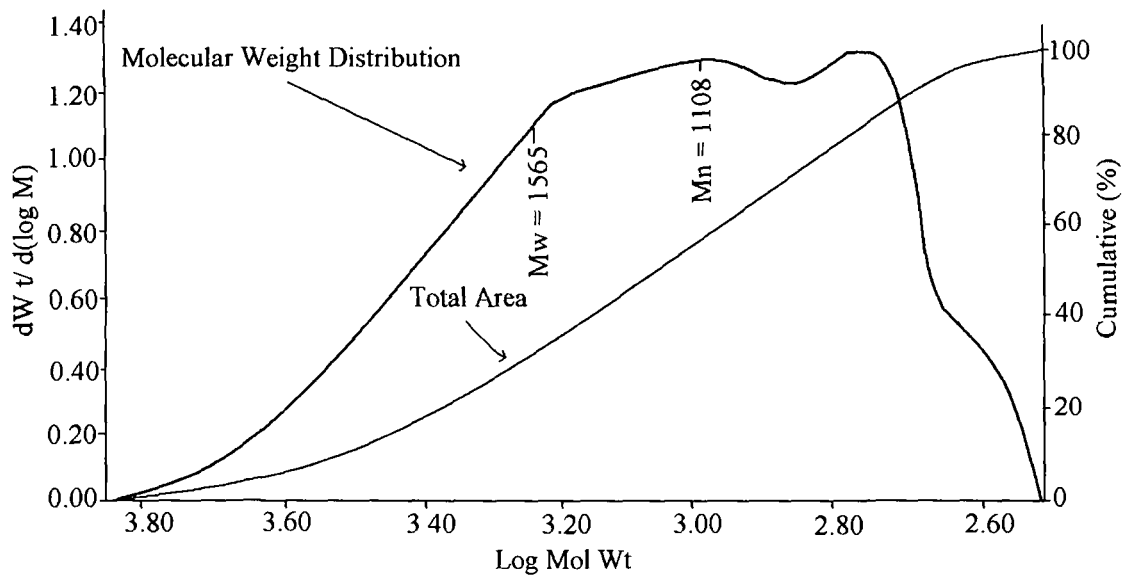


Figure 2.11 GPC chromatogram of PUE resin

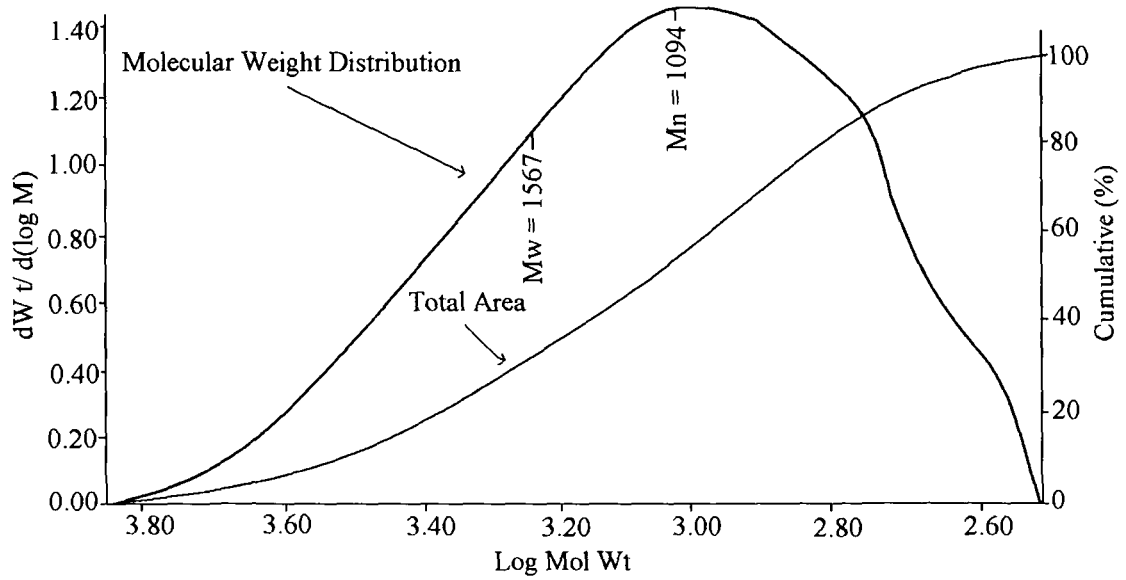


Figure 2.12 GPC chromatogram of PUA resin

Table 2.2 GPC data for PUE and PUA resins

Properties	PUE	PUA
Number average molecular weight ( $M_n$ , g/mole)	1108	1094
Weight average molecular weight ( $M_w$ , g/mole)	1565	1567
Polydispersity Index (PDI)	1.412	1.432

#### 2.3.2.4. Curing study of the resins

The chemical changes occurring in the network after the curing of the resins can be studied by FTIR spectroscopy. After curing at room temperature followed by post-curing at 120 °C for 2 h of the resins, the free NCO group band was found to be reduced drastically but not disappeared completely, as observed in the FTIR spectra (Figure 2.13 for PUE resins), which indicates that even after post-curing at 120 °C for 2 h, the cross-linking reaction was not completed. Again, with the increase of NCO/OH ratio, the formation of three dimensional network structure via allophanate, urea or biuret linkages also increases, which in turn increases the number of urethane groups [47].

In polyurethanes, NH groups form H-bonding with urethane or ester carbonyl (C=O), urethane alkoxy oxygen and with ether oxygen. This was expected to give a doublet (a band with two resolved branched peaks one at ca. 3350  $\text{cm}^{-1}$  for H-bonded NH and another at ca. 3500  $\text{cm}^{-1}$  for free NH) in the region ca. 3200-3500  $\text{cm}^{-1}$ . But unfortunately, this region was overlapped by broad OH stretching frequency and the peaks were not distinctly observed. However, this phenomenon was observed for the C=O absorption band if deconvolution was carried out for the slight broad band appearing in the region ca. 1715-1736  $\text{cm}^{-1}$  (Figure 2.13). The peak of the doublet towards the lower absorption region (ca. 1719  $\text{cm}^{-1}$ ) is due to H-bonded urethane carbonyl stretching, whereas the peak towards the higher absorption region (ca. 1733  $\text{cm}^{-1}$ ) is due to non H-bonded urethane carbonyl stretching [22, 48-49]. Furthermore, comparison of the H-bonded to the non H-bonded peaks in the FTIR spectra can give an idea about the extent of H-bonding [22].

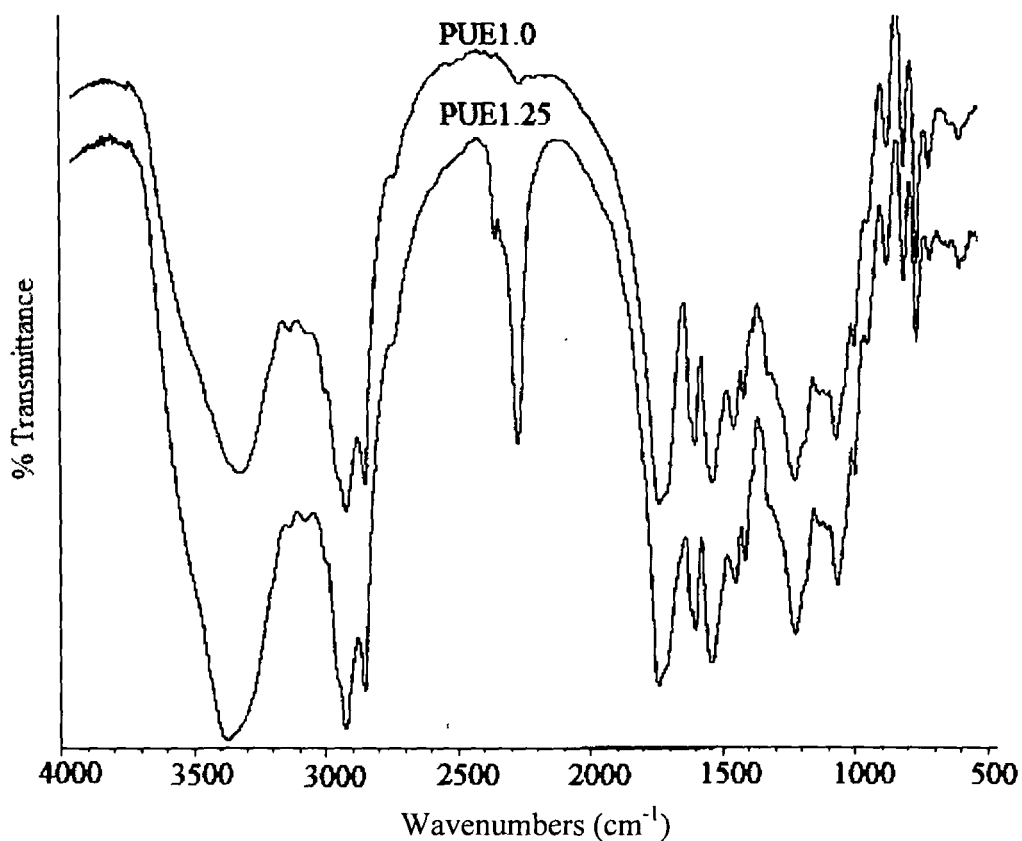


Figure 2.13 FTIR spectra of PUE resins after curing

As the value of NCO/OH ratio increases, the C=O stretching frequency further decreases but at NCO/OH = 2.0, again it increases a little. The splitting of C=O absorption and lowering of absorption value indicate the hydrogen bonding formation with urethane NH. It has also been noticed that the intensity of the lower absorption value increases with the increase of NCO/OH ratio, which further support the increase of hydrogen bond formation with the increase of urethane NH linkages. In a polyurethane with higher urethane concentration, the H-bonding is mainly formed with urethane C=O, whereas H-bonding with ether become more prominent as the urethane concentration decreased [50]. From Figure 2.13, it has also been noticed that the broad absorption band appearing at ca. 3316-3410  $\text{cm}^{-1}$  became sharper after curing which also indicated the increase in interaction of NH and OH groups present in the resin. Such interactions may also hint the phase separation occurring in the resin. The phase separation in polyurethanes can be characterized by measuring the intensity and position of the H-bonded NH stretching vibrations [51]. Usually, a significant amount of N-H.....O=C (urethane) H-bonding indicates extensive phase separation [52] which increases with the increase of NCO/OH ratio.

### ***2.3.3. Physical properties***

The dilute solution viscosity values of both the PUE and PUA resins were relatively low as evident from Table 2.3. It has also been found that the values increased slightly with the increase of NCO/OH ratio for almost same resinification times. However, in case of NCO/OH ratio 2.0, the resinification reaction took less time for completion. Actually, the viscosity of a polymer depends on molar mass, structure and conformation of the polymer molecules. With the increase in NCO/OH ratio, the molar mass increases and the molecular interaction increases as the number of urethane linkages increases which in turn increases polarity as well as the degree of H-bonding. As a result, viscosity is also expected to increase. The specific gravity values of the resins also increased steadily with the increase of NCO/OH ratio. This may be due to the formation of compact structures arising from increase of the aromatic content in the structure as well as the extent of hydrogen bonding with the increase of TDI content in the resins.

The hydroxyl value of both the PUE and PUA resins was found to be decreased continuously with the increase of NCO/OH ratio, whereas the isocyanate values increased (Table 2.3). This is obvious as the rate of the reaction of isocyanate with diols increases with the increase of NCO/OH ratio and thus leaves behind very less amount of free hydroxyl group in the reaction mixture. As the NCO/OH ratio increases, the molecular weight of the resins also increases as indicated by inherent viscosity measurements, as discussed earlier. This is further supported by the saponification value diminution with increase in NCO/OH ratio. The iodine values and acid values (Table 2.3) are not found to be changed much with NCO/OH ratio. However, the moderate acid values and iodine values especially up to NCO/OH ratio 1.25 indicate that the resin could be used for coatings and paint applications. This will also help the resins to be used as matrix for fiber reinforced composites, especially for the polar cellulosic fiber such as jute and bamboo [53].

### ***2.3.4. Coating performance***

The room temperature cured resins were subjected to post-curing at 120 °C for 2 h and then utilized for the determination of coating properties such as pencil hardness, gloss, adhesive strength, impact resistance, flexibility etc. However, the resins with

NCO/OH ratio 0.8 was not found to be cured at 120 °C or even at higher temperatures and hence was not studied further in this chapter. The most significant characteristic of the resins with NCO/OH ratio  $\geq 1.0$  is their ambient temperature curing under open environmental conditions. In the curing process, moisture plays a dominant role whereby the free NCO groups are converted into the corresponding amine with liberation of carbon dioxide followed by formation of urea linkages after the reaction with active hydrogen present in the chain. However, curing at room temperature may not consume all the free isocyanate groups and hence the post curing reaction at 120 °C for 2 h was performed to complete the process. During the process, curing takes place further via the formation of urethane, allophanate, urea and biuret linkages [19, 54, 55]. Such interactions cause a crosslinked, uniform and well-adhered structure which increases further with the increase of NCO/OH ratio due to the presence of more isocyanate groups in resin [48]. However, at lower temperature and humidity, the curing times tend to extend. The drying process became much faster at elevated temperature and higher humidity such as 50 °C and 90% relative humidity and the effect of NCO/OH ratio remains same as that for the ambient temperature cured resins [56].

The mechanical properties measured for evaluating the coating performance of the PUE and PUA resins with varying NCO/OH ratios are tabulated in Table 2.4. From the table, it has been found that the pencil hardness increased with the increase of NCO/OH ratio. This is expected as the cross-linking density increases with the increase of degree of hydrogen bonding, amount of rigid aromatic moiety and amount of reactive isocyanate groups with the increase of NCO/OH ratio. The results are further supported by FTIR studies, which indicate the presence of free isocyanate groups even after post curing (Figure 2.13). The adhesive strength also increased in the same order for both the resins. High adhesion capability is a characteristic of polyurethane which is expected from the presence of polar linkages such as urethane, ester, urea, allophanate etc. in the polymer matrix [40, 55]. Extent of such interactions (linkages) increases with the increase of NCO/OH ratio from 1.0 to 2.0 and hence adhesive strength also increases (Table 2.4). Vegetable oil based polyurethane is known to be flexible and the studied polyurethane is even more flexible due to the presence of flexible ether linkage of PEG, ester linkage and the flexible hydrocarbon chain of the oil. *Mesua ferrea* L. seed oil based PUE and PUA, all the resins showed sufficient flexibility as the films

can be bent into a very low diameter cylindrical form (Table 2.4). As the resins have good flexibility for all NCO/OH ratios, accordingly the impact resistance (toughness) is also expected to be good. The present study showed a marginal increase in this property with the increase of NCO/OH ratio. The reason behind this improvement is seemed to be contradictory. This is because of the fact that with the increase of NCO/OH ratio, the cross linking density, degree of hydrogen bonding and amount of rigid aromatic moiety also increases which make the cured resins more rigid. At the same time, the molecular weight of the resins also increases with the increase of NCO/OH ratio as supported by viscosity measurement of the resins before curing (Table 2.3) and hence the impact strength also improves. The optical behavior of the cured films as measured by gloss was also found to be excellent for both the PUE and PUA resins. The gloss was also found to be slightly increased with the increase of NCO/OH ratio due to the presence of urethane groups, long fatty acid chains and denseness in the structure [48].

#### ***2.3.5. Chemical properties***

Chemical resistance test was carried out in different media such as aqueous NaOH, HCl, NaCl, EtOH and distilled water (Table 2.5). All the PUE and PUA resins with varying NCO/OH ratio showed excellent chemical resistance in the tested media except in NaOH solution (particularly for PUE resins, where more degradation and adhesion loss was found). This poor alkali resistance is due to the presence of alkali hydrolyzable ester groups. Yet, these polyurethane resins showed comparatively better alkali resistance than the polyester or poly(ester amide) resins of the same oil [28]. The overall good chemical resistance behavior of the resins may be attributed to their crosslinked structure arising from the presence of rigid aromatic moiety in the polymer chain and strong intramolecular and intermolecular secondary interactions viz. polar-polar, H-bonding etc. Such crosslinked network prevents corrosive ions to penetrate into the cured resins [48]. However, the present study was not able to distinctly correlate the effect of NCO/OH ratio with the chemical resistance of the cured resins.

Table 2.3 Physical properties of PUE and PUA resins along with their polyol intermediates

Property	Mono Glyceride	PUE0.8	PUE1.0	PUE1.25	PUE1.5	PUE2.0	DEANO	PUA0.8	PUA1.0	PUA1.25	PUA2.0
Color	Dark brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown
Acid value (mg KOH/g)	6.2	14.03	12.12	12.02	8.75	8.07	9.02	8.21	7	4	3.9
Hydroxyl value	299.4	212.0	129.66	127.3	105.5	32.7	411.7	96.08	60.7	52.66	42.6
Saponification value (mg KOH/g)	-	413.23	352.6	316.6	327.25	243.9	245	261	232.3	156	131.6
Iodine value (g iodine/100 g)	-	67.76	45.0	40.11	40.35	41.12	245	69.6	61.6	46	45
Isocyanate value	-	-	1.0	25.2	45.3	67.8	-	1.7	33.4	44.7	77.1
Specific gravity	-	0.37	0.63	0.67	0.73	1.04	0.91	0.9	0.94	0.93	0.92
Inherent viscosity (dL/g)	-	0.087	0.11	0.092	0.12	0.15	0.077	0.21	0.25	0.4	0.55

Table 2.4 Coating properties of PUE and PUA resins along with their polyol intermediates

Property	PUE1.0	PUE1.25	PUE1.5	PUE2.0	PUA1.0	PUA1.25	PUA2.0
Touch free time (min)	45	40	35	25	15	10	8
Drying time (min)	85	75	65	50	45	35	30
Pencil hardness	HB	H	2H	3H	HB	H	2H
Gloss (at 45° for PUA and at 60° for PUE resin)	109	111	114	117	66	69	70
Impact strength (cm)	6-7	15-20	20-25	>30	3-4	4-5	7-10
Bending test (dia., cm)	<0.5	<0.3	<0.3	<0.3	<0.5	<0.5	<0.3
Adhesion (% for PUA and kN/m for PUE resin)	125.0	158.0	234.0	336.0	100	100	100

Table 2.5 Chemical resistance of the cured PUE and PUA resins

Medium	PUE1.0	PUE1.25	PUE1.5	PUE2.0	PUA1.0	PUA1.25	PUA2.0
5 weight % aqueous NaOH*	P	P	A	A	A	G	G
5 weight % aqueous HCl	A	G	G	G	G	G	G
10 weight % aqueous NaCl	E	E	E	E	E	E	E
20 weight % aqueous EtOH	A	G	G	G	A	G	G
Distilled water	E	E	E	E	E	E	E

\* Adhesion failure (P = poor, A = average, E = excellent, G = good)



### 2.3.6. Thermal properties

Figures 2.14-2.16 show TGA with DTGA curves for the *Mesua ferrea* L. seed oil based PUE resins with NCO/OH ratios 1.0, 1.5 and 2.0 respectively. The number of degradation steps was found to decrease with the increase of NCO/OH ratio. The resin PUE1.0 decomposed in three distinct stages (Figure 2.14) occurring at temperatures ca. 210 °C, 345 °C and 450 °C. The three step degradation is a characteristic of polyurethane corresponding to the decomposition of urethane bonds, ester or amide bonds and hydrocarbon chains respectively [48, 55]. On the other hand, the resin PUE1.5 decomposed via two distinct stages (Figure 2.15) occurring at temperatures of ca. 215 °C and 360 °C, whereas PUE2.0 resin showed only one step degradation characteristic at a temperature of ca. 220 °C (Figure 2.16). With the increase of NCO/OH ratio, the thermal behavior of the different moieties present in the resin also changes. Thermal stability of polyurethane resins depends mainly upon the equilibria of polymerization and depolymerization of the functional groups or linkages present in the polymer chains [55]. The allophanate and biuret linkages, which are formed during cross-linking reactions, reopen quite readily on heating at relatively higher temperature as they are very much thermolabile. Urethane linkages decompose at high temperature (ca. 200 °C) and the presence of aromatic moiety of the diisocyanates make the decomposition temperature even higher [55]. As the NCO/OH ratio increases, the amount of urethane linkage and aromatic moiety also increases and hence overall thermostability improves. The number of allophanate and biuret linkage increases accordingly. The decrease of number of distinct stages of degradation may therefore, be due to the fact that as the number of such linkages increases, so before the completion of one stage, the other stage starts.

The increase of NCO/OH ratio increases the cross-linking density of the polymer which draws the polymer backbones closer together making the material hard and restricting the molecular mobility. This increases the thermostability of the resin and also increases the softening point and glass transition temperature. The weight residue found at 550 °C for the resins were also found to be good which further supports their overall thermostability.

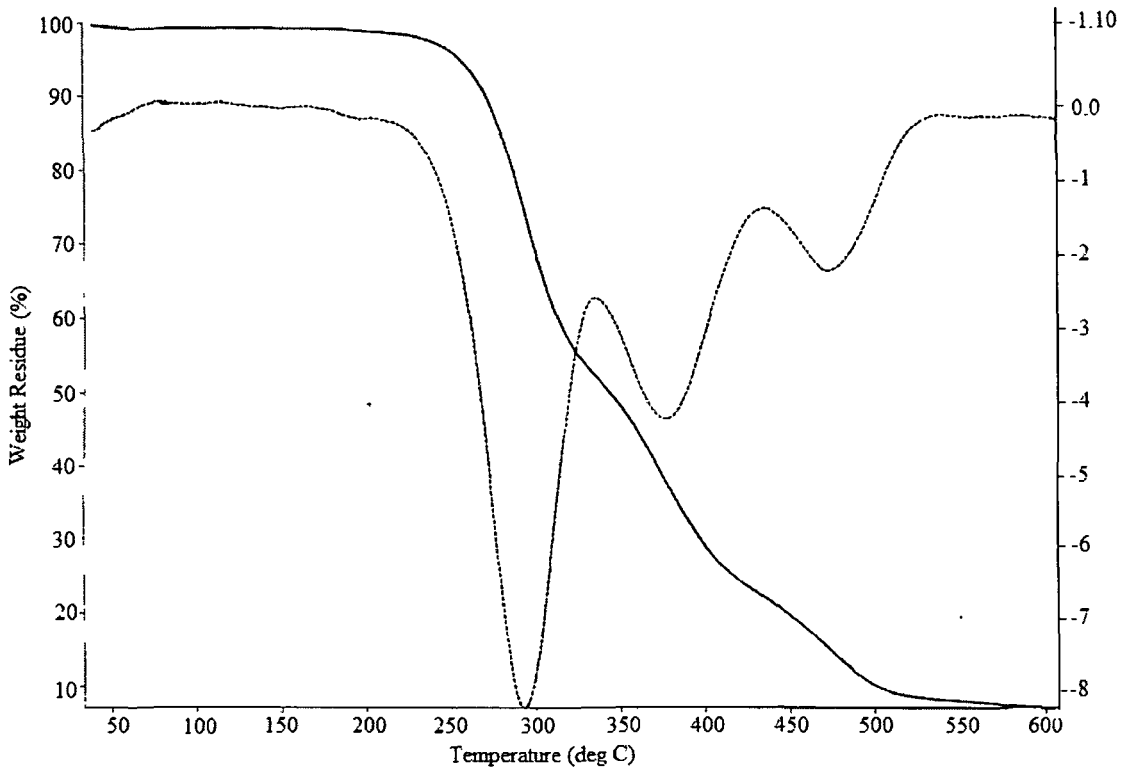


Figure 2.14 TG and DTG thermograms of the cured PUE1.0 resin

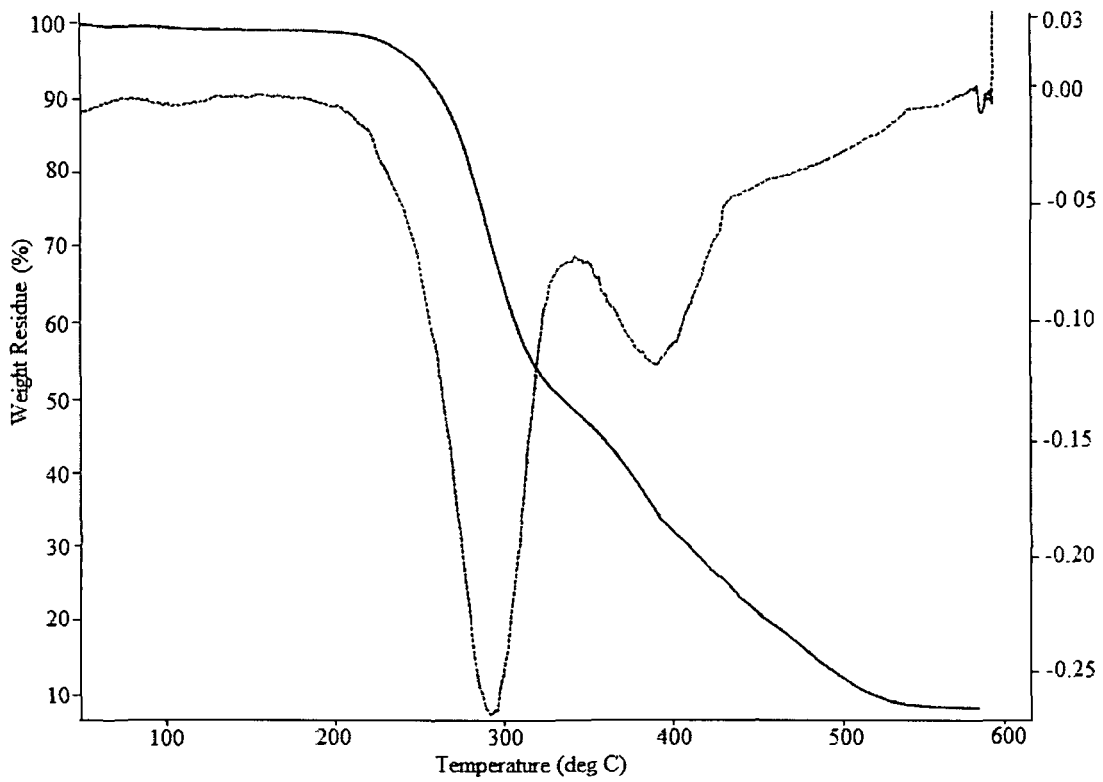


Figure 2.15 TG and DTG thermograms of the cured PUE1.5 resin

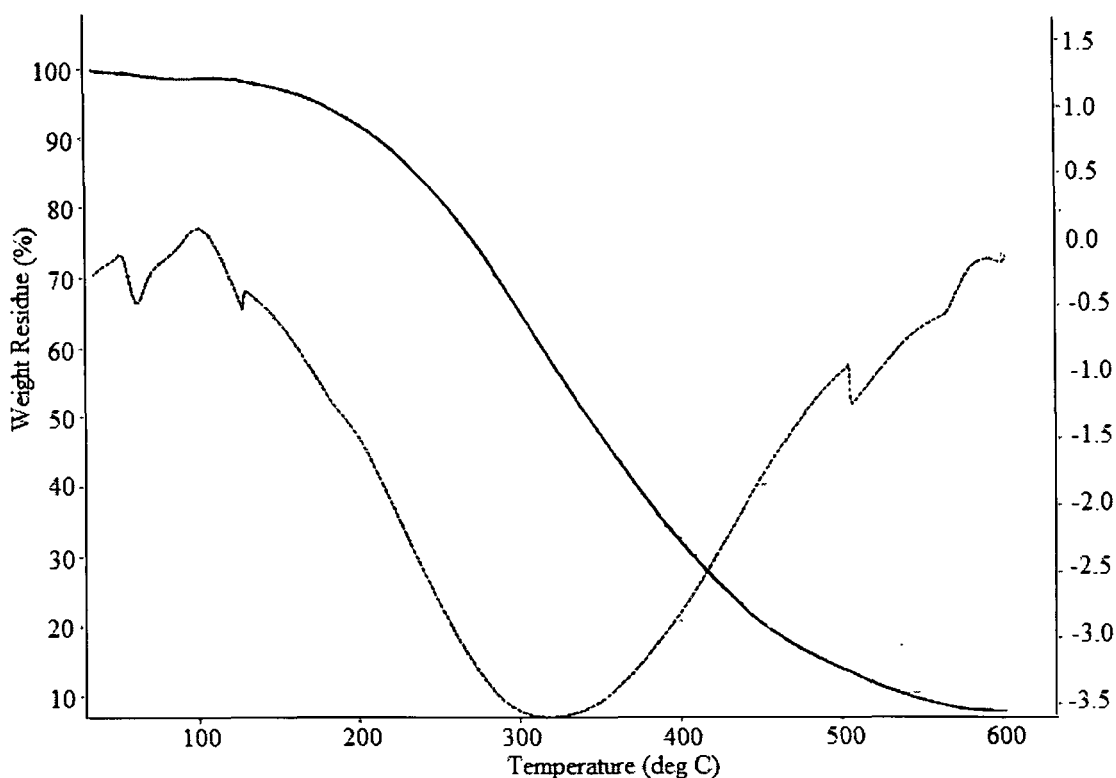


Figure 2.16 TG and DTG thermograms of the cured PUE2.0 resin

## 2.4. Conclusions

From this study, it can be concluded that the vegetable oil extracted from *Mesua ferrea* L. seeds has tremendous potential for the development of polyurethane resins with varying NCO/OH ratio. The synthesized polymers have been successfully characterized by the determination of various physical properties, spectroscopic studies (FTIR and <sup>1</sup>HNMR) as well as GPC analysis. The NCO/OH ratio has prominent effect on curing characteristic, physical properties and performance characteristics of both the PUE and PUA resins. The higher the NCO/OH ratio, faster is the curing time, harder is the materials and higher is the adhesive strength but lower is the gel time and pot life. Moreover, the cured resins also exhibit high thermostability which increases with increase in NCO/OH ratio. Thus *Mesua ferrea* L. seed oil based PUE and PUA resins can be utilized as surface coating materials. They may also be used as binders for composites like other vegetable oil based resins.

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## CHAPTER 3

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### Blends of *Mesua ferrea* L. seed oil modified polyurethane resins with epoxy and MF resins

#### 3.1. Introduction

Polymer blends are multi component polymeric systems that have widely been used for more than three decades [1] in various modern industries. The compatible blends represent one of the most rapidly growing areas in polymer science and are emerging to enhance the performance characteristics of the individual polymers. Polymer blends or mixtures are generally obtained by a simple technique known as blending which involves physical mixing of two or more polymers at different ratios. The enthrallment of polymer blending lies in the simplicity (as it can be processed with existing equipment and technology at low cost), various predictable components and capability of tailoring physical as well as chemical properties [2-3].

Polyurethane is a versatile polymeric material and the versatility becomes more momentous when they are synthesized from naturally renewable resources like vegetable oils as discussed in the earlier chapters. Vegetable oil based polyurethane resins have a number of advantages in surface coating applications. These include versatility in structure and properties, overall low cost, natural renewability, ease of applications etc. [4-5]. However, they suffer from a few serious disadvantages like low alkali resistance in case of polyester based polyurethanes [5-6], low hardness, non-drying nature of polyurethanes with NCO/OH ratio less than unity etc. Moreover, although the polyurethane resins with NCO/OH ratio greater than one are cured by moisture at ambient conditions, they exhibit very poor pot-life, as they are susceptible

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\* Parts of this work have been published in (i) *Euras Chem Tech J*, **2005**, 7, 251.

(ii) *Mater Sci Ind J*, **2006**, 6, 15.

(iii) *Pigment Res Technol*, **2007**, 36, 74.

to gel formation due to their high reactivity. To overcome such disadvantages or to obtain the desired level of properties, polyurethane resins can be modified by blending with other suitable and compatible commercially available resins such as epoxy, amino, silicone, ketonic etc. [7-10]. The compatibility of such polyurethanes with a wide variety of other resins originates from the low viscosity and from the structure of the resin that contains relatively polar and aromatic backbone as well as aliphatic side chains with low polarity. Blending technique may be used effectively to improve the mediocre properties of both the components. The significance of miscible polymer blends is to produce a new improved material from the less superior individual components. However, completely miscible polymer blends are very rare to get [11] although some semi-miscible blends with highly dispersed mixtures are also known to improve properties to an acceptable range [12].

Epoxy is a thermosetting macromolecular material available commercially for long time [13-14]. Among the epoxy resins, the resin obtained from the reaction of bisphenol-A with epichlorohydrin is the oldest and is still the most important commercially [15]. It has a number of unique properties such as outstanding adhesion, excellent mechanical properties, alkali resistance, thermal resistance, dimensional stability, good dielectric behavior and low shrinkage during cure [16-19]. However, applications of epoxy resin are often limited by some weak mechanical properties like low fracture strength, inferior weathering resistance and brittle behavior [17]. Epoxy resin is known to have good compatibility with polyurethane resin [20-23] and can cure the later by the cross-linking reactions between hydroxyl/ epoxy groups of epoxy resin and hydroxyl/ urethane groups of polyurethane resin in the presence of a base like poly(amido amine) (hardener for epoxy resin). Thus the combination of polyurethane features like flexibility and adhesion with epoxy features like mechanical properties and rigidity (brittleness) are expected to improve various properties like strength, adhesion, hardness, impact resistance etc.

