

**Designing and Development of Surface Functionalised Fly Ash
Reinforced Polyurethane and Epoxy Composites for Bulk
Utilization**

A Thesis

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University of Kota, Kota

By

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Under the Supervision of

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2019

CERTIFICATE

I feel great pleasure in certifying that the thesis entitled **“Designing and Development of Surface Functionalised Fly Ash Reinforced Polyurethane and Epoxy Composites for Bulk Utilization”** is submitted by **Ankit Sharma** under my guidance.

He has completed the following requirements as per Ph.D. regulation of the University.

- (a) Course work as per the University rules.
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Declaration

I, hereby, certify that the work, which is being presented in the thesis, entitled **“Designing and Development of Surface Functionalised Fly Ash Reinforced Polyurethane and Epoxy Composites for Bulk Utilization”** in partial fulfillment of their requirement for the award of the Degree of Doctor of Philosophy, carried under the supervision of Prof. Ashu Rani and submitted to the Department of Pure and Applied Chemistry University of Kota, Kota represents my ideas in my own words and where others ideas or words have been included, I have adequately cited and referenced the original sources. The work presented in this thesis has not been submitted elsewhere for the award of any other degree or diploma from any Institutions.

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“No one who achieves success does so without the help of others. The wise and confident acknowledge this help with gratitude.” – Alfred North Whitehead

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(ANKITSHARMA)

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ABBREVIATION	FULL FORM
PU	Polyurethanes
CRA	Curing agent
IR	Index ratio
EB	Electron beam
UV	Ultra violet
BPA	Bis – phenol A
TGIC	Triglycidyl isocyanurate
HTAPPO	Hexaglycidyl tris (m-amino) phosphine oxide
TGEPPPO	1,1',1''-Tris (m-phenoxy) phosphine oxide
Tg	Glass transition temperature
Tm	Melting point
EP	Epoxy polymeric
PUM	Polyurethane matrix
FA-r-PUC	FA reinforced Polyurethane composite
PEG	Polyethylene Glycol
CE	Chain extender/ binder
TDI	Toluene 2,4 diisocyanate
BD	1,4- butanediol
TMP	1,1,1-trimethylol propane
CLA	Cross linking agent
EPM	Epoxy matrix
FA-r-EPC	FA reinforced epoxy composites
EPC	Epoxy composites
DGEBA	DiglycidylEther of bis phenol A (IUPAC) 2-[[4-[2-4-(oxiran-2-ylmethoxy)phenyl]propan-2-yl]phenoxy] methyl] oxirane
TETA	Tetra ethyl tetra amine
FA- r-EPC	FA reinforced epoxy composites

FTIR	Fourier Transform Infrared Spectroscopy
FTIR-ATR	Fourier Transform Infrared Spectroscopy -Attenuated total reflection,
XRD	X-Ray Diffractometer
SEM	Scanning Electron Microscopy
UTM	Universal testing machine
F_m	Force maximum
TS	Tensile Strength
YM	Young Modulus
DSC	Differential Scanning Calorimetry
FA	Fly ash
RAFA	Raw Fly Ash
MAFA	Mechanically Activated Fly Ash
TAFA	Thermally Activated Fly Ash
CAFA	Chemically Activated Fly ash
HTPB	Hydroxyl terminated polybutadiene
HS	Hard segment
SS	Soft segment
PU_s	Polyurethane system
ASTM	American standard testing methods
MPa	Mega pascal
GPa	Gega pascal
PUC	Polyurethane composites
SF-FA-r-PUC	Surface functionalized fly ash reinforced polyurethane composites
CLFA	Calcined fly ash
UCFA	Uncalcined fly ash
CL-PUC	Calcined fly ash reinforced polyurethane composites
UC-PUC	Uncalcined fly ash reinforced polyurethane composites

T-PUC	Thermally activated fly ash reinforced polyurethane composites
R-PUC	Raw fly ash reinforced polyurethane composites
SF-FA-r-PUC	Surface functionalized fly ash reinforced polyurethane composites
PUM-A	Polyurethane matrix having BD: TMP:: 2:1
PUM-B	Polyurethane matrix having BD:TMP::1:2
R- EPC	Raw fly ash reinforced epoxy composites
CL- EPC	Calcined fly ash reinforced epoxy composites
UC- EPC	Uncalcined fly ash reinforced epoxy composites
T- EPC	Thermally activated fly ash reinforced epoxy composites
M-EPC	Mechanically activated fly ash reinforced epoxy composites

Chapter 1

The Perspective

ABSTRACT

Present chapter gives review of polymer components and matrices based on polyurethane and epoxy systems, the mechanistic course of reactions involved thereof, brief description of additives like surfactants, catalysts etc. Various polyols and epoxy resins with their curing components viz. isocyanates and amines, different types of fillers used for designing epoxy and polyurethane based composites are briefly discussed. The chapter significantly illustrates the need of developments in the synthesis and applications of polymeric composites, scope and objectives of the present research work.

In the present era, polymer chemistry is the branch of chemistry, which has created innovative integrated research fields in concurrence with the nano technology, material science, bio technology, etc, when the scientific involvement has resulted in the improve performances of the conventional polymeric products over the integrated polymeric composites, the focus of the scientific research is shifted towards the develop the composites of the desired properties for applications in a cost effective way of the formulation and evolution of the improved polymeric materials in almost every field of life has started using organic/inorganic hybrids where inorganic components of the composites are the fillers which govern the mechanical properties viz. surface smoothness, polymeric shrinkage and biocompatibility. Fillers from nano size to micron size their counter parts , different micro structures, shapes and amounts as well are developed [1,2] . The coupling of the fillers with the resin matrix governs the material performance. A large number of studies have been reported earlier for development of innovative polymeric composites or reinforced materials having different mechanical, thermal and physical properties using kaolin, organo clay silicates, nanocomposites, micro silica [3-5] etc, FA filler introduction are some common filler used by the previous researchers for developing PU and epoxy composites. Literature survey revealed that researchers have focused more on the variations of binders, curing agents and chain extenders rather than modifying the surface of the filler for improved interaction with the matrix, for designing the desired properties in a cost effective manner. The present research envisages the surface fictionalization of one of the low cost filler i.e fly ash (FA) widely used by the researchers for designing of the polymeric composites in bulk applications. FA is a solid waste material generated in huge amounts all over the world during coal burning process. Thermal power plants are generating tons of FA in India. Its main consumption remains in developing the cementitious materials, Zeolites, bricks,

landfill material, absorption materials etc. Its applications in FA reinforced polymeric materials are restricted due to unavailability of the desired FA for the requisite mechanical or thermal behaviour of the materials. During the present work, FA is activated for the surface modification for desired fictionalization and used as filler in two different PU and epoxy systems for comparing the effect of different types of polymeric systems.

Polyurethanes and epoxy are the class of polymers which are being used as a core matrix material and are important as are curable in ambient conditions and used as two component adhesives , sealants, insulators, backing materials[6] etc. Designing and development of innovative material as fillers is of utmost need of the present polymeric composites to reduce the cost of manufacturing and increase the strength with versatile applications.

The chapter 1 includes the basics and mechanistic aspects of polyurethane and epoxy synthesis using different raw materials, additives, catalyst, curing agents and fillers, the chapter also gives the objectives and importance of the present research work.

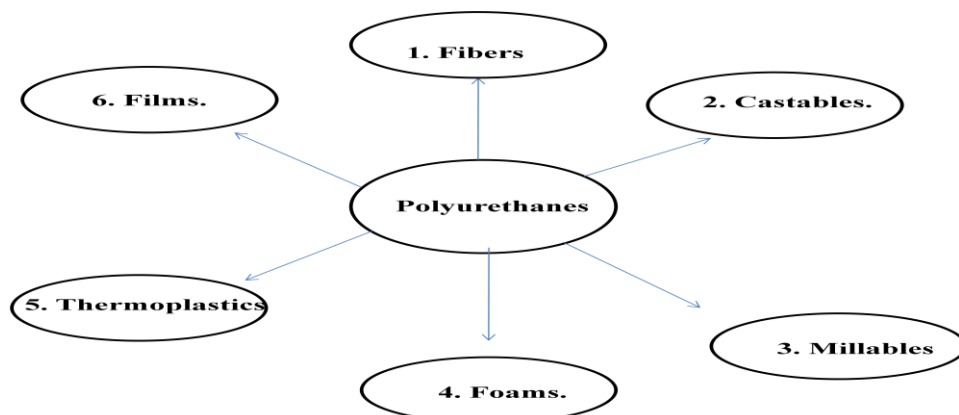
1.1 Polyurethane System

Polyurethanes (PU) are synthetic macromolecules made of organic units joined by carbamate (urethane) links , and are formed when polyols (binders) containing two or more hydroxyl groups per molecule reacts with two or more isocyanates group containing molecules called as the curing agent(CRA). The reaction between CRA and polyols is exothermic in nature; mixture becomes viscous and eventually forms solid mass. Polyurethane formulation may require additives like catalyst , blowing agents etc. synthesis can be done by careful stoichiometric calculations, reaction of diisocyanate with diols forms linear chain polyurethane while branched chain polyurethanes are formed when polyhydric alcohols (polyols) reacts with diisocyanate/ polyisocyanates.

1.1.1 Types of Polyurethane as Polymers

Polyurethanes can be developed in many forms by using various processing techniques [7, 8]. The classes of polyurethanes are as under.

1. Fibers. 2. Films. 3. Castables. 4. Thermoplastics. 5. Foams. 6. Millables

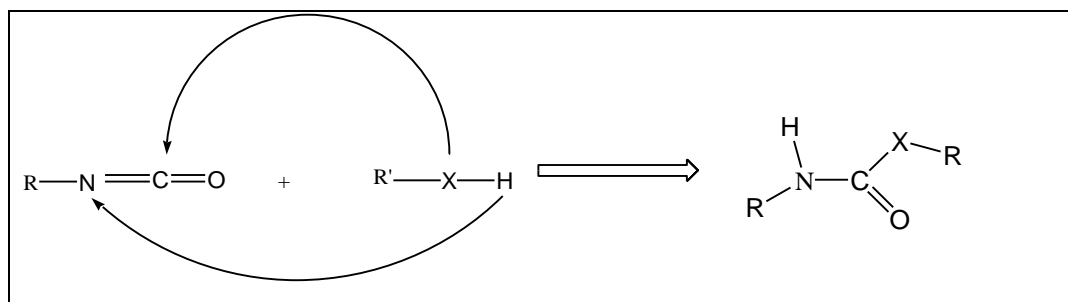


Fibres ; linear polymeric chains used in raw form or used as fibre-reinforced composites e.g *perlon*, *spandex* etc, **films** ; they are having two parts sprayable components used in making chemical resistant coating / paints or single component solid polymer cured by moisture like single pack PU paints, fully cured PU films mainly used in making thin walled components. **Castables**; They are used in making domestic roller blades, armamentarium etc. **Thermoplastics**; these are designed for application in biomedical purposes such as prosthesis, rubber tubings, grips, automotive parts, shoe soles etc. **Foam**: these are having three dimensional networks with aligned cells, which may be open or closed as per their end use applications, they can be **Rigid foams** these are used for the thermal and aural insulations. **Flexible foams**; They are being used for cushions, mattresses, carpet padding etc., **Integral spin polyurethanes**; They are used in making steering wheels, car dashboards etc. **Milliibles**; They are sulphur cured polyurethanes processed in rubber machinery.

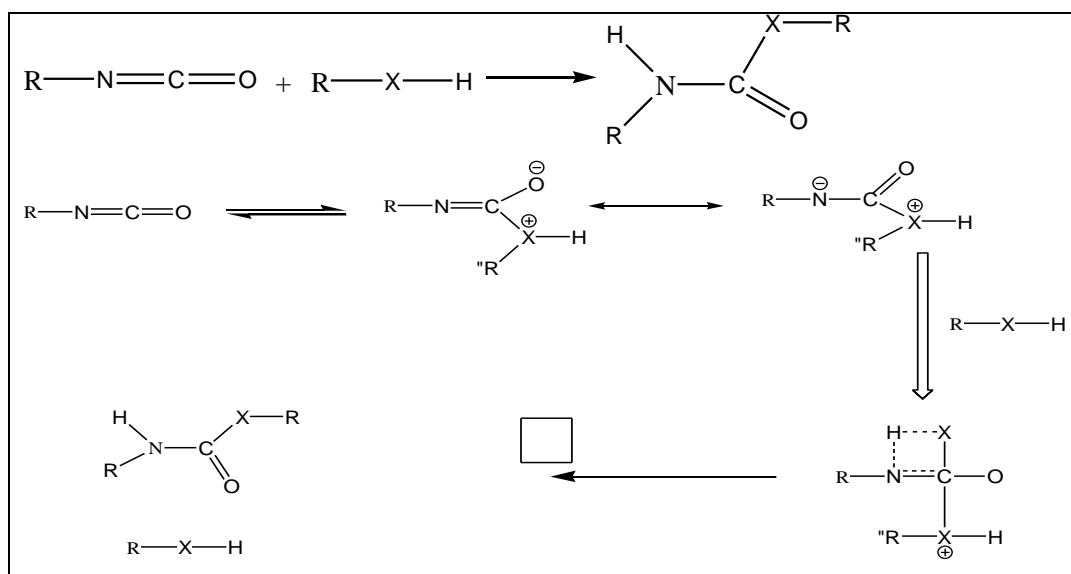
1.1.2 Chemistry of Polyurethane Synthesis

The polyurethane synthesis involves the nucleophilic addition reaction of electrophilic carbon atom of isocyanates group present between cumulative double bonds of nitrogen, carbon and oxygen (**Scheme. 1.1 and 1.2**). The electrophilic

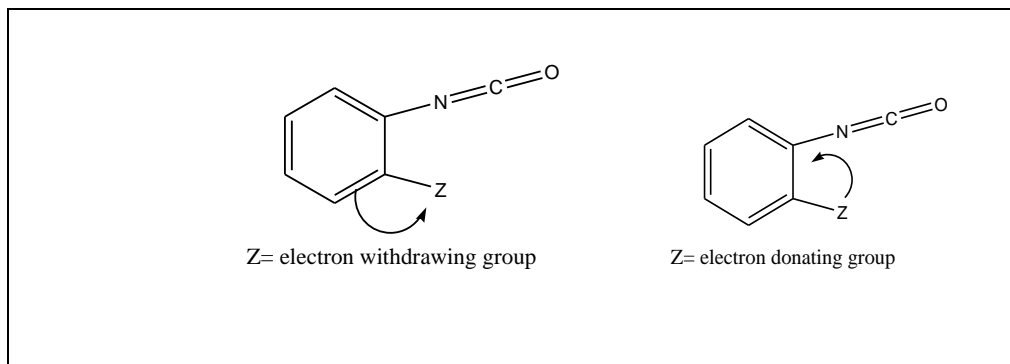
nature of carbon of NCO is more for aromatic system as compared to NCO of aliphatic structure and so the reactivity of the aromatic NCO is more than aliphatic NCO system [9-11]. Electron withdrawing groups at ortho and para positions of the aromatic system increases electrophilic character of carbon of NCO group and significantly increases the reactivity of nucleophilic addition reaction, while the electron donating group attached at ortho and para positions declines the electrophilic character of carbon of NCO group (**Scheme.1.3**), thereby decreases the reactivity for nucleophilic addition reaction of the NCO group as shown in the **Scheme.1.4**.



Scheme 1.1 Reaction of isocyanates with active hydrogen



Scheme 1.2 Reaction mechanism of polyurethane synthesis



Scheme 1.3 Electronic effect of groups on the NCO functionality

Electron donating groups	Ortho/Para positions	Electrophilic nature of carbon of NCO group decreases considerably
Electron withdrawing groups	Ortho/Para positions	Electrophilic nature of carbon of NCO group increases considerably

Scheme 1.4 Effect of groups position on the reactivity of NCO group

1.1.3 Types of Reaction in Polyurethane Synthesis

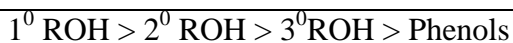
Two different types of reactions taking place during polyurethane synthesis are:

- (1) Primary reactions (2) Secondary reactions

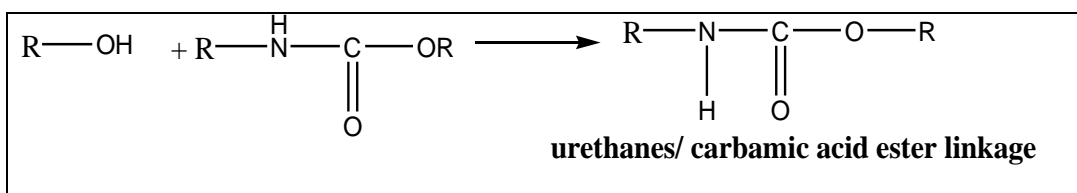
Primary reaction in polyurethane synthesis

Compounds having OH functionalities reacts with NCO group forming urethanes linked polymers or having carbamic acid ester linkages (**Scheme.1.5**). The ease of

OH functionalities participation in the reaction with NCO depends on the moiety with which OH is attached, of order as under:

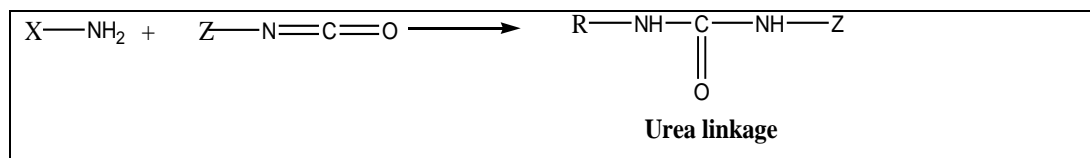


Among one, two and three degree alcohols the reactivity of three degree alcohol is least for NCO group due to steric hindrances of the alkyl group while for the phenol the OH lone pair are in resonance with the ring not available for the NCO functionalities [12].



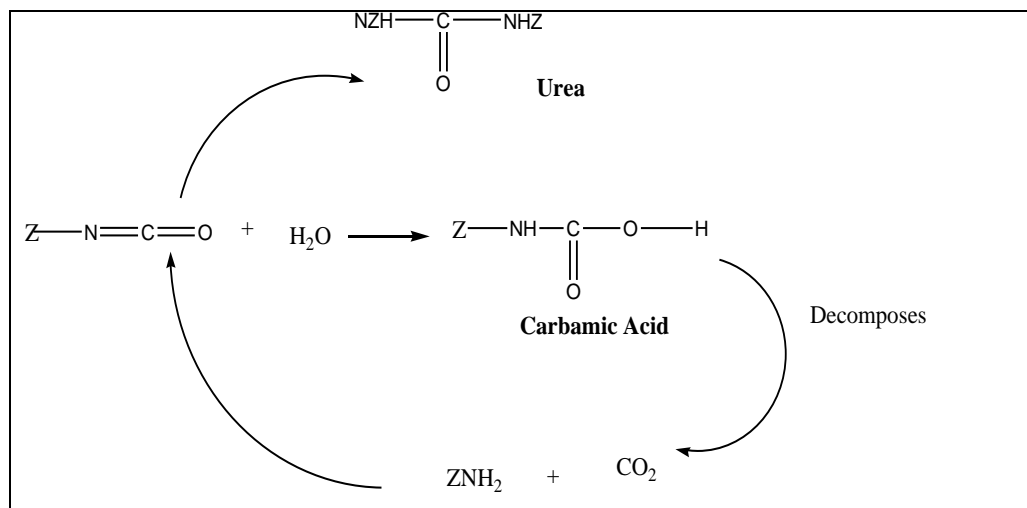
Scheme. 1.5 Carbamic acid ester linkage

(b) Compounds containing amines as the functional group when reacts with isocyanates forms product having urea linkage (**Scheme.1.6**)



Scheme. 1.6 Urea linkage formation

Isocyanates reacts with OH of water molecule to form unstable carbamic acid which later decomposes to an amine and carbon dioxide, acting as a blowing agent. (**Scheme.1.7**).