Since polyurethane with NCO/OH ratio less than unity has sufficient amount of free hydroxyl groups, it ensures good compatibility with polar amino resin and serves as reactive sites for polycondensation [24]. Among the various amino resins, melamine-formaldehyde (MF) resin is one of the most important resins in surface coating industry [25-26]. This resin can produce high performance coatings with respect to hardness, chemical resistance, scratch hardness, color retention, durability, good electrical

insulation property, thermal resistance etc. [27]. However, it is often found to form very hard and brittle coatings with poor adhesion after baking, so it cannot be used solely [28]. It is therefore generally used in combination with resins having flexible backbone with some polar groups [29-30]. Blending of MF resin is found to be done in literature with vegetable oil based polyester resins [27, 31]. To make MF resin soluble in most of the organic systems, it is often combined with an alcohol such as n-butanol and methanol [26]. The resulting blends exhibit good flexibility as well as good chemical resistance, hardness, thermostability etc. [32-34]. Furthermore, as the system may form a compatible blend, so the blend performances like strength properties, adhesion, hardness, impact resistance, chemical resistance etc. are also expected to be improved.

From the previous chapter, it has been found that *Mesua ferrea* L. seed oil based polyurethane resins with NCO/OH ratio  $> 1$  have strong tendency towards gel formation, whereas polyurethane resin with NCO/OH ratio  $< 1$  can be stored without gel formation even in an open atmosphere for a long period. As moisture plays no role in curing the latter polyurethane resins, so some curing agents are required which are compatible with polyurethane resins. One of the main objectives of this chapter is to develop a superior quality polyurethane resin by modifying the uncured polyurethane resin (NCO/OH ratio less than one) with commercially available bisphenol-A based epoxy resin by the solution blending technique at different weight ratios. Again, there is almost no report on improvement of coating properties of vegetable oil based polyurethane resins by blending with MF resin, although it has tremendous potential in this regard. Further, the cost of MF resin is much lower as compared to epoxy resin, so another objective of the present investigation is to develop and study the performance characteristics of the blends of *Mesua ferrea* L. seed oil modified polyurethane resin with partially butylated melamine-formaldehyde (MF) resin at different weight ratios.

## **3.2. Experimental**

### **3.2.1. Materials**

*Mesua ferrea* L. seeds were utilized for isolation of oil and the oil was purified as described in Chapter 2, section 2.2.1.

The *Mesua ferrea* L. seed oil based polyurethane resins PUE and PUA with NCO/OH ratio 0.5 were prepared by using the same methods as described in experimental section of Chapter 2, sections 2.2.2.1 and 2.2.2.2 respectively.



Bisphenol-A based epoxy resin, Araldite LY 250 and poly(amido amine) based hardener, HY 840 were obtained from Hindustan Ciba Geigy Ltd., India and was used as received. Specifications for the epoxy resin and the hardener are given in Table 3.1.

Table 3.1 Technical specifications of epoxy resin and hardener

Properties	Araldite LY 250 (Ciba Geigy)	Hardener HY 840 (Ciba Geigy)
Viscosity at 25 °C (mPas)	450-650	10,000-25,000
Epoxy equivalent (g/eq)	182-192	-
Epoxy content (eq/kg)	5.2-5.5	-
Amine value (eq/kg)	-	6.6-7.5
Density at 25 °C	1.15	0.98

Partially n-butylated (60% solid content) melamine-formaldehyde (MF) resin was received from Asian Paints India Ltd., Mumbai and was used as received. The technical specifications of MF resin are as given in Table 3.2.

Table 3.2 Technical specifications of MF resin

Properties	Values
Application viscosity at 25 °C (GP-02)	20-25s
Non-volatile matter (%)	60±2
Density at 25 °C	1.2
Thinning with xylene: n-butanol	90:10 (v/v)

*p*-Tolune sulfonic acid (PTSA) was obtained from Loba Chemie, India. The compound has melting point (m.p.) 100-105 °C, minimum assay 98.0%, maximum sulfated ash 0.2% and molecular weight ( $M_w$ ) 190.21 g/mole. It was used as received.

Xylene obtained from Merck has formula weight ( $F_w$ ) 106.17 g/mole, purity  $\geq$  98.0%, density at 20 °C 0.86 g/c.c. and boiling point (b.p.) 137-143 °C.

### 3.2.2. Instruments and methods

FTIR spectra of the blends were recorded before curing (solution) and after curing (films) in a FTIR spectrophotometer (Nicolet, Impact 410, USA). The TG analysis of the cured resins was done by Du-Pont 9900, USA thermal analyzer using

the nitrogen flow rate of 20 mL/min and heating rate of 10 °C/min. The tensile strength and elongation at break of the films were measured by using Zwick Z010, UTM, Germany at a jaw separation speed of 50 mm/min. The surface morphology of the blends was studied by using SEM of SU-SEM probe analytical scanning microscope, CAMECA, France (for PUE based blends) and SEM model No. LEO 412 EDIX, USA (for PUA based blends) after gold coating on the surface. The film thickness of the cured films was measured by Pentest, coating thickness gauge (Sheen Instrument Ltd., Model 1117, UK). The physical properties like specific gravity, touch free time and drying (curing) time, mechanical properties like impact resistance, hardness and flexibility (bending), and chemical resistance of the blends were determined according to the standard methods as mentioned earlier (Chapter 2, section 2.2.2). Percent of swelling (ASTM D-570) was determined by keeping the cured film in 100 ml conical flasks containing xylene at room temperature (ca. 27 °C). Weights were recorded before and after swelling until constant weights were obtained [35]. The adhesive strengths of the blends were also measured by the standard lap shear test using plywood as the substrate as mentioned in Chapter 2, section 2.2.2.

Dielectric properties such as dielectric constant and loss factor of both the PUE and PUA based blends were evaluated by taking dried thin films of the blend samples as discs of ca.  $0.8 \times 10^{-2}$  m diameter (d) and ca.  $1.0\text{-}2.0 \times 10^{-4}$  m thickness (t) using Hioki-3532-50 LCR Hi Tester. The measurements were performed at a temperature range of 300 K to 380 K at 50 kHz to 500 kHz frequency in a symmetric stainless level electrode system, which was placed inside the temperature controlled oven. The loss tangent (loss factor or dissipation factor) is obtained directly from the instrument, whereas the dielectric constant is calculated from the measured value of the capacitance ( $C_p$ ) by using equation (i).

$$\text{Dielectric constant} = C_p t / \epsilon_0 A \dots\dots\dots(i)$$

where  $\epsilon_0$  = permittivity of vacuum =  $8.85 \times 10^{-12}$  Farad/m and A = cross sectional area of the sample =  $\pi r^2$ , r is the radius of the film.

### 3.2.2.1. Synthesis of PUE and PUA resins

The poly(urethane ester) resin, PUE with NCO/OH ratio 0.5 was synthesized as per the method reported in Chapter 2, section 2.2.2.1. Briefly, an amount of 1.0 mole of

monoglyceride of *Mesua ferrea* L. seed oil, 0.5 mole of the chain extender [poly(ethylene glycol)], 0.05 weight % of dibutyl tin dilaurate (DBTDL) as the catalyst and 0.75 mole of toluene diisocyanate (TDI) were reacted using xylene as the solvent. The resin was obtained as a solution of (30±2.5) weight % solid content in xylene with yield of ca. 93-95%.

The poly(urethane amide) resin, PUA with NCO/OH ratio 0.5 was synthesized (Chapter 2, section 2.2.2.2) by using the same formulation except one mole of diethanolamide of the fatty acids instead of monoglyceride. This resin was also obtained as a solution of (30±2.5) weight % solid content in xylene with ca. 95% yield.

### 3.2.2.2. Preparation of PUE and PUA based epoxy blends (EM and EA)

The PUE/ epoxy and PUA/ epoxy blends were prepared by mixing PUE or PUA resin (30±2.5 weight % solid content in xylene) with epoxy resin (100 weight % solid content) and the poly(amido amine) hardener (50 weight % with respect to epoxy) in the desired proportions as shown in Table 3.3. The mixing was carried out with constant and vigorous stirring for about half an hour at (30±1) °C.

Table 3.3 Composition of PUE/ epoxy (EM) and PUA/ epoxy (EA) blends

Blend code*	PUE or PUA (weight %)	Epoxy (weight %)	Poly(amido amine) Hardener (weight %)
EM40	60 (PUE)	40	20
EM50	50 (PUE)	50	25
EM60	40 (PUE)	60	30
EA40	60 (PUA)	40	20
EA50	50 (PUA)	50	25
EA60	40 (PUA)	60	30

\*digits of the blend codes indicate the epoxy content

### 3.2.2.3. Preparation of PUE and PUA based MF blends (MM and MA)

The PUE/ MF and PUA/ MF blends were prepared by mixing PUE or PUA resin (30±2.5 weight % solid content in xylene) with MF resin (60 weight % solid content in xylene:butanol = 90:10 by volume) in the presence of PTSA as the acid

catalyst (0.5 weight % with respect to total resin). The compositions of the blends are shown in Table 3.4 (PUA with 15 weight % MF blend was not studied as it is not cured under the used conditions). The mixing was carried out with constant vigorous stirring for about half an hour at  $(30\pm 1) ^\circ\text{C}$ .

Table 3.4 Composition of PUE/ MF (MM) and PUA/ MF (MA) blends

Blend code*	PUE or PUA (weight %)	MF (weight %)
MM15	85 (PUE)	15
MM25	75 (PUE)	25
MM40	60 (PUE)	40
MA25	75 (PUA)	25
MA40	60 (PUA)	40

\*digits of the blend codes indicate the MF content (g)

#### 3.2.2.4. Preparation of blend films for curing and performance studies

Films of the blends were prepared by drawing the homogeneous mixture of the solutions of blends on glass plate of 120 mm X 100 mm X 2 mm using a micro adjustable thickness gauge (Sheen Instrument Ltd., UK) under ambient conditions. Similarly, coatings of blends on different substrates like commercially available mild steel strips, 150 mm X 100 mm X 1.44 mm for impact test and tin strips, 150 mm X 50 mm X 0.19 mm for bending test were prepared. After removal of sufficient amount of solvent under atmospheric conditions, the coated strips were degassed under vacuum at  $(45\pm 5) ^\circ\text{C}$  for 45 min to remove the last trace of solvent and volatile compounds. Then the coated blends were cured by heating at  $120 ^\circ\text{C}$  in an oven for specified time period. The cured blends were kept under ambient conditions for 24 h before further studies. The dried films from the glass plates were then peeled off by immersing the plates in warm water, followed by drying in a desiccator under vacuum and stored for 7 days before testing. The dry coating thickness of blends was measured by 'Pentest' coating thickness gauge (model 1117, Sheen Instrument Ltd., U.K.) and found to be 25-35  $\mu\text{m}$ .

### 3.3. Results and discussion

#### 3.3.1. FTIR study of resins and blends

##### 3.3.1.1. PUE and PUA based epoxy blends (EM and EA)

The FTIR spectra of the PUE and PUA resins have already been discussed in Chapter 2. The important peaks [36-37] for epoxy resin are listed in Table 3.5.

Table 3.5 The main FTIR bands and the corresponding functional groups of epoxy resin

Band ( $\text{cm}^{-1}$ )	Functional groups
2871-2965	Aliphatic C-H stretching vibration
3495	O-H stretching vibration
1606	Aromatic C-H stretching vibration
1456	Aromatic C-H bending vibration
827	Oxirane ring (epoxy group)

FTIR spectra of the PUE and PUA based epoxy blends (EM40, EM50, EM60, EA40, EA50 and EA60) are shown in Figures 3.1 and 3.2 before and after curing respectively. From the figures, it has been found that the important band for C=O of urethane which was present in case of resins at ca.  $1712\text{-}1720\text{ cm}^{-1}$  got shifted to ca.  $1730\text{-}1738\text{ cm}^{-1}$  which may be due to interaction of epoxy resin and the hardener with PUE and PUA resins. The intense band for epoxy group at ca.  $827\text{ cm}^{-1}$  in epoxy resin was found to be decreased in intensity in the blends (more in case of EM blends) after curing which hints interactions of epoxy with polyurethane resins. The presence of band with low intensity for epoxy group in the cured blends indicates that the reaction between epoxy resin and the curing agent [38] was not completed even after post-curing. This may be attributed to the formation of hindrance network structure with the progress of cross-linking reactions. Further, there is a noticeable sharpening and decrease of intensity for hydroxyl group peak centered at ca.  $3300\text{-}3330\text{ cm}^{-1}$  in the blends compared to the PUE and PUA resins. This may be due to the possibility of cross-linking reactions by the hydroxyl/ urethane groups of polyurethane resins with the hydroxyl/ epoxy groups of epoxy resin in the presence of amine hardener (Scheme 3.1) which precede over the H-bonding interaction between C=O of urethane groups of the polyurethane resins with the O-H of epoxy resin present in the systems.



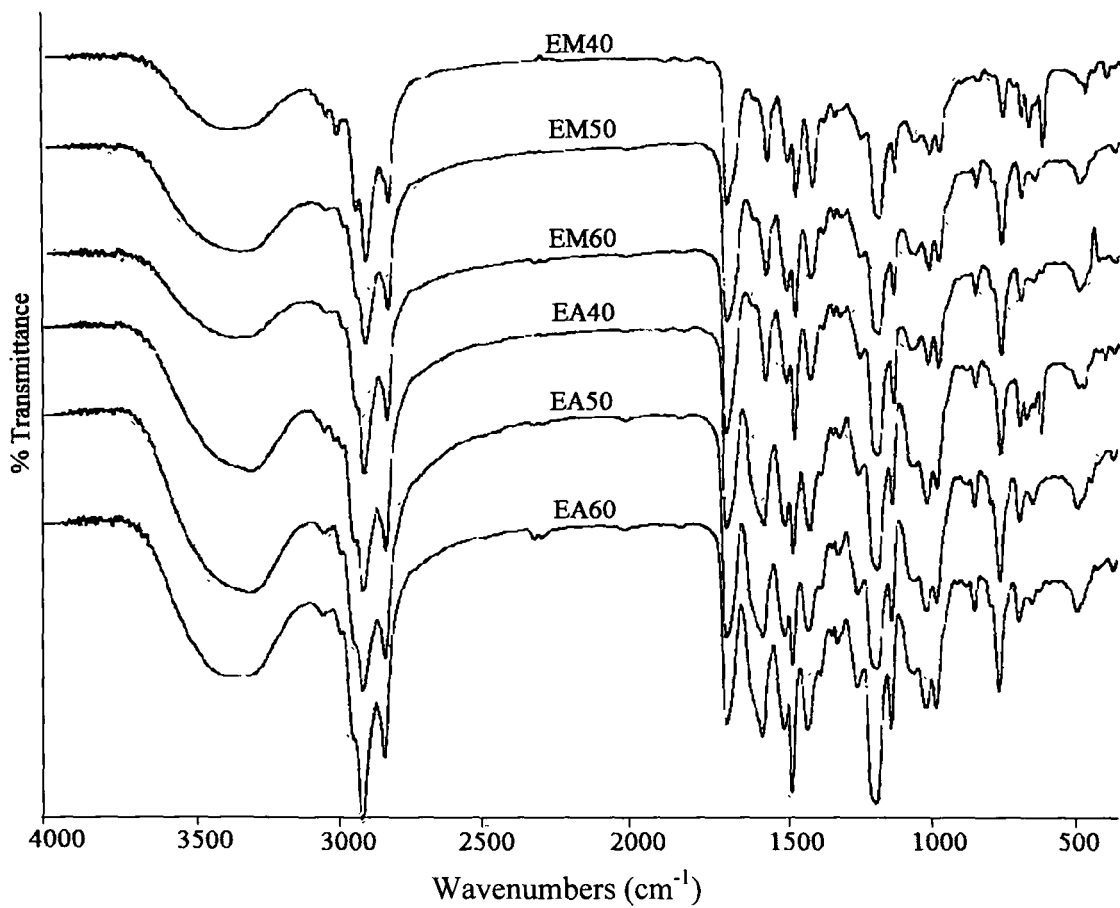


Figure 3.1 FTIR spectra of EM and EA blends before curing

### 3.3.1.2. PUE and PUA based MF blends (MM and MA)

The important bands [37, 39-40] for MF resin are listed in Table 3.6.

Table 3.6 The main FTIR bands and the corresponding functional groups of MF resin

Band (cm <sup>-1</sup> )	Functional groups
3360	Overlap of N-H and O-H stretching frequency
2958-2870	C-H stretching
1548	Overlap of N-H deformation and C-N stretching
1387	C-H bending
815	Triazine ring
932	C-H rocking of N-CH <sub>2</sub>

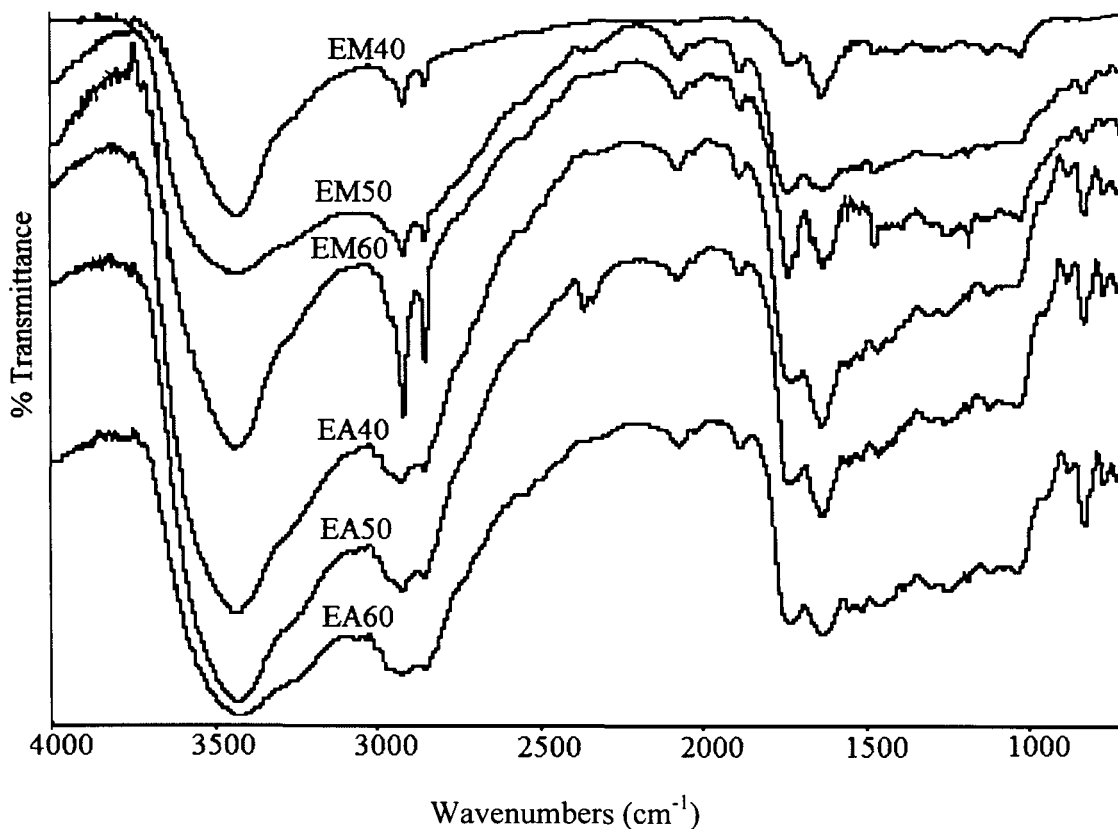
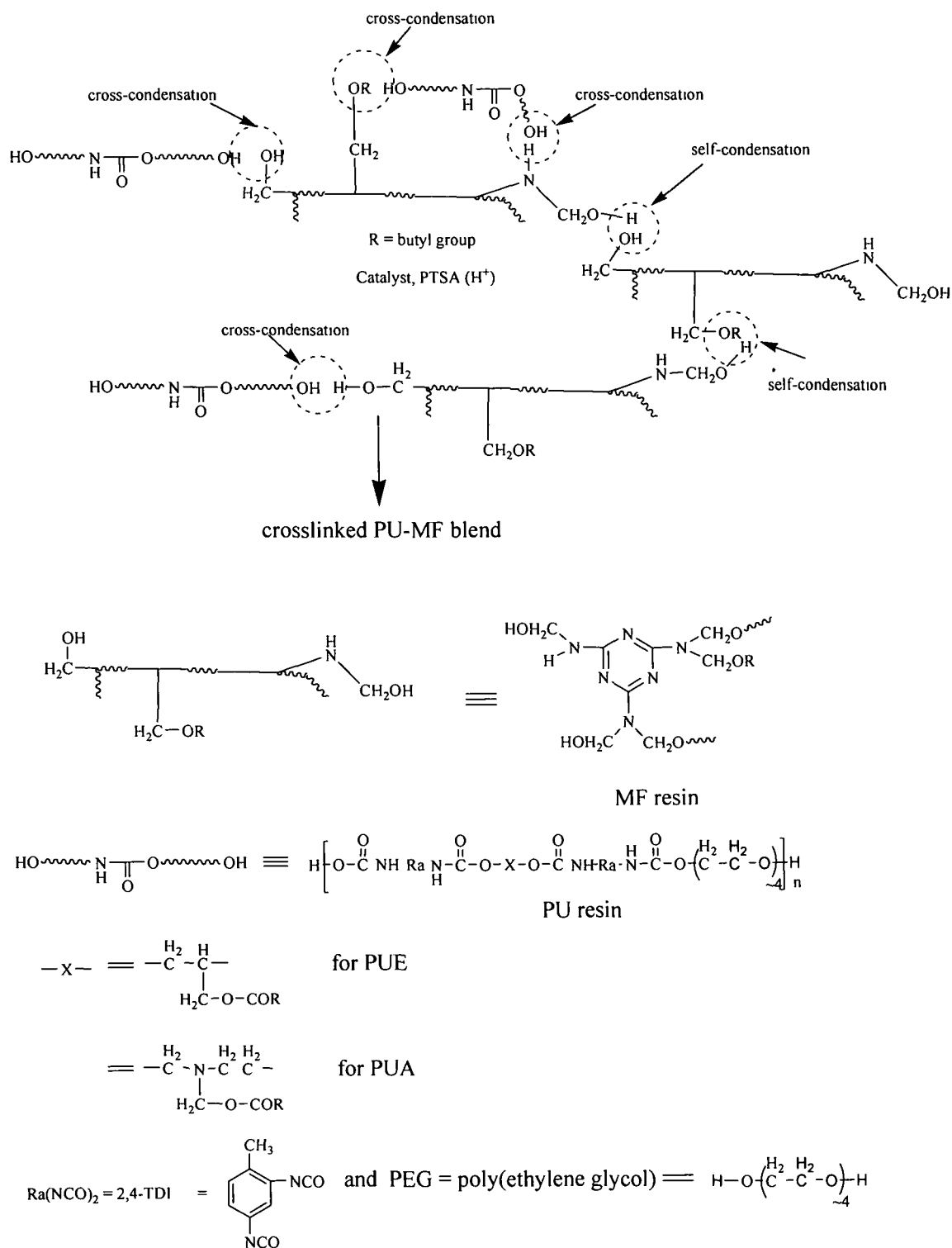


Figure 3.2 FTIR spectra of EM and EA blends after curing

From the understanding of curing reactions of alkyd resin with MF resin [32-34] as proposed by Wohnsiedler et al., it might be assumed that the similar type of cross-linking reactions could also cure polyurethane resins. As the studied polyurethane resins (both PUE and PUA with NCO/OH ratio of 0.5) have excess hydroxyl functionality, so there is a possibility of cross-linking reaction between the OH/urethane group of PU resins and OH/CH<sub>2</sub>OR (R=H or butyl) groups of MF resin as the most important cross-condensation reaction. Moreover, there is a possibility of self-condensation of MF resin leading to the formation of methylene bridges [32-34]. This is supported by observing an increase in intensity of the corresponding peaks at ca. 2851-2927 cm<sup>-1</sup> in the FTIR spectra (Figure 3.3) compared to the individual components. The formation of ether linkages (band at ca. 1071-1086 cm<sup>-1</sup>) by the cross-condensation reaction between MF and PU resins is also observed in FTIR spectra (Figures 3.3 and 3.4). The broad absorption band centered at about 3400 cm<sup>-1</sup> for blends before curing were found to be sharpened after curing (Figure 3.4). This clearly indicates that the OH groups of PU and MF and NH groups of MF and PU are involved in the curing reaction catalyzed by PTSA (Scheme 3.2). Absorption bands



corresponding to the usual NH, NCH<sub>2</sub>OR, CH<sub>2</sub>OH, triazine ring etc. functional groups of MF resin and OH, C=O, NH etc. functional groups of PUE/ PUA resins could also be seen [39-40] in the Figures 3.3 and 3.4.



Scheme 3.2 Proposed mechanism for cross-linking reactions between polyurethane and MF resins in the presence of PTSA catalyst

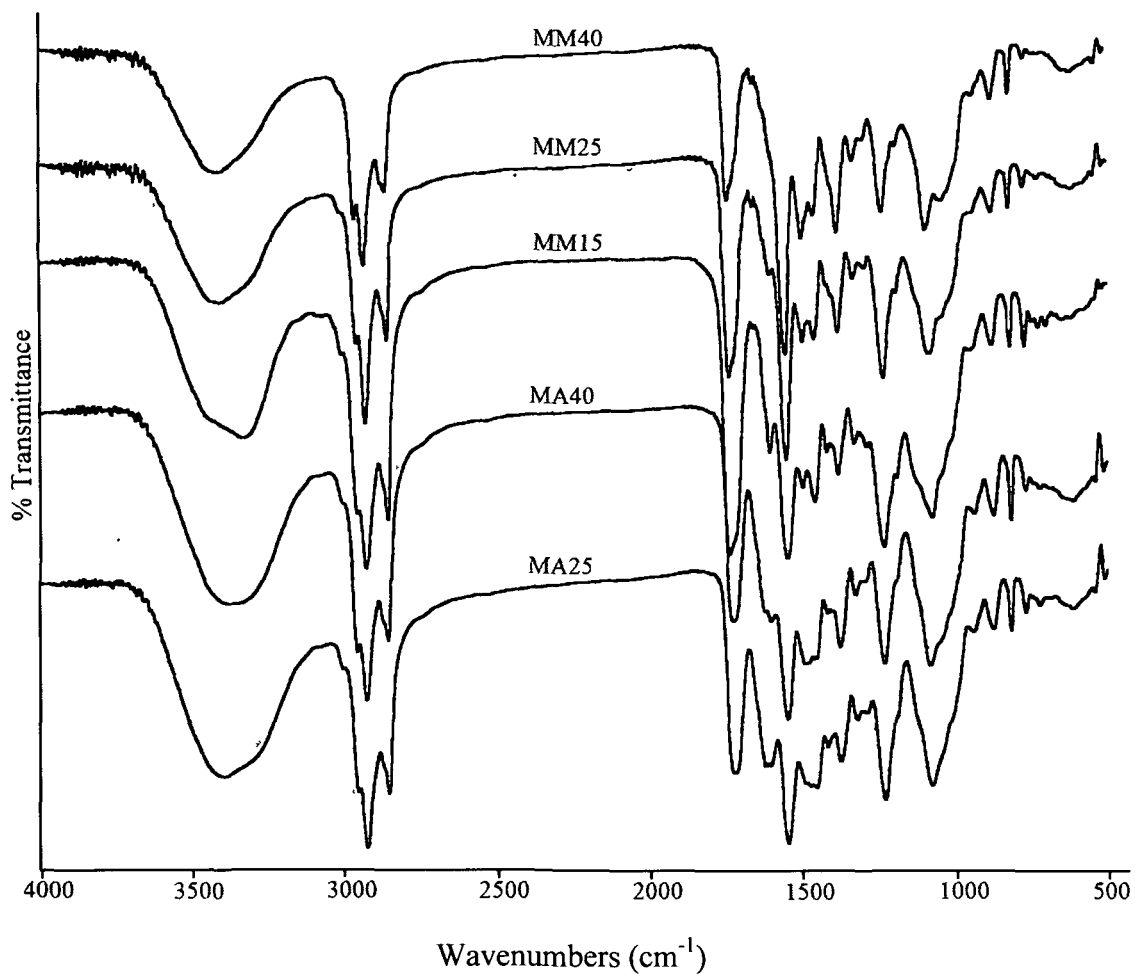


Figure 3.3 FTIR spectra of MM and MA blends before curing

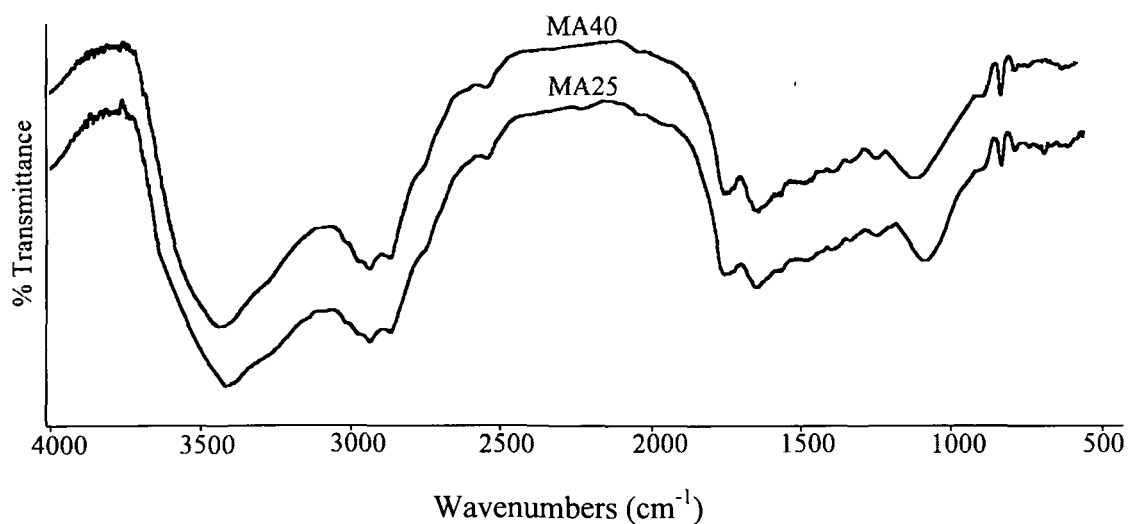


Figure 3.4 FTIR spectra of MA40 and MA25 blends after curing

### 3.3.2. Blend morphology

The ability to produce polymeric blends with improved combination of properties of the individual polymers depends upon the degree of homogeneity of the system. Polyurethane resins, in general, show a good compatibility with epoxy as well as MF resins in many industrially used solvents [7-10, 21, 27]. The solvent used in the present study, xylene has the desired compatibility, evaporation rate and ultimately uniform phase forming ability with the blend.

Among the SEM micrographs of the cured epoxy modified PUE/ PUA blends (Figure 3.5 a – f), EM50 (Figure 3.5 b) and EA50 (Figure 3.5 e) containing 50 weight % of epoxy resin showed excellent dispersion in polyurethane resin. There is no observable phase separation in the blends. However, degree of separation occurred to certain extent in the blends EA40 (Figure 3.5 d), EM40 (Figure 3.5 a) and EA60 (Figure 3.5 f), EM60 (Figure 3.5 c) which was more prominent in the former cases than the latter. The SEM study reveals that the blend of 50:50 (PU:Epoxy) ratio shows the best homogeneity. In all the cases, the haziness or turbidity was effectively eliminated by solution blending technique. Thus, the morphology of the solvent casted blend films depends on composition of blends, nature of solution, rate of evaporation of solvent and solution viscosity [41]. However, size of the domain of the disperse phase is largely governed by the level of polymer miscibility i.e., physical and chemical nature of the components. The reduction of domain size and relatively good interfacial adhesion of polyurethane resin and epoxy resin may be explained by better compatibility of the aromatic moiety present as well as polar-polar interaction between  $\pi$ -bonds of aromatic rings in both resins. In addition, the high compatibility may be ascribed to better interpenetrating network formation through the amine reaction of ester groups present in PUE resin along with other cross-linking reactions as discussed in the previous section (Section 3.3.1.1., Scheme 3.1). Thus the amine hardener also acts as a compatibilizing agent for these blends which is also reflected in the performance.

On the other hand, the SEM micrographs of the cured MF modified PUE and PUA blends are shown in Figure 3.6. The blends MM25 (Figure 3.6 b) and MA25 (Figure 3.6 e) showed excellent dispersion in polyurethane resin and exhibited no observable phase separation. However, certain extent of degree of separation occurred in the blends MM15 (Figure 3.6 c), MA40 (Figure 3.6 d) and MM40 (Figure 3.6 a)

which was more prominent in MM15 (Figure 3.6 c). Thus the SEM study reveals that the blend of 75:25 (PU:MF) ratio shows the best compatibility. The good compatibility may be attributed to the interfacial adhesion of polyurethane resin and MF resin blends. Besides, the improved compatibility may be due to interpenetrating network formation through reactions of PUE/ PUA resin with MF resin, which are already discussed (Scheme 3.2). The good compatibility is further reflected in the performance.

### **3.3.3. Curing study of blends**

All the blends were cured at 130 °C and the dried films were found to have thickness of ca. 25-35 μm. The curing study shows that the curing time (touch free time as well as drying time) decreases with the increase of epoxy/ MF content in the blends (Tables 3.7 and 3.8).

In the case of epoxy modified PUE/ PUA blends (i.e., EM and EA blends) this may be attributed to the increase of possibility of the reactions of epoxy/ hydroxyl groups of epoxy resin with hydroxyl/ urethane groups of polyurethane resins in the presence of amine hardener [42]. It has been reported [43] that the aromatic moiety of polyurethane resin accelerated the cross-linking reaction of epoxy in epoxy/ amine hardener/ urethane reaction system by the formation of an active complex of the hardener with the aromatic moiety of polyurethane in the curing reaction. The possible reactions of epoxy with hardener, epoxy with polyurethane and polyurethane with hardener are shown in Scheme 3.1.

On the other hand, the decrease in drying time with the increase of MF content in MF modified PUE/ PUA blends (i.e., MM and MA blends) may be credited to the increase of possibilities of the reactions: (i) cross-condensation reaction between NH or OH of MF resin and OH of PU, (ii) self-condensation reaction between OH and NCH<sub>2</sub>OR (where R = H or butyl group) of MF resin, (iii) self-condensation reaction between NCH<sub>2</sub>OR of MF resin and (iv) cross-condensation reaction between NCH<sub>2</sub>OR of MF and OH or NH of PU resin [32-34] as mentioned in Scheme 3.2. However, the most important reaction is the cross condensation reaction of NCH<sub>2</sub>OR of MF as stated above that occurs in presence of PTSA as the catalyst (Scheme 3.2). The curing is possible only after the initiation caused by PTSA. This has been proved satisfactorily as no curing was observed in the absence of catalyst.

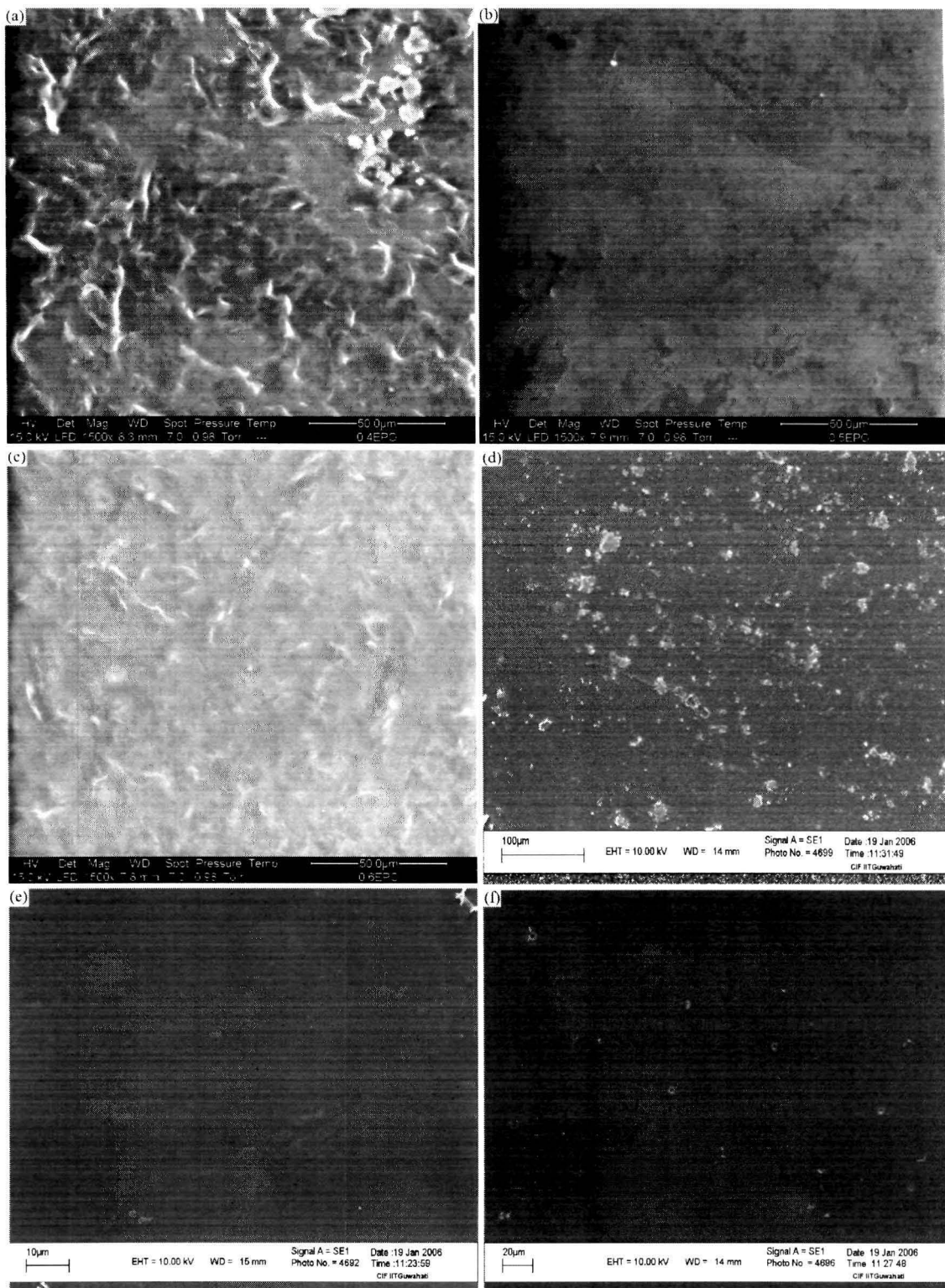


Figure 3.5 SEM micrographs of the epoxy modified PUE/ PUA blends (a) EM40, (b) EM50, (c) EM60, (d) EA40, (e) EA50 and (f) EA60

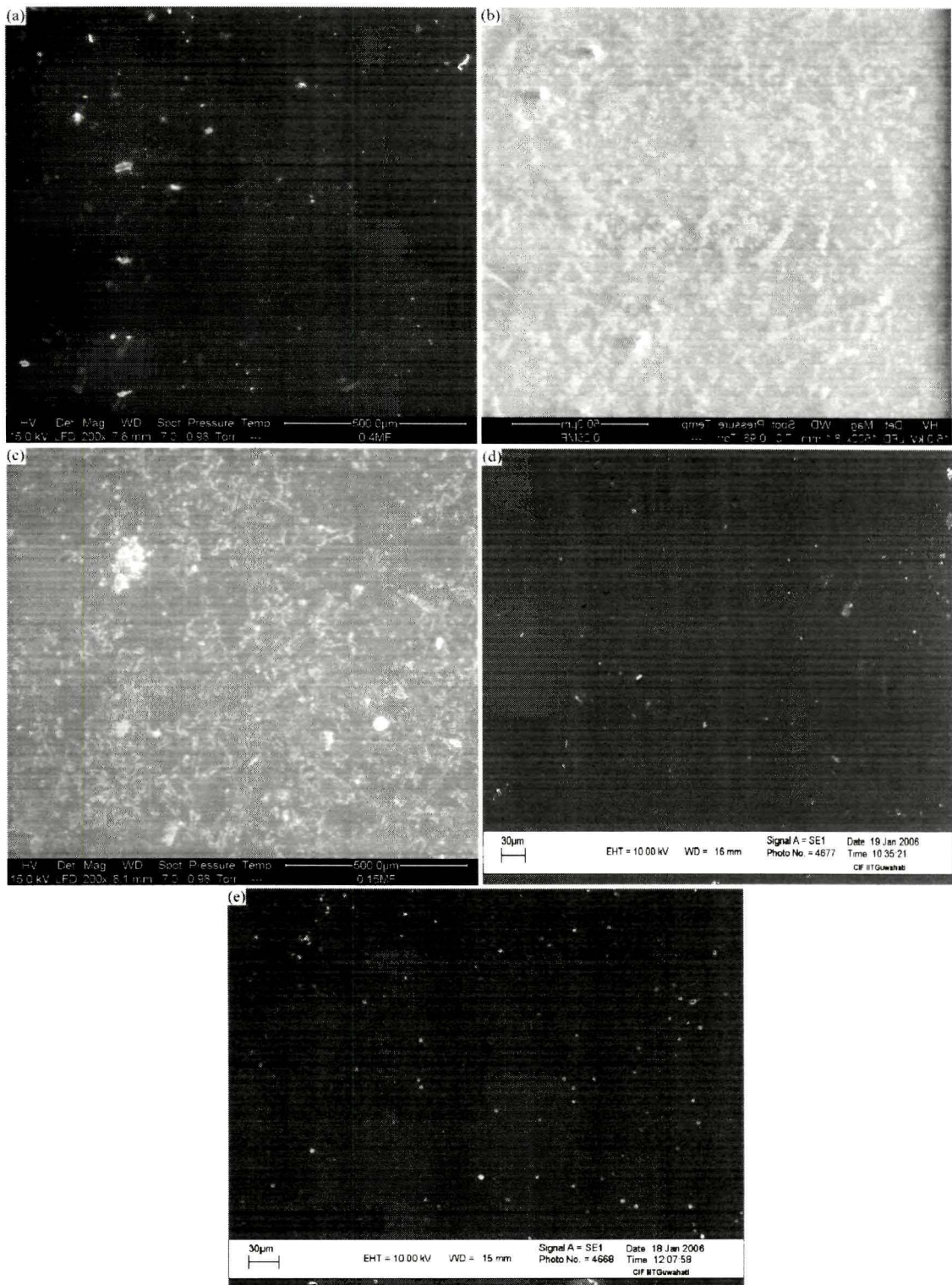


Figure 3.6 SEM micrographs of the MF modified PUE/ PUA blends (a) MM40, (b) MM25, (c) MM15, (d) MA40 and (e) MA25

### 3.3.4. Performance study of blends

Various performance characteristics of *Mesua ferrea* L. seed oil based polyurethane blends with epoxy and MF resins evaluated through various standard methods are mentioned in Tables 3.7 and 3.8 respectively.

From Table 3.7, it has been observed that the hardness increases with the increase of epoxy content in the blends up to 50 weight % for both EM and EA cases. This may be due to increase of cross-linking density, which is supported by swelling test in xylene and increase of H-bonding interaction between hydroxyl H-atom and urethane C=O group. However, the hardness decreases for EM60 blend but increases slightly for EA60 blend. This may be due to the fact that the extent of interpenetrating network formation decreases at 60 weight % of epoxy in the case of EM60 as observed by swelling test (Table 3.7), whereas in the case of EA60, the best network formation occurred at 60 weight % of epoxy content. Tensile strength depends on (i) cross-linking density, (ii) physical state of resins at the test temperature and (iii) compatibility [42]. The tensile strength of the EM blends shows a maximum at the 50 weight % of epoxy content which may be due to the best compatibility and optimum level of cross-linking density. But in the case of EA based blends, tensile strength increases continuously with the increase of epoxy content, which may be due to the occurrence of optimum cross-linking at 60 weight % of epoxy content. The observed results are due to the fact that the combination of cross-linking density, compatibility and rigidity are best suited for blends with 50 weight % and 60 weight % of epoxy for EM and EA blends respectively. As the cross-linking density and rigidity increases with the increase of epoxy content, so the elongation at break of the blends decreases for both the systems [42]. However, from the bending test it has been found that all the blends are sufficiently flexible. This may be due to the presence of flexible hydrocarbon chain of the fatty acids of the oil. The variation of impact strength with epoxy content of the blends in both EM and EA cases can be explained on the basis of toughness of the films. Thus the impact strength of the blends increases with the increase of mechanical strength and flexibility of the films. As the toughness (measured by total area under the stress-strain curve) increases with the increase of epoxy content for EM blends up to 60 weight % and up to 50 weight % for EA blends, the impact strength varies accordingly. The increase in adhesive strength with the increase of epoxy content in both the EM and EA blends may be credited to increase in number of polar epoxy and hydroxyl



groups in blends which may chemically react with the hydroxyl groups of the plywood substrate [44]. This increase of polarity also enhances the secondary interactions like H-bonding, dipole-dipole, dipole-induce dipole etc. which in turn increases the adhesive strength [45].

Table 3.7 Curing time and mechanical properties of PUE/ PUA and epoxy blends

Property	EA40	EA50	EA60	EM40	EM50	EM60
Touch free time (min)	60	40	35	10	5	5
Drying time (min)	80	55	50	15	10	8
Hardness (Shore A)	75	85	88	70	80	75
Bending test (dia., cm)	<0.5	<0.3	<0.3	<0.3	<0.3	<0.3
Impact resistance (cm)	3	7	8-10	4-5	6	9
Tensile strength (MPa)	9.3	12.7	20.7	47.0	71.0	25.6
Elongation at break (%)	51.5	37.6	28.6	17.8	21.0	43.7
Specific gravity	0.91	1.05	1.27	0.95	1.09	1.29
Swelling (%)	14.31	11.87	6.83	4.78	1.94	4.28
Adhesive strength (kN/m)	147.4	196.2	231.6	116.0	219.3	329.1

Again, from Table 3.8, it has been found that the hardness of the blends increases with the increase of MF content for both the MM and MA cases. In this case, H-bonding interaction responsible for cross-linking density occurs between hydroxyl/ amino H-atom and urethane C=O group. Again, tensile strength values of the blends show a maximum at 25 weight % of MF content due to the same reason as described in the case of epoxy blends. As the cross-linking density and rigidity increase with the increase of MF content, so the elongation at break of blends decreases for the EA blends and increases with epoxy content in the EM blends [42]. However, the bending test shows that all the blends are sufficiently flexible. This may be due to the presence of flexible hydrocarbon chain of the fatty acids of the oil. The variation of impact strength with MF content of blends in both the cases may again be explained from the angle of toughness of films as discussed earlier. Thus the impact strength of the blends increases with the increase of mechanical strength and flexibility of the films. Adhesive strength is found to be increased with the increase of MF content in the blends again due to increase of number of polar hydroxyl groups in the blends [45].



Table 3.8 Curing time and mechanical properties of PUE/ PUA and MF blends

Property	MM40	MM25	MM15	MA40	MA25
Touch free time (min)	5	10	25	25	55
Drying time (min)	10	15	50-55	45	75
Hardness (Shore A)	85	80	75	75	70
Bending test (dia., cm)	<0.3	<0.3	<0.3	<0.3	<0.3
Impact resistance (cm)	7-8	4-5	<2	5-6	2-3
Tensile strength (MPa)	52.3	74.2	19.7	20.1	29.7
Elongation at break (%)	1.6	7.0	27.4	11.6	26.1
Specific gravity	1.3	1.0	1.0	1.07	0.94
Swelling (% in xylene)	12.07	17.51	20.46	32.5	25.7
Adhesive strength (kN/m)	162	117.3	14.35	146.5	114.74

The impact of the nature of the host polyurethane resin on the performance of the blends cannot be overlooked as the performance characteristics of the PUE based epoxy or MF blends are found to be better as compared to those of the PUA based epoxy or MF blends. This may be due to higher cross-linking density of the former than the latter as supported by swelling test (Tables 3.7 and 3.8). This higher cross-linking density is understandable as more numbers of hydroxyl groups are present in PUE than in PUA. For example, tensile strength values were found to be higher for PUE based blends compared to that of PUA based blends (Tables 3.7 and 3.8). This is due to the fact that the ester groups of PUE react through ester exchange reaction with hydroxyl groups of epoxy/ MF and also H-bonding interaction [46]. Both these factors facilitate the network formation and hence increase the strength value. As such possibilities are missing in the case of PUA blends so their strength property is comparatively low.

### 3.3.5. Chemical resistance study

The good chemical resistance of all the blends may be ascribed to the good compatibility that arises from the presence of strong intra-molecular as well as inter-molecular secondary interactions like polar-polar and H-bonding, mutual cross-linking, presence of aromatic moiety etc. [47].

The chemical resistance test of the cured films was performed in various chemical environments for 10 days and the changes of weights were determined after the test. In the chemical resistance experiment carried out for EM and EA blends (Table 3.9), it has been seen that all the films showed very good chemical resistance in almost all the tested media, except in dilute alkali solution for EM40 blend. This is due to the presence of maximum amount of alkali hydrolyzable ester linkages in the blend. On the other hand, all the MM and MA blends (Table 3.10) showed excellent chemical resistance in almost all the tested media, except in dilute acid solution. This may be due to the reaction of a strong acid such as HCl with NH groups of MF resin. Again, even though MM based blends contain some amount of alkali hydrolyzable ester linkages, they showed good alkali resistance with the increase of MF resin content. This may be credited to the decrease of alkali hydrolyzable ester groups and increase of stable triazine moiety in blends. A little amount of water is absorbed in both the epoxy and MF based blends as indicated by their increase in weight after the experiment. Higher polarity of the blends favors the formation of more H-bonding with the water molecules, which might be responsible for water absorption. However, the extent of absorption is very low and will not affect the ultimate performance characteristics of the films.

Table 3.9 Chemical resistance of epoxy based PUE and PUA blends

Blend code	EA40	EA50	EA60	EM40	EM50	EM60
10% NaCl	-0.047	-0.13	-0.03	-0.009	-0.006	-0.005
20% EtOH	-0.08	-0.1	-0.034	-0.007	-0.021	-0.030
5% HCl	+0.017	+0.052	+0.016	-0.003	+0.0	-0.001
3% NaOH	-0.33	-0.1	-0.061	-0.042	+0.019	+0.053
Distilled water	+0.21	+0.106	+0.15	+0.14	+0.11	+0.084

+ indicates weight gain and – indicates weight loss

Table 3.10 Chemical resistance of MF based PUE and PUA blends

Blend code	MM40	MM25	MM15	MA40	MA25
10% NaCl	+0.0082	+0.013	+0.0166	+0.00279	+0.0148
20% EtOH	+0.017	+0.026	+0.0229	+0.0759	+0.0789
5% HCl	*	*	*	*	*
3% NaOH	-0.0216	-0.019	-0.065	-0.011	-0.0196
Distil. water	+0.103	+0.0256	+0.045	+0.0253	+0.011

\*Color of films faded and the films were damaged, + Indicates mass gain and – indicates mass loss

### 3.3.6. Thermal properties

The thermogravimetric analysis (TGA) of both the PUE and PUA based blends showed high initial degradation temperature (ca. 200 °C) for all the cases. The thermal stability of PUA and PUE based blends mainly depends on the equilibria of polymerization and depolymerization of various functional groups present in the polymer chains. The allophanate and biuret linkages formed during cross-linking reactions, reopen quite readily on heating at relatively higher temperature, as they are thermolabile [47]. However, the urethane linkages and aromatic moiety of diisocyanate decompose only at considerably high temperature [47].

The high thermostability of epoxy modified PUE and PUA based blends are due to the introduction of epoxy resin into the polyurethane matrix. The effect of epoxy loading on the thermal stability of the EM and EA blends was monitored by thermogravimetric analysis under the nitrogen atmosphere (Figure 3.7). The decomposition of the blends occurred in the temperature range of ca. 180-700 °C in a two step pattern. The incorporation of epoxy resin in the blend increases the cross-linking density, which brings the polymer backbones close together making the material hard. This reduces molecular mobility and hence increases the thermostability. The TGA curves for EM blends showed the initial decomposition to occur at ca. 200 °C with weight loss of ~ 15-17% only. This weight loss is most probably due to the decomposition of hydrocarbon parts of the oil, epoxy moiety and other linkages such as allophanate, biuret, ether etc. The second stage of degradation at higher temperatures is due to the decomposition of urethane linkages and rigid aromatic moiety.

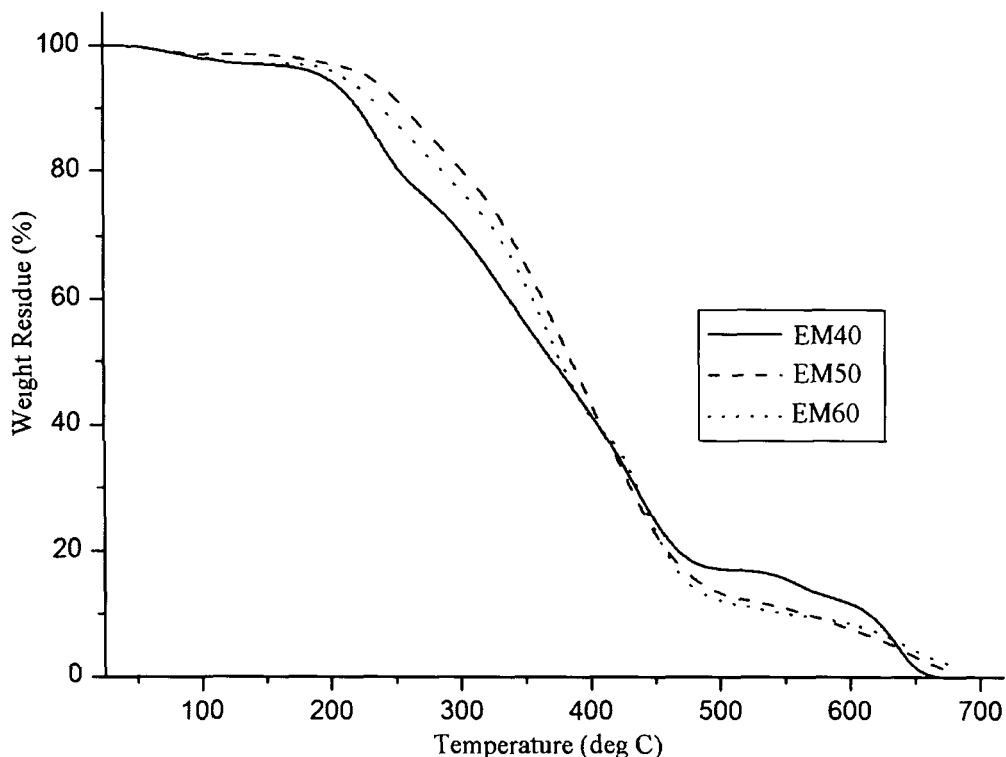


Figure 3.7 TG thermograms of EM blends

On the other hand, the thermal properties of both the PUE and PUA resins are again found to be significantly improved by introduction of MF resin into the polyurethane matrix. The effect of MF loading on the thermal stability of blends was also monitored by thermogravimetric analysis under nitrogen atmosphere (Figure 3.8). The decomposition of blends occurred in the temperature range of ca. 170-700 °C in a two step pattern. The incorporation of MF resin in the blend increases the cross-linking density, which brings the polymer backbones closer together making the material hard. The overall result is the reduction of molecular mobility and hence increase of the thermostability.

It has been further found from Figure 3.8 that the blends MM40 and MM25 showed almost same initial degradation temperature and 50% decomposition though the values are little less for MM15. This may be due to the fact that optimum level of cross-linking is obtained at 25 weight % of MF loading. The weight residue is the highest in the case of MM40 blend as it has the maximum amount of thermostable triazine unit. The weight loss in the first stage is most probably due to the decomposition of hydrocarbon parts of the oil and other linkages such as allophanate,

biuret, ether etc. The second stage of degradation at higher temperatures is due to the decomposition of urethane linkages and rigid aromatic moiety.

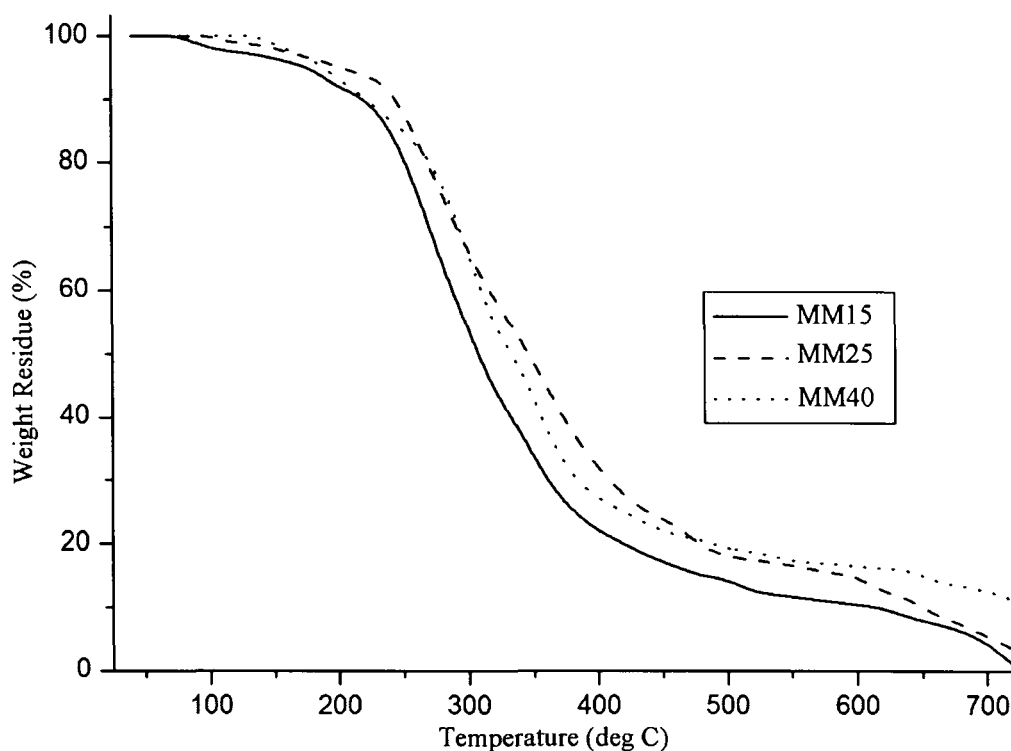


Figure 3.8 TG thermograms of MM blends

### 3.3.7. Dielectric properties

#### 3.3.7.1. Variation of dielectric constant with frequency and temperature

Dielectric constant is the ability of a dielectric material to store electric potential energy under the influence of an electric field. The dielectric constants obtained for EA and EM blends are shown in Figure 3.9, whereas for MA and MM blends are shown in Figure 3.10.

The dielectric constant of both epoxy and MF modified blends decreases with the increase of frequency, whereas the same increases first and then decreases with the increase of temperature (Figures 3.9 and 3.10). The initial high value of dielectric constant at lower frequencies may be due to the contributions from space charge polarization in the bulk material, structural defects and electrode effects [48]. Such dielectric behavior also indicates the possibility of the presence of an interfacial

polarization [49-50]. In general, the dielectric materials, especially polar materials like polyurethane, epoxy etc. contain some charges which can migrate to some distance through the dielectric on application of electric field. These charge carriers when impeded in their motion, they generate space charges and macroscopic field distortions. While migrating under electric field, these charges may get blocked at the electrode (conducting phase)-dielectric (non-conducting phase) interface, which results an interfacial polarization [51-52]. This distortion causes an increase in capacitance, which in turn increases dielectric constants at lower frequencies [49].

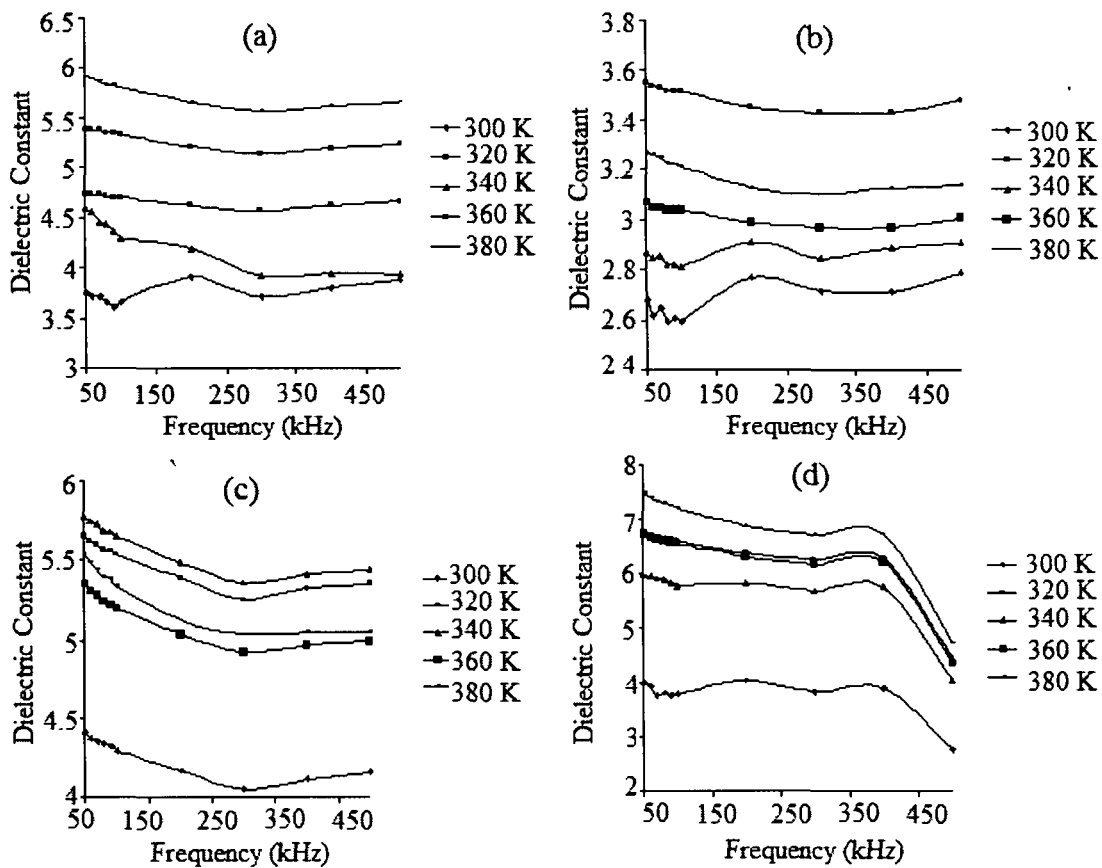


Figure 3.9 Variation of dielectric constant with frequency for epoxy modified PUE/PUA blends (a) EM50, (b) EM60, (c) EA50 and (d) EA60

Polyurethane is known for its flexibility. The presence of polar groups in the polyurethane chain makes it to orient in an electrical field producing high dielectric constant. On the other hand, molecular rigidity is responsible for restricting such orientations and subsequently causes reduction of dielectric constant. As these two factors namely, molecular flexibility and molecular rigidity, depends both on temperature and frequency, hence the studied polyurethane blends exhibit variable

dielectric constant values [47]. Furthermore, epoxy resin with hardener causes cross-linking of the matrix [41], whereas MF resin in the presence of an acid catalyst also causes cross-linking of the matrix [53]. The formation of cross-links reduces the number of free charge carriers, which is reflected in lowering of the total polarization and hence lowering of the dielectric constants.

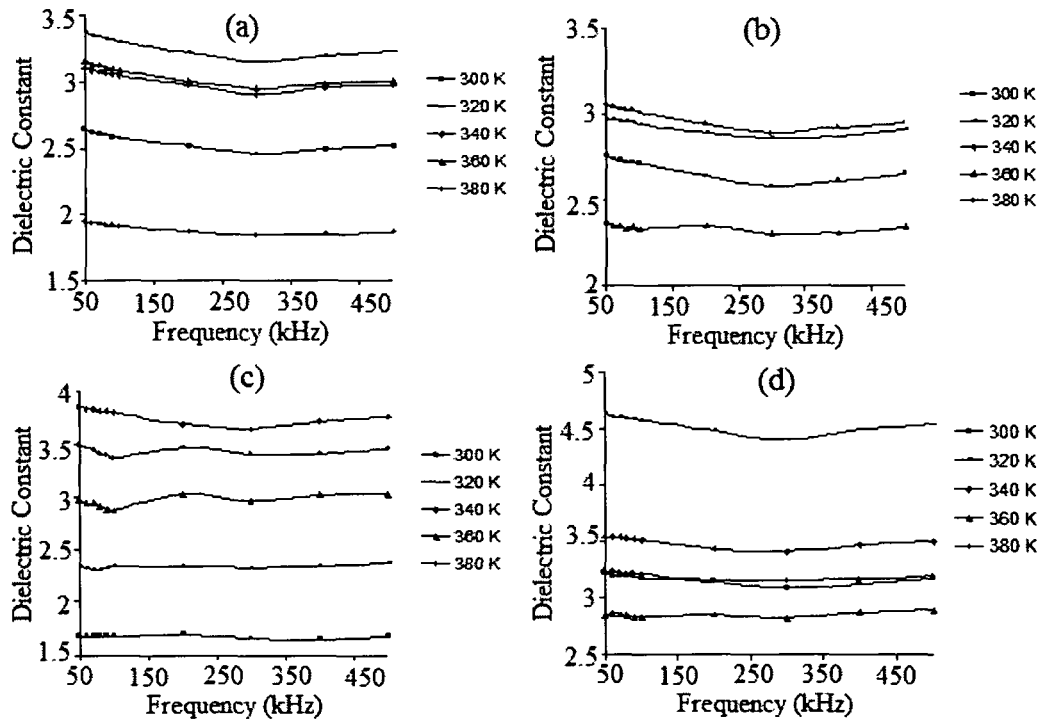


Figure 3.10 Variation of dielectric constant with frequency for MF modified PUE/ PUA blends (a) MA25, (b) MA40, (c) MM25 and (d) MM40

As the frequency of the external electric field increases, the polarization decreases and hence dielectric constant decreases. The dielectric constant decreases with the increase of frequency may be due to dielectric dispersion, result of the lag of molecules behind the alteration of the electric field at higher frequency. The relatively higher values of dielectric constant of the films may be due to higher intermolecular interactions through hydrogen bonding, dipole-dipole interaction, cross-linking etc. which decreases the mobility of molecules. The temperature dependence of the dielectric constant of the films can be explained from three dimensional network structure formations through cross-linking reactions. At first, the dielectric constant increases with increasing temperature which may be due to dipole orientation. As the

temperature increases the orientation of dipoles is facilitated and hence dielectric constant increases.