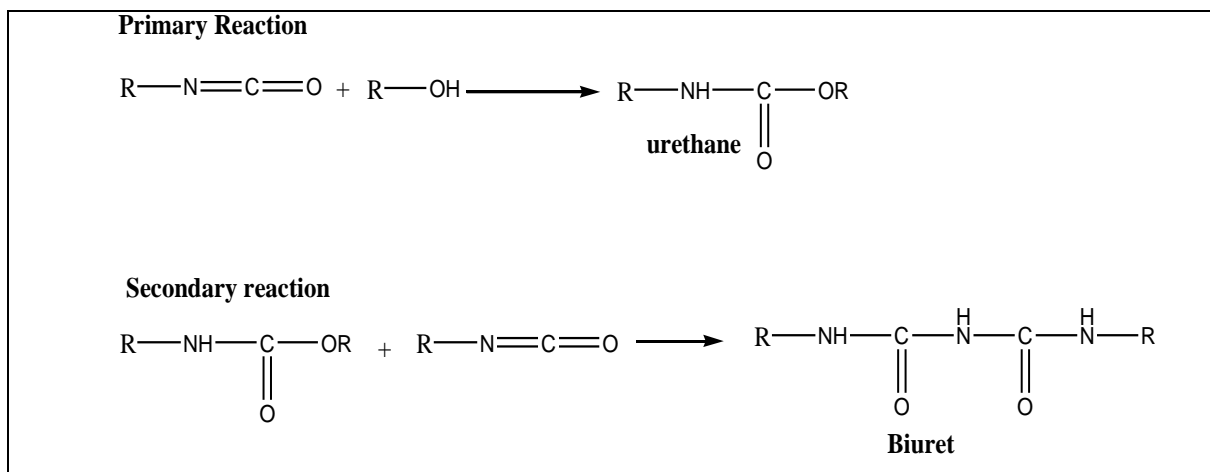
Scheme.1.7 Reaction of isocyanates with water molecules

PU and PU based composites generally stored in moisture free environment because slightly high index ratio (IR) i.e NCO/OH concentration ratio will make free NCO functionalities to react with OH of water molecules hence once cured the PU based system is oven stored at ambient temperature .

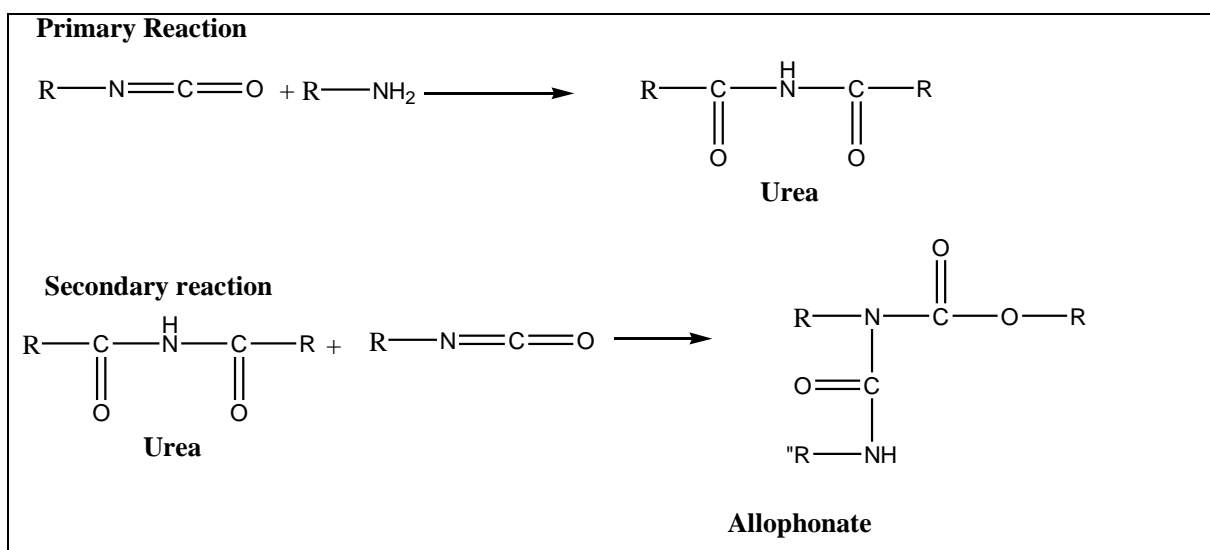
Once the amine is formed, it can react with the unreacted NCO functionalities to form urea linkages, essentially IR is of utmost significance in case of PU synthesis [13].

Secondary reaction in polyurethane synthesis

In the secondary reactions of PU synthesis, the formed products of primary reactions i.e urea and polyurethane can again react with the electrophilic carbon of NCO functionality as both of these have inherited hydrogen forming *biuret* (**Scheme.1.8**) and *allophont* respectively (**Scheme.1.9**).

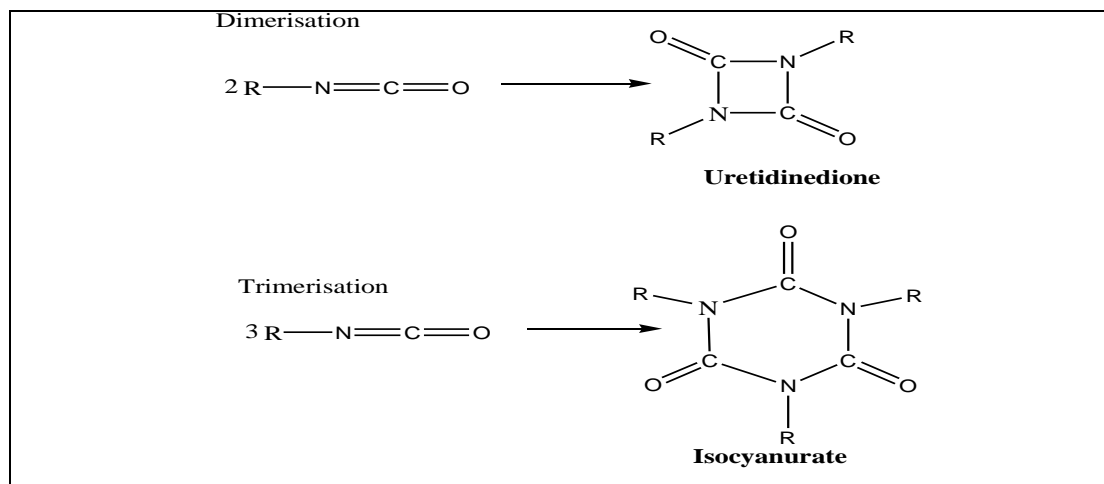


Scheme.1.8 Formation of biuret



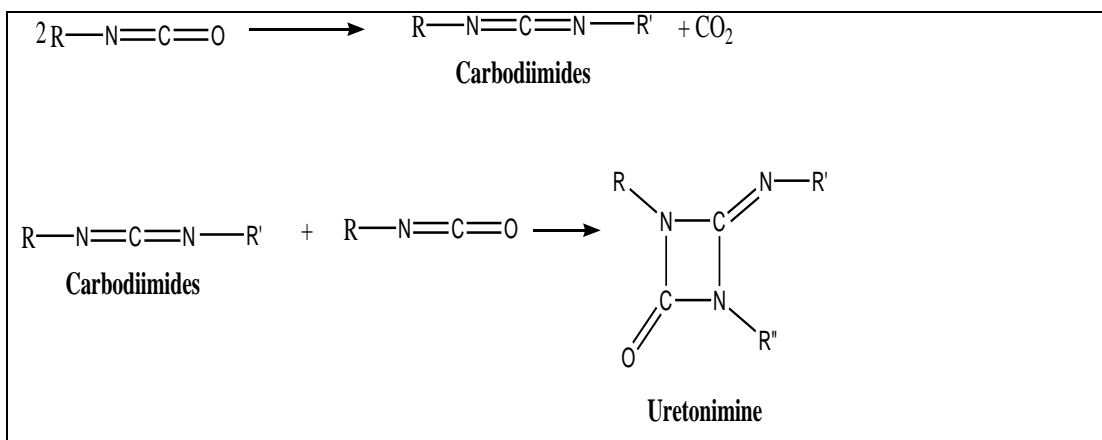
Scheme.1.9 Formation of allophonate

Allophonate and biuret are thermally stable and decompose into original compounds at 150⁰. [14], another type of secondary reaction is in between the molecules of isocyanates themselves, which can dimerise and trimerise to form Uretidinedione and isocyanurte respectively (**Scheme.1.10**)



Scheme.1.10 Dimerisation and trimerisation of isocyanates

Isocyanurate when reacts with another molecule forms carbodiimides which further reacts with isocyanate group to form Uritoneimine (**Scheme.1.11**).



Scheme.1.11 Formation of uretonimine


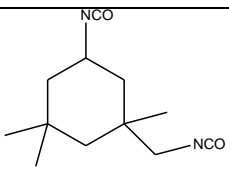
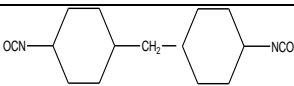
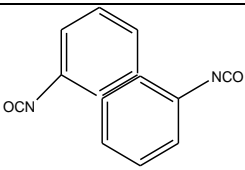
The secondary reactions wherein allophanates and biurets are formed can develop cross linkages in the PU system. The dimerisation and trimerisation of isocyanates can be enhanced by adding basic catalyst. The dimerisation of isocyanates to form uretidinediones during secondary reactions is restricted to aromatic isocyanates system as aliphatic isocyanates reaction product is thermally unstable however, trimerisation product isocyanurates can be formed by either system viz. aliphatic as well as aromatic isocyanates system.

1.2 Raw Materials in Polyurethane Synthesis.

1.2.1. Isocyanates

Generally the curing agents used in the polyurethane synthesis are isocyanates, which can be of aromatic or aliphatic in nature. Pertaining to the thermal/sunlight prone stability aliphatic isocyanates are more stable as compared to the aromatic isocyanate as such the aliphatic isocyanates are mainly used for coating purposes. [15, 16] As far as the aromatic isocyanate system is concerned the position, nature and steric hindrances provided to NCO functionalities decides the reactivity of the aromatic isocyanates curing system [17, 18]. For aromatic diisocyanates, the para position of the isocyanate makes toluene 1, 4-diisocyanate more reactive than the ortho position in toluene 1,2- diisocyanate owing to steric hinderance of methyl group over the NCO functionality. Source of the aliphatic and aromatic isocyanates used for polyurethane synthesis are given in **Table 1.1**

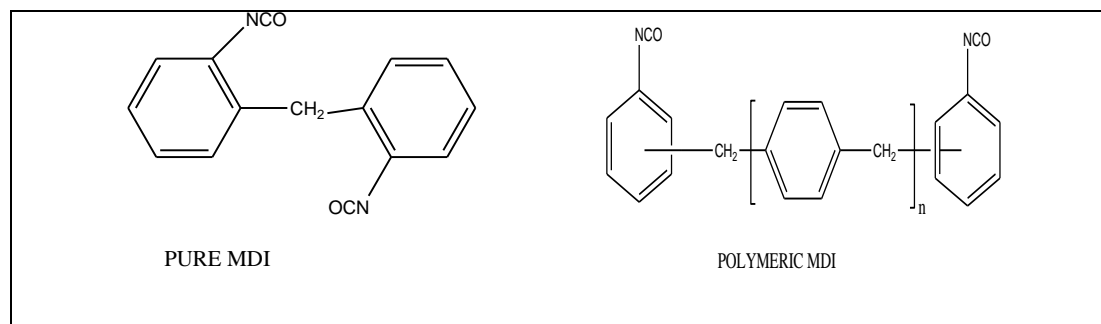
Table.1.1 List of aliphatic and aromatic isocyanates

S.No	Isocyanate Name	Structure	Aliphatic/ Aromatic
1	HDI(hexamethylene Diisocyanate)		Aliphatic
2.	IPDI(Isophorone diisocynate)		Cycloaliphatic
3.	HI2-MDI(4,4'-diisocyanato dicyclohexylmethane)		Cycloaliphatic
4.	NDI(1,5-Napthalene diisocyanate)		Aromatic

5.	TMXDI(Tetramethylxylene diisocyanate)		Aromatic
6.	PPDI (p-phenylene diisocyanate)		Aromatic
7.	CDI(1,4-cyclohexane diisocyanate)		Cycloaliphatic
8.	TDI(toluene diisocyanate)		Aromatic
9.	TMDI (trimethyl hexamethylene diisocyanate)		Aliphatic

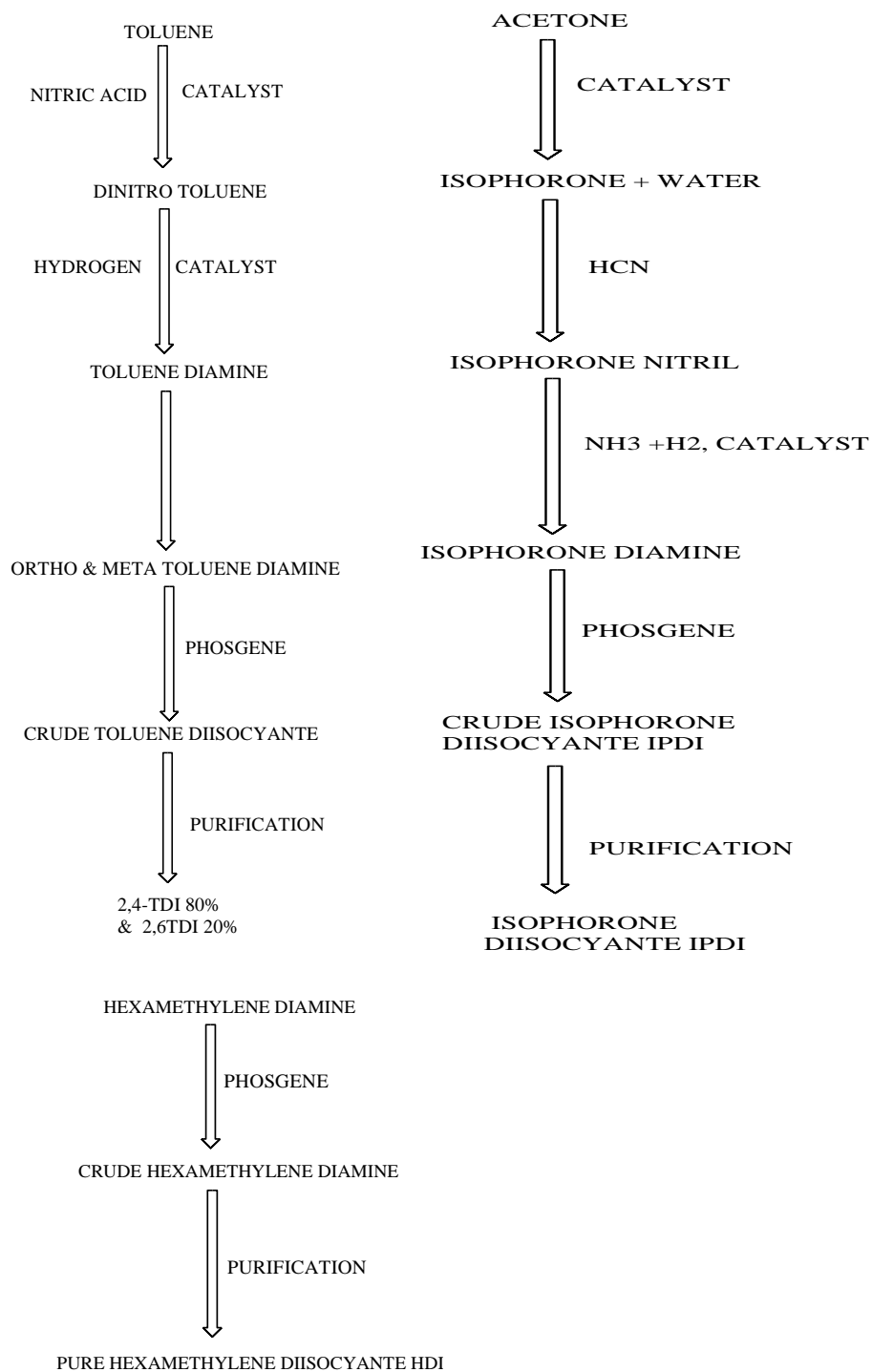
Materials as additives are added to the isocyanates to reduce the volatility, freezing points so to use in the toxic free environment. The pre polymeric forms of

isocyanates are also used for polyurethane synthesis. The pre polymer of MDI is shown in **Scheme 1.12**.