### 3.3.7.2. Variation of loss factor with frequency and temperature

The variation of loss factors of the epoxy modified blends (EM/ EA) and the MF modified blends (MM/ MA) with peaks at frequency between 250-350 kHz under isothermal condition are shown in Figures 3.11 and 3.12 respectively. The dielectric dispersion appears at high temperature which may be due to the rotating diffusional motion of the molecules from one quasi-stable position to another at the skeletal bond involving large conformational rearrangement of the main chain, which is known as primary dispersion region or the  $\alpha$ -relaxation. On the other hand, dielectric dispersion at the lower temperature is attributed to the dielectric response of the side groups, which can be considered to be more mobile or the small displacement of dipoles near the frozen-in position and is known as the secondary dispersion region or  $\beta$ -relaxation [54]. When a polymer is heated, the movement of the main chain starts and

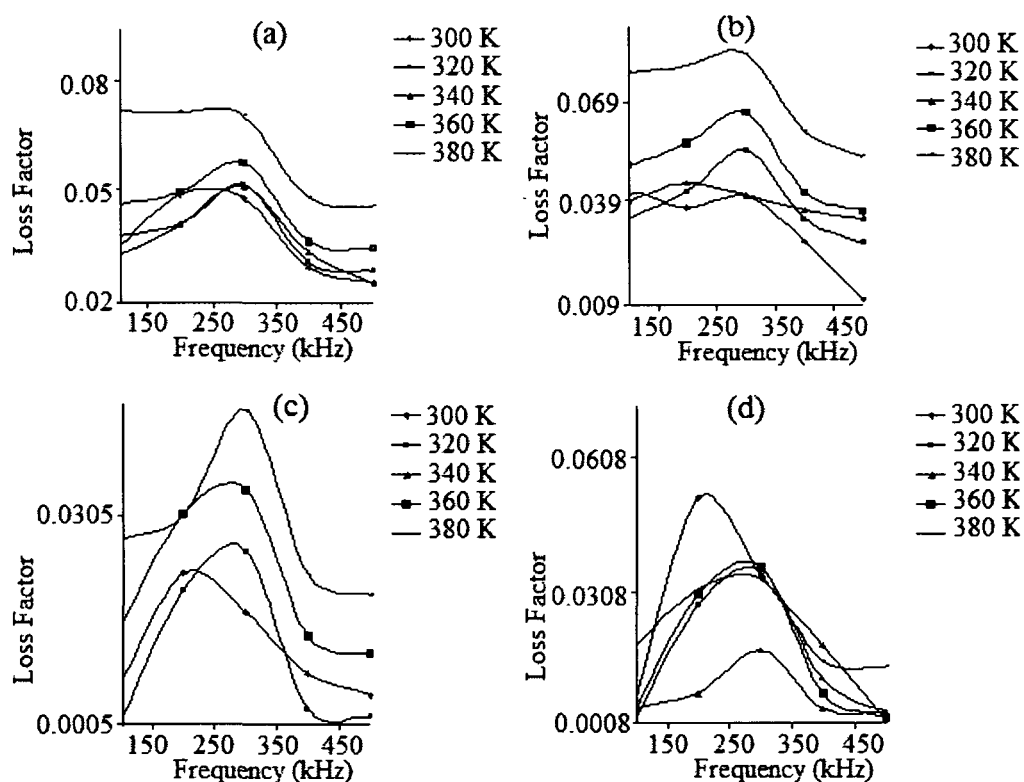


Figure 3.11 Variation of loss factor with frequency for epoxy modified PUE/ PUA blends (a) EA50, (b) EA60, (c) EM50 and (d) EM60



becomes maximum at glass transition temperature ( $T_g$ ), where maximum losses occur corresponding to the  $\alpha$ -relaxation peak [55]. As  $T_g$  is reached in addition to the normal expansion process, there will be an expansion of the rubber like polymer. This results sufficient space for rotational or translational motion of molecules to occur at  $T_g$ , accounting for the maximum dielectric loss at  $T_g$  [56].

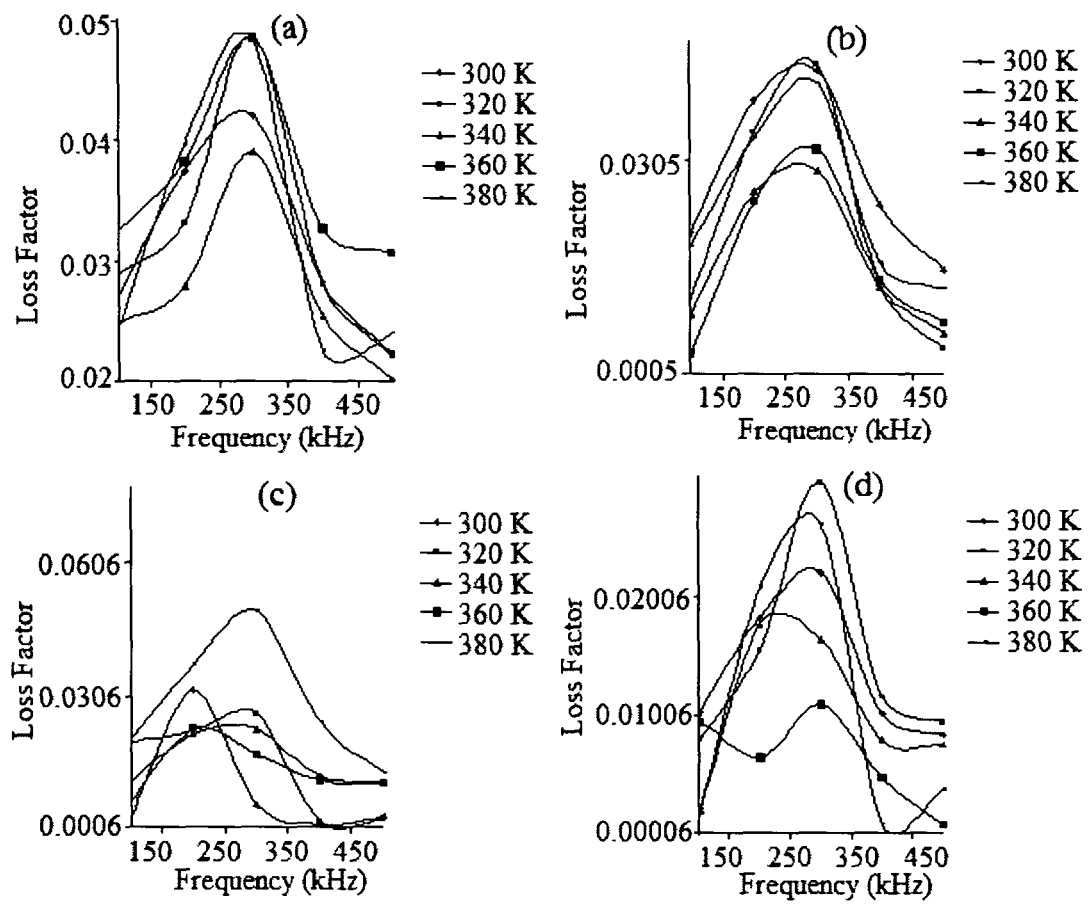


Figure 3.12 Variation of loss factor with frequency for MF modified PUE/ PUA blends (a) MA25, (b) MA40, (c) MM25 and (d) MM40

All the studied films exhibited only one peak appearing at 320-330 K over the entire frequency range. As this peak appears at relatively higher temperature and located in the neighborhood of  $T_g$ , so it may be termed as the  $\alpha$ -relaxation peak. This higher temperature peak may be due to the orientation in directions or locations of the polar groups OH, NH, C=O present in the polymer blend matrix (polymer backbone), which involves high activation energy. As the dipole orientations change due to segmental or translational motion of the main chain, so the relaxation time decreased and hence  $\alpha$ -relaxation could not be observed at lower temperature.

Loss factor for all the blends followed the same trend i.e., they increase first up to a certain frequency and then decrease as frequency increases at different temperatures (Figures 3.11 and 3.12). The magnitude of the loss factor increases with the increase of temperature. The initial increase of loss factor at lower frequency may be attributed to dipole polarization. As the frequency further increases, the dipole polarization effect tends to be zero and thus loss factor approaches towards small values. The increase of loss factor with temperature can be explained by dividing the relaxation phenomenon into three parts: (i) conduction losses, (ii) dipole losses and (iii) vibrational losses. At low temperature condition, losses are minimum as they depend on the product of ac resistivity and frequency. As the temperature increases, the ac resistivity increased and so the conduction losses increased. Thus the loss factor also changes in the same pattern.

### 3.4. Conclusions

From this study, it can be concluded that the performance characteristics of the *Mesua ferrea* L. seed oil modified polyurethane resins (both PUE and PUA) are well enhanced by blending with bisphenol-A based epoxy and with partially butylated MF resin using the solution blending technique. The study shows that all the blends showed good performance characteristics as well as compatibility between the components as observed by SEM. In the case of epoxy modified PUE and PUA blends, the blends EM50 and EA50 exhibit the optimum film performance, whereas in the case of MF modified PUE and PUA blends, the blends MM25 and MA25 exhibit the optimum film performance. Regarding thermal properties, the thermogravimetric analysis (TGA) showed initial degradation temperature near 200 °C under the nitrogen atmosphere for both the cases indicating their high thermostability. All the results indicate the potentiality of epoxy and MF modified *Mesua ferrea* L. seed oil based polyurethane blends towards high performance surface coating materials.

Further, the dielectric properties of epoxy and MF modified *Mesua ferrea* L. seed oil based polyurethane cured resins indicate that these materials may be used as insulators for solid state electronic devices in microelectronic industries.

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## CHAPTER 4

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### *Mesua ferrea* L. seed oil based polyurethane composites

#### 4.1. Introduction

The genuineness of polymer composites is ensuing from the amalgamation of continuous polymer matrix with tough and highly durable dispersed agent. Such biphasic materials are finding myriad of applications in different fields [1-3]. Conventional macro composites based on traditional reinforcing materials such as fibers like synthetic polymer, glass, carbon etc.; silicate and mica [4] are now largely replaced by natural fiber reinforced composite materials due to growing environmental awareness throughout the world. The main incentives for producing natural fiber reinforced green composites are their easy availability and processability, light weight, high specific strength, low toxicity, low cost and most importantly their bio-affable nature [5-7].

The avant-garde genre of composite materials is the nanocomposites, which becomes multidisciplinary in contemporary times and is challenging to the extreme. In this genre of composites, the inorganic reinforcing phase dimensions are in the nanometer range [8]. Clays are used unanimously as the nanofillers to develop nanocomposites. Incorporation of such layered nanofillers can significantly impact the microphase morphology of the polymers by acting as templates for structural development [8-9]. Nanocomposite formation results in dramatic enhancement of material properties which can be credited to the significant change occurring in microphase domain size and shape of the polymeric structure by incorporation of the nano-sized clay layers without affecting light weight characteristic of the pristine polymer. The efficiency of polymer nanocomposites is largely dependent on the degree

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(ii) *Bioresource Technol*, **2009** (in press).

of dispersion of the nanofillers in the polymer matrix [8]. The improved dispersion and distribution of nanofillers in the polymer matrices can be affected by application of ultrasound [10]. *Ex-situ* equipped with sonication is a simple technique by which nanocomposites may be obtained in a convenient manner [11].

Among the various polymer matrices exploited in the field of natural fiber reinforced composites, polyurethane is to be worth mentioned. A lot of research works are being progressed in this issue [12-14]. This is due to the structural versatility of polyurethane resins and their good compatibility with the lignocellulosic fiber like jute. However, such compatibility is obtained in an efficient manner only after modifying the surface chemistry of the jute fibers by alkali treatment [15-16]. This results in improvement of the interfacial adhesion by providing additional sites for mechanical interlocking that promotes more fiber matrix interpenetration at the interface [17-18]. These composite materials are now in great demand for their light weight, durability and cost effectiveness, especially in the automotive market. The versatility of polyurethane composites becomes more encompassed when clay layers with nanometer dimensions are incorporated into the polymer matrix. Some of the improved properties to be mentioned for polyurethane nanocomposites are higher modulus, greater strength, higher heat resistance, lower gas permeability, higher swelling resistance, better flame retardancy better electrical properties and lower elongation at break compared to the pristine polymer [19-22].

Recently, emphasis has been given on the development of renewable vegetable oil based polyurethane composites due to several environmental concerns and also due to ever mounting cost of petroleum based feed stocks [23-25]. *Mesua ferrea* L. seed oil has incredible potential in this regard as discussed in earlier chapters. Polyurethane resins [26-27] have been successfully synthesized from this vegetable oil (Chapter 2). Further, the performance characteristics of the *Mesua ferrea* L. seed oil based polyurethane resins can be enhanced to a considerable extent by blending with commercially available resins like melamine-formaldehyde (MF) and epoxy resins (Chapter 3) [28-29]. These blends may be fabricated either into macro composites by reinforcement with naturally renewable fibers like jute or into nanocomposites by reinforcement with layered silicates (nanofillers) due to the possible interactions of various functional groups present in the polymer backbone of the polyurethane blends with the hydroxyl groups of the fiber or nanoclay. Such interactions are expected to

improve a number of properties like hardness, elongation, mechanical strength, impact strength and dimensional stability [30-31].

From the previous chapter, it has been found that *Mesua ferrea* L. seed oil based polyurethane resins with NCO/OH ratio less than one can form compatible blend systems with commercially available bisphenol-A based epoxy and also with partially butylated MF resins. Thus the focal objective of the present chapter is the preparation, characterization and evaluation of performance characteristics of the epoxy and MF modified *Mesua ferrea* L. seed oil based polyurethane composites reinforced with jute fiber and nanocomposites reinforced with bentonite nanoclay.

## **4.2. Experimental**

### **4.2.1. Materials**

The jute fibers (density ca.  $1.5 \times 10^3 \text{ kg/m}^3$  as measured by pycnometer method) used in the present study as reinforcing agent was collected from the local market (Napaam, Tezpur, India).

Organically modified sodium bentonite nanofiller with octadecyl ammonium ions was obtained from Aldrich Chemicals and was used without further purification. Bentonite is much like that of montmorillonite (MMT) in structure and characteristics and belongs to the general family of 2:1 layered silicates.

NaCl, NaOH, HCl and xylene were obtained from Merck, India and were used as received.

### **4.2.2. Instruments and methods**

FTIR spectra of the post cured composite as well as nanocomposite samples were recorded in FTIR Nicolet, Impact 410 spectrophotometer, USA. Small quantities of the finely powdered composite samples were dispersed in KBr and further grounded to a fine mixture in a mortar before pressing to form transparent KBr pellets for analysis. The TG analysis of the cured composites and nanocomposites was done by Shimadzu TG 50, thermal analyzer under the nitrogen flow rate of 30 mL/min at the heating rate of  $10 \text{ }^\circ\text{C/min}$  from 50 to  $600 \text{ }^\circ\text{C}$ . DSC analyses were performed for the macro composites in a Perkin-Elmer Pyris DSC, USA at a heating rate of  $10 \text{ }^\circ\text{C/min}$  from 25 to  $400 \text{ }^\circ\text{C}$  under nitrogen flow rate of 20 mL/min. X-ray diffraction scattering

experiments were conducted for the nanocomposites film samples using a X-ray diffractometer “Miniflex”, (Rigaku Corporation, Japan) at room temperature. The X-ray was derived from nickel-filtered Cu-K $\alpha$  ( $\lambda = 0.154$  nm) radiation in a sealed tube operated at 40 kV and 40 mA. The scanning rate was 5.0  $^{\circ}$  min $^{-1}$  over a range of  $2\theta$  from 0 to 10  $^{\circ}$ . The tensile strength, flexural strength and elongation at break of all the composite (both macro and nano) specimens were measured by Universal Testing Machine of model Zwick Z010, Germany using samples of dimensions 100 mm X 10 mm X 3 mm. These mechanical properties along with thickness were measured on five specimens from each sample of composites to avoid irregularity. The surface morphology of the fractured tensile test samples were studied by using a JEOL scanning electron microscope of model JSM-6390LV SEM after platinum coating on the surface of the samples. Size and distribution of the nanoclay layers were studied by using JEOL, JEMCXII transmission electron microscopy (TEM) at operating voltage of 80 kV. Specific gravity, water absorption, impact resistance, hardness and chemical resistance of the composites were determined according to the standard methods as mentioned earlier (Chapter 2, section 2.2.2).

The water permeability of the nanocomposite films were measured in a desiccating chamber containing CaCl $_2$  as the drying agent under vacuum. Some small containers containing certain amount of initially weighed distilled water were taken, the caps of which were replaced by experimental nanocomposite films in an airtight manner to avoid any leakage. The containers were then placed in the well equipped desiccating chamber. The weight of the container was again taken after the experiment of 120 h. All the measurements were carried out at (30 $\pm$ 1)  $^{\circ}$ C and an average of three samples was taken for each measurement. The reduction in water content in the containers was calculated by using the following relationship,

$$\text{Percent weight loss of water} = [(W_i - W_f) / W_i] \times 100 \%$$

where  $W_i$  = initial weight and  $W_f$  = final weight of the water container.

#### 4.2.2.1. Preparation of EM50 and EA50 blend solutions

Both the polyurethane resins (PUE and PUA) with NCO/OH ratio 0.5 were prepared as reported in Chapter 3, sections 3.2.2.2 and 3.2.2.3. The EM50 and EA50 blend solutions were prepared by mixing PUE and PUA resins respectively (40% solid



content in xylene) with epoxy resin (100% solid content) separately in the presence of poly(amido amine) hardener (50 weight % with respect to epoxy) in the desired proportions as shown in Table 4.1. The mixing was carried out with constant vigorous stirring for about half an hour at  $(30\pm 1)^\circ\text{C}$ .

#### 4.2.2.2. Preparation of MM30 and MA30 blend solution

MM30 and MA30 blend solutions were prepared by mixing PUE and PUA based resins respectively ( $30\pm 5$  weight % solid content in xylene) with MF resin (60 weight % solid content in xylene:butanol = 90:10 by volume) separately in the presence of *p*-toluene sulfonic acid (PTSA) as an acid catalyst (0.5 weight % with respect to the total resin) in the desired proportions as shown in Table 4.1. The mixing was carried out with constant vigorous stirring for about half an hour at  $(30\pm 1)^\circ\text{C}$ .

#### 4.2.2.3. Preparation of jute fiber reinforced composites

##### 4.2.2.3.1. Treatment of jute fiber (JF) by alkali treatment method

Jute fiber (JF) obtained from the local market was first chopped uniformly into small pieces of ca. 1 cm in length. Well chopped fibers were scoured with 2% hot detergent solution and washed thoroughly with distilled water followed by drying in a vacuum oven at  $70^\circ\text{C}$  for ca. 1h. The dried fibers were dispersed in 2% NaOH solution for ca. 2 h with frequent stirring and then washed with distilled water for several times to leach out the absorbed alkali. The fibers were kept immersed in distilled water overnight and were again washed repeatedly to avoid the presence of any trace amount of alkali. Finally, the alkali treated fibers were made free of water by drying under sun and in the vacuum oven at ca.  $(60-70)^\circ\text{C}$  for 24 h and then stored at ambient temperature in a desiccator.

##### 4.2.2.3.2. Fabrication of jute fiber reinforced composites

The well dried alkali treated jute fibers in desired proportions (Table 4.1) were introduced separately into the solutions of the EM50, EA50, MM30 and MA30 blend solutions by hand lay out technique in four big trays. The compositions of these four composites are given in Table 4.1. After removal of sufficient amount of solvent under

atmospheric conditions, the polymer impregnated fibers were placed into mold of size 26 cm X 28 cm X 0.3 cm in each case. The mold was then subjected to hot curing by compressing in a hydraulic press (Peeco Hydraulic Pvt. Ltd., Kolkata, India) at ca. (130-140) °C under pressure of (35±5) kg/cm<sup>2</sup>. The molded articles were taken out after 4 h and thick plates of the composites with varying compositions were obtained. All the composite samples were stored for 48 h at room temperature before further testing and analysis.

Table 4.1 Compositions of the jute fiber reinforced composites

Composite Code	(% weight)		
	Polyurethane	Epoxy	MF
EM50/JF50*	50 (PUE)	50	-
EA50/JF50*	50 (PUA)	50	-
MM30/JF50*	70 (PUE)	-	30
MA30/JF50*	70 (PUA)	-	30

\* indicates 50% jute fiber loading with respect to the total resin content

#### 4.2.2.4. Preparation of nanocomposites

##### 4.2.2.4.1. Preparation of epoxy modified polyurethane nanocomposites

After proper and vigorous mixing of the epoxy based EM50 and EA50 blend solutions in xylene as the solvent for about half an hour at (30±1) °C, the solutions were taken in glass beakers. Desired quantity of the clay (Table 4.2) was allowed to swell separately in minimum amount of xylene for ca. 3 h. The clay solution was then mixed with the EM50 and EA50 blend solutions separately by constant stirring and then homogenized by applying ultrasound with the help of an ultrasonicator for ca. 30 min. Three sets of PUE based nanocomposite solutions and three sets of PUA based nanocomposite solutions were prepared in this manner (Table 4.2).

#### 4.2.2.4.2. Fabrication of the nanocomposite solutions into thin films

The thin films of both the series of nanocomposite solutions were prepared by drawing the homogeneous mixture of the solutions on glass plate of 120 mm X 100 mm X 2 mm using a micro adjustable thickness gauge (Sheen Instrument Ltd., UK) under the ambient conditions. After removal of sufficient amount of solvent under atmospheric conditions, the coated strips were degassed under vacuum at  $(45\pm 5)$  °C for 45 min to remove the last trace of solvent and volatile compounds. Then the coated nanocomposites were cured by heating at 130 °C in an oven for a specified time period. The cured nanocomposites were kept under ambient conditions for 24 h. Then the dried films were peeled off from the glass plates by immersing the plates in warm water. The films were kept in a desiccator under vacuum and stored for 7 days before testing. The thickness of the completely dried composites was found to be in the range of 25-35  $\mu\text{m}$ .

Table 4.2 Compositions of the nanocomposites

Nanocomposite Code*	(% weight)		
	Polyurethane	Epoxy	Clay
EM50/NC1.0	50 (PUE)	50	1.0
EM50/ NC2.5	50 (PUE)	50	2.5
EM50/ NC5.0	50 (PUE)	50	5.0
EA50/ NC1.0	50 (PUA)	50	1.0
EA50/ NC2.5	50 (PUA)	50	2.5
EA50/ NC5.0	50 (PUA)	50	5.0

\*digits of the nanocomposite codes indicate the nanoclay content (phr = part(s) of clay per 100 parts of total resin)

### 4.3. Results and discussion

#### 4.3.1. FTIR study

##### 4.3.1.1. Jute fiber reinforced composites

The completion of curing of the resins was confirmed for all the composites by disappearance of oxirane ring (band at ca.  $827\text{ cm}^{-1}$ ) in the structure of epoxy based composites and increase of intensity of ether linkage (band at ca.  $1225\text{-}1232\text{ cm}^{-1}$ ) [32-33] in both the cases as observed in FTIR spectra (Figure 4.1). The absorption bands

for the characteristic functional groups of the virgin blends remained almost unaltered in the composites which indicate the curing mechanism remaining to be almost the same. However, the absorption peak at ca.  $1730\text{-}1740\text{ cm}^{-1}$ , which is due to carbonyl stretching, becomes little broadened in the composites as compared to that of the virgin blends. This indicates more carbonyl groups of the composites to be involved in H-bond formation. Again, the broadness of the band at ca.  $3410\text{-}3430\text{ cm}^{-1}$  remains almost similar as that of the virgin blends due to two contradictory effects. The reaction of hydroxyl groups of the polyurethane / epoxy/ MF with the hydroxyl groups of the fibers causes sharpening of the bands, whereas H-bonding causes broadening.

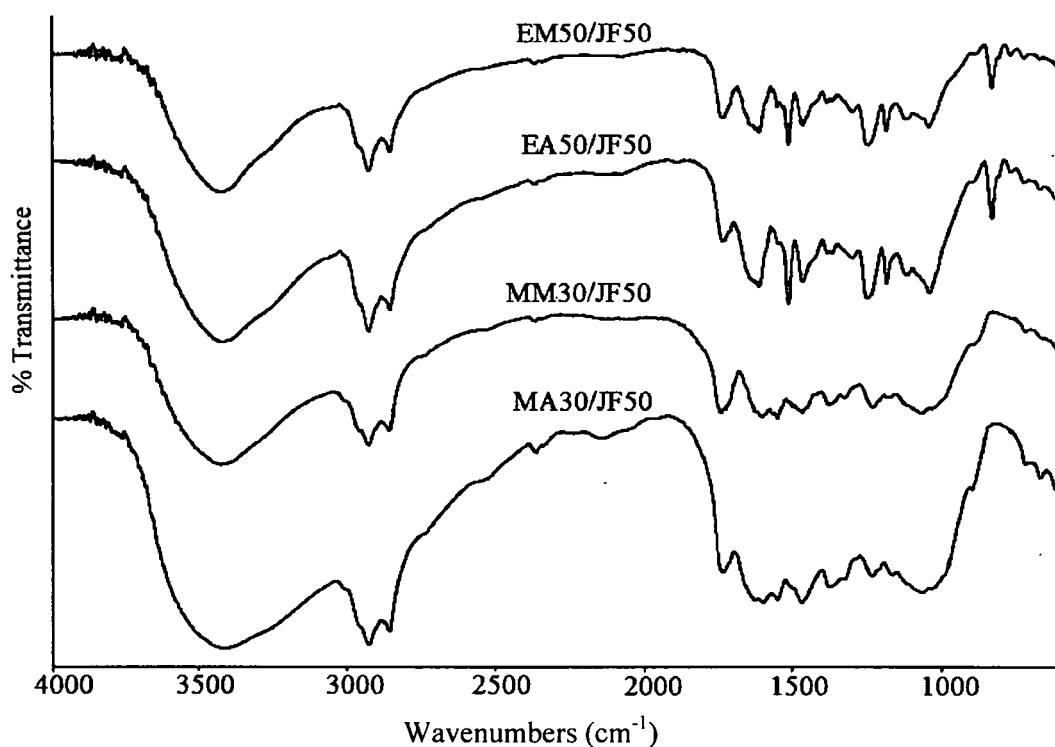


Figure 4.1 FTIR spectra of the jute fiber reinforced composites

#### 4.3.1.2. Nanocomposites

The absorption bands for the characteristic functional groups of the pristine polymer matrix remained almost same in the nanocomposites. This indicates that the segmented structure of polyurethane had not been affected much by the presence of nanoclay (Figure 4.2). This also reveals that the curing mechanism of the polymer was not influenced much by nanoclay loading. The bands appearing at ca.  $1030\text{ cm}^{-1}$  and at

ca.  $550\text{ cm}^{-1}$  region in the FTIR spectrum of the clay due to Si-O and Al-O stretching vibrations [34] and the band at ca.  $3500\text{-}3650\text{ cm}^{-1}$  for the OH stretching in Si-OH and Al-OH moieties located on the surface of the clay seem to be significantly minimized in the nanocomposites. This indicates interaction of OH group of clay occurring with the isocyanate group and free OH groups of the intercalated polymer chain. Thus the OH stretching band observed for the pristine polymers also sharpen in the nanocomposites [35].

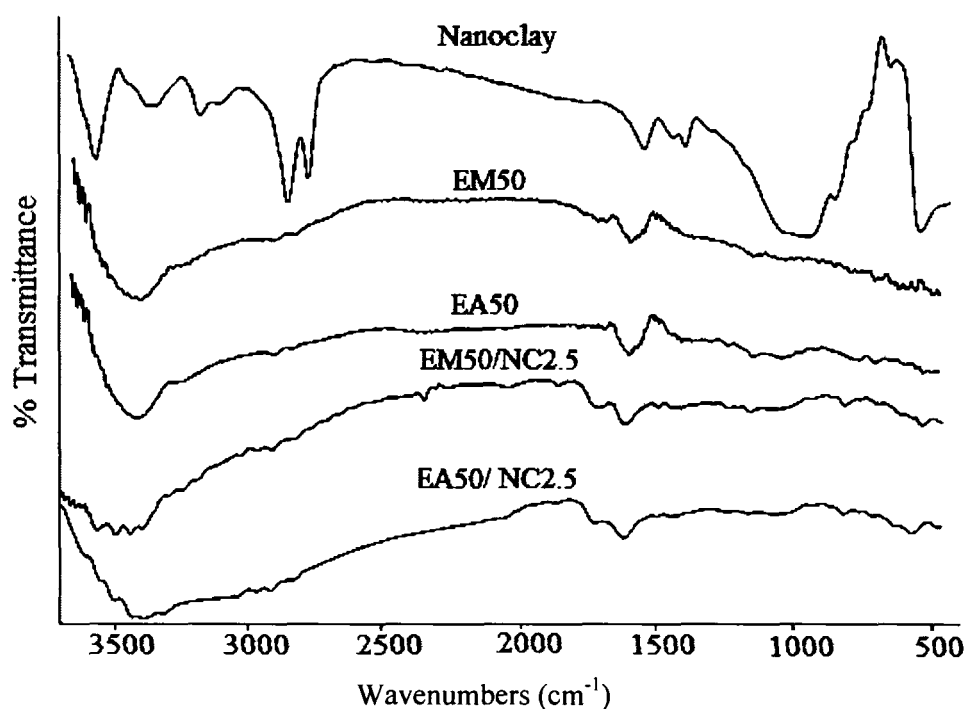


Figure 4.2 FTIR spectra of the nanocomposites and the pristine polymers

#### 4.3.2. Characterization of the nanocomposites by XRD analysis

The X-ray diffractograms of the bentonite clay and the nanocomposites along with the corresponding pristine polymers are shown in Figure 4.3. The interlayer spacing ( $d$ ) was calculated on the basis of Bragg scattering equation given as,

$$2d\sin\theta = n\lambda$$

where,  $\lambda$  is the wavelength (0.154 nm) of the X-ray radiation used in the diffraction experiment of the present study,  $d$  is the spacing between the diffractive lattice plane also known as the basal spacing,  $n$  is the order of plane which is 1 in the present case

and  $\theta$  is the measured half diffraction angle or glancing angle. The interlayer spacing for the clay was found to be 3.40 nm. The observation of strong XRD peaks at  $2\theta \leq 1.50^\circ$  for all the nanocomposites indicate that the interlayer spacing (d-spacing) of the clay have been increased or intercalated by the polymer chains to the range of 5.88-7.35 nm. The intensity of the XRD peak slightly decreases with increase in clay content in the nanocomposites indicating better intercalation at lower loading [8].

Thus, in all the nanocomposites, the intergallery distance has been found to be intercalated to a distance greater than that of pure clay. It confirmed intercalated or partially exfoliated nanostructure of clay with different extent of dispersion in the polyurethane matrix. Among the epoxy modified PUE (EM50) and PUA (EA50) nanocomposites, the degree of intercalation is found to be slightly higher in PUE as compared to PUA matrix (Figure 4.3) which may be due to better flexibility of the former.

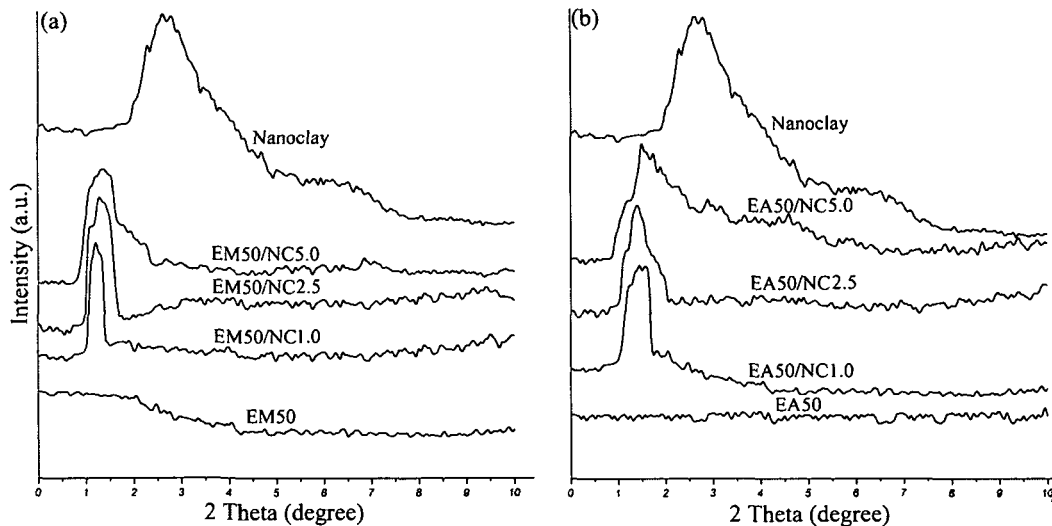


Figure 4.3 X-ray diffractograms of (a) EM50 and (b) EA50 based nanocomposites and pristine polymers

### 4.3.3. Morphological study

#### 4.3.3.1. Jute fiber reinforced composites

The scanning electron micrographs (SEM) of the fractured surface of the jute fiber reinforced polyurethane composites are shown in Figure 4.4 at two different magnifications. Use of alkali treated fibers in the composites improves the interfacial bonding by providing additional sites for mechanical interlocking, which results in strong wetting of the fibers by the matrix [17-18, 36]. The voids as observed in SEM

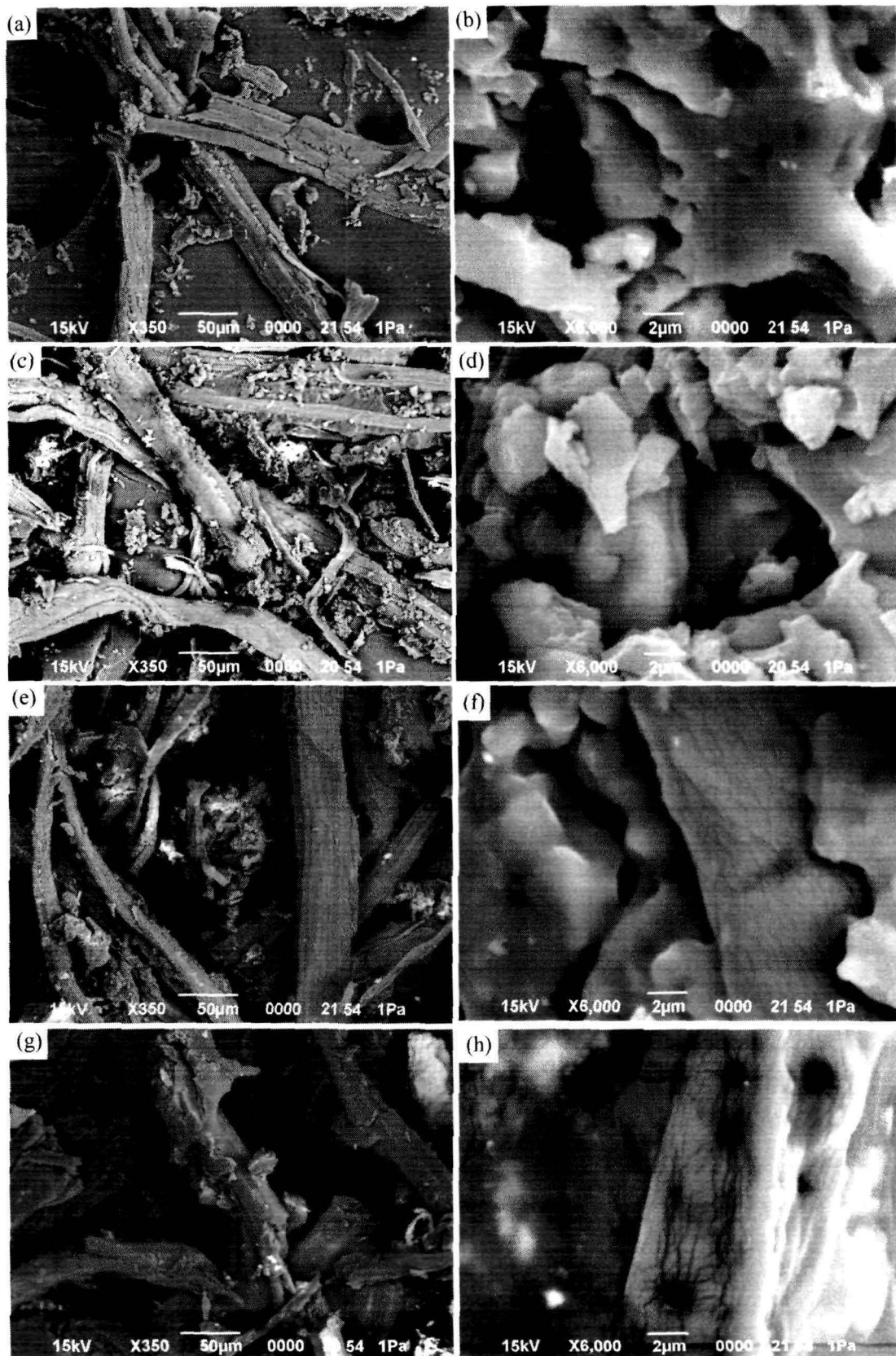


Figure 4.4 SEM micrographs of jute fiber reinforced composites (a) EM50/JF50 (350 X), (b) EM50/JF50 (6000 X), (c) EA50/JF50 (350 X), (d) EA50/JF50 (6000 X), (e) MM30/JF50 (350 X) (f) MM30/JF50 (6000 X), (g) MA30/JF50 (350 X) and (h) MA30/JF50 (6000 X)

micrographs are created due to pullout of fiber during fracture. More numbers of fiber pullout were observed in the case of MF modified polyurethane based composites, MM30/JF50 and MA30/JF50 due to lower level of polymer-filler adhesion than in the case of epoxy modified polyurethane based composites, EM50/JF50 and EA50/JF50 (Figure 4.4). Reduction in the amount of fiber pulled out in the latter case is due to the continuous stronger interfacial interactions between the polymer and fiber as evident from the cracks at the broken fiber ends (Figure 4.4). This may be ascribed to the interactions between jute fiber and epoxy modified polyurethane, which are significant due to the improved flexibility of the matrix. The SEM results indicate that the jute fibers play a definite role as a reinforcing agent in toughening the modified *Mesua ferrea* L. seed oil based polyurethane resins to form the green composites [37].

#### 4.3.3.2. Nanocomposites

The scanning electron micrographs of the fractured surface of the clay reinforced polyurethane nanocomposites are shown in Figure 4.5. Almost homogeneous morphology was observed for all the nanocomposites (Figure 4.5). Observation of protruding dots or lines indicate that the embedded clay layers were well adhered to the polymer surface [8]. The smooth and systematic pattern as observed from the SEM pictures of the fractured surfaces of all the nanocomposites hinted well dispersed clay layers in the polymers [38]. Such well dispersed dots and lines were found to be increased with increase in clay loading. Further, the partially exfoliated structure of the clay layers in the nanometer range can be seen in the TEM images (Figure 4.6). It provides a pictorial representation of the distribution of nanoclays inside the matrix. The clay layers approximately 2-5 nm thick are dispersed and disordered randomly in the matrix. This indicates that the clay layers are partially exfoliated and dispersed in the matrix.



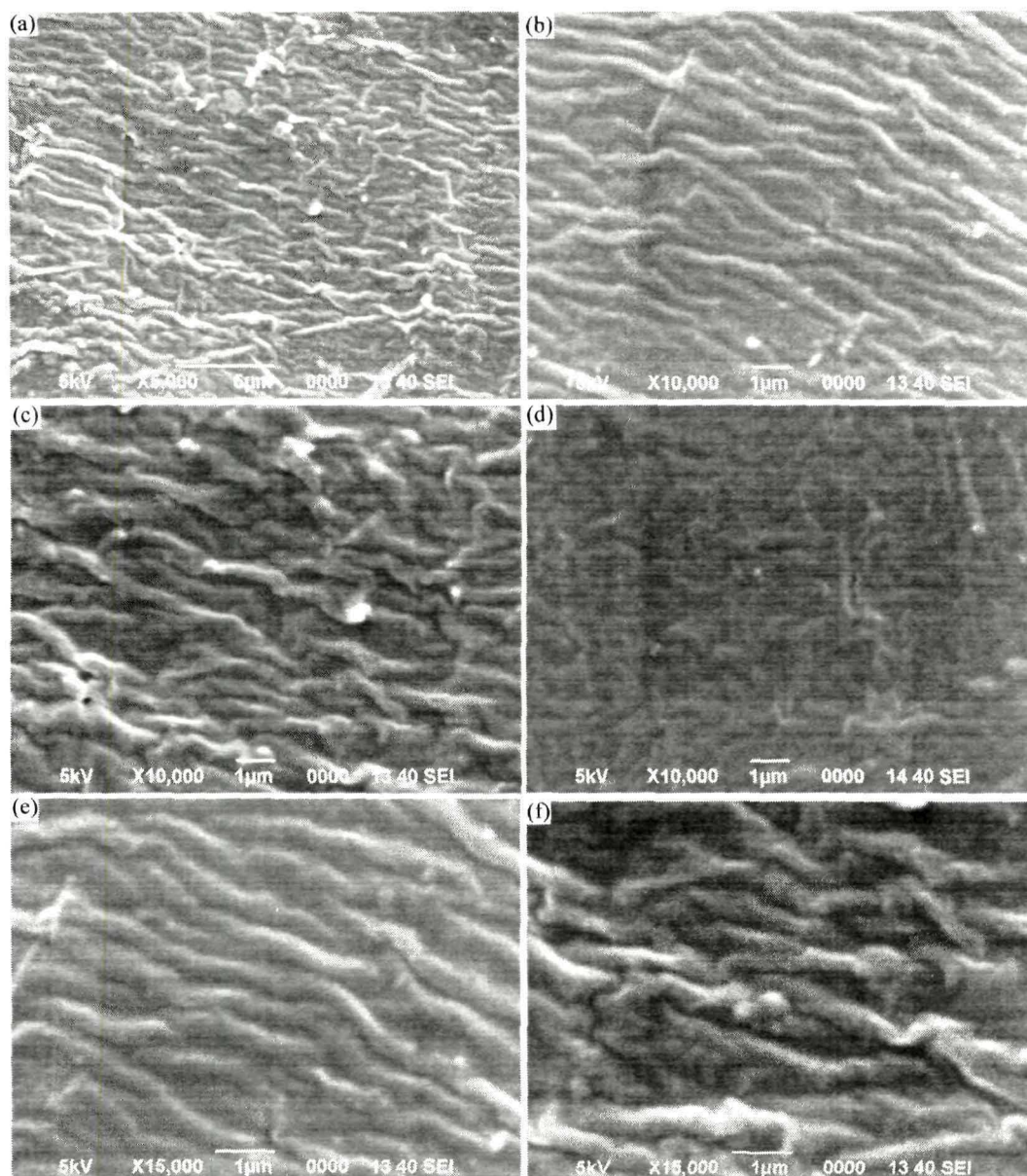


Figure 4.5 SEM micrographs of nanocomposites (a) EM50/NC1.0, (b) EM50/NC2.5, (c) EM50/NC5.0, (d) EA50/NC1.0, (e) EA50/NC2.5 and (f) EA50/NC5.0

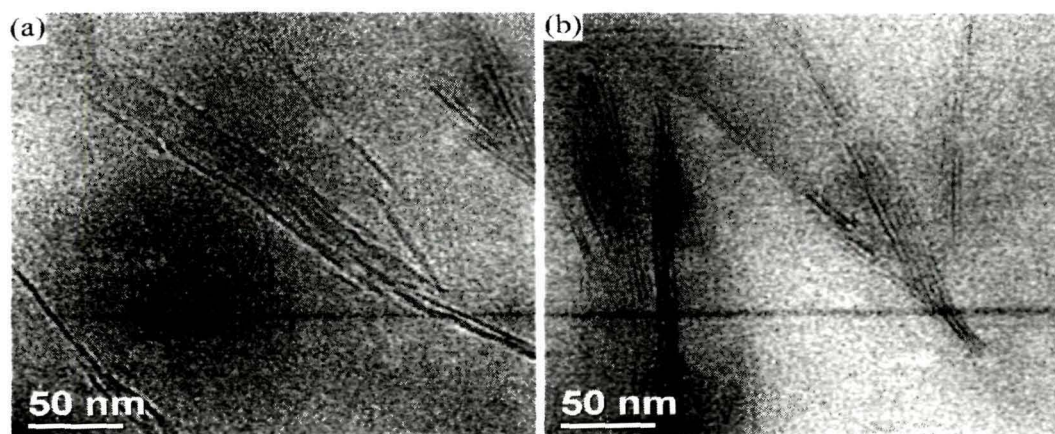


Figure 4.6 TEM images of nanocomposites (a) EM50/NC2.5 and (b) EA50/NC2.5

#### 4.3.4. Performance characteristics

##### 4.3.4.1. Physical properties of the jute fiber reinforced composites

Well chopped alkali treated jute fiber was used as the reinforcing agent in the present investigation as alkali treatment is branded to cause delignification that results in significant roughening [39-40] of the fiber's surface. This encourages strong fiber-matrix adhesion which is very important from the viewpoints of enhancement of mechanical property [39-40]. Interfacial adhesion depends on partial chemisorption (covalent and H-bonding interactions) of the matrix occurring on the surface of the fibers. The reinforcing effect of the jute fiber could be understood from the improved interfacial interactions such as H-bonding between the hydroxyl group of cellulosic jute fiber and epoxy/ hydroxyl groups of the matrices, polar-polar interactions etc. [15]. The tensile and flexural strengths (Table 4.3) were found to be well enhanced for epoxy modified polyurethane based composites, EM50/JF50 and EA50/JF50 as compared to the MF modified polyurethane based composites, MM30/JF50 and MA30/JF50. This may be attributed to the superior interfacial adhesion in the former case (supported by SEM, Figure 4.4) which results better and continuous stress transfer from the matrix to the fibers. Such observations also indicate the extent of compatibility between the fiber and the matrix to be higher in the epoxy based composites. The comparatively low compatibility in the MF based composites may be due to the rigidity of the matrix (MF resin) causing random orientation of the sandwiched jute fibers [41-42].

Table 4.3 Physical properties of the jute fiber reinforced composites

Properties	EM50/JF50	EA50/JF50	MM30/JF50	MA30/JF50
Tensile strength (MPa)	32.4	36.0	15.6	4.0
Flexural strength (MPa)	42.6	50.3	29.2	9.75
Break load (MPa)	39.9	45.1	29.8	14.5
Elongation at break (%)	12.0	16.1	6.6	0.9
Hardness (Shore A)	93	96	85	55
Specific gravity (g/cm <sup>3</sup> )	1.16	1.10	0.88	1.02

Among other mechanical properties, the hardness value (Shore A) was found to be the highest (~ 96) for the composite, EA50/JF50 and the lowest for MA30/JF50 composite (~ 55) (Table 4.3). This can again be explained on the basis of fiber-matrix

interactions of the composites and their compatibility. The higher hardness of the epoxy based composites as compared to the MF based composites is due to better compatibility between matrix and fiber arising from the higher reactivity of the strained epoxy moiety. However, between the two MF modified polyurethane composites, MM30/JF50 and MA30/JF50, the hardness value was found to be considerably higher for the former. This is due to improved adhesion and distribution of polymer in the fibers in case of the former. Both epoxy and MF modified *Mesua ferrea* L. seed oil based polyurethane composites were found to possess low densities (Table 4.3) as can be expected from the low density of alkali treated jute fibers. Thus the synthesized composites can play crucial role as light weight materials.

#### 4.3.4.2. Physical properties of the nanocomposites

The drying time (Table 4.4) of the nanocomposites were found to be comparatively lower than the pristine polymers. The epoxy modified PUE nanocomposite was found to be dried even by ten minutes only. This may be due to the presence of large numbers of OH groups of the delaminated nanoclay in the matrix. The specific gravity values of the nanocomposites were found to be almost unaltered as in the pristine polymers (Table 4.4). Thus the light weight characteristic of the pristine polymer is retained in the nanocomposites also, as the amount of nanoclay is low.

The tensile strength and scratch hardness values of the synthesized nanocomposites were found to be well enhanced as compared to that of the pristine polymers (Table 4.4). The reinforcing effect, caused by the intercalation or exfoliation of clay layers, reduces the amount and size of voids and hence increases the length of the crack spreading path during tensile drawing [34]. This effect can also be explained from the angle of cross-linking density, which could be expected from the reaction between OH and NCO groups of the polymer matrix with the OH groups of the bentonite clay during the process of curing. Again, high surface to volume ratio of the nanofiller increases bridge, tail and loop interactions with the polymer which facilitates the aforementioned chemical interactions. These interactions are definitely more in the EM50 nanocomposites as reflected from their higher tensile strength and scratch hardness values than the EA50 nanocomposites (Table 4.4). Further, the values were found to be increased with increase in clay loading from 1 to 5 weight % in both the cases. However, the elongation at break values were found to be decreased with clay

content which may be due to the stacked clay layers that cause molecular restriction of the polymer chain. The impact strength values were found to be slightly improved as evident from Table 4.4. Bending test showed that the nanocomposites films can be bent without any crack even after wrapping in a 0.3 mm diameter rod. This indicates retention of flexibility in all the nanocomposites. Thus the overall performance characteristics of the epoxy modified PUE and PUA i.e., EM50 and EA50 nanocomposites were found to be enhanced in comparison to the pristine polymers. Between PUE and PUA based nanocomposites, the PUE based nanocomposites were found to be better in all aspects which is due to better delamination of nanoclay by more flexible ester based polyurethane chains (Figure 4.5).

Table 4.4 Mechanical properties of the nanocomposites and the corresponding pristine polymers

Property	EM 50	EM50/ NC1.0	EM50/ NC2.5	EM50/ NC5.0	EA 50	EA50/ NC1.0	EA50/ NC2.5	EA50/ NC5.0
Drying time (min)	15	12	10	10	55	20	15	15
Specific gravity	0.95	0.96	0.97	0.98	0.93	0.95	0.96	0.97
Tensile strength (MPa)	17.0	20.8	27.9	32.3	12.7	17.8	21.2	25.3
Elongation at break (%)	37.6	38.0	22.2	3.7	21.0	18.6	3.7	2.8
Impact strength (cm)	56	60	62	63	57	63	67	67
Scratch hardness (kg)	2	5	8	10	2	5	8	10
Bending (dia., cm)	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0

#### 4.3.5. Thermal properties

##### 4.3.5.1. Jute fiber reinforced composites

The DSC thermograms of the jute reinforced composites (Figure 4.7) indicated that all the composites possess high glass transition temperatures ( $T_g$ ) (marked by arrows). This hints good fiber dispersion, efficient wetting and good fiber matrix

adhesion [43]. However, the  $T_g$  values obtained for MF modified polyurethane based composites (184-188 °C) were comparatively lower than that obtained for the epoxy

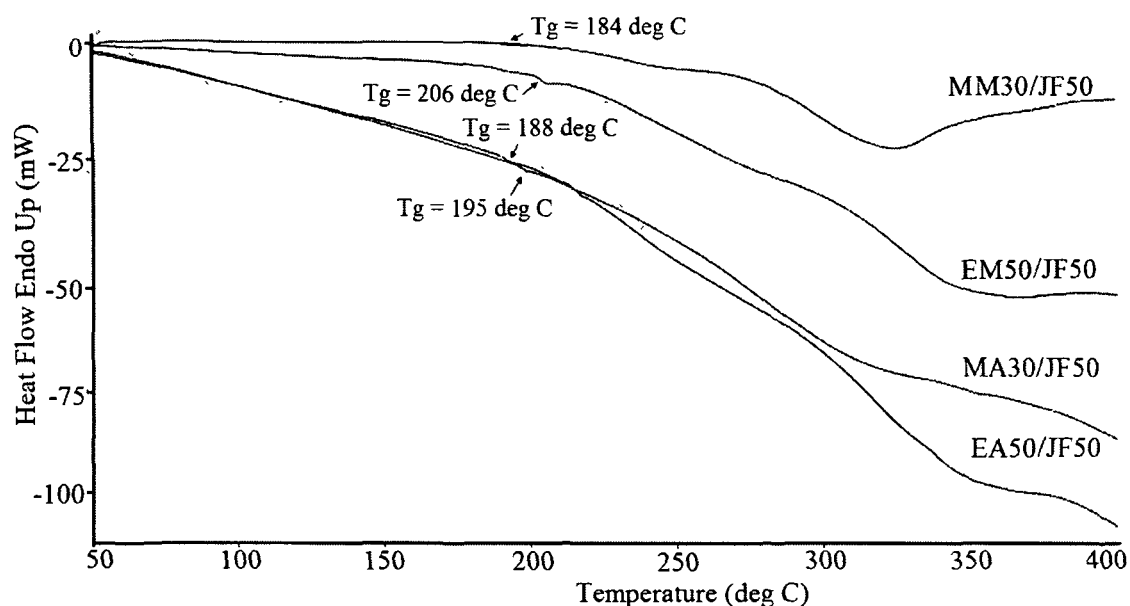


Fig. 4.7 DSC thermograms of the jute fiber reinforced composites

modified polyurethane based composites ( $T_g=195-206$  °C). It can be partly attributed to the more plasticizing effect of the dangling polymeric chains i.e., entanglements which were not included in the network during cross-linking and left dangling in the former case [44]. This may also be attributed to phase separation of hard and soft domains due to fiber matrix incompatibility which is more in the MF modified polyurethane based composites. All the composites were found to be stable up to temperatures greater than ca. 200 °C as evaluated by thermogravimetric analysis (Figure 4.8). Further, degradation up to ca. 600 °C occurs in a three step process. It is evident from the thermograms (Figure 4.8) that incorporation of jute fibers into both the epoxy and MF modified polyurethane matrix enhances the thermal stability to a considerable extent as compared to the virgin blends [28-29]. Thus the overall high thermostability of the composites indicates improved fiber-matrix interfacial adhesion.

#### 4.3.5.2. Nanocomposites

All the nanocomposites exhibited almost one step degradation (Figure 4.9) instead of two step degradation in the pristine polymer [28-29]. This indicates high degree of intercalation of the nanofiller by the matrix. The initial degradation

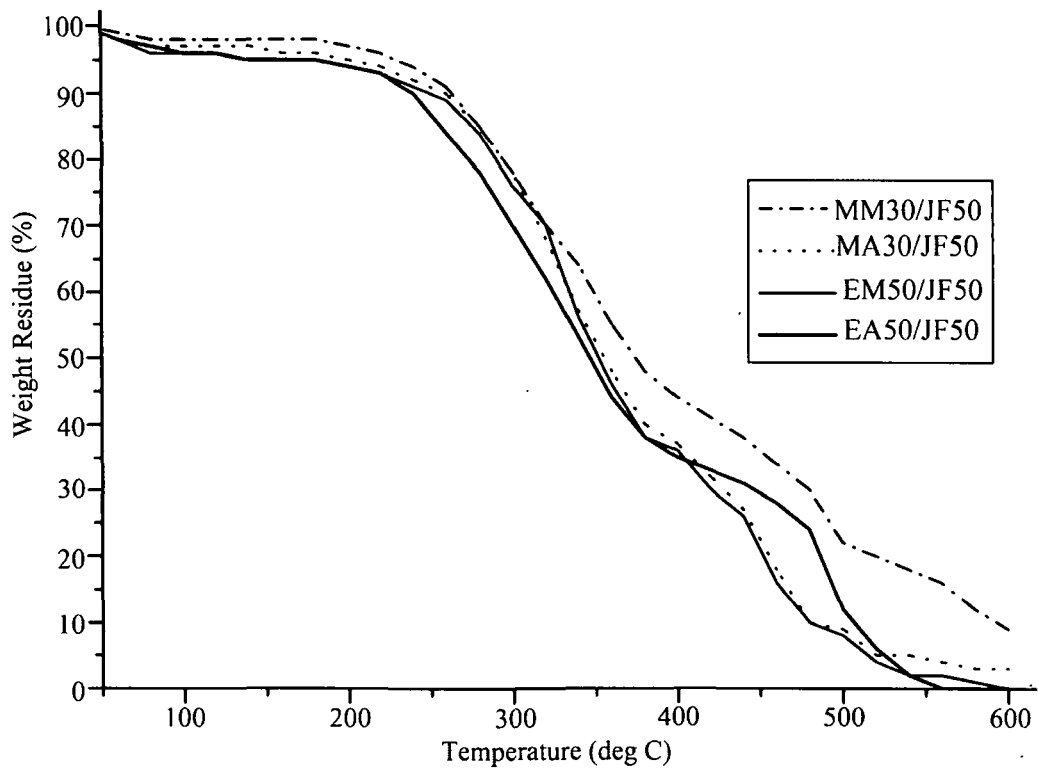


Fig. 4.8 TG thermograms of the jute fiber reinforced composites

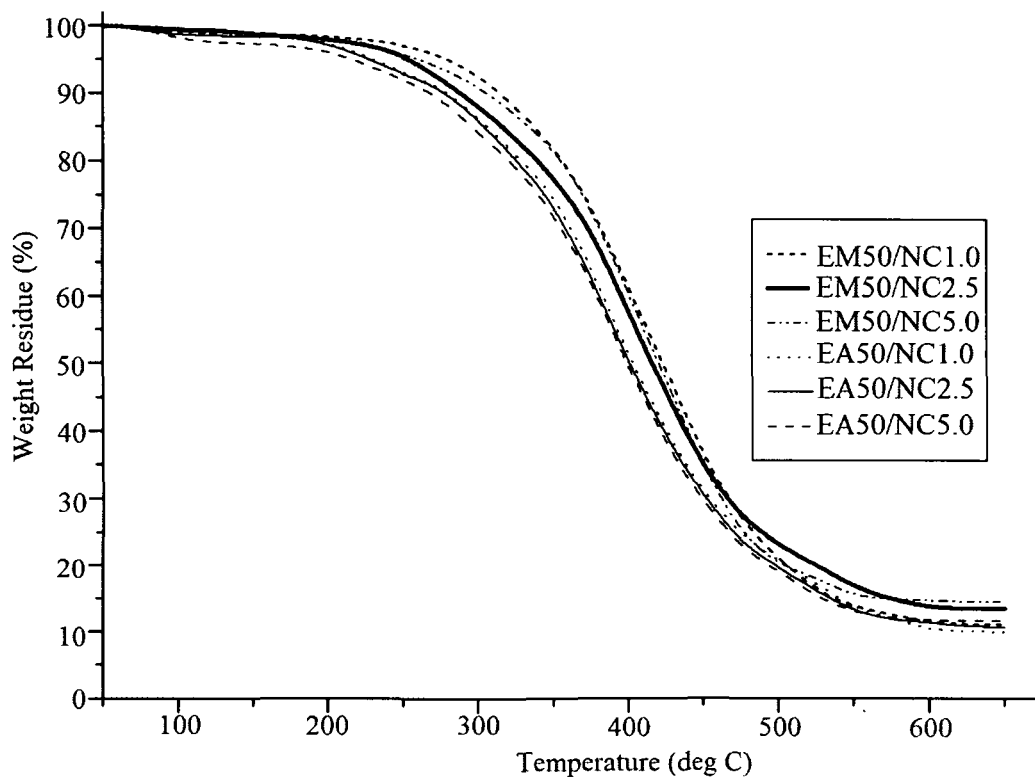


Fig. 4.9 TG thermograms of the nanocomposites

temperatures (decomposition onset) were found to be increased up to ca. 250 °C in the nanocomposites. Such high thermostability of the nanocomposites is explicable as the clay nanofiller acts here as a thermal insulator and mass transport barrier to the volatile products generated during decomposition by providing longer paths for them to escape [45]. Further, a close surveillance of the TGA curves (Figure 4.9) hints the thermostability to be increased with increase in clay loading from 1 to 5 weight %. This is due to the delay in thermal degradation arising from the clay layers [34] which disperses the polymer chains into their intergallery region. Among the PUE and PUA based nanocomposite series, the first series is found to possess more thermal stability possibly due to more cross-linking density in the network.

#### 4.3.6. Chemical resistance study

##### 4.3.6.1. Jute fiber reinforced composites

The hydrophilic nature of jute fiber is due to the presence of hydroxyl and ether groups in the cell walls which attract water molecules through H-bonding [46-47]. All the composites were found to absorb water to a measurable extent. The water absorption results are represented pictorially in Figure 4.10.

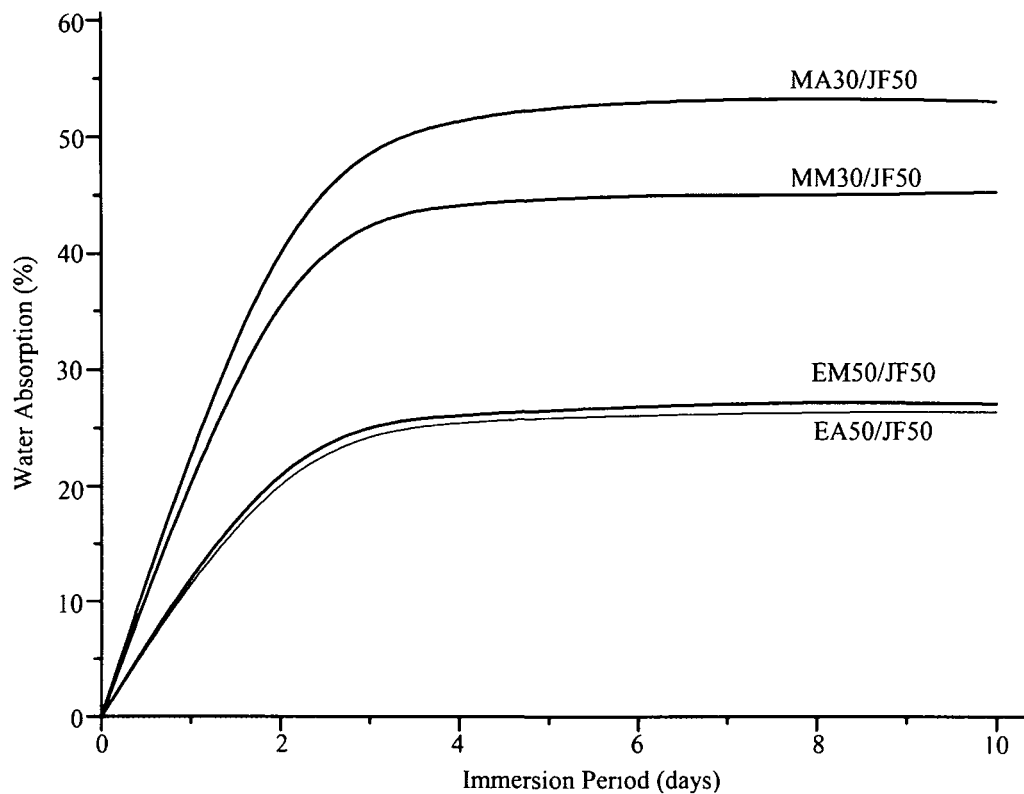


Figure 4.10 Water absorption of the jute fiber reinforced composites

The percent (%) of water absorption is found to be in the order: EA50/JF50 < EM50/JF50 < MM30/JF50 < MA30/JF50. The lower water absorption of the epoxy based composites is due to the greater compatibility of the matrix with the fiber. The fibers got fully masked with the matrix which causes stronger adhesion resulting in greater hydrophobicity and hence show lesser water absorption. The factors responsible for poor water resistivity of MF based composites are weak fiber matrix adhesion, agglomeration of the jute fibers and incomplete encapsulation of the matrix by the fibers. Figure 4.10 further depicts the water absorption as a function of time. The percentage of water absorption after 2 days is quite high due to the porous structure of jute fibers which allows transportation of water through their capillaries into the gaps and flaws at the interfaces between the fibers and matrix. Thereafter, the rate of water absorption becomes slow. Immersion in water caused debonding between the matrix and the fibers as the time progressed. The absorption of water reached a maximum value in six days and then remained almost unchanged as observed up to ten days.

The results obtained for chemical resistance of the composites in aqueous acidic (10% HCl), basic (3% NaOH) and salt (10% NaCl) environments are given in Table 4.5. Weight gain was observed in all the cases in the order of NaOH > HCl > NaCl. This is due to the absorption of water by the cellulosic fiber present in the composites.

Table 4.5 Chemical resistance of the jute fiber reinforced composites

Medium	Duration (days)	% weight gain			
		EM50/JF50	EA50/JF50	MM30/JF50	MA30/JF50
3% NaOH	2	34.5	39.9	46.0	55.6
	4	36.2	40.7	47.1	55.7
	6	34.4	40.1	47.0	53.6
	8	32.1	36.2	44.4	52.1
	10	30.4	34.1	44.3	51.7
10 % HCl	2	23.5	25.0	30.7	47.2
	4	23.6	25.6	31.6	48.9
	6	23.8	25.5	31.9	49.0
	8	23.6	24.7	32.0	46.1
	10	23.4	24.6	31.1	46.2
10 % NaCl	2	20.6	20.9	32.0	37.1
	4	21.4	22.0	32.9	39.9
	6	21.7	22.6	33.6	40.4
	8	22.3	22.8	33.7	40.6
	10	22.3	22.7	33.6	40.6



However, a loss in weight was observed after four days for the composites in NaOH solution and after six days in HCl solution. This may be possibly due to the presence of acid/ alkali hydrolyzable ether and ester groups and the presence of large number of OH groups in all the composites. Besides such irreversible reactions (chemical degradation by ester hydrolysis), the other factors responsible for this type of observation are cracking and leaching. The fiber ends and the fiber matrix interfaces provide easy routes for the cracks to grow that causes more absorption of water, whereas leaching causes decrease in weight [48].

#### 4.3.6.2. Nanocomposites

The chemical resistance results for the nanocomposites (after 10 days) are given in Table 4.6. All the nanocomposites were found to exhibit better chemical resistance in comparison to the pristine polymers in all the media. It is evident from the table that both the EM50 and EA50 based nanocomposites absorbed water to lesser extent than the pure polymers. Water molecule can easily diffuse into the amorphous region of a polymer. In nanocomposites, the introduction of crystallinity by the presence of clay layers retards the water diffusion process and hence water absorption occurs to lesser extent [45]. The poor chemical resistance of the pristine EM50 against NaOH was seen to be somewhat compensated in the nanocomposites as indicated by lower extent of loss in weight. The other media also showed better resistance to the nanocomposites. The overall improved chemical resistance of the nanocomposites may be attributed to the increase of intramolecular and intermolecular H-bonding as well as other secondary forces operating between the nanofiller and the polymer matrix and increase of diffusion path length.