Scheme.1.12 Formation of prepolymer of MDI

Synthetic routes of synthesis of some isocyanates:

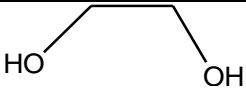
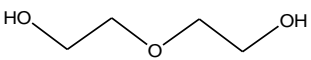
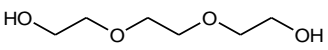
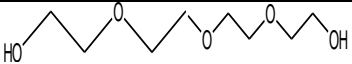
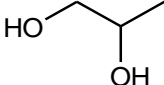
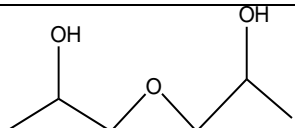
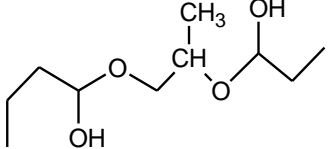

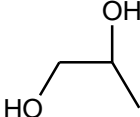


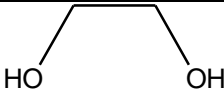
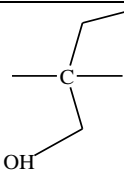
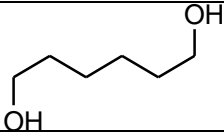
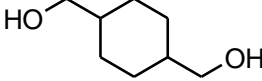
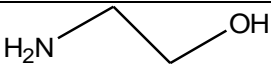
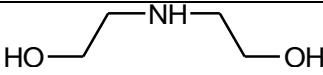
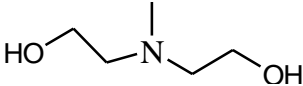
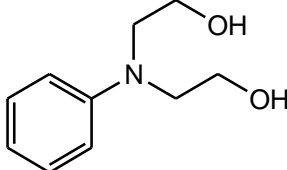
Scheme 1.13 Synthesis of isocyanates

1.2.2. Polyols/ Binders/Chain Extender

Polyols are compounds with two or more hydroxyl functional groups, which on reaction with isocyanates develop urethane links. Polyols used have mainly functionalities between 2 to 8 wherein the average molecular mass ranges from 200 to 8000 gmol⁻¹ (Randall and Lee 2002) [19]. Polyols used are hydroxyl terminated polyester polyols, hydroxyl terminated polybutadiene HTPB, hydroxyl terminated polyethers polyols etc. Some polyols used in PU synthesis are listed below in **Table 1.2 to 1.4.**

Table.1.2 List of dihydroxy polyols used as binders/ chain extenders

Name	Structure	Mol.wt
<u>Ethylene glycol</u>		62.1
<u>Diethylene glycol</u>		106.1
<u>Triethylene glycol</u>		150.2
<u>Tetraethylene glycol</u>		194.2
<u>Propylene glycol</u>		76.1
<u>Dipropylene glycol</u>		134.2
<u>Tripropylene glycol</u>		192.3
<u>1,3-Propanediol</u>		76.1
<u>1,3-Butanediol</u>		92.1

<u>1,4-Butanediol</u>		92.1
<u>Neopentyl glycol</u>		104.2
<u>1,6-Hexanediol</u>		118.2
<u>1,4-Cyclohexanedimethanol</u>		142
<u>Ethanolamine</u>		61.1
<u>Diethanolamine</u>		105.1
<u>Methyldiethanolamine</u>		119.1
<u>Phenyldiethanolamine</u>		181.2

As far as the structural morphology of PU is concerned , they are composed of the hard segment HS and the soft segment SS, the SS of PU is rendered by polyol part, which gives the characteristic physical behaviour to the polyurethane system. Depending on the end use of the synthesized PU, the soft part rendering polyol system is chosen.

If the hydrolytic resistivity is the requisite trait of PU than polyether based polyol imparts hydrolytic susceptibility. Polydiene based polyols are good candidate for environment resistant polyurethane synthesis, excellent resistance for hydrolysis, photo and thermal degradation hydrogenated polybutadiene and polydiene based polyol/SS are the best suitable candidates.

Table 1.3. Some of the trihydroxy polyols used as binders/chain extenders

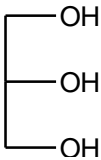
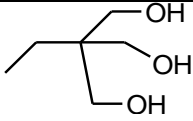
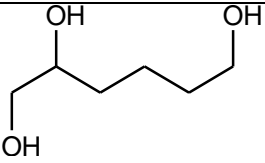
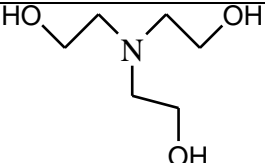
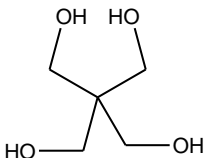
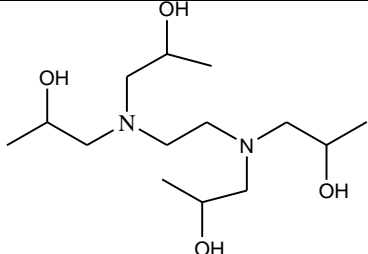
Name	Structure	Mol.wt
Glycerol		92.1
Trimethylolpropane		134
1,2,6-Hexanetriol		149.2
Triethanolamine		149

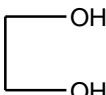
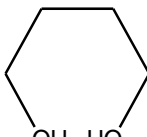
Table. 1.4 Some of the tetrahydroxy polyols as binders/chain extenders

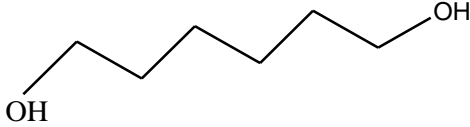
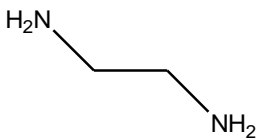
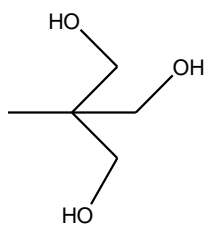
Name	Structure	Mol.wt
<u>Pentaerythritol</u>		136
N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylenediamine		278

1.2.3. Cross Linkagers

Cross linkagers covers the bifunctional and polyfunctional compounds both categories are generalized under active hydrogen bearing compounds. In polyurethane synthesis, cross linkagers are segregated into two components aliphatic diols / triols /diamines by which the PU synthesized are softer as compared to the aromatic diols/ triols/ diamines[20]. Cross linkagers essentially affects the mechanical, thermal and hydrolytic stability of the synthesized PU finished products. Some of the cross linkagers popularly used for PU synthesis are listed in **Table 1.5**

Table 1.5. List of cross linking agents

S.No:	Name	Structure
1.	Ethylene glycol	
2.	1,4-butanediol	

3.	1,6- hexanediol	
4.	Ethylene diamine	
5.	1,1,1-trimethylol propane	

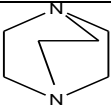
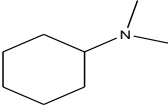
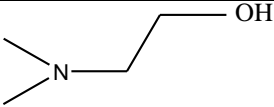
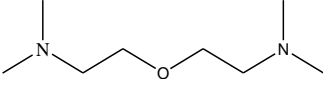
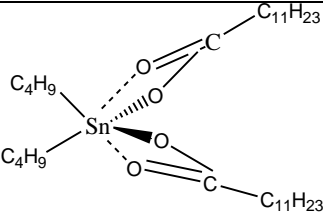
1.2.4 Catalyst

Polyurethane synthesis can be catalyzed by tertiary amines and organometallic compounds of mercury, tin and lead [21, 22].

By enhancing the nucleophilicity of the diols components tertiary amines act as a lewis acid and catalyzes the PU synthesis, mercaptide oxides and alkyl tin carboxylate oxides accelerate the polyurethane synthesis.

Tertiary amines show more reactivity with water molecules as compared to polyols as such they are used as the blowing agents, or the blowing catalyst for the polyurethane foams. For the synthesis of elastomers, organometallic salts of mercury act a catalyst while for the rigid PU foams lead's organometallic salts are used as the catalyst. Organometallic salts of tin are the best candidate as catalyst for PU synthesis as they doesn't have hazardous environment, moreover they show more affinity for the hydroxyl group of polyols as compared to water molecules. Some of the generally used catalysts are summarized in **Table 1.6**.

Table 1.6. List of catalysts for polyurethane synthesis

Trade Name	Chemical name	Chemical structure
TEDA/DABCO	Triethylenediamine. 1,4-diazabicyclo[2,2,2] octane	
DMCHA	Dimethylcyclohexylamine	
DMEA	Dimethylethanolamine	
A-99	bis(2dimethylaminoethyl) ether	
Dibutyltin dilaurate		

Catalyst utilization for the PU synthesis involves the balance of the three chemical routes.

- (A) Reaction between Polyol and isocyanates i.e Urethane formation.
- (B) Reaction between water and isocyanates i.e Urea formation.
- (C) Trimerisation of isocyanates i.e formation of Isocyanurate rings.

1.2.5. Surfactants

Surfactants are the amphiphilic compounds which lower the surface tension of the two phases. When they are used for foam based PU, they emulsify the liquid components, stabilize the cell structure and restrict them to collapse, and they also regulate the cell size [23-25]

In synthesis of Non-foam/ rigid PU synthesis the surfactant causes air release (act as antifoaming agents) they also eliminates the surface defects like sink marks, pin holes

etc. Some generally used surfactants are the co polymer of polydimethyl siloxane – polyoxalkene, silicon oils, nonylphenol ethoxylates.

1.3. Epoxy System

Epoxy resins are thermoset resin, which forms infusible mass when heated developing thermally stable cross linked structural network [26-29]. They are used extensively in making light weight and mechanically strong structure/ composite materials.

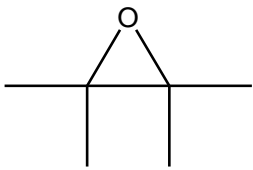
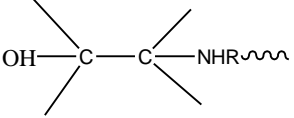
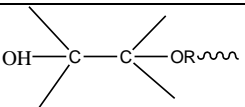
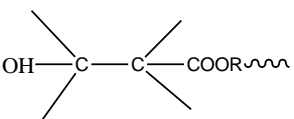
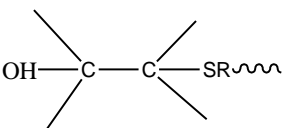
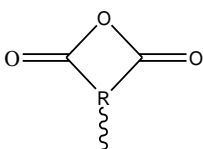
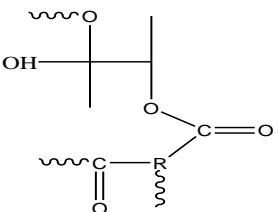
The pre polymers and the cured resin both are named as epoxy resin, two components are there; one is epoxy resin and the other is the hardener wherein the hardener causes curing of the epoxy resin material developing amorphous structure having good mechanical properties viz. tensile strength, young modulus etc bearing good thermal and chemical resistance.

The epoxy resin's fundamental chemical structure has a three member ether ring called epoxy, epoxide, oxirane or ethoxyline. The world wide application of the epoxy material includes adhesives, binders, coatings etc [30, 31]. When an epoxy matrix is reinforced with fibers /fillers they form composites which are used from polymer industries to aerospace engineering [32, 33]. The epoxy matrix / composites are analyzed for the various properties viz. young modulus, tensile strength, notch sensitivity, compression strength, flammability, impact resistance and for material availability and the cost effectiveness of the processing. The list of curing agents and the cured epoxy resins are given in **Table 1.7**.

Epoxy rings being three member ring is a highly strained structure which owes to its high reactivity with the electrophilic and the nucleophilic reagents, which are having active hydrogens like carboxylic acids, thiols, aliphatic and aromatic amines, anhydrides and so on. Once epoxy resin reacts with these active hydrogen containing

compounds they lose their epoxy functionalities but are still called as the epoxy resins. The active hydrogen compounds are called as the curing agents or the hardener which provides the three dimensional network to the epoxy resin [34-38].

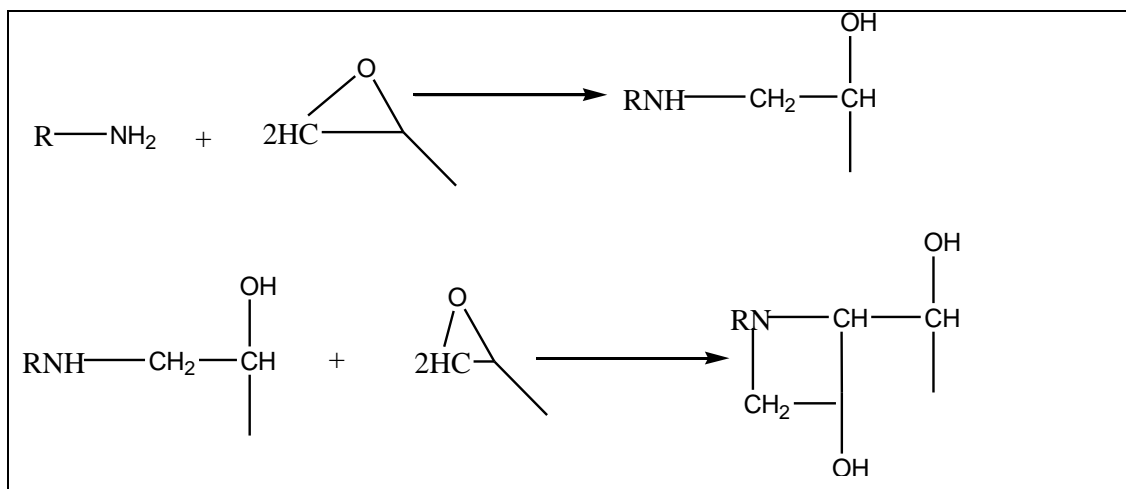
Table.1.7 Reaction products between epoxy resin and the various curing agents

EPOXY RESIN	CURING AGENTS	CURED EPOXY RESIN
	$\sim\text{R}-\text{NH}_2$ AMINES	
	$\sim\text{R}-\text{OH}$ ALCOHOL	
	$\sim\text{R}-\text{COOH}$ ACIDS	
	$\sim\text{R}-\text{SH}$ THIOLS	
	 ANHYDRIDES	

Pertaining to the end use of the cured epoxy resin the curing agents are selected, to improvise certain properties of the epoxy structure in addition certain additives are also added like plasticizers, solvents, fillers, diluents, accelerators etc.

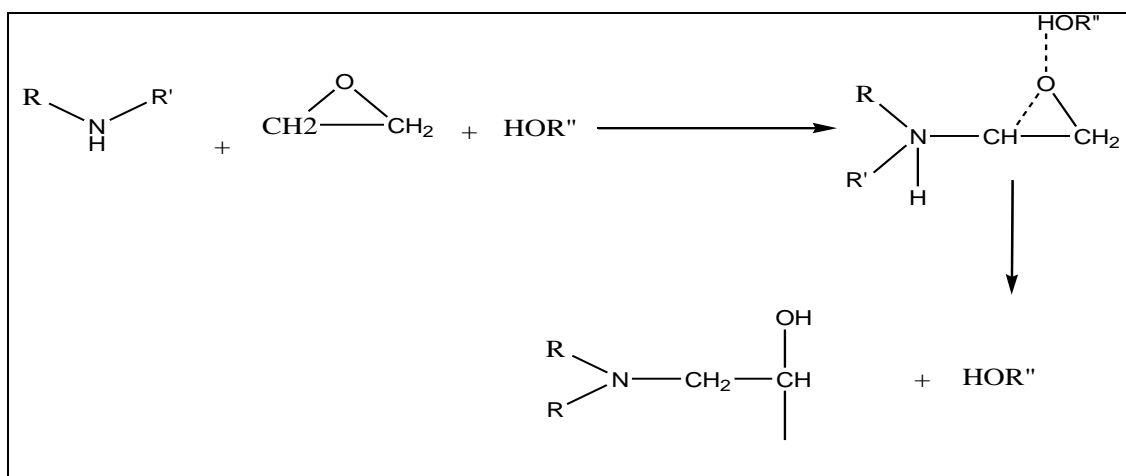
1.3.1 Curing of the Epoxy Resin

Curing agents / hardener generally used worldwide are having amine (primary or secondary), as the functional group. The reaction between curing (amines) and epoxy resin is shown in **Scheme.1.14**.



Scheme 1.14 Reaction between epoxy resin and amines

The curing of the epoxy resin accelerates in the presence of the hydroxyl functionalities wherein there is the protonation of the oxygen atom of the epoxy group developing partial positive charge on the carbon atom of methylene group of the epoxy resin [39, 40] and enhancing its susceptibility for the nucleophilic amines, the proposed mechanism is given in **Scheme.1.15**



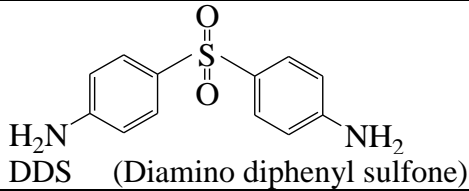
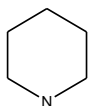
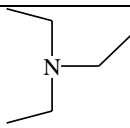
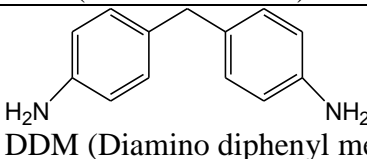
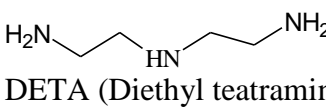
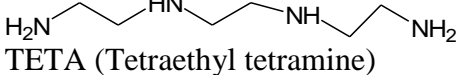
Scheme. 1.15 Curing of epoxy resin in presence of hydroxy compound

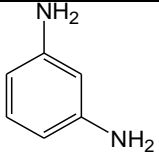
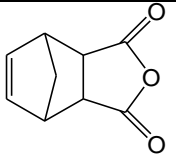
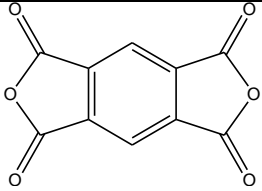
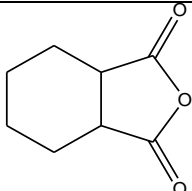
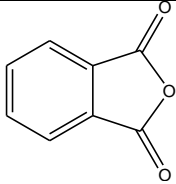
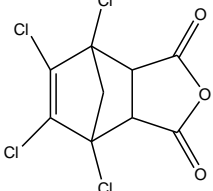
Amines cured epoxy resin have a wide application in making composites and coating of high performance for electrical encapsulation and other purposes, they show high chemical resistance and low moisture resistance.

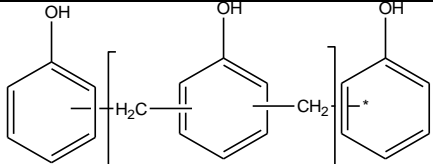
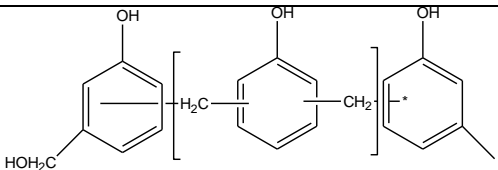
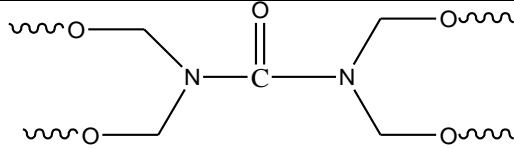
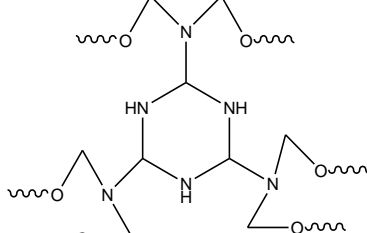
- **Hardeners /Curing agents**

Generally hardeners are effective at the ambient temperature, but those which are less reactive at the ambient temperature show effective curing properties at higher temperature, hardeners of this Category are called as latent hardeners. The list of hardeners with their applications is given in the **Table1.8**.