Table 4.6 Chemical resistance of the nanocomposites

Medium	EM50	EM50/ NC1.0	EM50/ NC2.5	EM50/ NC5.0	EA50	EA50/ NC1.0	PUA/ NC2.5	PUA/ NC5.0
Distilled H <sub>2</sub> O	+0.11	+0.07	+0.07	+0.1	+0.21	+0.05	+0.11	+0.114
10% NaCl	-0.021	+0.0	-0.05	+0.0	-0.1	-0.037	-0.036	-0.027
5% HCl	+0.0	-0.018	-0.05	+0.0	+0.05	-0.026	+0.04	-0.1
3% NaOH	-0.19	-0.071	-0.062	+0.0	-0.1	+0.02	-0.035	+0.0

\*+ indicates weight gain and – indicates weight loss

#### 4.3.7. Water permeability study

The enhancement of barrier properties by the formation of true nanocomposite is a well established phenomenon [20]. In an attempt to study such barrier properties, extent of water vapour permeation was measured in the present investigation. Herein, it has been seen that there is a 2 to 4 fold reduction in the rate of permeability of water vapour with increase in clay loading from 1 to 5 weight % in the nanocomposites (Figure 4.11). This can be explained on the basis of tortuosity mechanism. The intercalation/ exfoliation of clay platelets in the polymer matrix offers a long tortuous path (mean free path) for the guest molecules to pass through and hence the permeation get retarded [21]. Such tortuosity gets increase with the increase of clay loading in the matrix and hence barrier properties also improved.

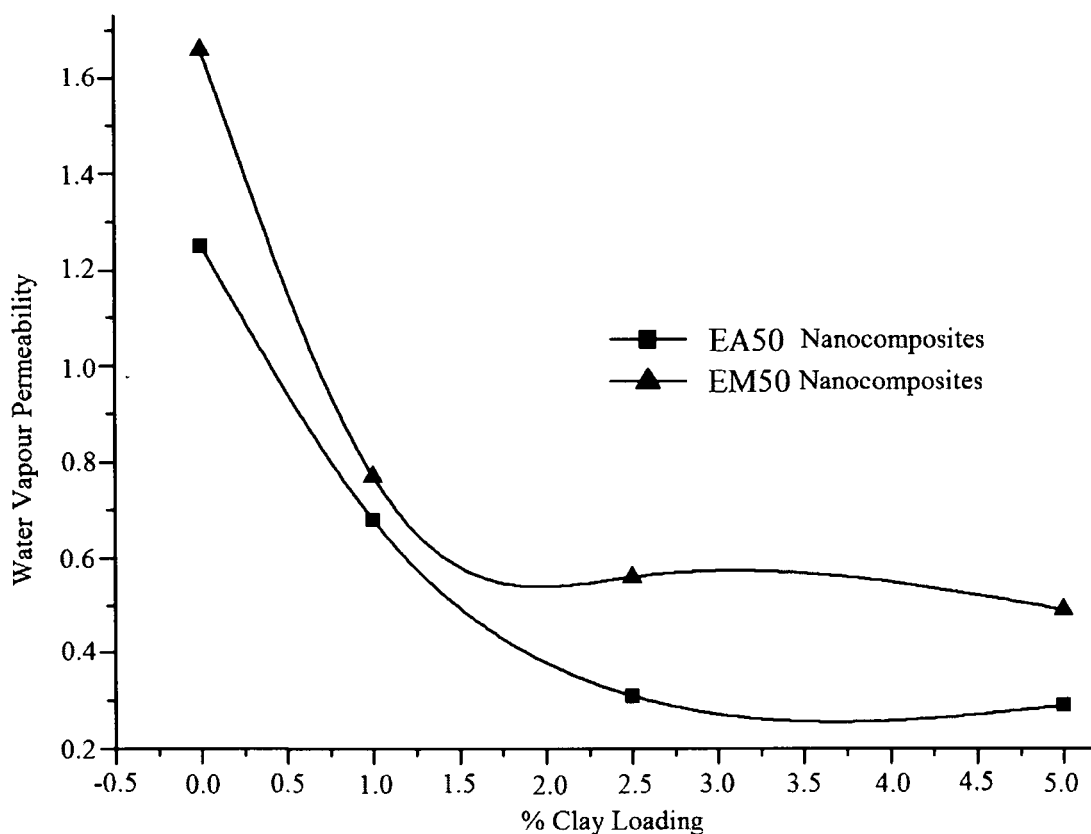


Fig. 4.11 Water vapour permeability of the nanocomposites

#### 4.4. Conclusions

From this study, it can be concluded that the performance characteristics of the *Mesua ferrea* L. seed oil modified polyurethane resins can be well enhanced by the formation of both composites and nanocomposites.

The results of jute fiber reinforced *Mesua ferrea* L. seed oil based green composites showed that composite materials with sound mechanical properties, arising from good dispersion and wetting of fibers in the polymer matrix, have been obtained. Various properties are found to be dependent on the nature of the matrix. They also possess excellent chemical resistance and hydrolytic stability in water, acid and salt solutions which can make them useful for low load bearing applications. Epoxy based composites were found to be better in all aspects than the MF based ones.

In the case of nanocomposites, organically modified nanoclay is found to be a good nanofiller in modifying epoxy based *Mesua ferrea* L. seed oil modified polyurethane (both EM and EA) resins. FTIR, XRD, SEM and TEM analyses reveal intercalation of the polymer chains by the silicate layers. The nanocomposites possess good barrier effects as can be seen from water vapour permeability measurements. All the nanocomposites exhibit tremendous improvement in performance characteristics as compared to the pristine polymers. PUE nanocomposites were found to be better in all aspects than the PUA nanocomposites.

Thus the present study concludes that cost effective and environment friendly value added composite materials with high performance characteristics can be obtained from epoxy and MF modified *Mesua ferrea* L. seed oil based polyurethanes.

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## CHAPTER 5

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### **Biodegradability of MFLSO based polyurethane blends and nanocomposites**

#### **5.1. Introduction**

With the advent of modern technologies, various brands of versatile polymeric materials have been evolved to meet need of the hour. But unfortunately, most of them are creating great environmental anxiety all over the world. This is understandable as most of the polymers are of synthetic origin and are non bio-responsive. In other words, these materials are non-biodegradable which is causing hazard to the modern society. Attempts are being encouraged in current times to develop partially or totally biodegradable polymers of semi-synthetic or bio-origin as the viable alternatives for synthetic non-biodegradable polymers [1-3]. This is obvious as polymeric materials including nanocomposites based on biodegradable polymers are going to be the forerunner polymeric materials in near future and are the next generation materials to reduce global environmental pollution [4-6]. Ample scopes are there for the end use of such biodegradable polymers as binders for paints and composites, medical, agricultural and disposable packaging materials. Further, these materials may have the potential to be used as biocompatible biomaterials [7-10].

The durability of biodegradable polymeric materials under various environmental conditions and degradability after their service life are now the essential fields of research worldwide. Since the establishment of biodegradability of polyurethanes by Ossefort and Testroet [11], a lot of research has been advanced in this connection. Polyester polyurethanes are comparatively more biodegradable as suggested by Darby and Kaplan [12]. Polyurethane is also known for its biocompatibility as reflected from various biomedical applications [7]. Another

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\*Parts of this work have been published in *Bioresource Technol*, 2009 (in press).

advantage of this type of polymer is the possibility to tailor the composition for slower or faster rates of degradation depending upon the usage conditions and their mode of disposal after use as waste into soil.

Soil burial method is a largely employed method for biodegradation study of polymeric materials due to its simplicity and similarity to real field conditions of waste disposal [3, 13-14]. However, the accuracy of the method is not in control because of the noise produced by evolution of CO<sub>2</sub> during the test [15]. Evaluation of gravimetric weight loss is a reliable evidence to estimate the extent to which degradation takes place in the buried films [16-17]. Further, measurement of loss in mechanical properties provides further information regarding biodegradation. The biodegradability of the buried films can further be analyzed by studying the changes occurring in chemical constitution and surface morphology with the aid of FTIR, TGA as well as SEM techniques. Microbial degradation by broth culture technique is another technique for biodegradation study which is more quantitative as compared to the soil burial method [18-19]. Microbial degradation of polyurethanes is being reported with a number of fungi, bacteria and enzymes [20]. The degradation is estimated from the growth count of the bacterial population on the cultured polymer. *Pseudomonas aeruginosa* is one such well-known bacterium that can degrade polyurethanes [21].

Besides biodegradability, another important prerequisite for an ideal biomaterial is cytotoxicity which is also vital from biomedical application viewpoints [10, 19]. Two methods are generally employed for estimating cytotoxicity of polymers namely the direct contact method and the MTT method [10]. However, anti-hemolytic test can be a direct evidence of non-cytotoxicity and protection power of the polymer to the cells from harmful free radicals. Red blood cells (RBC) are very much susceptible to free radical attack and lose the cell membrane integrity and heme protein comes out of the cell membranes which can be estimated [22].

Vegetable oil based polymers are expected to possess high biodegradability due to their bio-origin. They can also be chemically modified to compete and replace conventional petroleum based polymers [23]. From the previous chapters, it has been seen that *Mesua ferrea* L. seed oil modified polyurethane blends with epoxy and MF resins as well as the epoxy based polyurethane clay nanocomposites are potential polymeric materials. Thus the main objective of this chapter is to study the

biodegradability and cytotoxicity of these polymeric systems to examine their applicability as green binders for composites or as biomaterials.

## **5.2. Experimental**

### **5.2.1. Materials**

Thin films of the epoxy and MF modified *Mesua ferrea* L. seed oil based polyurethane (PUE) blends namely EM50 and MM25 were prepared and fabricated by using the methods as mentioned in experimental section of Chapter 3, sections 3.2.2.2 and 3.2.2.3 respectively.

The *Mesua ferrea* L. seed oil based polyurethane (PUE and PUA) nanocomposites films namely EM50/NC1.0, EM50/NC2.5, EM50/NC5.0, EA50/NC1.0, EA50/NC2.5 and EA50/NC5.0 were obtained as described in Chapter 4, section 4.2.2.4.

The minerals  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_3\text{BO}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{MoO}_3$  used for the bacterial broth preparation were obtained from Merck, India. The *Pseudomonas aeruginosa* strains MTCC 7815, MTCC 7814 and PN8A1, and the ingredients required for the anti-hemolytic test were obtained from the Department of Molecular Biology and Biotechnology (Department of Biotechnology, DBT Centre, Government of India), Tezpur University.

### **5.2.2. Instruments and methods**

The CHN analysis of the experimental soils used in soil burial test was done by using a CHN analyzer (Perkin Elmer model 2400, series II). FTIR spectra of the soil buried blend samples were recorded in FTIR Nicolet, Impact 410 spectrophotometer in the same manner as mentioned in the earlier chapters. The TG analysis of the biodegraded blends and nanocomposites was done by Shimadzu TG 50 thermal analyzer under identical conditions as it was done for the virgin blends (Chapter 3, section 3.2.2). The tensile strength and elongation at break of the blend samples were measured by Universal Testing Machine, Zwick Z010 using samples of dimensions 100 mm X 10 mm X (0.25-0.35) mm. The surface morphology of the microbial degraded



blends and nanocomposites were studied by using a JEOL scanning electron microscope of model JSM-6390LV SEM after platinum coating. The optical density (OD) for bacterial population during biodegradation study was measured at a wavelength of 600 nm and the percent of RBC hemolysis inhibition was calculated by measuring OD at the wavelength of 540 nm using Varian UV-visible spectrophotometer of model Cary 100 Bio, Germany.

#### 5.2.2.1. Biodegradation of the blends by soil burial method

The soil burial test was carried out using three different soils (Table 5.1) of three different locations of Assam, India (Titabar, Solmora and Tezpur University campus). The soil samples were finely powdered after properly drying under sun light for 72 h and the foreign particles were removed manually. The soils were then placed in 250 mL glass beakers followed by addition of 100 mL water. Each sample was cut into pieces of size 100 mm X 10 mm X (0.25-0.35) mm and was dried under vacuum at ca. 50 °C until constant weight was obtained. The samples were then placed into the pasty soils of the beakers. Three sets of beakers for each soil of each sample (including positive and negative controls) were taken which were planned to be removed during biodegradation test after time periods of 60, 120 and 180 days respectively.

The beakers containing the blend samples were buried in a soil bed at a depth of around 18-20 cm from the top of the ground surface. The experimental soil bed was partitioned into three principal blocks and three different sets of all samples were placed. The beakers containing samples were removed from first, second and third blocks of the soil bed after 60, 120 and 180 days respectively. Three samples were buried for each blend, positive control (gelatin film) and negative control (polypropylene film) specimens in every block to avoid irregularity in measurement. The soil burial test was carried out under ambient conditions with regular addition of water (except in rainy days). Samples were taken out carefully from each beaker and washed repeatedly with water to remove the adhered soil, plant wastes and other debris, if any, from the surface of the films. Utmost care had been taken in handling to avoid any damage or cracking of the films. The samples were finally dried at ca. 50 °C under vacuum until constant weights were obtained. The percent weight loss of the films was calculated by using the following relationship,

$$\text{Percent weight loss} = [(W_i - W_f) / W_i] \times 100 \%$$

where  $W_i$  = initial weight and  $W_f$  = final weight of the test sample.

Table 5.1 Specification of the soils

Soil Code (Location)	Ttb <sup>a</sup>	TU <sup>b</sup>	Sol <sup>c</sup>
% Carbon content	0.88	2.45	3.81
% Hydrogen content	0.22	0.21	0.04
% Nitrogen content	0.85	0.23	2.07
% Organic matter content	1.52	4.22	6.57
pH	5.7	6.5	6.6
Type	hard, silty, sandy	silty, sandy, clay	farmland, sandy

<sup>a</sup> Ttb = Titabar soil, <sup>b</sup> TU = Tezpur University Campus soil and <sup>c</sup> Sol = Solmora soil

#### 5.2.2.2. Biodegradation of the blends and nanocomposites by broth culture technique

A nutrient broth medium for culture was prepared by dissolving 2.0 g  $(\text{NH}_4)_2\text{SO}_4$ , 2.0 g  $\text{Na}_2\text{HPO}_4$ , 3.61 g  $\text{KH}_2\text{PO}_4$ , 1.75 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.2 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 50 mg  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 1 mg  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ , 50  $\mu\text{g}$   $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ , 70  $\mu\text{g}$   $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 10  $\mu\text{g}$   $\text{H}_3\text{BO}_3 \cdot 5\text{H}_2\text{O}$  and 10  $\mu\text{g}$   $\text{MoO}_3$  in 1.0 L of demineralized water. An amount of 10 mL of this liquid culture medium was poured into 100 mL conical flasks and was sterilized using autoclave at 121 °C and 15 lb pressure for 15 min. The autoclaved media were then allowed to cool down to room temperature and polymer films were applied to the media under sterile condition inside a laminar air hood. Media containing no polymer film were also cultured as negative control.

#### *Microbe selection*

Three *Pseudomonas aeruginosa* strains were selected for the study with strain number MTCC 7815, MTCC 7814 and PN8A1. Pure culture of each bacterial strain was prepared using urea as carbon source along with the mineral media that are mentioned above for a period of 48h at 37 °C. 100  $\mu\text{L}$  of the culture medium containing  $1 \times 10^8$  / mL microbes as calculated from McFarland turbidity method [24-26] was inoculated to the conical flask containing 10 mL media for each test. The flasks were

then incubated under sterile condition at 37 °C for the degradation study. The samples were collected for spectrophotometric observation at 600 nm against blank culture media on weekly basis under sterile condition. Bacterial growth was calculated from the absorbance data using McFarland turbidity as the standard.

#### *McFarland standard preparation*

In microbiology, McFarland standards are taken as a reference to adjust the turbidity of bacterial suspensions to keep the number of bacteria in a given range. It was obtained by mixing specified amounts of 1% BaCl<sub>2</sub> and 1% H<sub>2</sub>SO<sub>4</sub> solutions which creates turbidity due to the precipitation of BaSO<sub>4</sub> in the solution. Five McFarland standards were prepared by mixing solutions of BaCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> in different proportions (Table 5.2). The plot of absorbance at the wavelength of 600 nm against known population gives a straight line of the following equation,

$$y = 18.96x - 1.629$$

where 'y' is the bacterial population and 'x' is the absorbance of the cultured broth. The constants 18.96 and 1.629 are the slopes and intercepts respectively of the straight line [24-26].

Table 5.2 McFarland Nephelometer standards

McFarland Standard No.	0.5	1	2	3	4
1% BaCl <sub>2</sub> ( mL)	0.05	0.1	0.2	0.3	0.4
1% H <sub>2</sub> SO <sub>4</sub> ( mL)	9.95	9.9	9.8	9.7	9.6
Cell Density (approx. 1 X 10 <sup>8</sup> CFU/mL)*	1.5	3.0	6.0	9.0	12.0
Absorbance at 600 nm	0.132	0.257	0.451	0.582	0.669

\* CFU stands for Collony Forming Unit

#### 5.2.2.3. Cytotoxicity by anti-hemolytic test

Erythrocytes were separated from plasma and the buffy coat was washed 3 times with 5 volume of (PBS) phosphate buffer saline (pH 7.4). To collect the RBC,

centrifugation was performed at 3000g for 10 min at 25 °C. The obtained packed cells were suspended in 4 volume of PBS to perform the experiment.

The experimental blend and nanocomposite films with uniform thickness were cut to obtain 10 mg weight for each. The surfaces of all the films were sterilized under ultraviolet light for 30 min under a sterile laminar air hood.

The RBC protection assay of the films was performed using the method mentioned by Zhu et al. [22] with little modifications. In short, 2 mL of erythrocyte suspension was used to treat with 10 mg of each type of films. H<sub>2</sub>O<sub>2</sub> was added to the solution to get a total concentration of 100 µM. Gentle shaking was done while incubating at 37 °C for 90 min. 200 µL of the RBC suspension was collected at an interval of 30 min from t = 0 min to t = 90 min and diluted to 8 times using PBS solution. The samples were then centrifuged at 3000g for 5 min at 25 °C and the absorption of the supernatant liquids was measured at a wavelength of 540 nm against a PBS blank solution. The percent of inhibition was measured using the following equation,

$$\text{Percent RBC Hemolysis Inhibition} = [(A_{\text{H}_2\text{O}_2} - A_{\text{sample}}) / A_{\text{H}_2\text{O}_2}] \times 100 \%$$

### **5.3. Results and discussion**

#### ***5.3.1. Physical appearance and gravimetric weight loss of the soil buried blends***

The mode and extent of biodegradation of a polymer depend on the microbial population in a given environment, temperature, pH, humidity and the composition as well as properties of the polymeric material [27-28]. Very low carbon content of the used soils (Table 5.1) indicates that polyurethane is the sole carbon and energy source for the microorganisms under the experimental conditions. Some microorganisms present in soil are capable of rupturing ester linkages present in the polymer [11, 29]. The polymer is degraded into some volatile components (molecules) which can then be metabolised by both fungi and bacteria.

All blend samples after biodegradation were inspected for any physical change. Every sample, except the gelatin film, was found to retain its size and shape approximately. Gelatin films (positive control) were found to be disappeared completely, whereas the polypropylene films (negative control) were completely

remained intact. The surfaces of the blend films were found to be rough and uneven. Some films of MF blends got disintegrated on application of little pressure into small pieces. Observation of some splits and cracks, particularly in the films recovered after 120 and 180 days indicates biodegradation of the blends by microorganisms.

The biodegradation of the films was further confirmed through the studies of loss in weight as well as strength. Percent weight loss for the 60, 120 and 180 days buried samples of EM50 and MM25 films along with the positive and negative control specimens in all the three soils are presented in Table 5.3. The weight loss was found to be increased with the increase of degradation period. Surface erosion is one of the predominant degradation processes which is taking place through a constant surface area and hence the degradation from the planar surface area was more than the sides of the films. Moreover, according to earlier reports polyester degradation mainly proceeds through surface attack by various microorganisms present in the soils [27, 30]. Hence, ester based polyurethane (PUE) is expected to follow the same trend of degradation and thus the weight of the films decreases with time. Further, the bisphenol-A based epoxy and MF resins are well known non-degradable polymers. Thus the biodegradation rate of these blends is dependent on the composition of the non-biodegradable component present in the system. The relatively low biodegradation of MM25 films may be attributed to the rigid non-degradable triazine moiety of the MF resin. The extent of deterioration observed in the films was almost similar in all the three soils.

Table 5.3 Percent weight loss of the soil buried blend films

Sample Code	Percent Weight Loss									Extent Of Biodegradation
	After 60 days			After 120 days			After 180 days			
	Ttb	TU	Sol	Ttb	TU	Sol	Ttb	TU	Sol	
EM50	6.6	7.4	7.6	6.9	9.7	10.3	11.0	13.7	14.1	**
MM25	7.6	8.0	8.0	11.4	12.0	12.2	12.8	15.3	16.4	**
PP	0.00	0.11	0.11	0.11	0.00	0.12	0.13	0.11	0.13	*
Gelatin	100	100	100	100	100	100	100	100	100	***

\* Non-biodegradable, \*\* Semi-biodegradable and \*\*\* Biodegradable

### 5.3.2. FTIR study of the soil buried blends

FTIR study of the soil buried samples showed considerable extent of evidence in support of biodegradation. A close look at the absorption spectra of the samples, EM50 and MM25 after 60, 120 and 180 days of soil burial, a number of distinct changes have been observed (Figures 5.1 and 5.2) as compared to the spectra before biodegradation [31-32].

The first observation was in the hydrocarbon C-H stretching region at ca. 2851-2927  $\text{cm}^{-1}$ . The intensity of the band was almost unaltered in 60 days biodegraded samples, whereas it diminished gradually after 120 and 180 days of exposure. This is possibly due to the presence of some hydrocarbon degrading bacteria in the soils (more significant in Solmora soil) which degraded the samples by attacking at the hydrocarbon parts of the polymer network. The second observation dealt with the absorption band at ca. 1725-1745  $\text{cm}^{-1}$  and at ca. 1045-1065  $\text{cm}^{-1}$  which arises from ester carbonyl and ester C-O stretching vibrations respectively [33-35]. Gradual diminution in intensity of both the bands after soil burial indicated biodegradation to occur through change in polymeric structure by rupture of the ester linkages. No

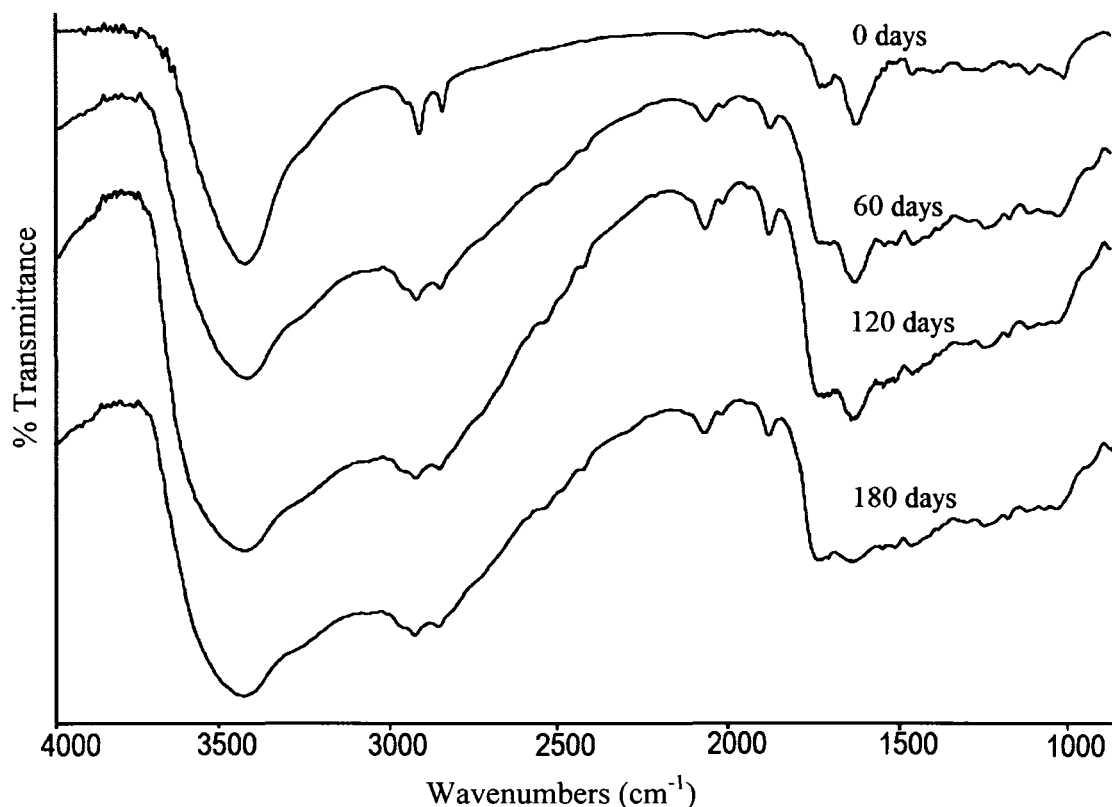


Figure 5.1 FTIR spectra of the soil (Solmora) buried EM50 blends

significant change was observed for the absorption bands at ca.  $815\text{ cm}^{-1}$  (triazine ring). In other words, there is no indication of biodegradation in this region as there is no change in the intensity of the bands. The FTIR study of the biodegraded samples leads to the conclusion that the biodegradation occurred to the blend samples is chiefly due to the reduction of ester linkages caused by some esterase microorganisms and due to the reduction of the hydrocarbon moieties caused by some hydrocarbon degrading microorganisms present in the soils [11].

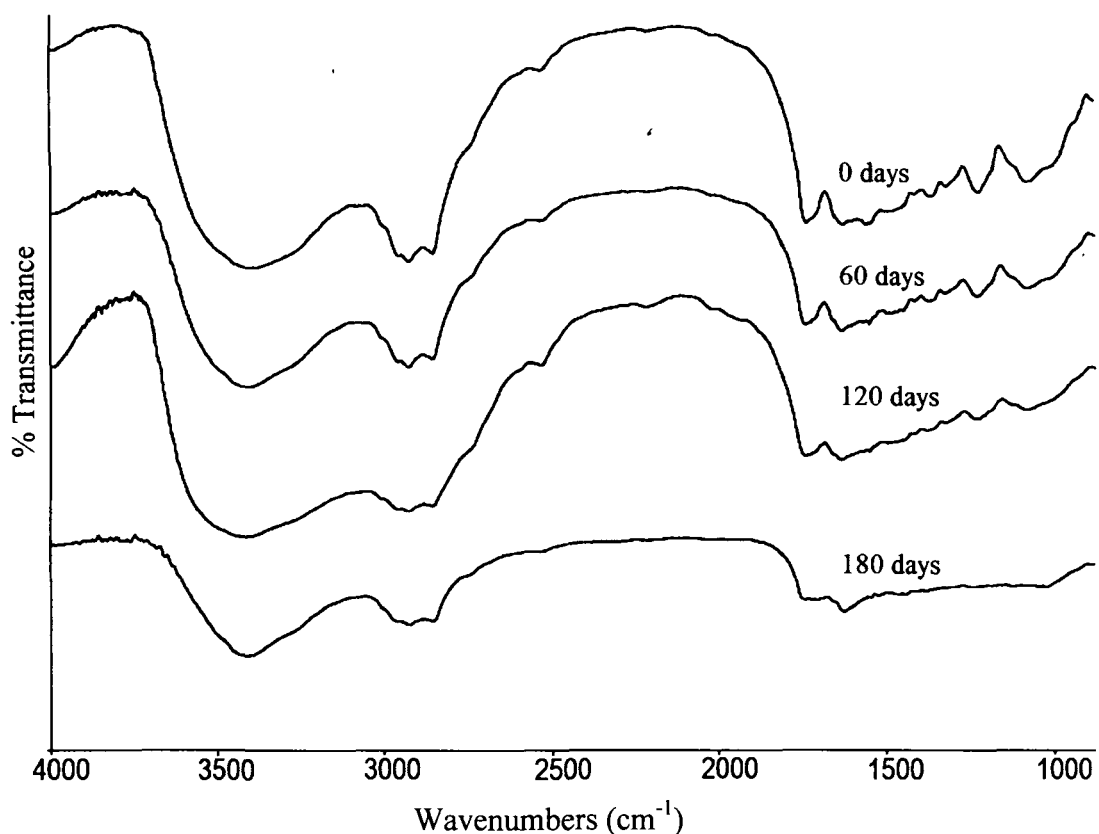


Figure 5.2 FTIR spectra of the soil (Solmora) buried MM25 blends

### 5.3.3. Morphological study of the soil buried blends

The results obtained from FTIR spectroscopic studies were also supported by SEM analyses. The smooth surface of the EM50 and MM25 blends [31-32] became rough after attack of microorganisms (Figure 5.3). The roughness of the surface for both the blends was found to be increased in the order  $60 < 120 < 180$  days biodegraded samples. Even, some pores (as seen in the form of black spots) were observed in the biodegraded samples of 120 days of exposure (Figure 5.3). This result indicates an increase in the extent of biodegradation with duration of soil burial

exposure. The rough and wrinkled texture was found to be more in EM50 than MM25 blends.

#### 5.3.4. Mechanical property measurement of the soil buried blends

The tensile strength (T.S.) of the soil buried EM50 blend films were measured and were found to be decreased with increase in soil burial exposure period in all the soils (Table 5.4). The extent of decrease in tensile strength is the highest for Solmora soil which further confirmed that the degradation is also the highest in such systems. However, in the case of MM25 blend samples in Titabar and TU campus soils, the strength initially (60 days) remains almost constant, though after 120 and 180 days of exposure the strength decreases in similar manner. However, the variation of elongation at break (E.B.) for both the blends does not follow any particular trend. For the positive control PP films, no change in strength property was observed (Table 5.4) which confirmed its non-biodegradability.

Table 5.4 Mechanical properties of the soil buried blend films

Sample Code	Property	After 60 days			After 120 days			After 180 days		
		Ttb	TU	Sol	Ttb	TU	Sol	Ttb	TU	Sol
EM40	T.S. (MPa)	22	22.2	24.4	20.0	21.1	19.5	13.2	17.7	15.6
	E. B.(%)	2.9	2.1	3.4	4.7	2.3	3.2	2.7	2.1	2.0
MM25	T.S. (MPa)	9.7	10.2	14.2	10.4	10.3	7.8	4.4	5.6	4.8
	E.B. (%)	2.6	2.9	1.2	2.0	2.8	1.0	-	2.2	0.8
PP	T.S. (MPa)	19.1	19.0	19.1	18.9	19.0	18.9	18.9	18.3	18.3
	E.B. (%)	91.9	90.9	91.8	78.4	83.4	78.6	77.2	74.0	75.2

\*Each reading is based on the average of three samples

#### 5.3.5. Thermal properties of the soil buried blends

To understand the pattern of biodegradation, TG curves obtained for the biodegraded samples were compared with the respective non-biodegraded samples [31-32]. The TG curves for both the epoxy and MF modified PUE based blends are shown in Figures 5.4 and 5.5 respectively. From the figures it has been seen that in case of the TG curves for 60, 120 and 180 days biodegraded EM50 samples, a gradual conversion



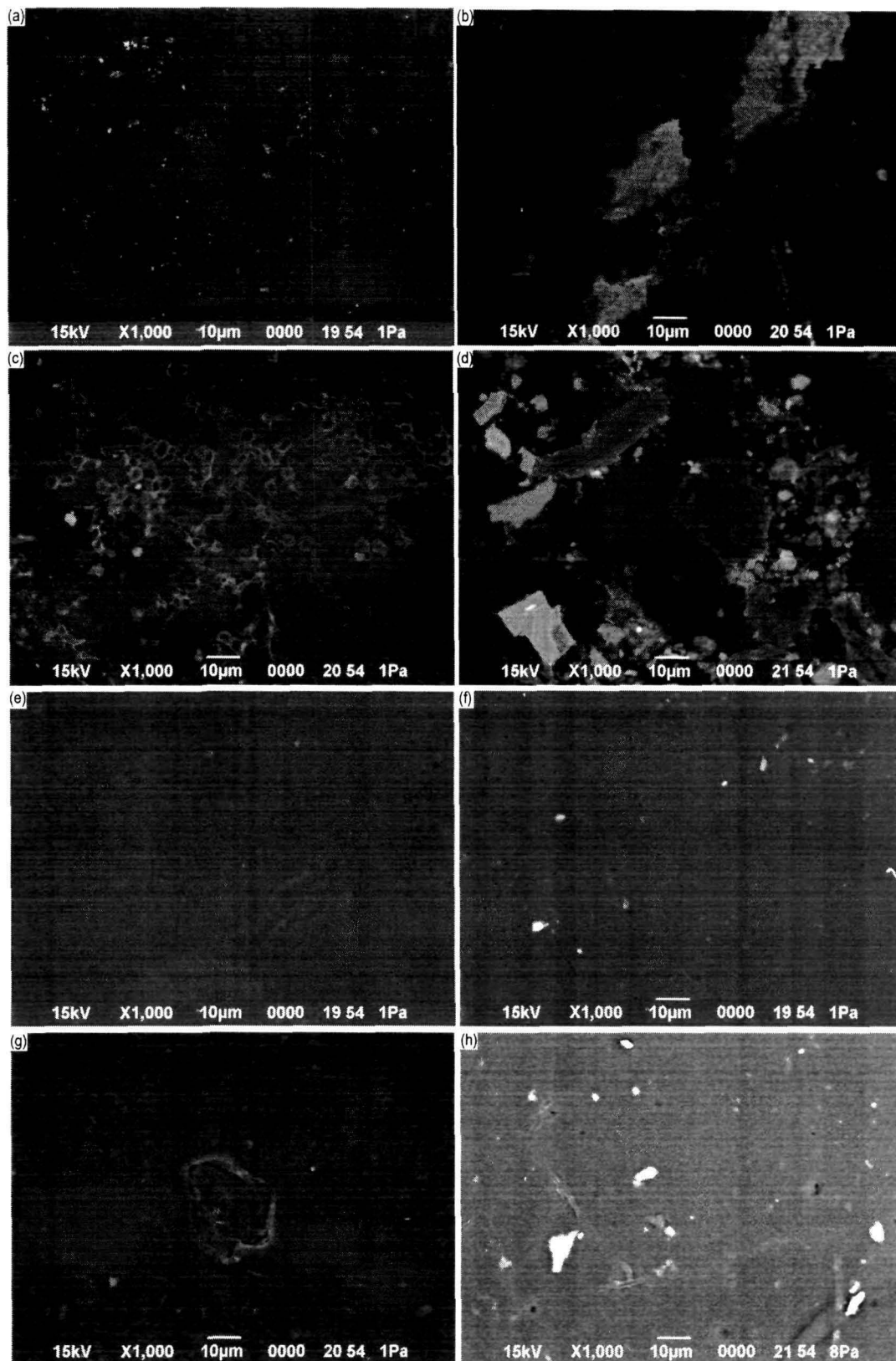


Figure 5.3 SEM micrographs of (a) non-biodegraded EM50, (b) 60 days soil biodegraded EM50, (c) 120 days soil biodegraded EM50, (d) 180 days soil biodegraded EM50, (e) non-biodegraded MM25, (f) 60 days soil biodegraded MM25, (g) 120 days soil biodegraded MM25 and (h) 180 days soil biodegraded MM25 blends (for Solmora soil only)

from two step degradation pattern to single step degradation had occurred (Figure 5.4) with the increase of exposure time of biodegradation. The second step of degradation (ca. 400-500 °C) which was proposed to be arisen from the rupture of ester or urethane linkages and aromatic moiety present in the polymer backbone in the non-biodegraded samples had gradually disappeared during biodegradation. This suggests the biodegradation of EM50 blends to occur by breaking of the ester linkages.