Table 1.8. List of hardeners with their applications

1.	 <p>DDS (Diamino diphenyl sulfone)</p>	Composites, electrical encapsulation, coating adhesive
2.	 <p>PIPERIDINE</p>	General purpose
3.	 <p>TEA (Triethanolamine)</p>	Adhesive
4.	 <p>DDM (Diamino diphenyl methane)</p>	Adhesive, filament winding,
5.	 <p>DETA (Diethyl tetramine)</p>	Civil engineering, adhesive
6.	 <p>TETA (Tetraethyl tetramine)</p>	General purpose

7.	 <p>MPD (Metaphenylenediamine)</p>	Laminates
8.	 <p>NADIC METHYL ANHYDRIDE</p>	High HDT(heat deflection temperature)
9.	 <p>PYROMELLITIC DIANHYDRIDE</p>	Improvises HDT(heat deflection temperature)
10.	POLYAMIDOAMINES	Used in sealents, concrete bonding maintenance of coating, adhesives.
11.	POLYAMIDES	Marine coating, trade sale paints.
12.	 <p>HEXAHYDRO PHTHALIC ANHYDRIDE</p>	Used in casting
13.	 <p>PHTHALIC ANHYDRIDE</p>	Filament winding, potting, encapsulation
14.	 <p>CHLOROENDIC ANHYDRIDE</p>	Flame retardant

15.	 NOVOLAC	Powder coating, moulding compounds
16.	 RESOL	Drum and pail coating, baked enamels
17.	DICYANODIAMIDE	Singlr package adhesive, powder coating
18.	ISOCYANTES	powder coating
19.	POLYMERCAPTANS & polysulphides	Sealants and adhesives
20.	 UREA-FORMALDEHYDE RESIN	Fast bake enamels, topcoats and stove primers.
21.	 MALAMINE FORMALDIHYDE RESIN	Stove paints

Various curing methods are implied for the epoxy resins including chemical curing which generally performed under ambient temperature. It can be done by radiations EB (electron beam) and UV (ultra violet) curing through microwave are also used for curing of epoxy resins. The methods of curing affects the mechanism of curing for example when done through radiations the mechanism follows chain polymerization pathway. The curing methodology affects the mechanical properties of the cured matrix system. During curing of epoxy resins, polymerization proceeds with the linear chain growth followed by branching which forms the cross linked three dimensional structures [41, 42].

Curing results in transformation of viscous phase into elastic gel, the temperature at which the transformation occurs is called as the gel point with the development of cross linking in the polymers its viscosity increases and T_g also increases. As the T_g approaches curing temperature the viscous liquids transforms into elastic gel and converts into glassy solids.

- **Catalytic Curing of the epoxy resins**

Tertiary amines such as dimethyl diamino phenol, triethyl amine and benzyldimethylamine are acting as accelerators for the curing of the epoxy resin. While boron trifluoride monomethylamine (BF₃NH₂C₂H₅) has been used as the catalyst as well as an accelerator and crosslinking agent.

1.3.2. Types of Epoxy Resins

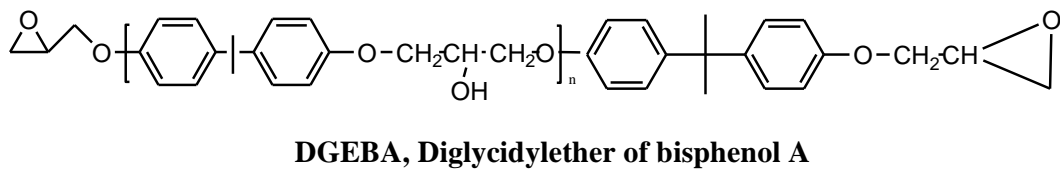
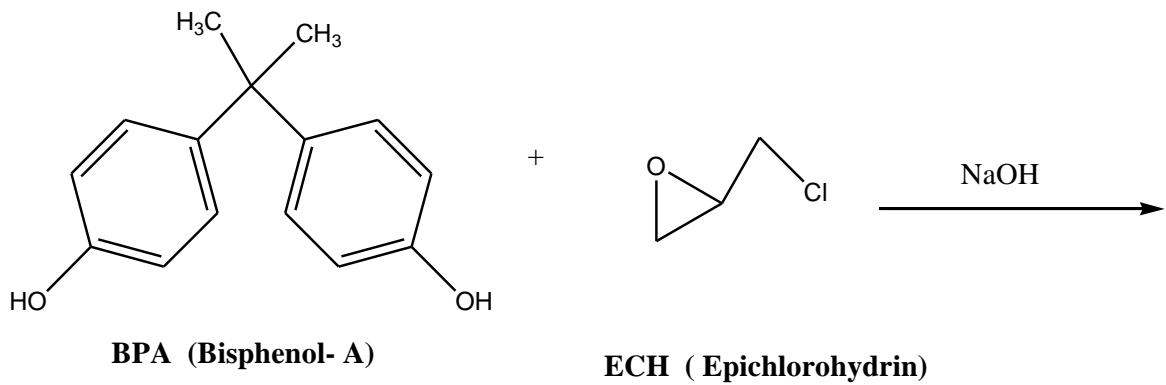
Essentially the resins have epoxy/oxirane as the main functional group which has the potential reactivity with various functionalities rendering epoxy resin as a versatile resin. The properties of the cured resin can be modified by the addition of fillers, plasticizers, diluents and solvents accelerators[43, 44]. Depending on the type of end use various epoxy resins and curing agents are available, some of them are discussed here.

Glycidyl epoxy resin from bis phenol

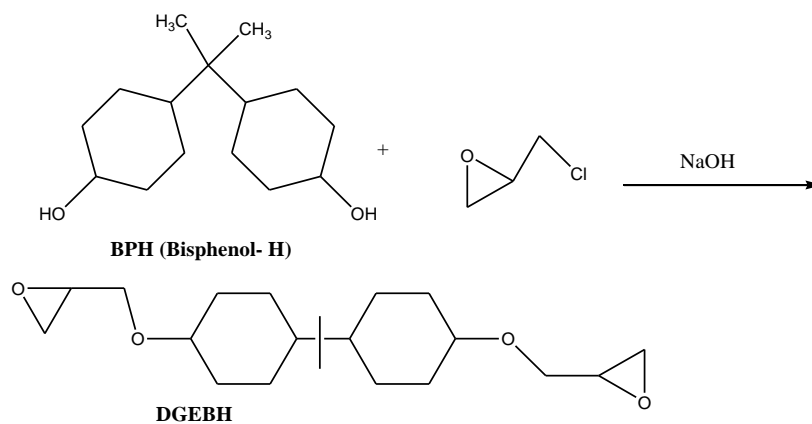
bis – phenol A

General class of epoxy resins are produced by reaction of bis – phenol A (BPA) and epichlorohydrine in presence of sodium hydroxide [45-47].

The chemical structure of DGEBA basically depends on the stiochiometric ratio of BPA and ECH where n of DGEBA can be from 0.2 to 12.



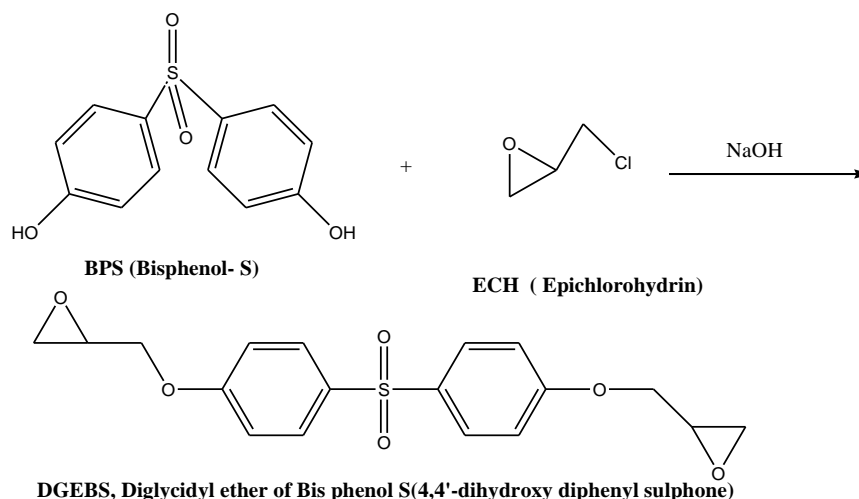
bis phenol- H , which is hydrogenated bis phenol A when reacted with ECH in the presence of NaOH forms the diglycidyl ether of Bis phenol –H.



DGEBH is a good candidate for weather resistance imparting material.

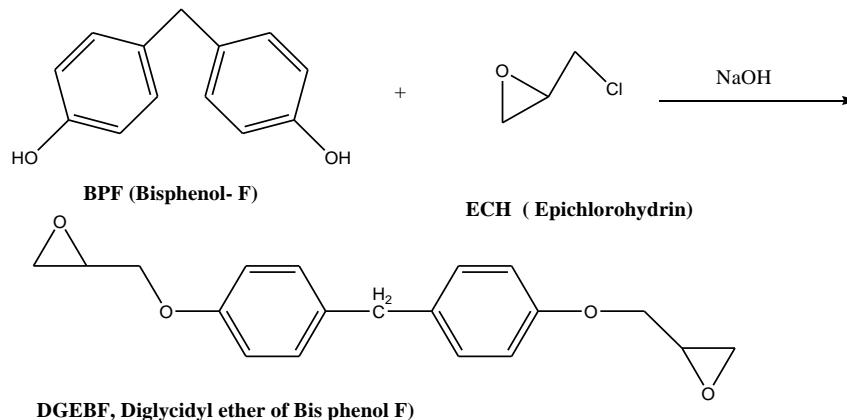
Bis phenol S

Bis phenol S (4, 4'-dihydroxy diphenyl sulphone) is used to prepare its diglycidyl ether DGEBS when reacted with ECH in presence of sodium hydroxide.



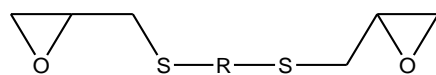
Bis phenol F

Bis phenol F is used to prepare diglycidyl ether DGEBS using ECH and NaOH

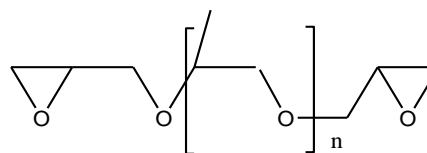


DGEBA used as mainly epoxy resin is of wide application , yet the cured product suffers less mechanical properties viz. low elongation, lower strength and lower flexibility to overcome these flaws aliphatic epoxy resins are substituting aromatic ones having less viscosity and can be easily handled[48-50] .

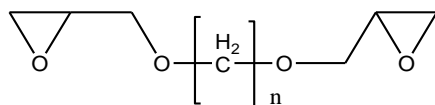
Some commercial aliphatic epoxy resins are;



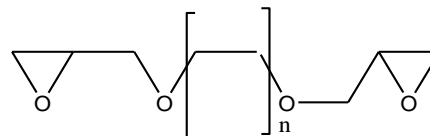
Epoxidised Thiol



shell Epon 812



Araldite RD-2



DOW-DER 732

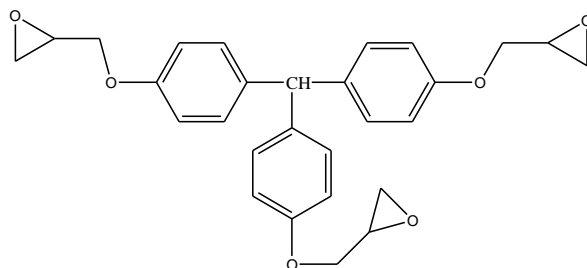
- **Epoxy resin based on functionality**

With the increase in the functionalities of the epoxy resins, the extent of cross linking increases, this improves the mechanical, thermal, and electrical properties of the cured epoxy system.

(a) Trifunctional epoxy resins (functionality , f=3)

➤ **Tris (hydroxyl phenyl) methane**

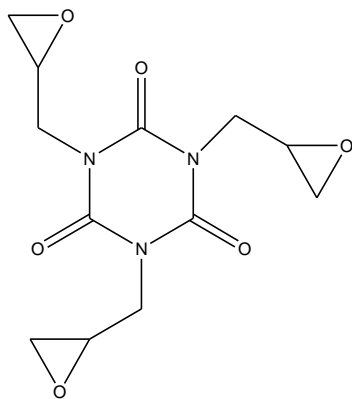
Epoxy resins with trifunctionality are mainly based on the tris(hydroxyl phenyl) methane. this epoxy resin is the best candidate for the end use pertaining to the moisture resistance, high temperature properties retention viz. electrical, mechanical etc[51-53]



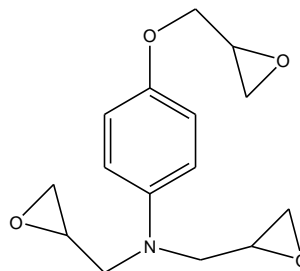
tris(hydroxyl phenyl) methane

➤ **Triglycidyl of p-amino phenol**

A product of cyanuric acid and epichlorohydrin traded as PT 810, chemically triglycidyl isocyanurate (TGIC) possesses weather resistivity so is used in the powder coating another trifunctional epoxy is triglycidyl of p-amino phenol TGEPA



TGIC



TGEPA

(b) Tetra functional epoxy resins (functionality, f=4)

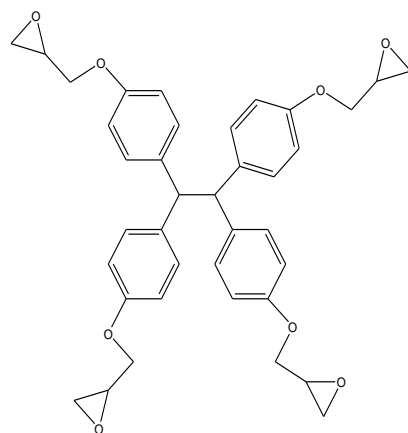
With the increase in the demand of a better material having excellent properties as the matrix and in composite preparation tetrafunctional epoxy resins were synthesized with better mechanical [54-58] electrical [59-61] and adhesive properties [62,63], some of the general tetra functional epoxy resins used are as under.

➤ **Araldite 0163**

Tetraglycidyl ether of tetrakis (4-hydroxyphenyl) ethane also traded as Araldite 0163 by CIBA-GEIGY and EPON 1031 by shell chemical company.

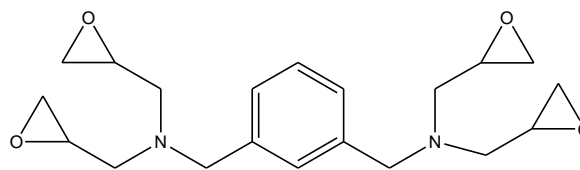
➤ **N, N, N', N'- tetraglycidyl m-phenylenediamine**

N, N, N', N'- tetraglycidyl m-phenylenediamine having f=4 possess low viscosity, low temperature curing best adhesion and moisture resistance properties.



tetraglycidyl ether of tetrakis(4-hydroxyphenyl) e

(A)

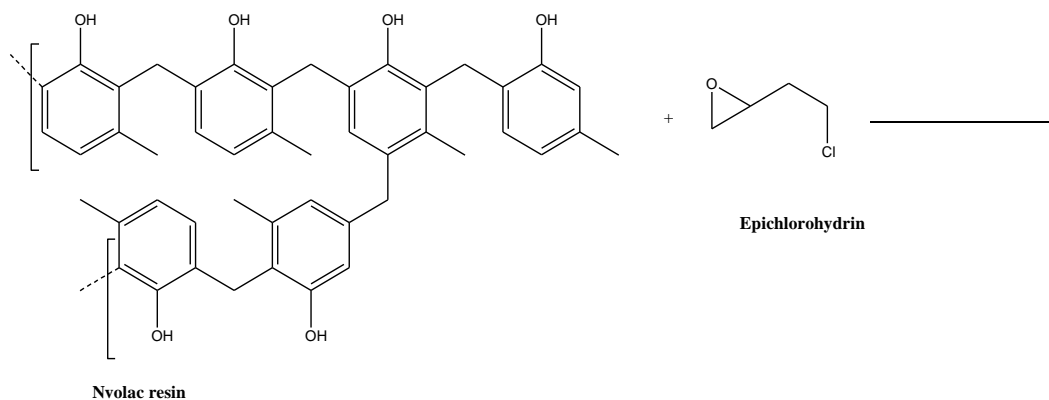


N,N,N',N'- Tetraglycidyl m-phenylenedia

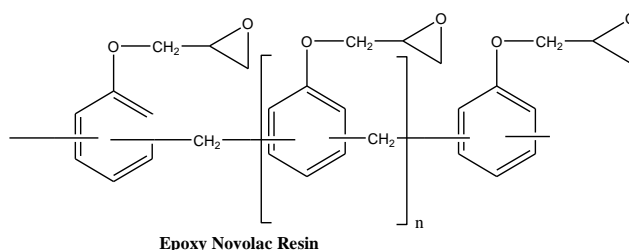
(B)

- Epoxy Novolac resin**

When epichlorohydrin and resins reacts in the presence of sodium hydroxide it forms polyglycidyl ether of novolac resin



Novolac resin



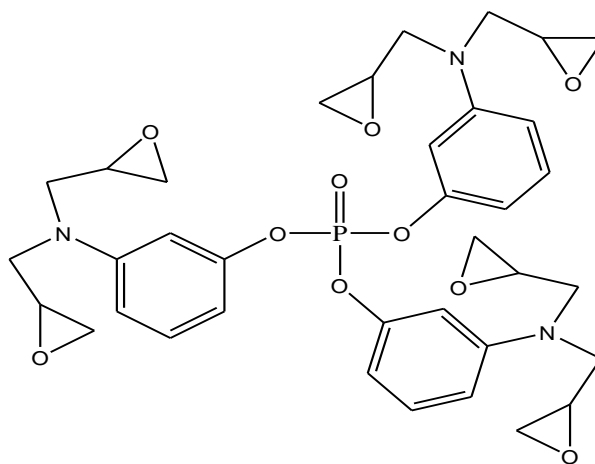
Novolac are the reaction product of phenol formaldehyde wherein formaldehyde and phenol ratio is less than one, excellent properties of epoxy novolac resin like

electrical lamination, high temperature adhesiveness etc made them best candidate of this line.

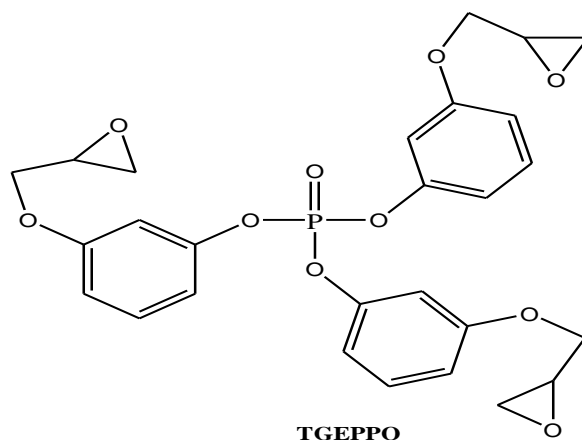
- **Flame retardant epoxy resins**

When chlorophenols are used, the cured product is having flame retardancy, antimony secondary butoxide when added to the final resin at 110°; it further enhances the flame retardant properties. Compounds of phosphorous also render flame retardant behaviour of epoxy resins. Phosphorous- halogen composition having phosphorous and halogen as 2% phosphorous and 6% chlorine imparts self extinguishable epoxy resins.

Flame retardant when incorporated in the chemical backbone of the epoxy resin imparts permanent flame retardancy behaviour as the flame retardancy shall be dispersed throughout the matrix. Some of the flame retardants used having the phosphorous in the matrix backbone are Hexaglycidyl tris (m-amino) phosphine oxide (HTAPPO) and triglycidyl ether of 1,1',1''-Tris (m-phenoxy) phosphine oxide (TGEPPPO).