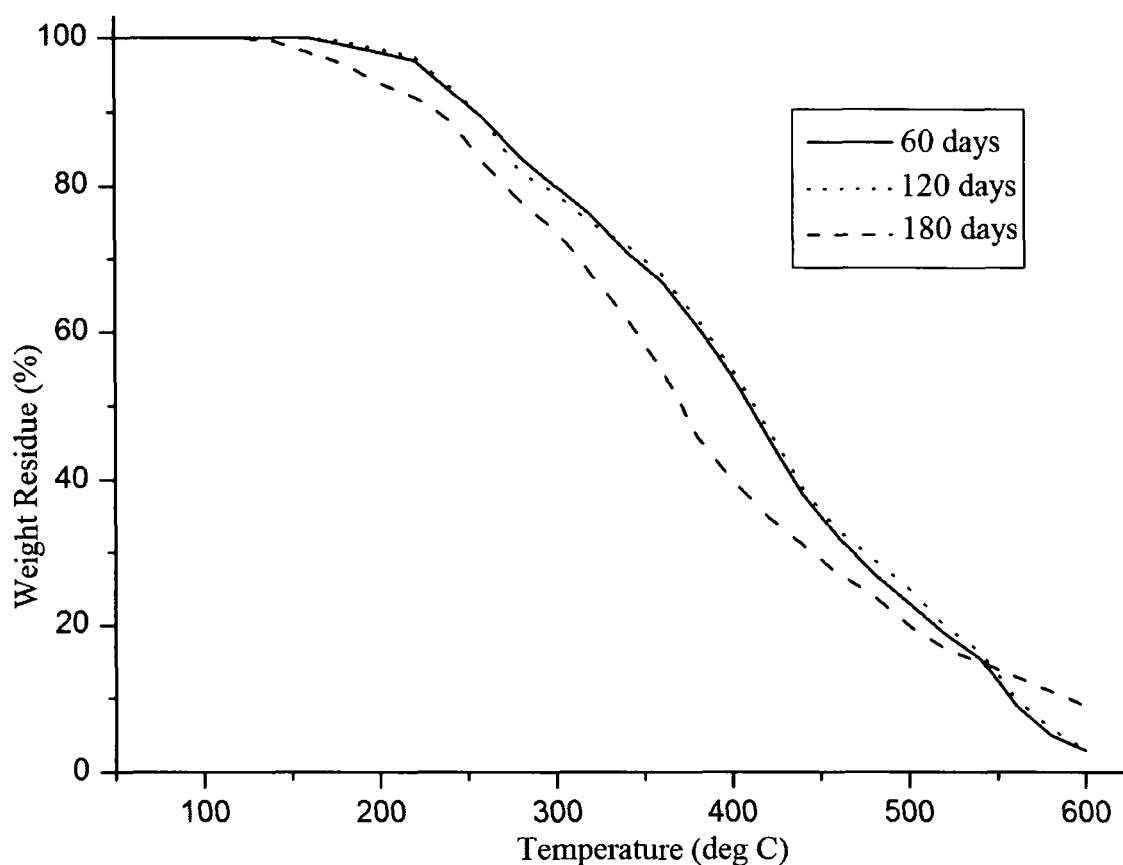


Figure 5.4 TG thermograms of soil (Solmora) buried EM50 blends

Again in case of MM25 blends also, the peak corresponding to the second step decreased gradually after biodegradation (Figure 5.5), which was more prominent in the 180 days biodegraded sample. In other words, the second step corresponding to rupture of ester links disappeared gradually as the exposure period to microorganism attack was increased from 60 to 180 days.

Thus the TG analysis revealed that one major pathway for biodegradation is ester hydrolysis. The rate of disappearance of the second step was more prominent in EM50 blends than in MM25 blends (Figures 5.4 and 5.5). This indicates the rate of

biodegradation by ester hydrolysis is more in epoxy modified *Mesua ferrea* L. seed oil based polyurethane blends than in MF modified ones.

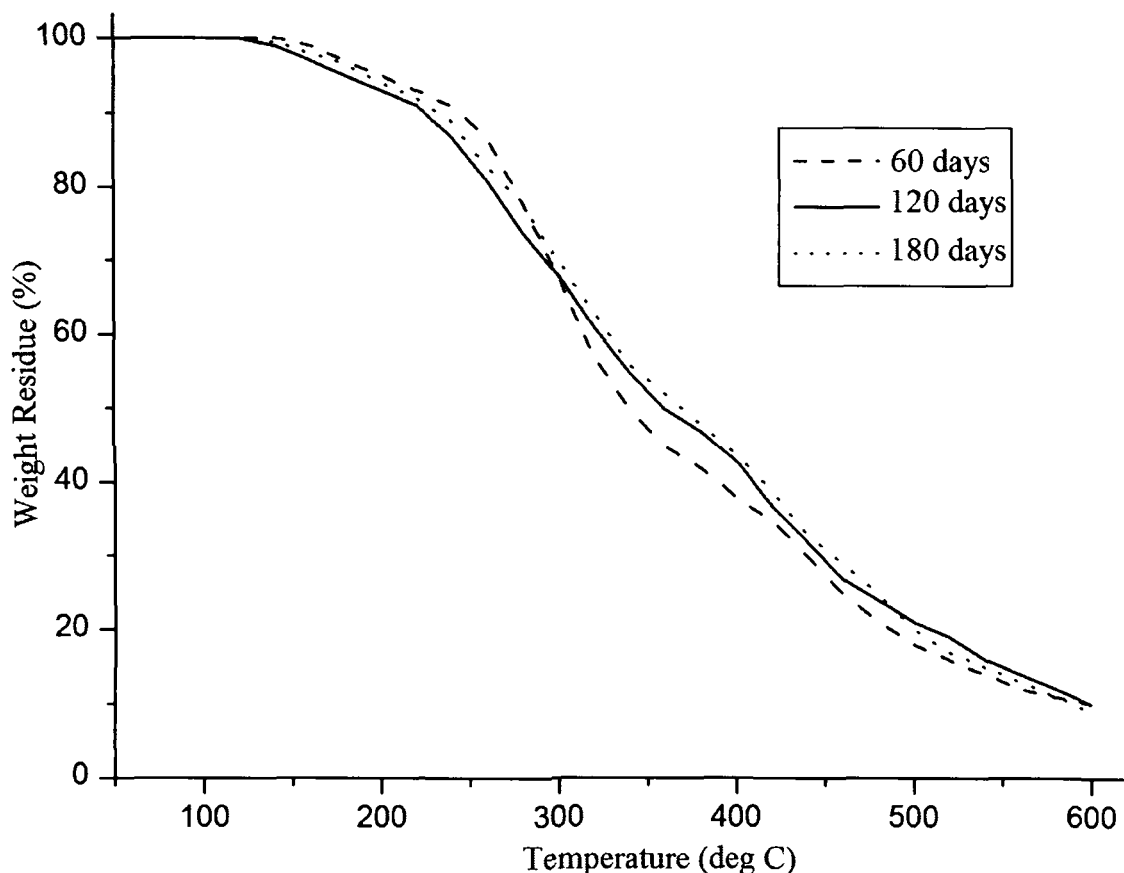


Figure 5.5 TG thermograms of soil (Solmora) buried MM25 blends

### 5.3.6. Biodegradation study of the blends by broth culture technique

After getting hints of biodegradability of the *Mesua ferrea* L. seed oil based polyurethane blends, the extent of biodegradation of the blends was further estimated conveniently via “Broth Culture Technique” by direct exposure of the films to different strains of *Pseudomonas aeruginosa* bacteria. The film samples were kept in broth culture media for 12 days and were found to be deteriorated to a large extent especially for the EM50 blends. The rate of decrease in weight was found to be a bit higher as compared to the soil buried samples. This is due to the direct exposure of the films to the microbes in the broth culture technique. The growth of bacteria on the polymeric films was found to be different for different *Pseudomonas aeruginosa* strains (Figure 5.6). This is due to difference in the microbial specificity for specific substrate. Three

bacterial strains were used in the present study namely MTCC 7814, MTCC 7815 and PN8A1. It is clear from the figure that the growth of all the bacterial strains increases with the increase of bacterial exposure time. However, the rate of growth for all the strains is more in the case of EM50 blends containing broth, as can be observed from the slopes. The calculation of the number of bacteria grown (count of bacterial population) in broth containing the films was done using McFarland turbidity method [25-26]. The scanning electron micrographs (SEM) of both the blends EM50 and MM25 (Figure 5.7) clearly hints that the EM50 blend is more biodegradable as compared to the MM25 blend.

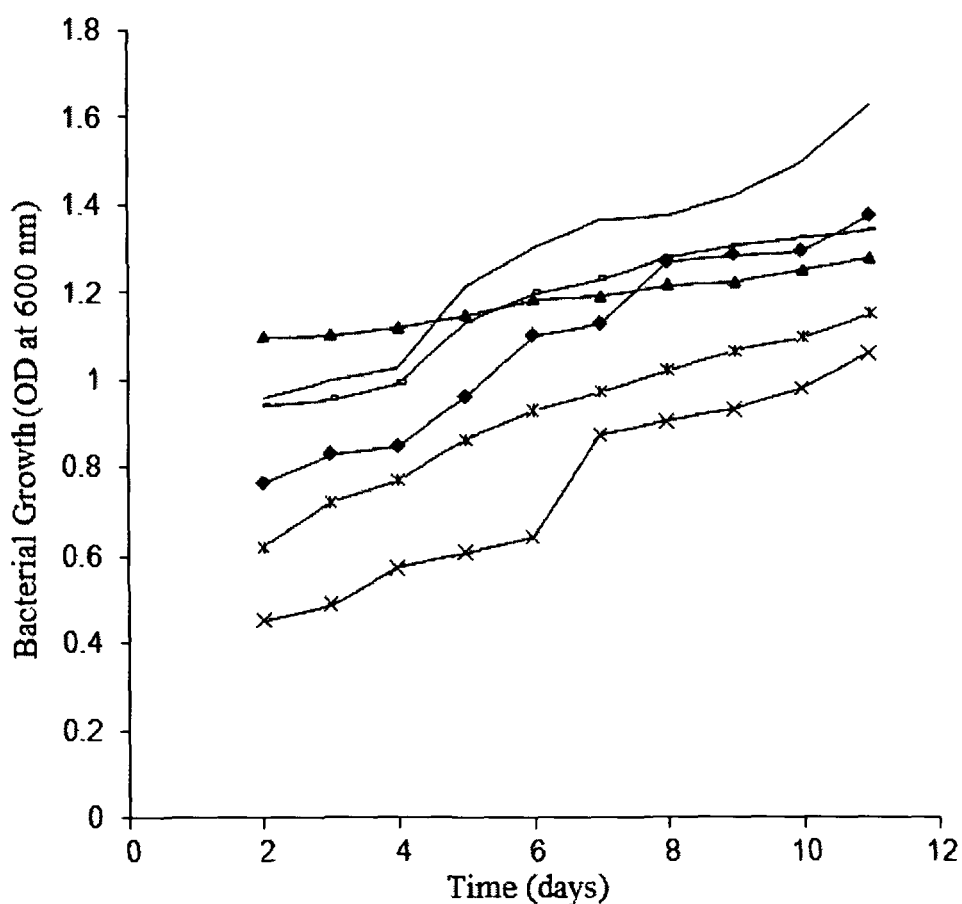


Figure 5.6 —◆— *P. aeruginosa* MTCC 7815 growth on EM50, —▲— *P. aeruginosa* MTCC 7815 growth on MM25, —×— *P. aeruginosa* MTCC 7814 growth on EM50, —⊗— *P. aeruginosa* MTCC 7814 growth on MM25, — — *P. aeruginosa* PN8A1 growth on EM50, — — *P. aeruginosa* PN8A1 growth on MM25 blends

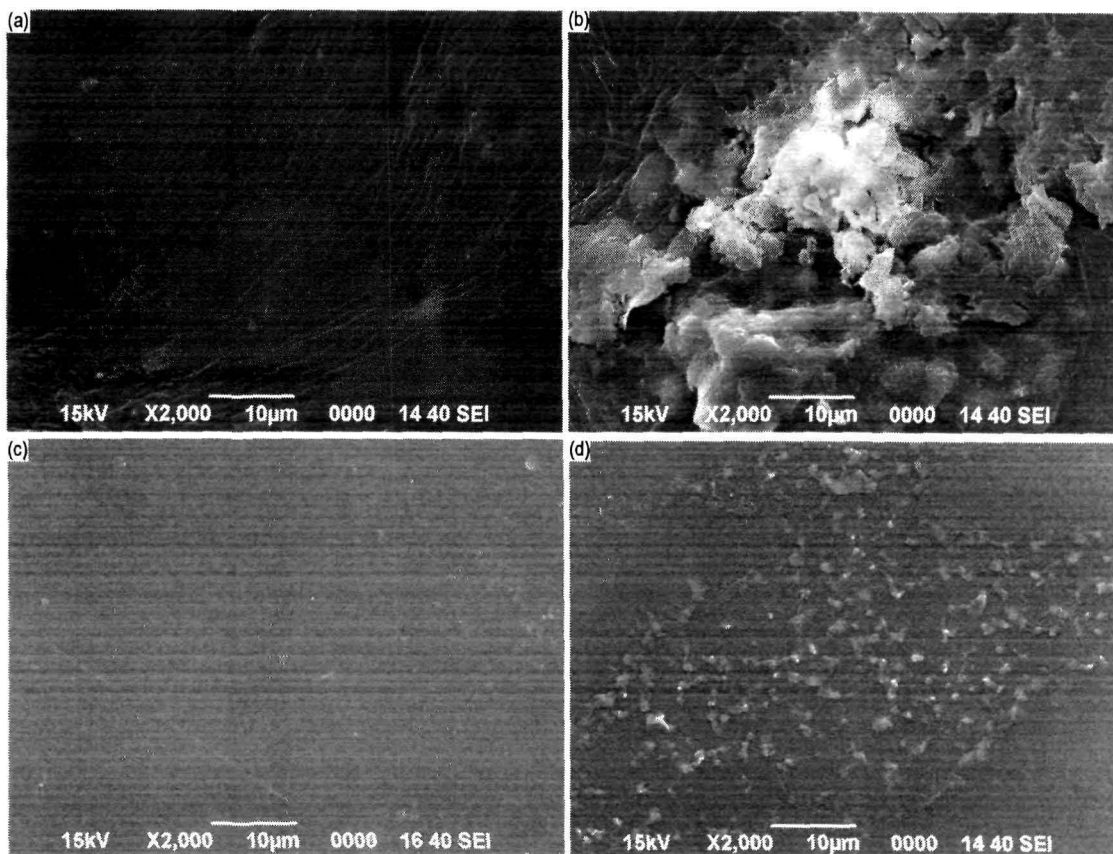


Figure 5.7 SEM micrographs of (a) non-degraded EM50, (b) *P. aeruginosa* degraded EM50, (c) non-degraded MM25 and (d) *P. aeruginosa* degraded MM25 blends

### 5.3.7. Biodegradation study of the nanocomposites by broth culture technique

A striking aspect of the polyurethane nanocomposites is their high biodegradation rate as compared to the pristine polymer particularly the polyester based ones [36-37]. The biodegradation of both the epoxy modified MFLSO based PUE and PUA (i.e., EM50 and EA50) nanocomposites were quantitatively estimated by direct exposure to three different *Pseudomonas aeruginosa* bacterial strains by broth culture technique as was done for the blends. After keeping the samples in broth culture media for six weeks, they were found to be deteriorated to a significant extent especially for the EM50 nanocomposites. Again, the rate of biodegradation was found to be higher than the corresponding pristine polymers for both EM50 and EA50 cases. The extent of growth of *Pseudomonas aeruginosa* bacterial strains MTCC 7814, MTCC 7815 and PN8A1 on various nanocomposites films as well as on the corresponding pristine polymeric films can be observed from Figures 5.8, 5.9 and 5.10 respectively.

It is evident from the figures that the growth of all the bacterial strains increases with the increase of bacterial exposure time. One key observation made from these figures is the difference in extent of growth in all the nanocomposites as well as on the pristine polymers which is not much significant up to two weeks of bacterial exposure. But after two weeks, the biodegradation rate increases remarkably as can be realized from the bacterial population data obtained by using McFarland turbidity method. This was particularly observed for the EM50 nanocomposites which may be credited to the catalytic role played by the clay in hydrolyzing the ester groups. The presence of unreacted terminal hydroxyl groups in the clay layers can cause heterogeneous hydrolysis after absorbing water in the presence of microbes. This process is known to take some time for initiation [37] which might be the reason for tremendous improvement of biodegradation only after two weeks in the present study. The process caused severe damage to almost all the nanocomposites which could be observed from the SEM micrographs of the recovered nanocomposite films after six weeks of bacterial exposure (Figure 5.11).

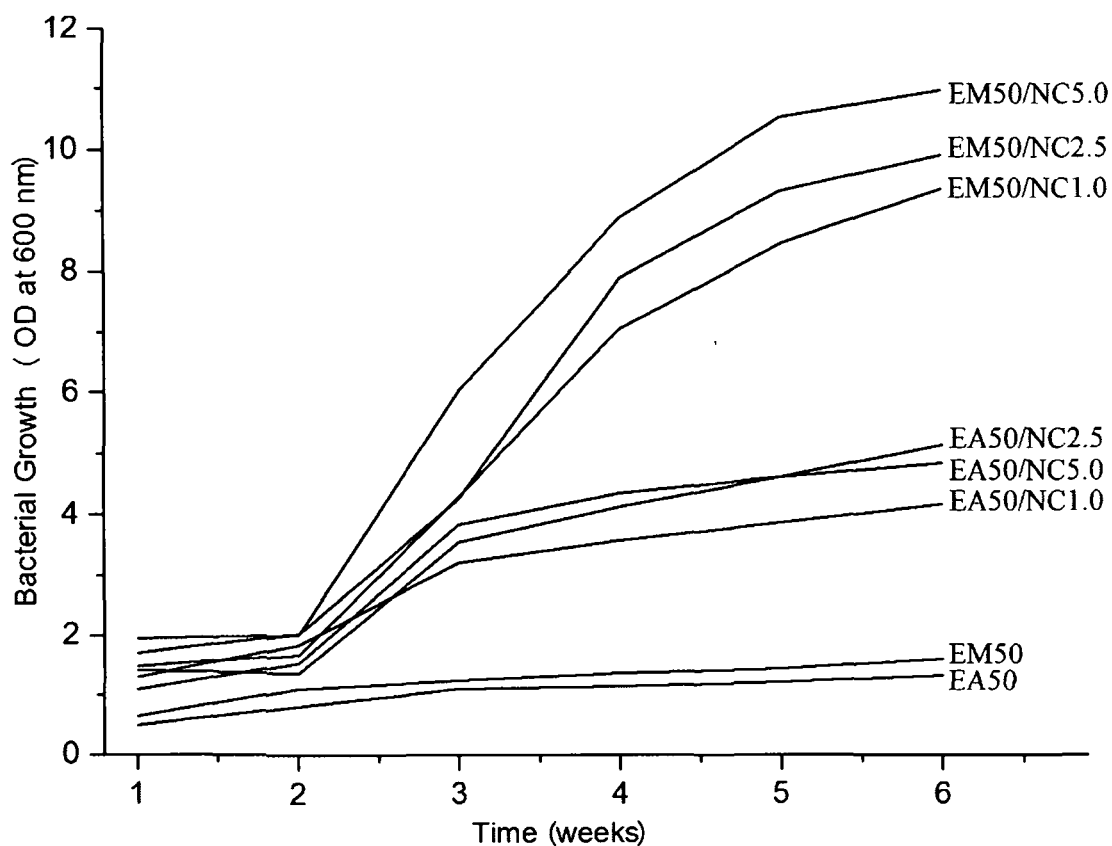


Figure 5.8 Growth of *Pseudomonas aeruginosa* bacterial strain MTCC 7814 on nanocomposites and pristine polymers

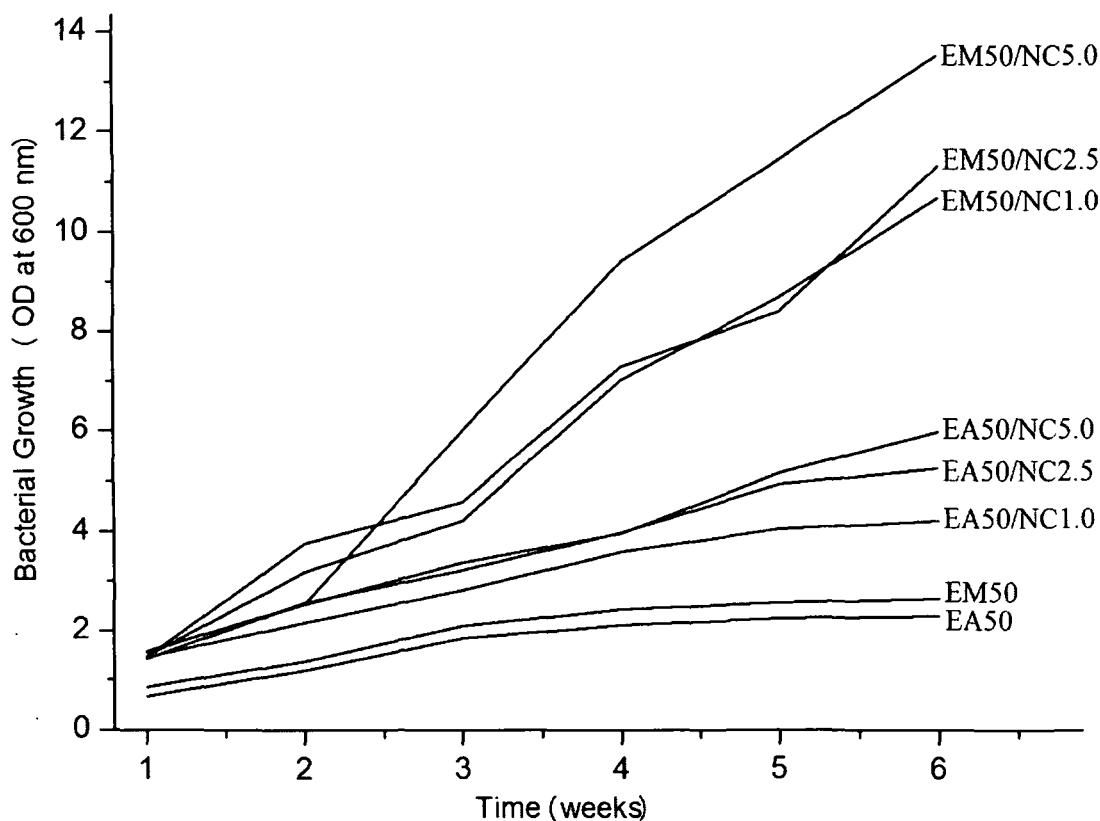


Figure 5.9 Growth of *Pseudomonas aeruginosa* bacterial strain MTCC 7815 on nanocomposites and pristine polymers

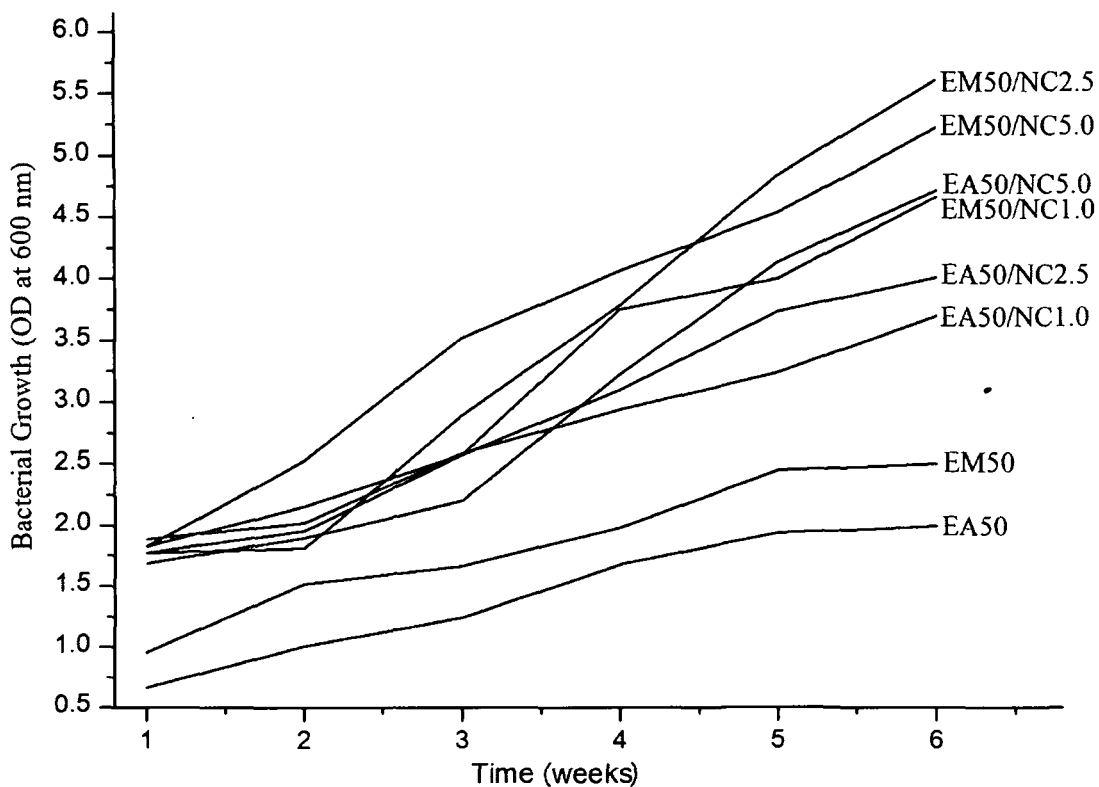


Figure 5.10 Growth of *Pseudomonas aeruginosa* bacterial strain PN8A1 on nanocomposites and pristine polymers

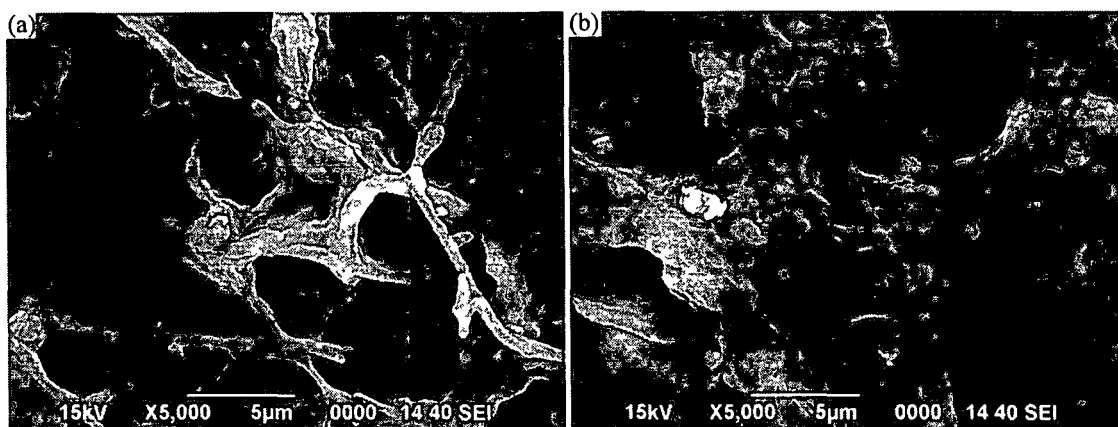


Figure 5.11 SEM micrographs of the biodegraded nanocomposites (a) EM50/NC2.5 and (b) EA50/NC2.5

### 5.3.8. Cytotoxicity assay by anti-hemolytic test

The RBC hemolysis inhibition data obtained from the anti-hemolytic test carried out in time intervals of 0, 30, 60 and 90 min for all the nanocomposites and virgin films (blends) (Figure 5.12) showed overall non-cytotoxicity.

It is evident from this Figure 5.12 that the nanocomposite EA50/NC1.0 showed the highest and constant hemolysis prevention from detrimental free radicals. The EM50/NC1.0 on the other hand was found to be more efficient in preventing hemolysis after time interval of 30 and 60 min of observation but a decline in inhibition was observed after 90 min as compared to EA50/NC1.0. The hemolysis prevention capacity of the EM50 and EA50 nanocomposites decreased gradually with time which might be attributed to saturation after reacting with free radicals [22]. Both the virgin EM50 and EA50 films showed less RBC hemolysis prevention capacity in the assay. Such observations indicate that presence of clay layers in the nanocomposites definitely plays a crucial role in RBC hemolysis prevention. Again, a close look at the plots for different nanocomposites shows that the hemolysis prevention and hence non-cytotoxicity increases with decrease in clay loading from 5 to 1 weight % in both the EM50 and EA50 based systems. Thus the cytotoxic assay indicates epoxy modified PUE and PUA based nanocomposites to possess capability of hemolysis prevention from harmful free radicals. It can be concluded from the anti-hemolytic study that the nanocomposites are not only non-toxic to the living cells but they are also able to prevent the cells from the attack of harmful free radicals.