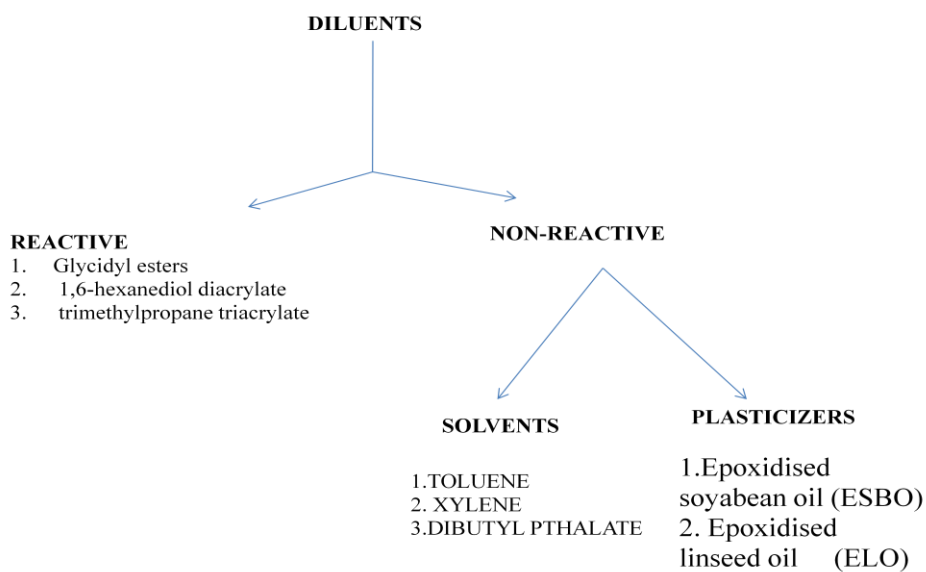
HTAPPO



Epoxy resins with the flame retardant properties are of various applications like they can be used as the electrical laminates, for adhesive coating, as encapsulation and potting compounds and structural laminates.

1.3.3. Diluents

Diluents are added for improvising the handling properties by lowering the viscosity as well as the thermal and chemical resistance are substantially reduced. Classification of diluents is shown in **Scheme1.16**. Some commercially available diluents are;



Scheme1.16 General Classification of diluents

Though solvents acting as diluents effectively decrease viscosity of highly viscous epoxy resins like DGEBA, but if trapped in the cured system leads to develop the cracks and also reduces the compressive modulus. This drawback is taken care by selecting a suitable diluents/diluents for the desired epoxy system.

1.4. Fillers

Fillers are conventionally treated as solid particulate additives to the polymeric matrix, which when added to the matrix bring variations (due to their geometrical features, surface area) in its thermal properties like Tg (glass transition temperature) Tm (melting point) thermal conductivity, thermal insulation etc and physical properties like tensile strength, young modulus, % elongation, break point, flexure strength and others, as a result the addition of the fillers can bring a large modification in the properties of the polymers[64-68]. Addition of the fillers brings many changes in many properties of polymers depending on the nature of the filler. Using various types of fillers we can modify the properties of the polymer products [69-71]. Fillers are classified as: Inorganic and Organic Fillers on chemical basis, shape and size or aspect ratio [72-74]. As given under:

1.4.1. Organic Fillers

The category includes ; **Natural polymers** like starch , wood flour , Cellulose fibers, , flax, sisal , cotton, , and fibers, **Synthetic polymers** like polyester, aramid , polyvinyl alcohol and Polyamide, graphite fibers , carbon nanotubes, graphite Carbon fibers, carbon black and flakes,

1.4.2. Inorganic Fillers

The category of inorganic fillers includes; **Metals** : steel and Boron, **Silicates**; asbestos Talc, kaolin, mica, montmorillonite wollastonite, ,and feldspar, **Salts**; phosphates, hydrotalcite, CaCO_3 , BaSO_4 , and CaSO_4 , **Hydroxides**; Al(OH)_3 and Mg(OH)_2 .

Fillers are also classified on the basis of their shapes and the aspect ratio .Aspect ratio is the ratio of the length of the filler to the cross sectional diameter of the filler Fibers used as the filler in the composites have the high aspect ratio [75-77]. Fillers according to the shape and size or aspect ratio are classified some examples are given in **Table 1.9**

Table.1.9. List of fillers based on aspect ratio

Shape	Aspect ratio	Example
Cube	1	Calcite and Feldspar
Sphere	1	Glass spheres
Block	1–4	Barite , Silica, Quartz, and Calcite
Plate	4–30	Hydrous alumina, Talc, and Kaolin
Flake	50–200++	Montmorillonite , Graphite ,Mica, and Nanoclays
Fiber	20–200++	Carbon nanotubes , Glass fibers , Wollastonite, , Asbestos fibers &Wood fibers,

1.4.3. The Fillers are classified on the Basis of their Primary Functions too:

Fillers on the basis of their uses in various fields have been classified as stated below.

- **Mechanical properties modifying fillers.**

The fillers aspect ratio can definitely affect the mechanical properties of the composites like the tensile strength, modulus, break point, yield point,

➤ **Low aspect ratio:** glass spheres, wollastonite, CaCO_3 , wood Flour, kaolin and Talc.

➤ **High aspect ratio:** natural fibers, carbon nanotubes, mica, carbon/graphite fibers

- **Permeability / Impermeability of fillers.**

Fillers can decrease the permeability of the matrix or can reduce permeability to considerable extent by using those fillers which have less aspect ratio i.e the cross section diameter of the filler is more as compared to the length of the filler[78-81], the various examples of such fillers are:: glass spheres, CaCO_3 , wollastonite, wood, kaolin, flour and talc, glass flakes, talc, nanoclays, mica, where as fillers with enhanced permeability thus with high porosity are CaCO_3 in dispersed polymers.

- **Fire retardancy fillers:** Fillers used as fire retardant are Hydrated fillers like: $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ etc

- **Bioactivity fillers**

Fillers like silicate glasses, tricalcium phosphate, hydroxyapatite, etc have been of great importance in the field of biomedical field as they have been used for the Bone regeneration[82-85].

- **Electrical & magnetic fillers;**

Fillers can be of ferromagnetic; non magnetic and conductive in nature examples are mica, carbon black, carbon fibres, etc which can modify the nature of the matrix being conductive and magnetic in nature.

- **Degradability fillers**

The fillers like starch and cellulose if used in the matrix the prepared polymeric composites can be of degradable in nature.

- **Surface fillers.**

Certain fillers can be used to modify the surface properties of the polymeric system, like Graphite, PTFE, silica, CaCO_3 , MoS_2 .

- **Radiation absorbing fillers**

Lead glass, oxides of leads, metal particles etc are having the properties of absorbing the radiations and can be used in the preparation of the modified composites having radiation blocking properties.

- **Processability fillers**

Fillers used for modifying the processability of the polymer formation like variations in the, anti-sag property, thickening properties, thixotropic property and acid scavenging are colloidal hydrotalcite, silica, bentonite and others [86-89].

How filler improvise matrix properties.

The physical and mechanical properties of the composites can easily be modified by using the particulate fillers TiO_2 , SiO_2 , graphite, Al_2O_3 , short glass fibers, fly ash particles, glass beads, clay etc types of inorganic particulate fillers, have been used as reinforcing material for providing low strength and low stiffness to the polymeric matrix which provides advantage of their constituent phases[90-92].

To provide more stiffness to the polymeric matrix, addition of the micron sized inorganic filler is required [93-95]. The strength of the polymeric matrix mainly depends to the extent the stress is transferred from the matrix to the particulate filler, more the bonding between the filler and the matrix more shall be the efficiency of the stress transfer phenomenon and more shall be the strength of the polymeric matrix resin [96-97]. This is the underlining fundamental for improvising the strength of the polymer matrix resin. [98, 99].

Thermosetting polymer matrix resin suffers from crack growth, when reinforced with inorganic particulate fillers, they were effective enough in imparting toughness to the matrix. [100].

1.5. Fly Ash (FA)

During combustion of coal, residue produced is known as fly ash, its composition is determined by the type of coal being used in the power plants, but generally fly ash has significant amount of aluminium oxide, iron oxide, silicon oxide (crystalline and amorphous form) and trace amount of thallium or vanadium, cadmium, mercury,

cobalt, selenium, chromium, manganese, arsenic, molybdenum, boron, lead, beryllium, strontium

Fly ash is hazardous waste, whose disposal can be harmful for humans and animals, and can pollute air, water or land. Pertaining to its hazardous nature exhaustive research has been done for its recycling both economically and environmentally wise. Making the use of Fly ash as substitute of Portland cement not only increases the chemical resistance and durability but also decrease green house gas, the footprint of concrete.

Other potential uses of fly ash include applications in construction industry, such as road sub-base or light weight aggregate synthesis of zeolites or production of adsorbents for the removal of different chemical compounds such as organic gases heavy metals ,dyes ,mercury nitrogen and sulfur oxides and other pollutants

When fly ash surface is activated, its adsorption capacity is greatly increased. World's fifth largest resource is fly ash so its other potential applications must be explored. Fly ash can be used as one of the filler in the polymer matrix substituting the conventional fillers which nowadays generally used in the polymer industries. Fly ash has many polar groups on its surface and its surface can be subsequently modified which can easily increase the filler – matrix interaction and thereby modifying the properties of the composites.

The present research work mainly focuses on the filler “FLY ASH” for the epoxy and polyurethane based matrices. Crude fly ash and surface functionalized fly ash has been used. Surface functionalized fly ash mainly deals with the surface modification of fly ash like the mechanical activation, chemical activation, and thermal activation, and how this surface modified filler has altered the PU and Epoxy based composites mechanical and other properties are the main focal point of the present research work using fly ash as filler.

1.6. Scope of the Research Work

Coal generated Fly Ash (FA) is a micro spherical particulate solid waste by-product, which is obtained at higher temperature from the various coal burning power plants all over the world. The FA is reported to have composition as, SiO_2 (62%), Al_2O_3 (23%), Fe_2O_3 (7%), CaO (1.6%), MgO (0.8%), TiO_2 (1.3%), Na_2O (2.8%) and trace elements (1.5%) .

FA is mainly a silico-aluminate material with an admixture of several other metal oxides present in varying amounts depending on the composition of coal. Besides its application in the synthesis of geopolymers , zeolites , cementitious materials, catalyst etc. The unique property of FA is its porosity and particle size to support various functional moieties making it as a perfect filler replacing other conventional fillers viz. kaolin, talc, mica, silica, glass etc. in the polymer matrix.

The main aim of research work is the appropriate treatment for the functionalization of the FA by thermal, mechanical and chemical treatments to design simple, novel and less time consuming synthetic methods for the preparation of polyurethane/epoxy composites using functionalized FA as the filler for its bulk utilization.

The developed composites will be tested for the, tensile strength, young modulus, percent elongation, break point etc to design light weight materials with high mechanical strength of requisite characters for its specific utilizations.

1.7. Importance of the Proposed Research Work

The disposal of FA poses a serious problem and is of great concern for the land disposal and the potential environmental pollution. There is a global interest of its utilization. Utilization of the FA as a filler material in polymer composites is cost effective also. Studies reveal that toughened resin composites enhance the properties compared to the neat matrix.

Present research work envisages on the bulk utilization of the fly as in developing reinforced polyurethane/epoxy composites wherein the industrial wastes FA has been

the key compounds as filler in the matrix of the composites which not only solves the hazardous waste utilization problem, but also designs an innovative composite for the utilization in the various fields of science and engineering.

The fly ash is used so far in its raw form for developing the PU and Epoxy composites affecting physio-chemical, mechanical and thermal properties for desired applications.

The present research work is important in designing and developing the surface functionalized fly ash containing significant number of hydroxyl moieties to provide better linkage with polyurethane and epoxy matrix forming the fly ash reinforced composites, cost effective widely applicable in various polymer products . the research is significant to give an overview of used of surface functionalized FA as filler in two different polymeric matrices to explore the possibility of application of FA in developing composites of desired mechanical and thermal properties.

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**Materials, Methods and Characterizations:
Polyurethane (PU) and Epoxy Polymeric
Synthesis**

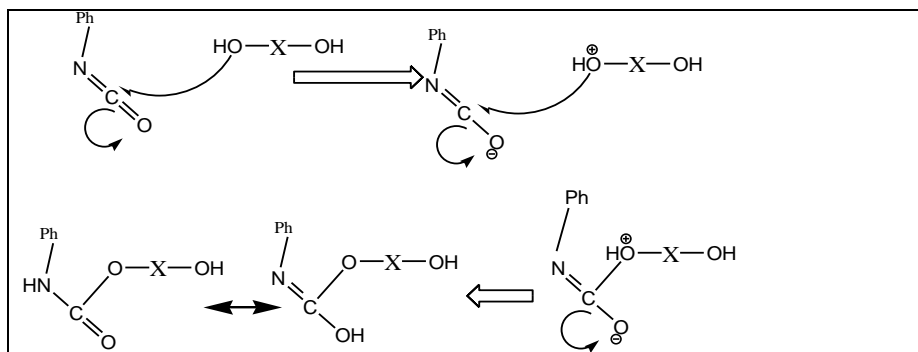
ABSTRACT

A systematic description of various chemicals, methodology for synthesis of polyurethane and epoxy polymeric systems, mold with mold release applied for different polymer matrices and composites, characterization techniques etc are described in this chapter. Fly ash used as filler for synthesis of composites is thoroughly investigated for physico-chemical, structural, and morphological properties. The method of OH functionalization of fly ash through chemical, thermal and mechanical activations is described and suitable characterization results are presented.

2.1 Introduction

Polyurethane Polymeric systems

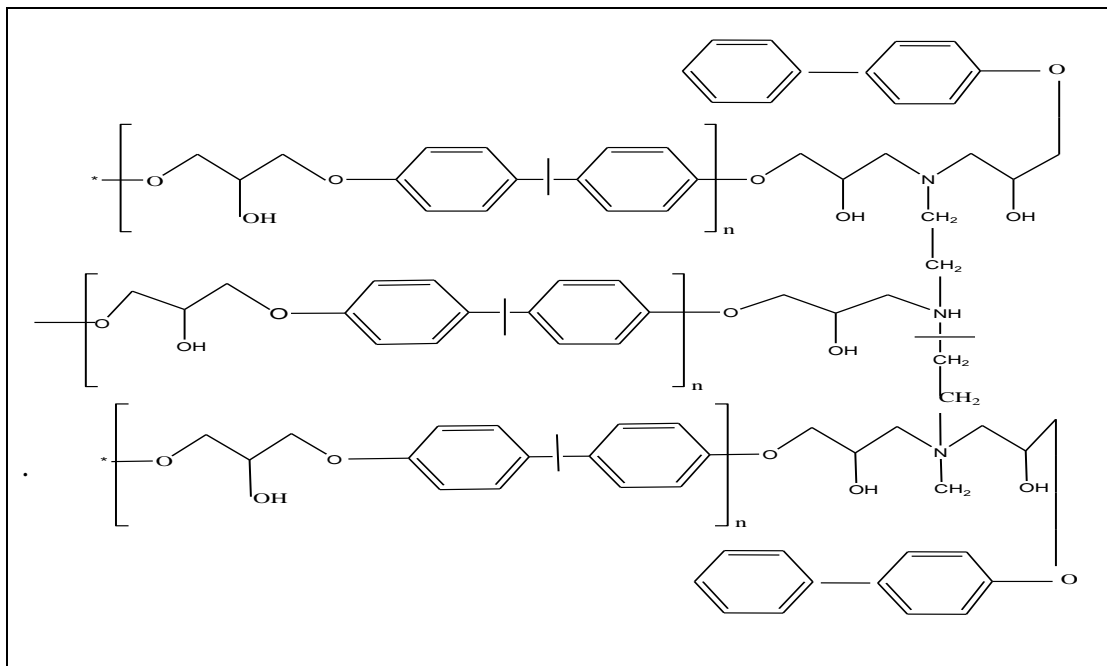
Polyurethanes (PU) have basic components diols/polyols as chain extenders /binders, di/polyisocyanates as curing agents and different chain linkers/cross linkers, which when react in presence of catalysts and other additives form a chain of repeating organic units joined by carbamates(urethane -NH-COO-) links (**Scheme 2.1**). The property of PU system not only depends on the ratio of the constituent monomer units but also on the chain length, chemical structure, molecular volume and functionality of the monomers [1-3].



Scheme2.1 The general mechanistic approach of PUM synthesis

Epoxy Polymeric systems

Epoxy polymeric (EP) systems have basic components different resins with epoxy/oxirane functional group, curing agents/ hardeners having amine group, chemical additives and fillers. Chemical reaction of epoxy monomer units with amine based curing agents forms a cross linking three dimensional structure (**Scheme 2.2**) primarily depending on resin hardener ratio, pressure, temperature and mixing techniques [4-5]



Scheme 2.2. Epoxy cross linked structure

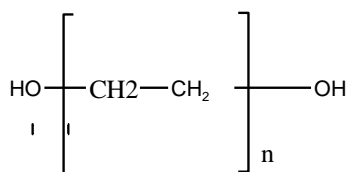
A systematic description of various chemicals, methodology for synthesis of polyurethane and epoxy polymeric systems, mold with mold release applied for both the polymeric matrices and composites, characterization techniques etc are described in this chapter briefly.

2.2 Materials

2.2.1. Chemicals for PU System

In the present research work polyurethane PU matrix (PUM) and FA reinforced PU composite (FA-r-PUC) are synthesized chemicals used for synthesizing polyurethane matrices and composites are;

- **Polyethylene Glycol(PEG) $H(OCH_2CH_2)_nOH$** ; Polyethylene glycol with trade name PEG-600, AR grade, Sigma Aldrich make having melting point-17-23⁰C, flash point-182–287 °C, density-1.125 was used as chain extender/ binder (CE) .



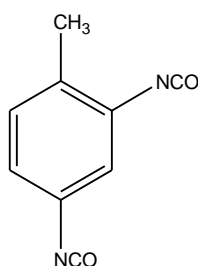
Polyethylene glycol

IR spectrum of PEG-600 (**Figure.2.1**) shows presence of broad and less intense peak at around 3451cm^{-1} corresponding to the OH groups, while strong and intense peak around 2865cm^{-1} is assigned to the $-\text{CH}_2-$ present in the monomer chain [6](**Table 2.1**)

Table2.1 IR frequencies of Polyethylene Glycol

-OH- stretching	3451 cm^{-1}	-CH₂- Bending	1454cm^{-1}
-CH₂- stretching	2865 cm^{-1}	C-O stretching	1092 cm^{-1}
C-C stretching	1248 cm^{-1}		

- **Toluene 2,4 diisocyanate (TDI) $\text{C}_9\text{H}_6\text{N}_2\text{O}_2$** ; Toluene 2,4 diisocyanate, AR grade, Sigma Aldrich make, molecular weight-174.16, M.P-19.5-21.5⁰C, B.P-251 °C (484 °F; 524 K), density-1.084g/ml is used as curing agent (CRA).



Toluene 2, 4-diisocyanate (TDI)

IR spectrum of TDI (**Figure.2.2**) shows a characteristic peak of NCO at 2240 cm^{-1} corresponding to the stretching band of NCO groups. Aromatic nature of CRA is shown by the presence of peak at 3184 cm^{-1} due to $=\text{C-H}$ stretching, overtones from $1721\text{-}2000\text{ cm}^{-1}$ and $\text{C}=\text{C}$ ring stretching at 1441cm^{-1} , 1522cm^{-1} , 1614 cm^{-1} . The presence of methyl group on benzene ring is confirmed by the stretching band

(symmetric & asymmetric) at 2924 cm^{-1} in addition bending of methyl group is assigned by a peak at 1382 cm^{-1} [7]. (Table 2.2)

Table 2.2 IR frequencies of TDI

<i>NCO stratching</i>	2235 cm^{-1}	<i>overtones</i>	$1721\text{-}2000\text{ cm}^{-1}$
<i>-CH₃- stretching</i>	2924 cm^{-1}	<i>C=C stretching</i>	$1441\text{ cm}^{-1}, 1522\text{ cm}^{-1}$ 1614 cm^{-1}
<i>-CH₃- bending</i>	1382 cm^{-1}	<i>=C-H stretching</i>	3184 cm^{-1}

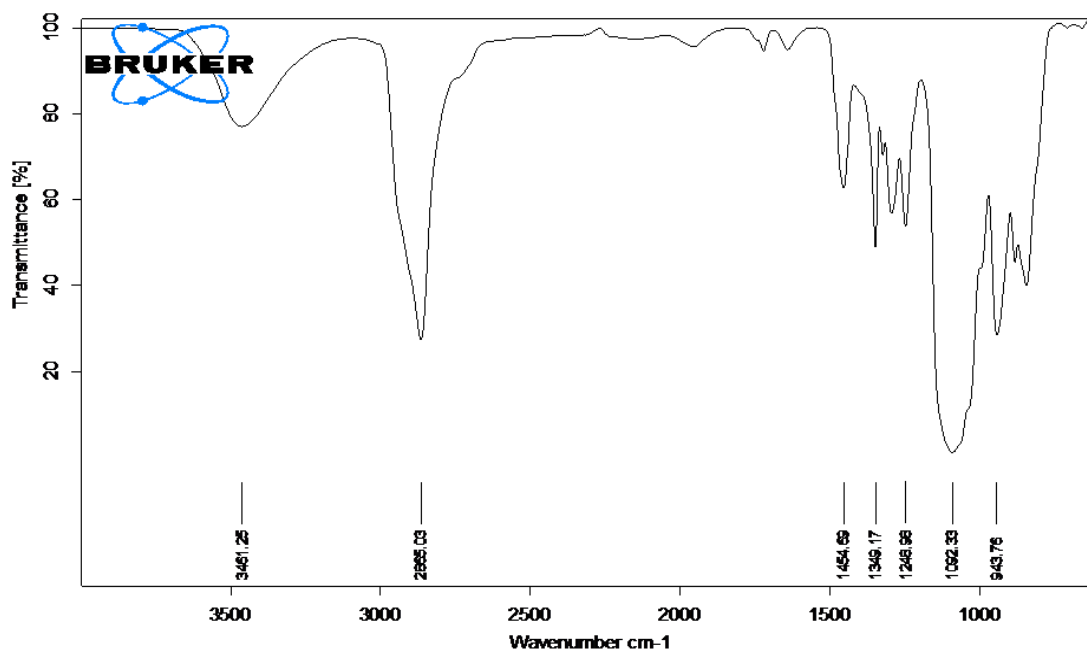


Figure.2.1. IR spectra of polyethylene glycol

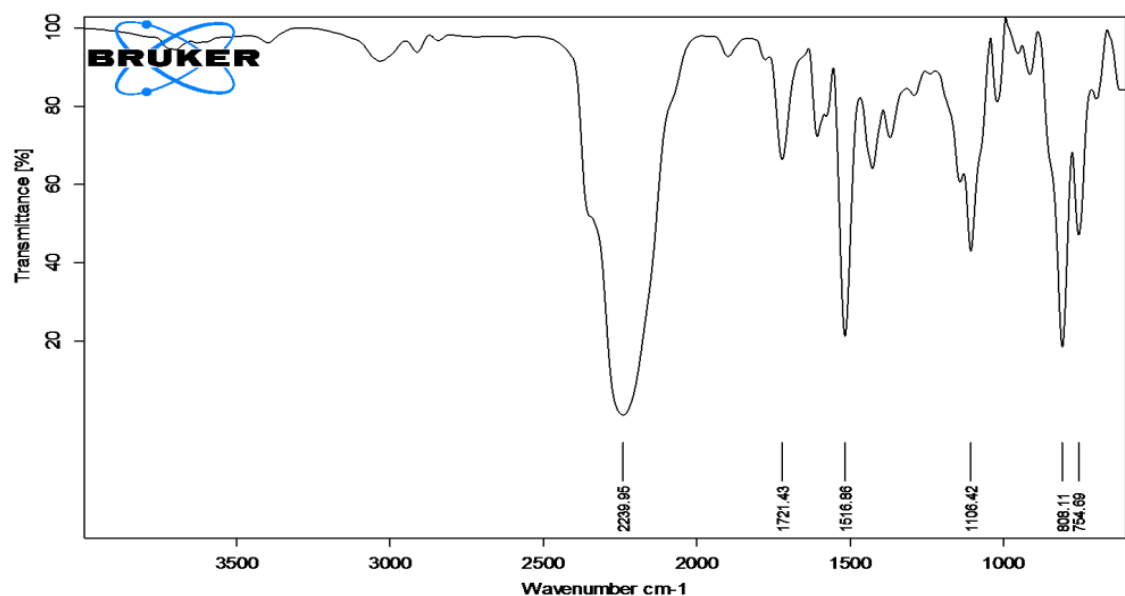
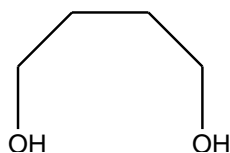


Figure 2.2 IR spectra of TDI

- **1,4- butanediol (BD)** $C_4H_{10}O_2$; 1,4- butanediol, AR grade, Sigma Aldrich make,



1, 4-butane diol (BD)

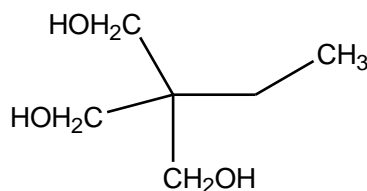
Molecular weight-90.12g/mol, m.p-20.1 °C (68.2 °F; 293.2 K), b.p-235 °C (455 °F; 508 K), density-1.0171 g/cm³ (20 °C) is used as a component of cross linking agent.

The IR spectrum of BD as presented in **(Figure 2.3)** shows characteristic peak of OH groups at around 3200-3600cm⁻¹. The presence of symmetric and asymmetric stretching of -CH₂- groups is shown by the peaks at 2936 cm⁻¹ and 2868 cm⁻¹ while peak at 1433 cm⁻¹ corresponds to the -CH₂-bending frequency. **(Table 2.3)**

Table 2.3. IR frequencies of BD

<i>O-H stretching</i>	3299 cm^{-1}	<i>-CH₂- Bending</i>	1433 cm^{-1}
<i>-CH₂- stretching(Asymm)</i>	2936 cm^{-1}	<i>C-C stretching</i>	1174 cm^{-1}
<i>-CH₂- stretching (Symm)</i>	2868 cm^{-1}	<i>C-O stretching</i>	1047 cm^{-1}

1,1,1-trimethylol propane (TMP) C₆H₁₄O₃: 1,1,1-trimethylol propane AR grade, Sigma Aldrich make having molecular weight-134.18, m.p -59-60⁰C , b.p-296-298⁰C, density-1.084g/ml is used as another component of cross linking agent. .



1,1,1-trimethylol propane (TMP)

The IR spectrum of TMP (**Figure.2.4**) shows OH stretching band at 3225 cm^{-1} , CH₃ and CH₂- symmetric and asymmetric peaks are seen in between 2886 cm^{-1} to 2966 cm^{-1} . Bending frequency of CH₃ group is confirmed by a Peak at 1345 cm^{-1} while peak at 1471 cm^{-1} corresponds to the bending of -CH₂- group. Peaks at 1002 cm^{-1} and 1006 cm^{-1} correspond to C-C and C-O stretching respectively [8].(**Table 2.4**)

Table2.4. IR frequencies of TMP

<i>O-H stretching</i>	3225 cm^{-1}	<i>-CH₃- bending</i>	1345 cm^{-1}
<i>-CH₂- stretching</i>	2966 cm^{-1}	<i>C-C stretching</i>	1002 cm^{-1}
<i>-CH₃- stretching</i>	2886 cm^{-1}	<i>C-O stretching</i>	1006 cm^{-1}
<i>-CH₂- bending</i>	1471 cm^{-1}		

Cross linking agent (CLA) used in the synthesis of PU polymeric systems during the work was homogenous mixture of BD (1, 4-butane diol) and TMP (1,1,1 trimethylol propane) in different w/w ratios (1:1, 1:2 and 2:1).

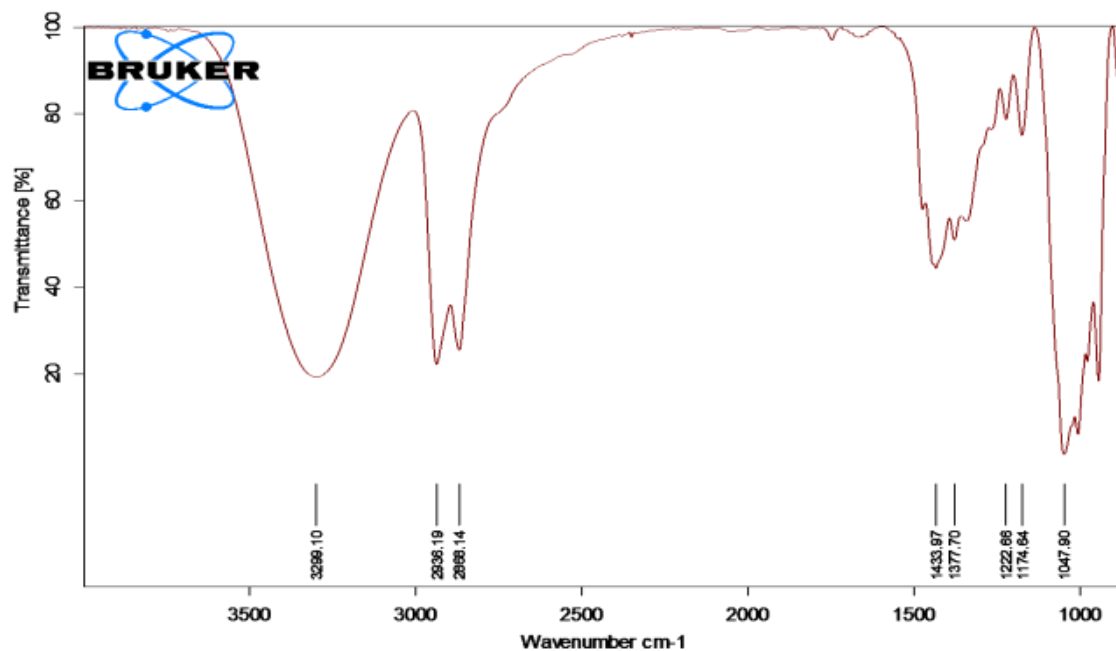


Figure 2.3 IR spectra of 1,4- butanediol(BD)

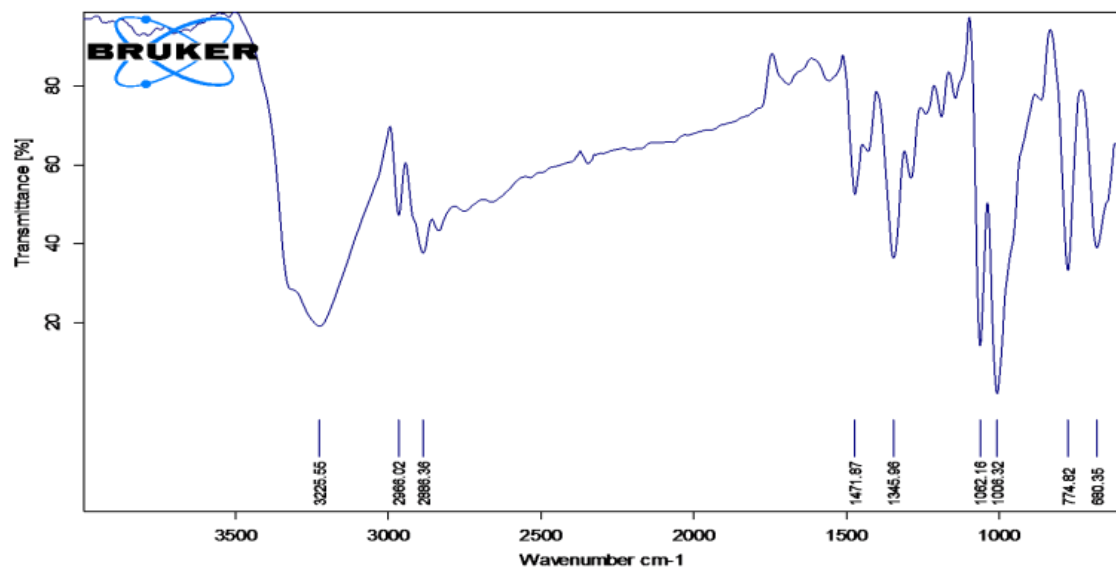


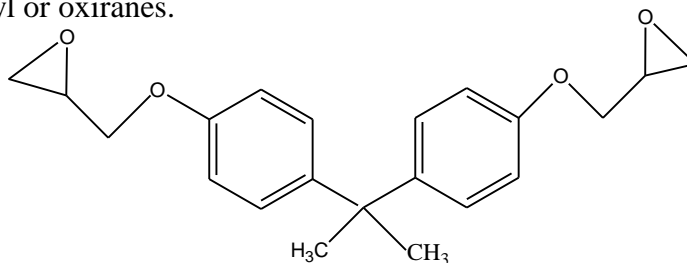
Figure 2.4. IR spectra of 1,1,1 trimethylol propane(TMP)

2.2.2. Chemicals for Epoxy System

Chemicals used for the preparation of epoxy matrix (EPM) and FA reinforced epoxy composites (FA-r-EPC) are as follows.

- **Bisphenol A diglycidyl ether (DGEBA) $C_{21}H_{24}O_4$:**

DGEBA, trade name LY561-LAPOX which is chemically Diglycidyl Ether IUPAC 2-[[4-[2-4-(oxiran-2-ylmethoxy)phenyl]propan-2-yl]phenoxy] methyl] oxirane, has been used in the research work was of AR grade, Atul Chemical make, chemical formula molecular weight $340.419 \text{ g mol}^{-1}$, density; $1.16\text{-}1.19 \text{ g ml}^{-1}$. Epoxy resin are polymeric materials generally possess at least two epoxide group, epoxide groups are also called as glycidyl or oxiranes.



2-[[4-[2-4-(oxiran-2-ylmethoxy)phenyl]propan-2-yl]phenoxy]methyl] (DGEBA)

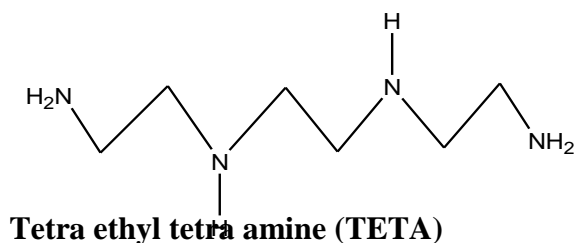
The IR spectra of LY561 (**Figure 2.5**) shows peak at 1027 cm^{-1} attributed to C-O-C stretching, peak at 912 cm^{-1} corresponds to C-O stretching while peak at 824 cm^{-1} , 764 cm^{-1} are of C-O-C, and -CH₂- rocking respectively of the oxirane group. The presence of aromatic ring is confirmed by benzene ring stretching bands at 1607 cm^{-1} , 1506 cm^{-1} , 1461 cm^{-1} . The chemical structure also possess methyl group whose presence is shown by peak at $2971\text{-}2880 \text{ cm}^{-1}$ corresponding to symmetric and asymmetric stretching of C-H of CH₃ while peak at 1355 cm^{-1} corresponds to -CH₃- bending frequency.[9](**Table 2.5**)

Table2.5. IR frequencies of DGEBA

Stretching of C-H of the oxirane	3057 cm ⁻¹	Stretching C-O-C of ethers,	1027 cm ⁻¹
Stretching of C-H of CH ₃ (symmetric & asymmetric)	2971- 2880 cm ⁻¹	Stretching C-O of oxirane group,	912 cm ⁻¹
-CH ₃ - bending	1355 cm ⁻¹	Stretching C-O-C of oxirane group,	824 cm ⁻¹
Stretching of C=C of aromatic rings,	1607 cm ⁻¹ , 1506 cm ⁻¹ , 1461 cm ⁻¹	CH ₂ Rocking	764 cm ⁻¹
Overtone	1650-2000 cm ⁻¹		

- **Tetra ethyl tetra amine (TETA) C₆H₁₈N₄:**

Amine based hardener TETA has been used in the present research work which is chemically N,N'-bis (2-aminoethyl) -1,2-ethanediamine with trade name HY 951, LAPOX of AR grade purchased from Atul Chemicals, having molecular formula molecular weight 146.238 gmol⁻¹, density 982 mgml⁻¹, m.p -34.6⁰C , b.p 266.6⁰C.