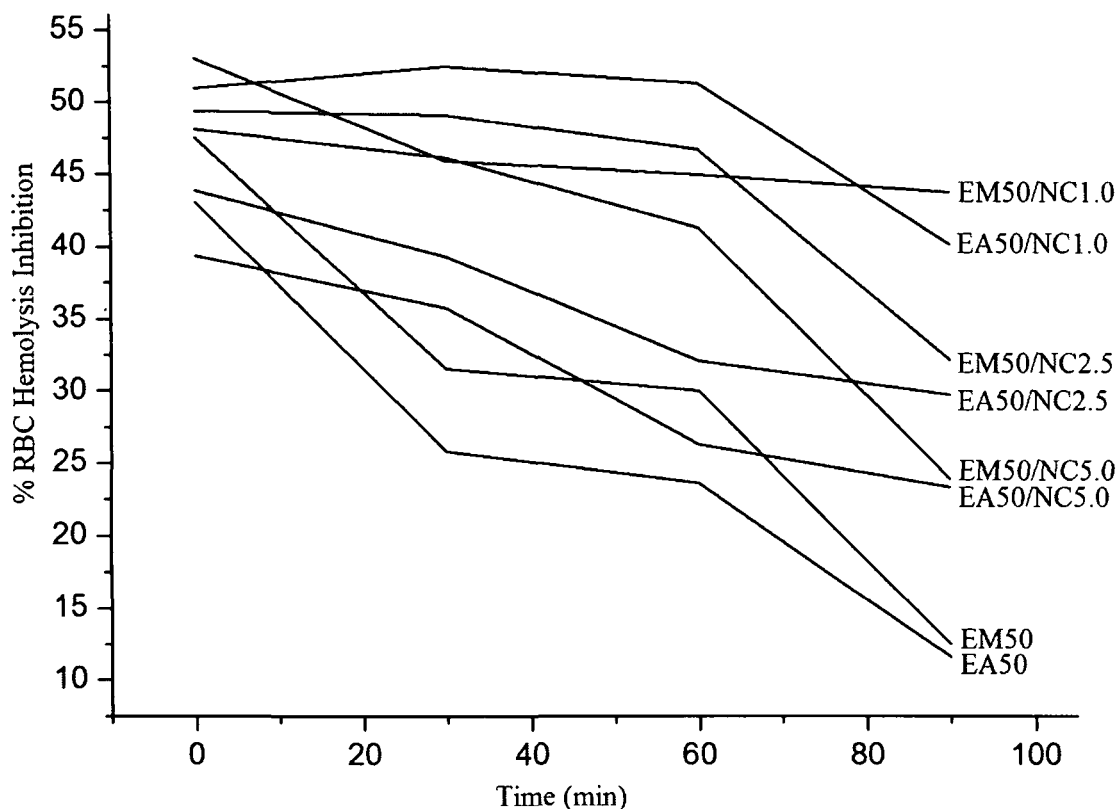


Figure 5.12 RBC hemolysis inhibition of the pristine polymers and nanocomposites

#### 5.4. Conclusions

From the present study, it can be concluded that the epoxy modified polyurethane blend, EM50 and the MF modified polyurethane blend, MM25 derived from a sustainable resource, *Mesua ferrea* L. seed oil (MFLSO) exhibit considerable amount of biodegradation as signified from both soil burial and broth culture test methods. The study further predicts the EM50 blend to be more biodegradable than the MM25 blend. The biodegradation of the polymeric blends were realized from the increase in percent weight loss of the films and decrease in mechanical properties with time in the soil burial method and increase in the extent of growth of *Pseudomonas aeruginosa* bacterial strains on the polymeric films with time in the broth culture technique. The comparison of the TG curves, FTIR spectra as well as SEM micrographs of the biodegraded EM50 and MM25 with the non-biodegraded virgin blends further demonstrates biodegradation and predicts the chief mechanism behind biodegradation assay to be the rupture of ester linkages.

*Mesua ferrea* L. seed oil based EM50 and EA50 modified clay nanocomposites are found to be more biodegradable than the pristine polymers as reflected from the

broth culture technique. The rate of biodegradation was found to be a little higher for the EM50 nanocomposites than the EA50 ones. All the nanocomposites have been found to fulfill the requisites as potential biomaterials. Furthermore, they are biocompatible as can be seen from their biodegradation by *Pseudomonas aeruginosa* bacterial strains during the biodegradation experiment. The better biocompatibility is also reflected from the non-cytotoxicity test results. Thus from the present study, it can be concluded that the MFLSO based polyurethane nanocomposites have incredible prospect to be utilized as biomaterials.

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## CHAPTER 6

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### Application of MFLSO based polyurethanes in industrial paints

#### 6.1. Introduction

Paints and coatings are industrial products used for protecting objects from destructive corrosion and for providing desired aesthetical properties (color and gloss) to the material [1-2]. Further, they are of vital importance in the protection of materials against environmental influences (moisture, radiation, biological deterioration etc.) or damage from mechanical and chemical origin for both interior and exterior applications. In the prehistoric era, peoples used to decorate their caves by painting with natural paints [3]. However, after the introduction of cheap mineral oil, the use of natural resources in paints and coatings declined gradually [4-5]. But the depleting petroleum based feedstock and growing environmental concerns have driven consumers to use eco-friendly paints and coatings in all swings since last few years.

The prime component of paint is the binder, which is generally a natural or synthetic resin, vegetable oil, natural protein or fat etc. They are mainly responsible to form a thin continuous film and adhere to various components in the paint system [4-5]. The binder along with solvent system is often called vehicle. In addition, modern paints consist of some other components [3, 6] such as dispersing agents, wetting agents, viscosity controlling agents, anti-settling agents, anti-skinning agents, antioxidants, antifoaming agents, adhesion promoters, desiccants, driers, biocides, light stabilizers, etc. [7-8]. The basic properties of a paint for instance drying, gloss, durability, flexibility, adhesion, scratch resistance, abrasion resistance and chemical resistance depend mainly on the nature and composition of the binder, though some minor

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\*Parts of this work have been published in *Prog Org Coat*, **2009**, 65, 131.

\*This work has been appreciated in *Mater Today*, **2009**, 12 (5), 11.

variations can also be made by manipulating the composition of other components in the paint. Pigment provides required aesthetic appearance i.e., color and hiding to the paint, protects the paint from ultra-violet (UV) light and corrosion and can also increase elasticity, hardness and abrasion resistance [9]. The efficacy of a pigment depends on its particle size distribution and the dispersion in the binder system.[10]. The ease of processing and wetting of pigment can be facilitated by reducing the viscosity through introduction of proper solvent system. The solvent system may either be a single solvent or be a mixture of solvents and the system should be sufficiently volatile so that no trace of it remains after finishing stage of the paint. ‘

Among various existing binder systems, polyester polyol based polyurethane resins are to be worth mentioned as they are dominating the market owing to their excellent performance versatility. They possess excellent gloss, corrosion resistance, abrasion resistance, scratch resistance, chemical resistance, flexibility and UV durability. Polyurethanes, in particular, have found immense number of applications in high performance coatings for the automotive, appliance and wood industries [1, 11]. The blends of *Mesua ferrea* L. seed oil based polyurethanes with commercially available bisphenol-A based epoxy resin [12] and partially butylated MF resin [13] were found to exhibit satisfactory performance characteristics as surface coating materials (as discussed in chapter 3). Further, epoxy resins are known to provide durable coatings with high mechanical strength and good adhesion to most of the substrates [7, 10, 14]. Paints based on polyester combined with MF resin are also known as highly durable [15-16]. Thus blends of polyurethane resin with MF resin are also expected to possess similar characteristics.

In this chapter, *Mesua ferrea* L. seed oil based polyurethane blends with epoxy and MF resins were utilized separately as binder material for industrial stoving paints. The performance characteristics of the resulting paints were compared with industrially used similar type of stoving paints (standard paint) obtained from castor oil based resin.

## **6.2. Experimental**

### **6.2.1. Materials**

*Mesua ferrea* L. seeds were utilized for isolation of oil and the oil was purified as described in Chapter 2, section 2.2.1.

The resin poly(urethane ester) (PUE) of *Mesua ferrea* L. seed oil was obtained as per the earlier reported method [17] (Chapter 2, section 2.2.2.1).

Other materials related to paint formulations such as titanium dioxide, MF resin, epoxy resin, n-butanol, baryte, silica, solvent CIX and UF resin were all of commercial grade and were obtained from Shalimar Paints India Ltd., Kolkata. The technical specifications of partially butylated MF resin and bisphenol-A based epoxy resin have already been mentioned in Chapter 3, section 3.2.1.

### **6.2.2. Instruments and methods**

The TG analysis of the cured paint samples was done by Shimadzu TG 50, thermal analyzer under the nitrogen flow rate of 30 mL/min at the heating rate of 10 °C/min from 50 to 600 °C. The surface morphology of the paints was studied by using a JEOL scanning electron microscope of model JSM-6390LV SEM after platinum coating on the surface of the samples.

The physical properties like viscosity, specific gravity and non-volatile content of *Mesua ferrea* L. seed oil based PUE/MF and PUE/epoxy paints (test paints) along with the standard paints were measured using the standard IS methods [18-20]. The fineness of the grounded particles during paint preparation was checked using Hegman Gauge (Sheen Instrument Ltd., UK). The performance characteristics of all the paints were evaluated by determining scratch hardness [21], flexibility, adhesion [22] and gloss [23] as per the ASTM methods. The tests for corrosion resistance [24], salt spray resistance [25] and UV exposure resistance [26] were also performed using the standard IS methods.

The thin films of all the paint samples were prepared by following the same procedure as was mentioned in Chapter 3, section 3.2.2.4. The thickness of the coated paint films was measured by Pentest, coating thickness gauge (model 1117, Sheen Instrument Ltd., U.K.) and were found to be in the range of 30-35 µm.

#### **6.2.2.1. Preparation of paints**

The formulations utilized for preparing the standard as well as the test paints are given in Table 6.1.

Table 6.1 Formulation of test and standard paints

Ingredients	PUE/epoxy Paint	PUE/MF Paint	Function
TiO <sub>2</sub>	10	24	White inert pigment with high opacity and tint resistance
Baryte	12	-	Acts as fillers and imparts physical reinforcement to the paint film
Silica	15	-	Acts as filler used to control viscosity of any solvent based paint
Epoxy	20	-	Important binder to impart chemical resistance, adhesion and hardness to the paint film
PUE/ Standard resin	18	46	Binder
Xylene	16	7	As a polar solvent for polar binder system
n-Butanol	8	5	As a polar solvent for polar binder system
UF resin	1	-	Acts as flow promoter
MF resin	-	16	As a cross-linking resin for stoving paint
Solvent CIX	-	2	As a polar solvent for good flow property to the paint system

\*All data are in weight percent

Both the polyurethane test paints (MF and epoxy based) were prepared in two different porcelain ball mills using butylated MF and epoxy based polyurethane resins respectively as binders in the grinding stage (Scheme 6.1). Firstly, the pigment (titanium dioxide), extenders, respective resins and around 20% of solvent were charged in the ball mill. The grinding of the pigments and extenders was done for around 18 h to attain the grinding particle sizes of 10 micron, as measured by Hegman Gauge. After reaching the required grinding size, the ingredients were dropped into some containers and mixed with polyurethane ester (PUE) resin and finally adjusted with remaining solvents and other additives to achieve application viscosity of paint [80-100 s in FC4 (Ford cup) at 30 °C]. Finally the mixture solution was kept for 24 h for sufficient wetting before panel preparation for further study.



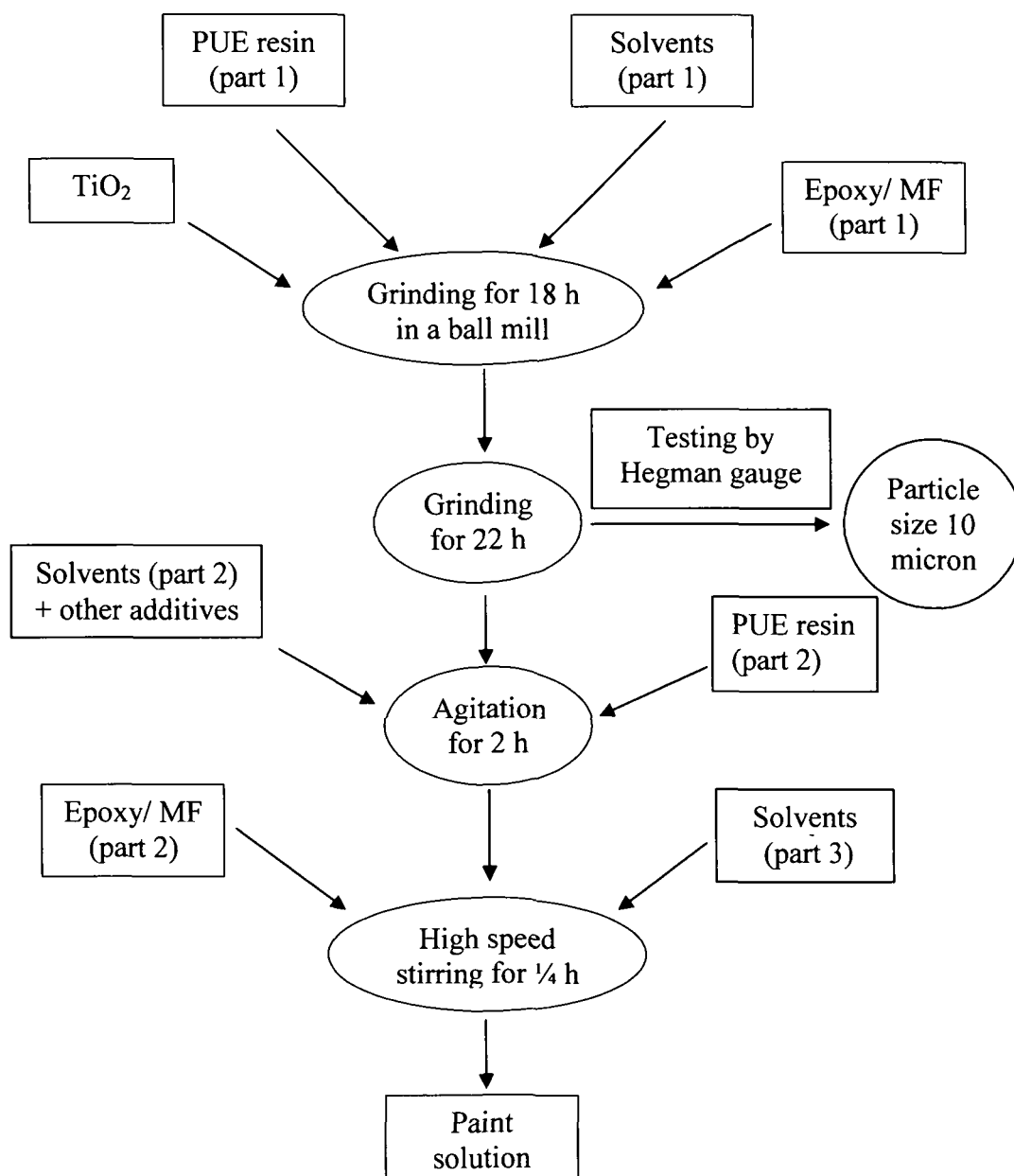
#### 6.2.2.2. Preparation of test panels

The prepared paints were subjected to dilution of 46% solid content by adding xylene as the solvent. Then panels of mild steel (150 mm X 100 mm X 1.25 mm) free from surface imperfections were made ready by removing the excess oil and by roughly degreasing the surface with petroleum hydrocarbon to avoid any embedding emery in the surface. The paint solution was then sprayed with the help of a spray gun from a distance of 15-20 inches on the mild steel plates placed on spray booth. After the preparation of the panels, they were kept in open air for 10 min followed by drying in an oven at 150 °C for 30 min.

### 6.3. Results and discussion

#### 6.3.1. *Paint preparation*

The blends of MFLSO based PUE resin with MF resin (70:30 weight ratio) and with epoxy resin (50:50 weight ratio) were found to exhibit optimum performance characteristics as discussed in Chapter 3. Hence, these blend formulations were utilized as binder systems to prepare the stoving paints and to evaluate their performance characteristics. The pigment particles generally exist in the form of clusters or aggregates. Hence disintegration is required in order to cause proper dispersion of the pigment particles into the paint medium. During paint preparation, pigment particles were grounded along with other additives in a vehicle to cause fine dispersion [27]. The grinding process was continued until the dispersion reached acceptable range for the paints as tested by Hegman gauge (particle sizes of 10 micron). A stable dispersion was then obtained by the process of wetting of the dispersed phase in the binder medium. High speed stirring was performed finally in order to cause dispersion occurring with additional vehicle to get the final stoving paint with optimum level of performance characteristics [28]. The whole process of paint preparation is shown in Scheme 6.1.



Scheme 6.1 Preparation of paints

### 6.3.2. Physical properties

Various physical properties like viscosity, specific gravity and non-volatile content were determined for all the paint samples (Table 6.2). The viscosity of the PUE/epoxy test paint was found to be little higher as compared to the corresponding standard paint, whereas the viscosity of the PUE/MF tests paint was found to be little lower than the corresponding standard paint. However, the viscosity values are well acceptable to the paint industries. Other physical properties of the test paints were

found to be comparable with the standard paints. These results indicate that both the test paints possess the required physical properties for paint application.

Table 6.2 Physical properties of the paints

Properties	PUE/Epoxy Test Paint	Epoxy Standard Paint	PUE/MF Test Paint	MF Standard Paint
Viscosity (s at 30 °C)	36	32	36	40
Specific gravity	1.28	1.30	1.21	1.18
NVC* (weight %)	65.6	65.3	61.04	56.75

\*Non-volatile content

### 6.3.3. Performance characteristics

The performance characteristics determined for all the paints are given in Table 6.3. The drying times of the test paints particularly the PUE/epoxy paint are comparable to the respective standard paints and hence can attract the customers. Pot life of a paint is the time up to which it remains stable without any phase separation in the stored container for a particular period of time. Both the test paints as well as the standard paints possess pot life more than 4 months without loss of homogeneity indicating their excellent storage availability. This is due to their low skinning tendency (skinning tendency is the formation of gel which initiates at the surface of the binder or resin i.e., in contact with the external atmosphere due to cross-linking caused by oxidation of the polymer) and appropriate viscosity of the binder systems. The gloss of the *Mesua ferrea* L. seed oil based paints is found to be comparable to that of the industrially used paints. This good light reflecting property of the paints is due to the surface smoothness of the binder systems [29-30]. Panels with uniformly coated paint were fastened and bent over conical mandrels of different radii. All the samples tested for flexibility passed the bending test successfully for the rod of 6.25 mm diameter without any crack in the bent films. This is mainly due to the flexibility of the films which is a characteristic feature of vegetable oil based poly(urethane ester). The high flexibility of the paints is due to the flexible hydrocarbon chains present in the fatty acids and the ether linkages arising from the cross condensation reactions between the free hydroxyl groups of the polyurethane resin and the MF or epoxy resins [12-13], in

addition to the other possible self condensation reactions. It is these hydroxyl groups and the ether linkages present in the binder systems of the paints which is responsible for the high adhesion of the test paints. Besides such covalent crosslinks, there are possibilities of some pseudo crosslinks resulting from hydrogen bonding between urethane groups of PUE, methylol groups of MF and epoxy groups which are also responsible for improved adhesion. At low levels of stress, the hydrogen bonding remains intact, whereas at higher stress levels the hydrogen bonding is no more effective permitting extension without the breakage of covalent crosslinks. The hydrogen bonds again reform when the stress is released. The scratch hardness determined for the test paints are found to be lower than the standard paints. This may be due to the lower degree of cross-linking density of the test paint than the standard paint. However the values determined are sufficiently high to satisfy the requirements for applications as stoving paints.

The protective properties of the paints against corrosion were determined by exposing them to various chemical environments for specified exposure times. Both the standard paints were resistant to corrosion up to 96 h, whereas the test paints were found to be resistant up to 48 h as indicated by color fading. The corrosion resistance test is important as it reflects the actual field performance of the paints. Initial damage of the paint is indicated by color fading which is mainly due to the attack of moisture through oxidation or rust formation on the metal surface [8]. Although the corrosion resistance is found to be somewhat lower for the test paints than the corresponding standard paints, this data is sufficient to fulfill the service requirement for stoving paint applications.

The salt spray test evaluates the resistance of the paint samples to the corrosive chemical environments. The test panels were kept in the environment of corrosive chemicals such as moisture, NaCl etc. All the test and standard paints were found to possess excellent salt spray resistance of greater than 15 days. Such good chemical resistance of the paints is due to the low degree of penetration of the corrosive chemicals through the paint films. The strong three dimensional network and the presence of rigid aromatic as well as triazine moieties in the network prevent the chemicals to pass through the paint films. Almost similar results for all the four paints may be credited to maturation, which causes the same extent of dimensional stability [8]. Regarding UV resistance as observed after exposure of eight days, very low

reduction in gloss (ca. 20-25%) was observed for all the paints. The films remain intact for PUE/epoxy paint which indicates their stability towards harmful UV rays. However, for the PUE/MF test paint, the film cracks and brittles after eight days. This is possibly due to the presence of aromatic rigid triazine moiety in the network of the binder system. Thus the PUE/epoxy based test paint is more efficient than the PUE/MF based test paint towards UV exposure.

Table 6.3 Performance characteristics of the paints

Properties	PUE/Epoxy Test Paint	Epoxy Standard Paint	PUE/MF Test Paint	MF Standard Paint
Touch free time* (min)	20	12	5	5
Hand drying time* (min)	150	120	30	30
Curing time*	7 days	7 days	35 min	35 min
Pot life (months)	> 4	> 4	> 4	> 4
Scratch hardness (g)	500	1500	800	800
Flexibility (6.25 mm)	passed	passed	passed	passed
Gloss (at 60 <sup>0</sup> )	62	65	60	75
Salt spray resistance (days)	> 15	> 15	> 15	> 15
Corrosion resistance (h)	48 (color fade)	96 (color fade)	48	96
UV resistance (8 days, Gloss reduction)	up to 25% (film intact)	up to 22% (film intact)	up to 20% (film brittles)	no change (film intact)

\* Room temperature for PUE/Epoxy paints and 150 deg C for PUE/MF paints

#### 6.3.4. Thermal properties

The thermogravimetric analysis (TGA) (Figure 6.1) showed two step degradation patterns for all the paints. It is evident from Figure 6.1 that the test as well as the standard paints is thermally stable up to ca. 250 °C and the overall thermostability of the test paints are comparable to that of the standard paints. Further,

50% decomposition for all the paints occurred at ca. 330-420 °C, whereas 90% decomposition occurred at ca. 500 °C for MF modified PUE based stoving paint and at temperatures above 600 °C for epoxy modified PUE based stoving paint. Again, the percent of weight residue left for the test paints were found to be comparable to that of the corresponding standard paints. Among the two test paints, the amount of weight residue was higher for PUE/epoxy based test paint (ca. 15% at 600 °C). Such remarkable thermostability is due to the various thermostable units present in the binder system [12-13].

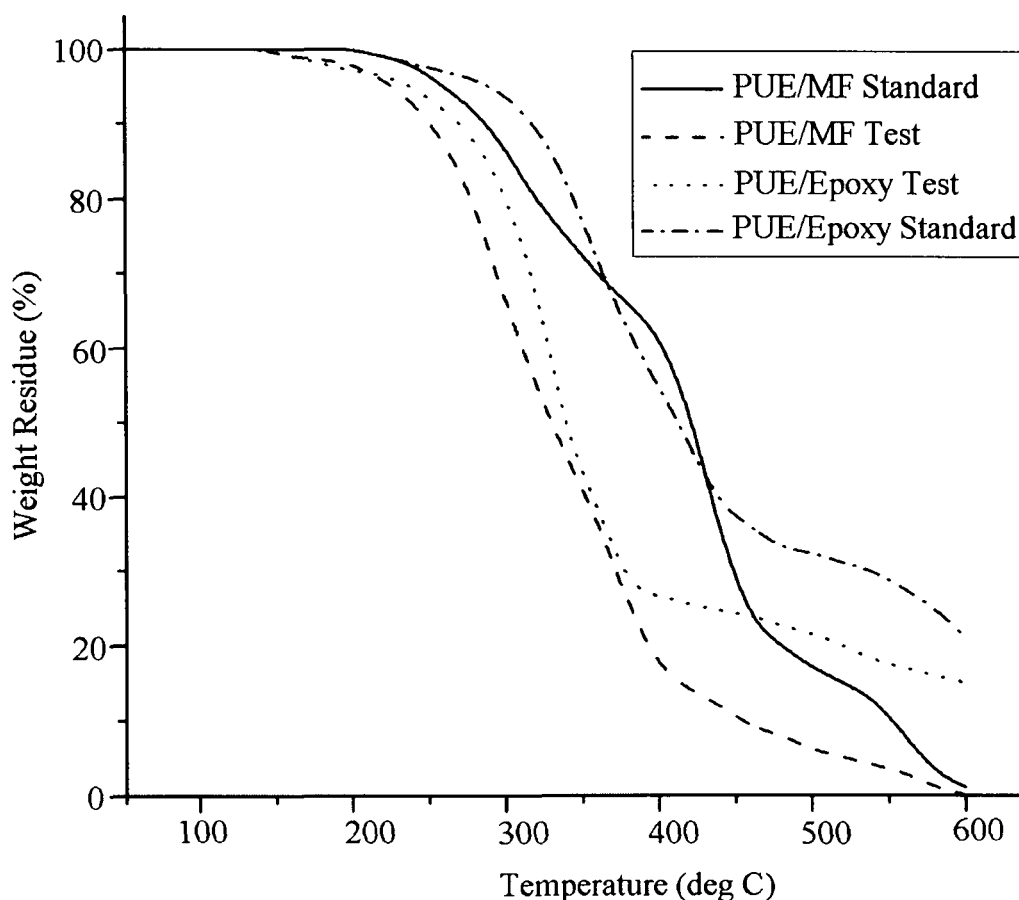


Figure 6.1 TG thermograms of the paints

### 6.3.5. Morphological properties

The scanning electron micrographs (SEM) of the test and standard paints are shown in Figure 6.2. It is evident from the figure that the uniformity in distribution of the dispersed phase inside the matrix of the PUE/epoxy test paints is comparable to that of the corresponding standard paints. There is no observable phase separation in any of

the paints indicating their stability (high pot life). The morphology of the paint films actually depends on the nature and composition of the binder system, rate of evaporation of the solvent and viscosity of the system [9, 12-13]. The good compatibility of the blend components makes the domain size of the dispersed phase of the paints very small. Moreover, the dispersed phases get broken in smaller sizes into the matrix by applying high mechanical stress during ball milling.

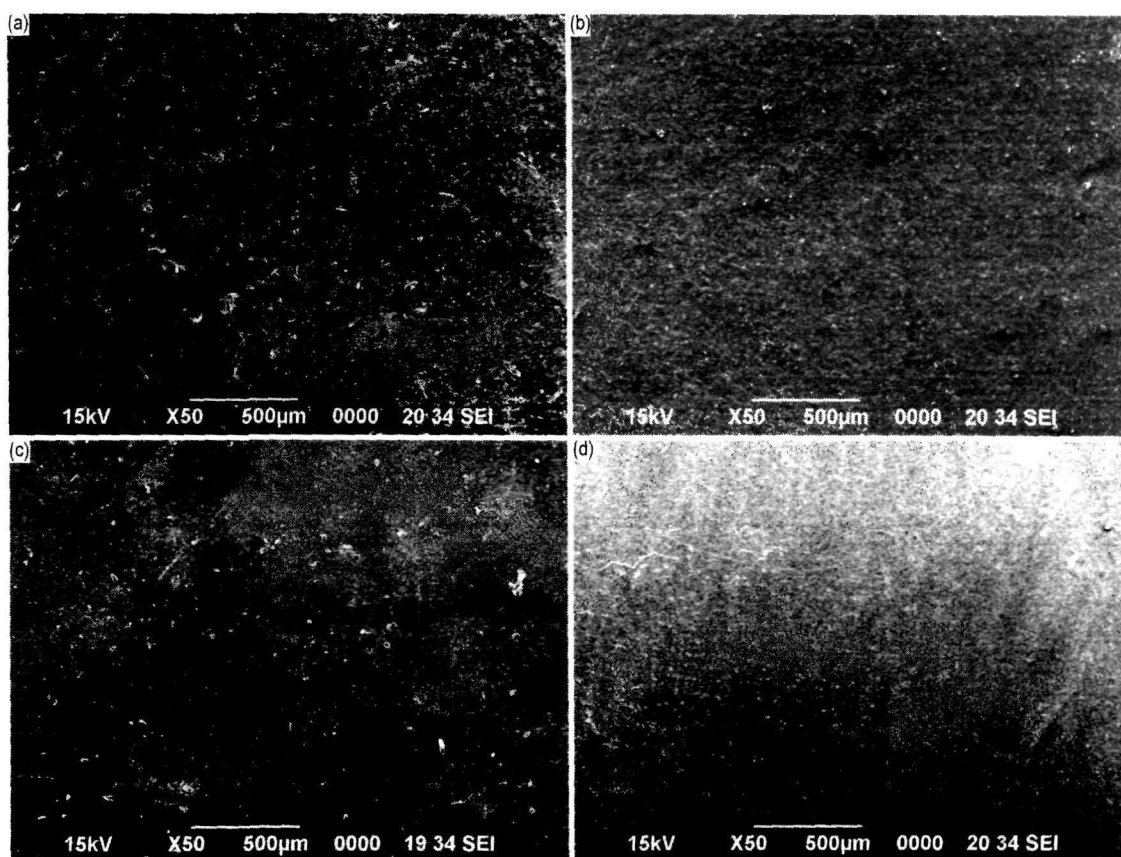


Figure 6.2 SEM micrographs of (a) PUE/Epoxy Test, (b) PUE/Epoxy Standard, (c) PUE/MF Test and (d) PUE/MF Standard paints

#### 6.4. Conclusions

From the present study, it can be concluded that *Mesua ferrea* L. seed oil (MFLSO) based polyurethane resins in combination with commercially available partially butylated MF and bisphenol-A based epoxy resins can be used successfully as green binders for the preparation of industrial stoving paints. Various parameters that reflect the performance characteristics of the test paints are found to be comparable with the standard industrial paints. Among the two test paints, the PUE/epoxy based one is seem to be more effective than the PUE/MF based paint as far as performance

characteristics are concerned. Furthermore, they are highly durable as reflected from their superb resistance towards various chemicals, corrosion and ultraviolet light. The study reveals their perspectives for successful utilization as high performance stoving paints in the automotive, appliance and wood industries. Higher pot life, lower cost involved in the raw materials and less environmental hazardness are the three key factors that can make the *Mesua ferrea* L. seed oil based polyurethane paints more versatile to magnetize consumers.



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## CHAPTER 7

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### Conclusions and Future Scope

#### 7.1 Summary and conclusions

The present thesis reports the work on synthesis, characterization, properties evaluation and application of *Mesua ferrea* L. seed oil based polyurethane resins. The first chapter of the thesis highlights a brief review on vegetable oil based polyurethanes including the importance, general techniques of preparation, characterization, properties and application. The whole technical work of the present investigation is divided into five different parts.

In the first part, the synthesis, characterization and properties evaluation of two *Mesua ferrea* L. seed oil based polyurethane (PU) resins, poly(urethane ester) (PUE) and poly(urethane amide) (PUA) with varying NCO/OH ratio were described.

In the second part, the enhancement of coating performance characteristics of the PUE and PUA resins (NCO/OH ratio = 0.5) by blending with commercially available bisphenol-A based epoxy resin and with partially butylated melamine-formaldehyde (MF) resin at different weight ratios were reported.

The third part of the technical work dealt with preparation, characterization and evaluation of performance characteristics of the epoxy and MF modified *Mesua ferrea* L. seed oil based polyurethane composites reinforced with jute fiber and nanocomposites reinforced with bentonite nanoclay.

A description regarding the biodegradation of the aforementioned *Mesua ferrea* L. seed oil based polyurethane blends and nanocomposites by soil burial and broth culture techniques was made in the fourth part of the work.

The final part of the technical work is on utilization of the *Mesua ferrea* L. seed oil based polyurethane resins as binder materials for the preparation of two industrial stoving paints.

From the present investigation, following conclusions have been drawn

- i) A highly potential non-edible vegetable oil, *Mesua ferrea* L. seed oil was successfully utilized for the first time to prepare industrially important polyurethane resins.
- ii) The synthesized polyurethanes were characterized successfully by the conventional analytical and spectroscopic techniques.
- iii) Blending with commercially available epoxy or melamine-formaldehyde resin significantly improved the film properties especially thermal stability and chemical resistance of *Mesua ferrea* L. seed oil based polyurethane resins. The blend at 50:50 ratio of PUE resin to epoxy resin and the blend at 75:25 ratio of PUE resin to MF resin showed optimum performance.
- iv) Formation of both conventional composites as well as nanocomposites caused tremendous improvement in performance characteristics of the resins.
- v) Biodegradability and cytotoxicity studies of the *Mesua ferrea* L. seed oil based resins and nanocomposites showed their potentiality as biomaterials.
- vi) The *Mesua ferrea* L. seed oil based polyurethane resins were used for the first time to investigate the viability of commercial utilization as binders for industrial stoving paints. The performance characteristics of the test paints were found to be comparable with the corresponding industrially used standard castor oil based stoving paints. Among the two tested paints, the PUE/epoxy based one had seen to be more effective in terms of performance characteristics than the PUE/MF based paint.

Thus the overall major achievement of the present investigation is the successful utilization of a less significant renewable raw material to industrially important products of great significance.

## 7.2 Future scope

There are some future scopes of *Mesua ferrea* L. seed oil based polyurethane resins to be worth mentioned for further studies.

- i) Study on the nature and extent of H-bonding in the polyurethane resins and their variation with NCO/OH ratio by using different spectroscopic techniques to understand the structure-property relationship, comprehensively.
- ii) Development of water borne polyurethane resins.
- iii) Development of polyurethane resins with versatile structures and compositions by inter-esterification of *Mesua ferrea* L. seed oil with other commercially useful vegetable oils.
- iv) Investigation of polyurethane resins as binders for flame retardant and metal insulating coating materials.
- v) Evaluation of *Mesua ferrea* L. seed oil based polyurethane nanocomposites for different biomedical applications.

## List of Publications

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11. Karak N., Deka H. and **Dutta S.** "Vegetable oil based hyperbranched and conventional resinous polyurethane/ clay thermosetting nanocomposites", **2009** (communicated).

12. **Dutta S.** and Karak N. “Past, present and future of vegetable oil based polyurethanes as surface coating materials”, **2009** (ready for communication).

***Papers published as conference proceedings (Conference presentations)***

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