The IR spectra of TETA (**Figure.2.6**) reveals the presence of both primary and secondary amine group which is assigned by a broad band at 3269 cm⁻¹ corresponding to H-N-H asymmetric and symmetric stretching of the primary amine group, while single type stretching for secondary amine. The presence of methylene group is shown by the presence of peaks at 2920 cm⁻¹ and 2853 cm⁻¹ corresponding to the symmetric and asymmetric stretching frequency respectively of -CH₂- group,

which is further confirmed by the peak at 1453cm⁻¹ corresponding to -CH₂- bending vibration frequency [10].(**Table2.6**)

Table2.6. IR frequencies of TETA

	Primary Amine	Secondary Amine
N-H stretching	3269 cm^{-1} (Symm+Asymm)	3269 cm^{-1}
N-H bending	1649 cm^{-1} , 1549 cm^{-1}	Absent
N-H (wagging)	723 cm^{-1}	723 cm^{-1}
Stretching of C-H of CH_2 (symmetric & asymmetric)	2920 cm^{-1} & 2853 cm^{-1}	
- CH_2 - bending	1453 cm^{-1}	

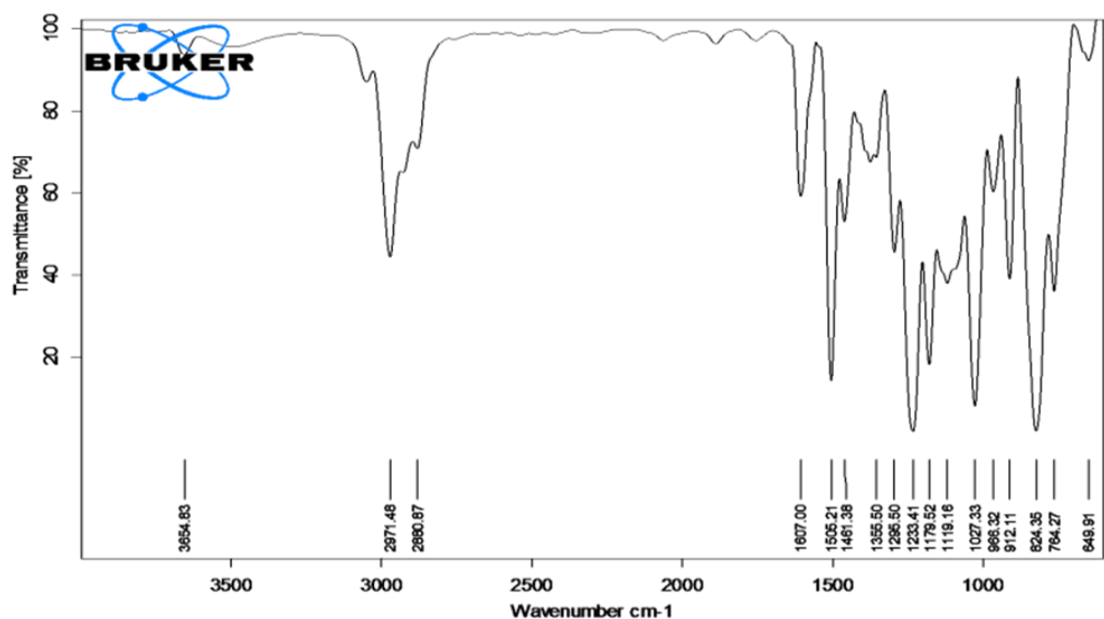


Figure 2.5 . IR spectra of Bisphenol A diglycidyl ether (DGEBA)

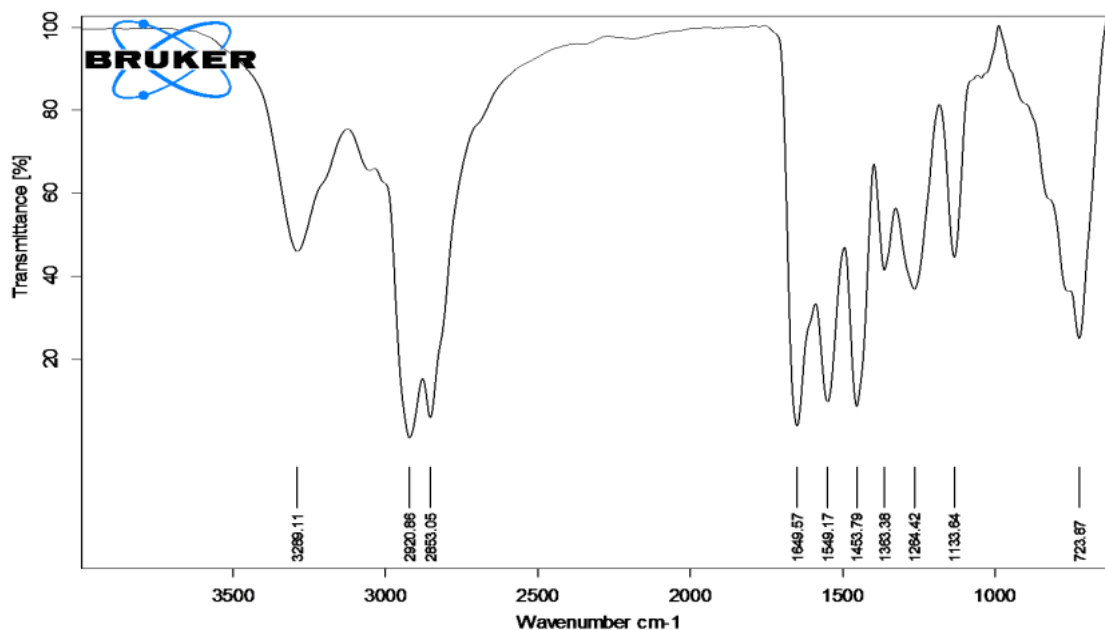


Figure 2.6 . IR spectra of Tetra ethyl tetra amine (TETA)

2.2.3. Mold and Mold Release

Iron molds are fabricated as per the ASTM D638 type IV standard pertaining to preparation of polymer samples for testing the mechanical properties (**Figure 2.7**) [11]. All the polymeric materials were casted in the metal (iron) mold (**Figure.2.8**) lined with mold release and cured for 24 hours at room temperature. Polymer samples with approximate dimensions of 14mm (width); 7mm (thickness); and 60mm (gauge length) are prepared during the research.

Mold release

Commercial Silicone spray (ALFA-40) procured from Jivika New Delhi is used as a mold release, for the easy release of PUM and FA reinforced PU composites (FA-r-PUC) from the metal molds. Non-Silicone spray (8329) procured from MG Chemicals, Noida used as mold release for the easy release of EPM and FA reinforced epoxy composites (FA- r-EPC) [12].

2.3 Synthetic Methodology

2.3.1. Polyurethane Synthesis

Liquid polyol components viz. PEG-600, BD and TMP were taken in a beaker fitted with mechanical agitator. Requisite amount of filler was added and mixed thoroughly to make a viscous paste to which CRA pre dried at 105⁰C in vacuum oven (to avoid reactions between isocyanates and water which forms CO₂ bubbles making PUC highly porous) was added for synthesis of FA-r-PUC. For PUM synthesis no filler was added in the above method. The resin mass thus prepared was poured in the mold lined with mold release. Curing was done for 24 hours; the samples were removed from the molds thereafter to test for various properties.

2.3.2. Epoxy Synthesis

For synthesis of FA-r-EPC method reported in earlier studies was adopted. Filler was mixed in Epoxy resin LY 561 to form homogenous paste using mechanical agitator and amine based hardener HY 951 in the resin hardener weight ratio 1:1 was added[13,14]. The mix was latterly subjected to vacuum for removal of the entrapped air and poured into mold lined with suitable mold release. For EPM synthesis no filler was used.

A schematic representation of the method is shown in **Scheme 2.3**.

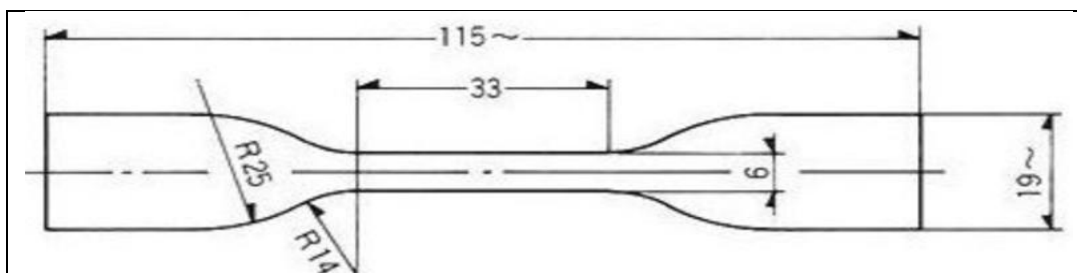


Figure.2.7 Design showing the ASTM standards D638 type IV format



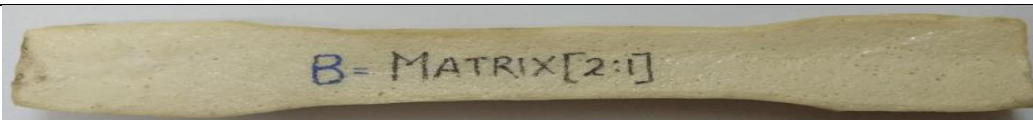
Figure2.8 Iron mold used for sample preparation



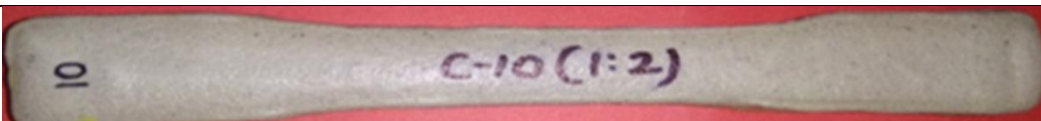
Epoxy Matrix



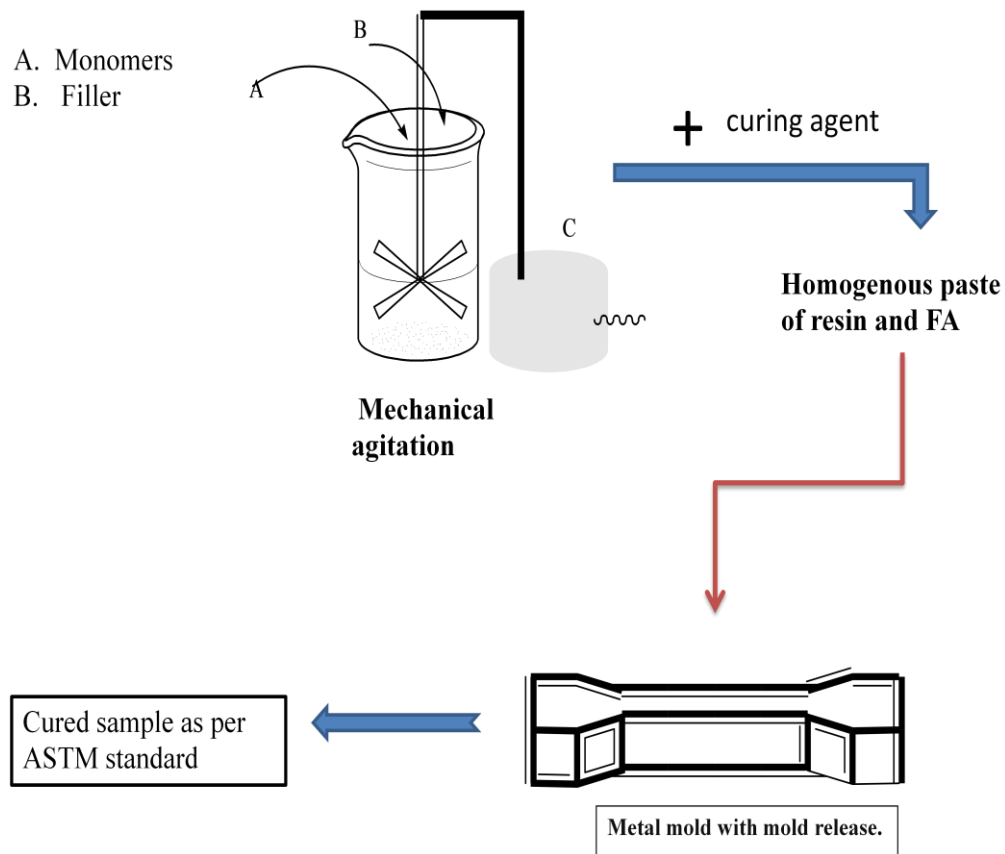
FA-reinforced Epoxy Composites



Polyurethane Matrix



FA-reinforced Polyurethane Composites



Scheme 2.3 Synthetic route of polymer samples

2.4 Analytical Techniques

Structural analysis of the raw and OH-functionalized fly ash and the evaluation of mechanical property of the prepared polymer matrices and their FA-reinforced composites were done by various analytical tools whose brief description is as under.

2.4.3. Fourier Transform Infrared (FTIR) Spectroscopy

For determining the chemical composition and chemical structure of the raw material and the synthesized products FTIR is a good analytical tool. FTIR is very helpful in the field of polymer science also, as it gives the estimation of the functional groups of

the raw materials/monomers and the finished polymeric products with high wave number precision, which can be used for tracing the mechanistic synthetic route of the reactions. In the present research work FTIR (TENSOR27, Bruker, USA) has been used for Filler and polymer characterization.

2.4.4. FTIR-ATR

It is a spectroscopic analytical tool based on attenuated total reflection, in this technique IR radiation passes through ZnSe crystal and then interacts with the sample, it characterizes the substance either in liquid or in solid. In the present research work the FTIR-ATR used is ALPHA model of, Bruker make, USA.

2.4.5. X-Ray Diffractometer (XRD)

The XRD is used in determination of the crystalline pattern, which is observed due to reflection from the crystalline phases of the filler or the matrix domain of the polymer under study. In this technique when the sample is subjected to the X-ray irradiation the scattering pattern obtained, wherein the intensity of the scattered radiations depends on the scattering angle θ . The variation in the electron density is mainly causes the scattered pattern. Powder X-ray diffraction studies was done by using (Philips X'pert) analytical diffractometer using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) in 2θ range of $5-65^\circ$. Structural properties viz. crystal phase, crystallinity, crystallite size of fly ash samples were determined using XRD technique. The fly ash samples were scanned in 2θ range of $0-80^\circ$ with scanning rate of 0.04°s^{-1} . The planes of crystal lattice are assigned h, k, and l called as miller indices. Planes h,k,l intercepts the a –axis of unit cell in h section b axis in k sections and the c – axis in l sections. The lattice planes and the incident X-Ray beam is oriented at specific angle θ to allow diffraction, beams which get reflected at lattice planes in distance $dhkl$ undergo interference to give maximum intensity, which finally appears as signal/peak in diffractogram. When the path difference $2dhkl$ is an integer of

wavelength (λ), than it can be mathematically co related with the equation called Bragg's equation (2.1)

$$n.\lambda = 2.dhkl.\sin\theta \quad \dots\dots\dots(2.1)$$

In X-ray diffractogram , graph is plotted between reflected intensity versus diffracted angle 2θ . The peak position gives information about lattice parameters.

2.4.6. Planetary Ball Mill

It is a grinder having a hollow shell having grinding balls capable of rotating at high rpm and can reduce the size of the material due to impact and attrition. In the research work planetary ball mill model RETSCH PM 100 (Inkarp, Germany) having an agate jar with 5mm size agate balls wherein the filler FA was charged and subjected to mechanical activation for 15 hrs at 350 rpm is used.

2.4.7. Scanning Electron Microscopy (SEM)

SEM is a surface morphology elucidation technique in which highly focused electron beam is used to get a very high resolution image of surface topography, showing excellent depth of field. The scanning electron microscope model ZEISS make Germany (EHT=20KV, WD=16.5mm, Mag=150KX) was used for analyzing the FA reinforced epoxy and PUC for examining the filler distribution in the matrix and witness the extent of polymerization.

2.4.8. Universal testing machine (UTM)

For the determination of the Mechanical Property of polymeric matrix/composites UTM model UTE-40, is used following the standard procedure for measurement of properties as stated below. The mechanical properties viz. Tensile Strength, Young Modulus, %Elongation, Yield point etc of the prepared polymeric materials were evaluated using ASTM standards. The specimen were prepared and were placed in

between grips of UTM machine being equipped with software automatically recording the change in gauge length with cumulatively increment of load on specimen. Results are obtained in terms of F_m (Force maximum) displacement at F_m , maximum displacement, ultimate strength and elongation with a graphical representation of load v/s displacement.

Tensile Strength: -

The tensile strength measures the ultimate resistance of the solid material before it breaks, it is reported as the force per unit width, the units of measurement are Pa or MPa or N/m^2 or $lb/inch^2$ or Psi.

Young Modulus: -

Young modulus (σ) is the measure of the stiffness of solid material and gives the relationship between stress (F/A) and Strain (proportional deformation, $\Delta L/L$) of the material under test in the linear elastic zone. The SI units of modulus are Pa or GPa.

$$\text{Young modulus } \sigma = \frac{[F/A]}{[\Delta L/L]}$$

2.4.9. Rockwell Hardness Tester

Hardness of any solid material is measured in terms of force needed for penetration to a specified depth; hardness is the function of temperature and constitution of the material. Hardness of FA-r-PUC and EPC and their matrix thereof were evaluated by Rockwell hardness tester which is based on the indentation of the material. The results on the Rockwell scale are dimensionless numbers denoted as HRA, HRB, HRC etc.

2.4.10. Differential Scanning Calorimetry (DSC)

For analyzing the thermal behaviour of the polymeric material, Differential Scanning Calorimeter model DSC 204F1 Phoenix by NETZSCH, Germany is used wherein

the sample is heated in inert atmosphere over a temperature gradient and a graph is obtained between difference of heat flow between reference and the sample material and the temperature, phase transition of polymeric material is identified by the thermogram. Glass transition temperature, T_g , is the temperature at which polymer become soft and elastomeric, while below T_g the polymer act as hard glass. T_g value depends on the chemical composition and chemical structure of polymer. DSC also evaluates melting temperature T_m and crystallization temperature T_c , also. As phase transition requires heat energy, the DSC thermogram are endothermic in DSC scan. Sample were weighted and thermally analyzed from 30^0 C to 230^0 C using liquid nitrogen (40ml/min).

2.5. Filler/Fly ash

Coal generated fly ash (FA) has been collected from Kota Thermal Power Station (KTPS) situated in the Kota city. FA is a solid waste powder generated during coal burning at higher temperatures and remains as waste by product in power plants all over the world. FA is mainly a silico-aluminate material with an admixture of several other metal oxides present in varying amounts depending on the composition of coal. Earlier composition of FA obtained from KSTPS is as, MgO (0.8%), TiO_2 (1.3%), CaO (1.6%), Na_2O (2.8%), Fe_2O_3 (7%), Al_2O_3 (23%), SiO_2 (62%), and trace elements (1.5%) besides its application in the synthesis of geopolymers, zeolites, cementitious materials, catalyst etc, the unique property of FA is its porosity and particle size to support various functional moieties making it as a perfect filler replacing other conventional fillers viz. kaolin, talc, mica, silica, glass etc. in the polymer matrix. During the present research work differently activated FA samples are used and are described as follows

2.5.1. Raw Fly Ash (RAFA)

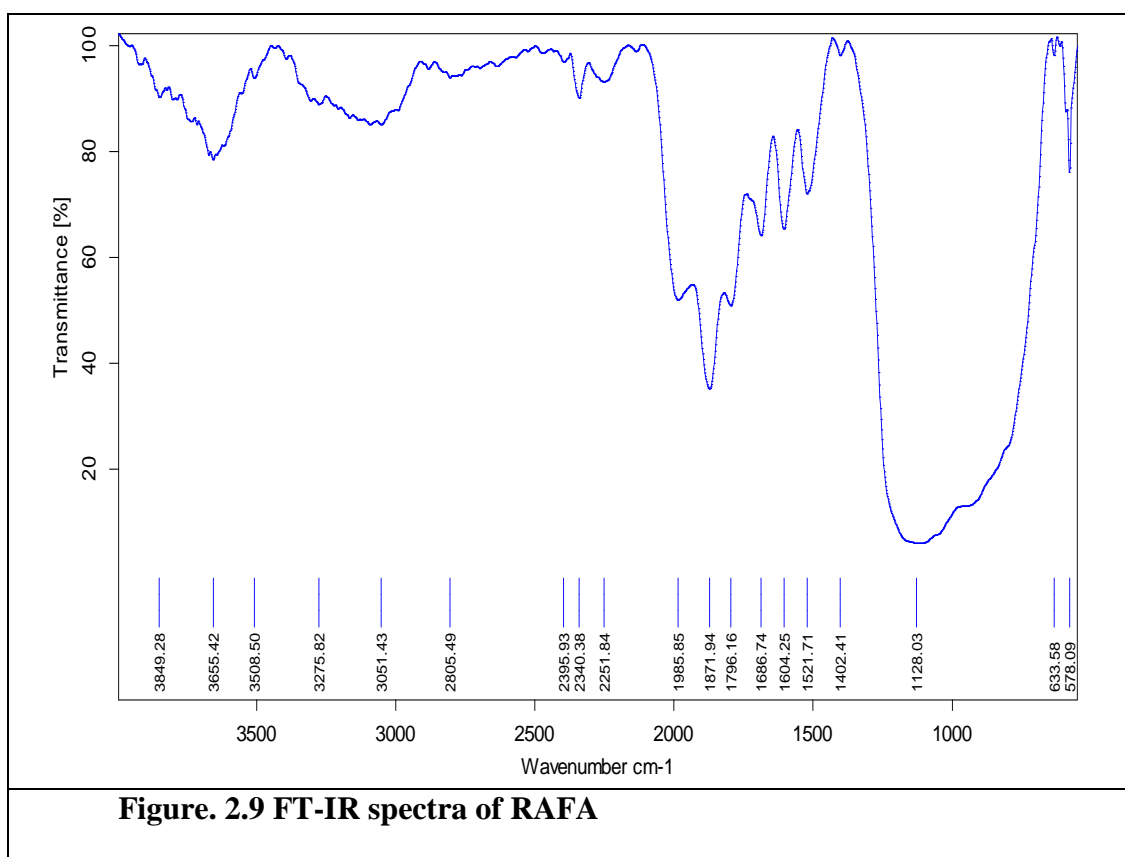
FA directly collected from KSTPS is used as filler in PU and Epoxy composites is denoted as RAFA. In the FT-IR spectra of RAFA (**Figure.2.9**) the peak around 3400-

3000 cm^{-1} corresponds to $-\text{OH}$ of $-\text{Si}-\text{OH}$ groups of aluminosilicate filler FA, the peak also attributes to the OH of surface adsorbed water molecules, OH group is extensively involved in H-bonding. Peak at 1650 cm^{-1} corresponds to the bending mode of $-\text{OH}$. Other IR peaks are Si-O-Si symmetric stretching (798 cm^{-1}) Si-O-Si bending vibrations (460 cm^{-1}) and Z-O-Si (Z=Al, Si) asymmetric stretching (913, 1090, 1160 cm^{-1}). A peak around 996 cm^{-1} , 1081 cm^{-1} and 1185 cm^{-1} corresponds for vitreous phase of unreacted FA, mullite and quartz various peaks are summarized in the **Table 2.7**

Table 2.7 Characteristic IR peaks of RAFA

S.No:	Chemical Functional group/ Vibration band	Characteristics absorption range, Wavelength (cm^{-1})	Reference
1	Surface $-\text{OH}$ of $\text{SiOH}/\text{Al}_2\text{O}_3$	3826.87, 3655.42, 3508.50	15
2	O-Al-O-H/Crystalline water	3275.82	16
3	Surface $-\text{OH}$ group	3051.43	17
4	CH_2 Stretch	2805.49	18
5	H- SiO_3	2251.84	19
6	$\equiv\text{Si}-\text{H}$ (monohydride)	1985.85	15
7	C-H Stretching	1871.94	20
8	C=O Stretching	1796.16	21
9	δ -OH bending vibration	1686.74	22
10	Carbonate/ CO_3^{-2}	1604.25	23
11	CO_3^{-2} group Symmetric Stretch	1521.71	24

12	CaO/CO ₃ ²⁻	1402.41	25
13	Si-O-Si stretching	1128.03	26
14	Calcium oxide	633.58	27
15	C-OH, Twist	578.09	28, 29



SEM Analysis of RAFA

The SEM image of RAFA reveals the spherical shape and smooth surface having iron particles clusters, quartz formed due to partial decomposition of dark quartz and pyrite. FA also exhibits wide distributed char, carbonaceous matter of irregular shapes and dimensions. FA also has agglomerates i.e particles of different size aggregated that may be solid or hollow cenospheres [30]. **(Figure. 2.10)**

XRD Analysis of RAFA

The identification of the crystal phase is based on the identification and comparing the reflection set of the sample with pure reference crystal phases or with data base **(Table 2.8)**. The crystallite size of crystalline phase is evaluated by the Scherrer formula [31-35]; Crystallite size = $K\lambda/W.\cos\theta$ K = shape factor, λ = wavelength of X-ray radiation use, W = difference of broadened profile width of the experimental sample (W_b) and standard profile width of the reference sample (W_s), θ = angle of diffraction. [36-37] **(Figure.2.11)** XRD diffractogram show that RAFA is nano-crystalline with crystallite size ranges from 33 to 60 nm. The broad gibbosity in XRD patterns ranges 2θ is in between $15-35^\circ$ indicates the coexistence of amorphous components also.

Table 2.8: XRD details of RAFA

Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Area [cts*°2Th.]	Particles Size (nm)
16.516	0.1005	5.38833	48.11	15.50	81
20.851	0.1507	4.25951	29.33	14.26	54
25.998	0.1172	3.42713	45.03	13.26	71
26.277	0.1003	3.39025	72.82	20.57	81
26.897	0.1505	3.34012	100.01	56.43	54
30.924	0.1505	2.88550	13.72	7.74	52
33.2662	0.1003	2.69486	28.55	13.42	81
35.4766	0.1507	2.54581	33.23	12.50	55
39.2657	0.2341	2.29416	12.64	9.50	33
40.861	0.3345	2.20857	38.96	22.01	26
42.178	0.1674	2.12147	11.18	12.62	48
60.6777	0.2341	1.52456	16.47	20.43	36

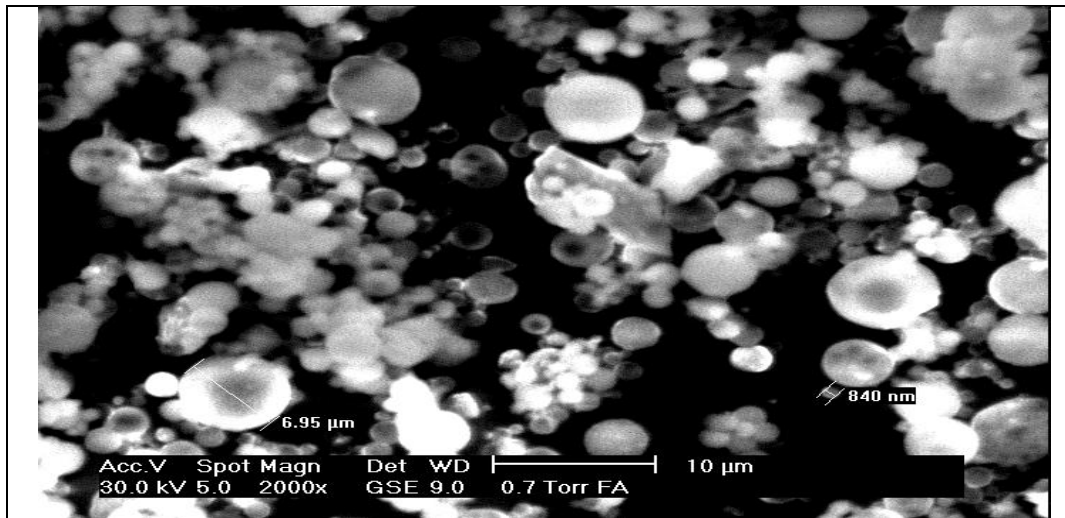


Figure. 2.10. SEM image of RAFA

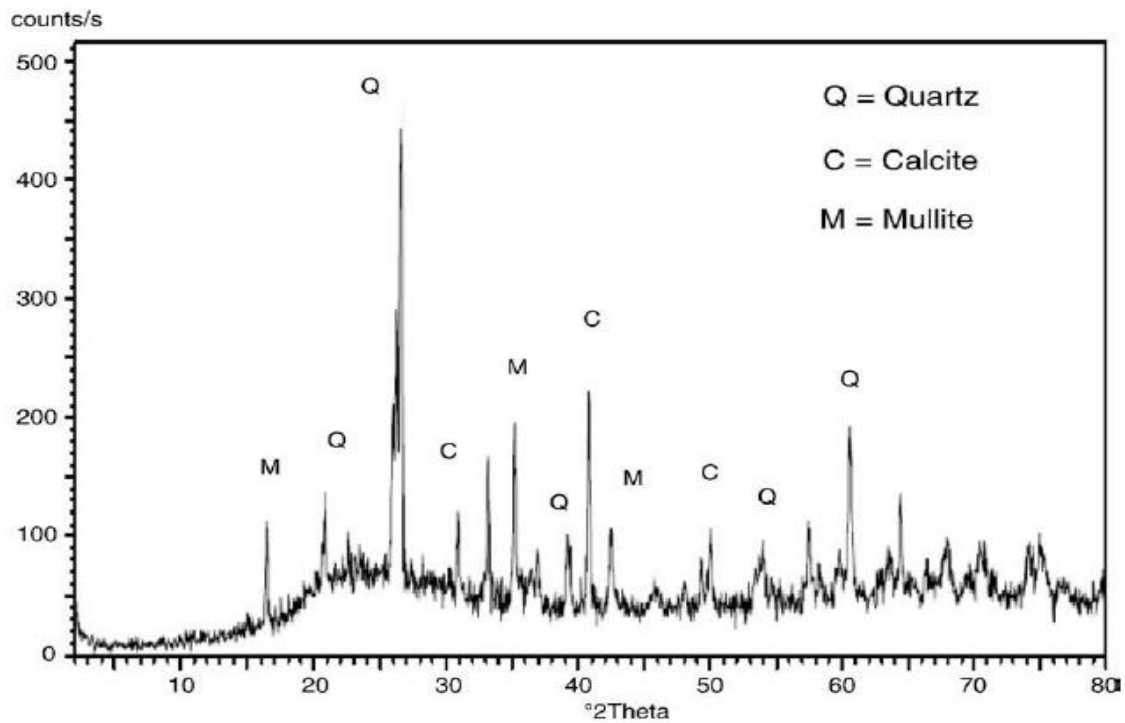


Figure.2.11. X-ray diffraction pattern of RAFA

Raw fly ash (RAFA) is activated mechanically, thermally and chemically for finding the possibility of OH functionalization. RAFA is converted into three different surface activated forms, methodology and characterization results are stated as below.

2.5.2. Mechanically Activated Fly Ash (MAFA)

Mechanical activation is a value addition in property of FA which enhances the reactivity of FA by increasing the surface area of surface and bulk as a whole. Fly ash reactivity is increased on mechanical activation due to bulk changes like structural changes and transformation of phases. MAFA for the present research work is obtained by feeding raw FA in high energy planetary ball mill.

Experimental Procedure

FA after washing with distilled water is dried for 24 hours at 100⁰C. After drying FA is subjected to planetary ball mill (Retsch PM-100, Germany) possessing an agate jar with 5mm grinding balls [38, 39] the filler is milled at 250 rpm for the time period of 5 to 10 hrs .

Characterization

FT-IR analysis of MAFA

After milling of RAFA for 5 hrs, it was seen that there was increment in the broadness of peak between 3600-3300 cm⁻¹ (**Figure 2.12**) which signifies the formation of Si-OH groups and breaking down of quartz structure [40]. The broadening of IR peak at 1095 cm⁻¹ (**Table 2.9**) which corresponds to Si-O-Si asymmetric stretching vibrations [41] signifies the structural rearrangements in RAFA after 5 hrs milling. Peak at 697 cm⁻¹ corresponding to Si-O-Si symmetric stretching also shows changes in the intensity of Peaks, these changes in the intensity of the peaks indicates the structural changes of the RAFA after mechanical activation.

Table 2.9. IR stretching frequency table of RAFA and MAFA

S. No.	Chemical Functional groups/Vibration band	RAFA	MAFA (15h)
1.	Surface-OH group of SiOH/Al ₂ O ₃ (Maxima.)	3632	3432
2.	O-H Stretch (Alcoholic & water	3553	3301
3.	C-H stretching vibration	2827	-
4.	ν OH stretching	2343	-
5.	H-SiO ₃	2241	-
6.	=Si-H (monohydride)	1984	1989
7.	Calcium Carbonate	1872	1870
8.	H-O-H bending vibration	1681	1614
9.	CaO	1524	1524
10.	Si-O-Si asymmetric stretching	1100	1095
11.	Si-O-Ca stretching	-	1050
12.	Carbonate group	-	-
13.	Calcium oxide (CaO)	610	610
14.	C-OH,TWIST	570	565

SEM analysis of MAFA

SEM image of MAFA (**Figure. 2.13**) reveals that there are structural changes after mechanical activation of RAFA by milling for 5 hrs, which is shown by the structural variation of large particles with increase surface roughness. High affect, is on the morphology of smooth spherical cenospheres with breaking of silica structure.

XRD analysis of MAFA

From XRD data it is clear that with mechanical activation there is an increment in the amorphous components as revealed by the broad gibbosity pattern in diffractogram at

2theta corresponding to 15° to 35° there is a decrease in the size of crystallites wherein the quartz phase suffers the most (**Figure.2.14**). Evaluation of peak heights after milling reveals the same effect. quartz (silica) exhibits strong peaks at 20.7° , 26.5° , 26.66° , 40.66° , 49.96° and 54.2° while peaks at 16.4° , 42.2° and 26.2° corresponds to the mullite (alumino silicate) phases of 2θ values.(table 2.4). Peak corresponding to the value 33.56 and 35.62 are of iron oxide phases [42]. Ball milling minimises the crystallinity of the fly ash, & augments its amorphous domains. The intensity of peak corresponding to quartz phase is reduced with the increases in the milling. (**Table 2.10**)

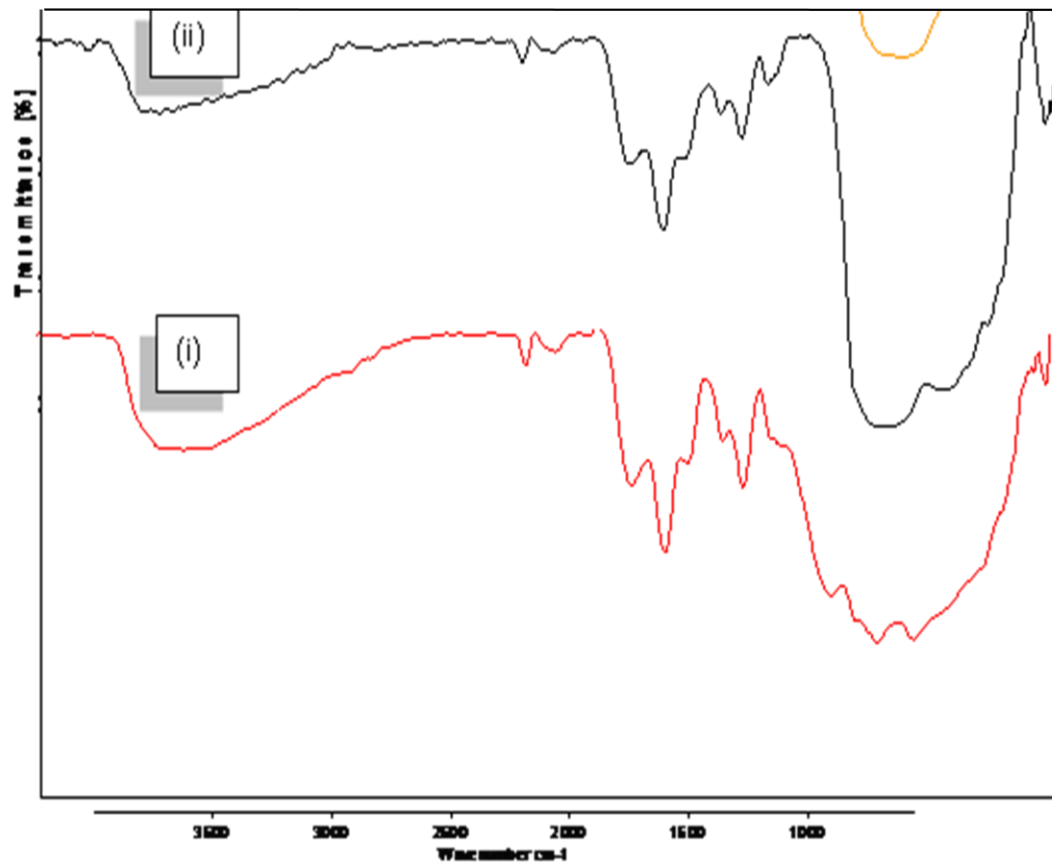


Fig.2.12 FT-IR spectra of (i) RAFA (ii) MAFA

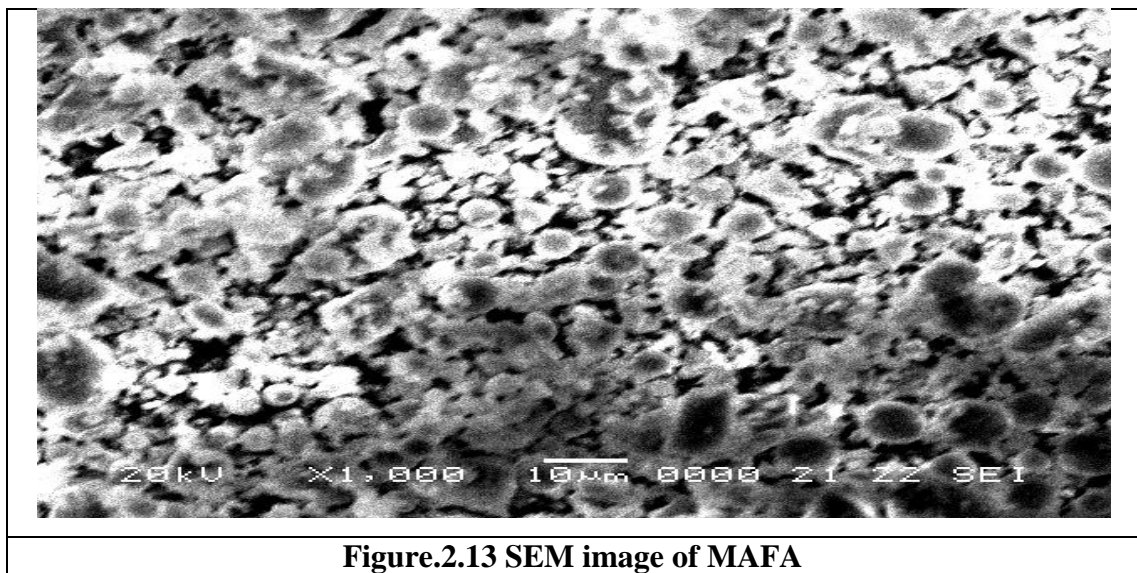


Figure.2.13 SEM image of MAFA

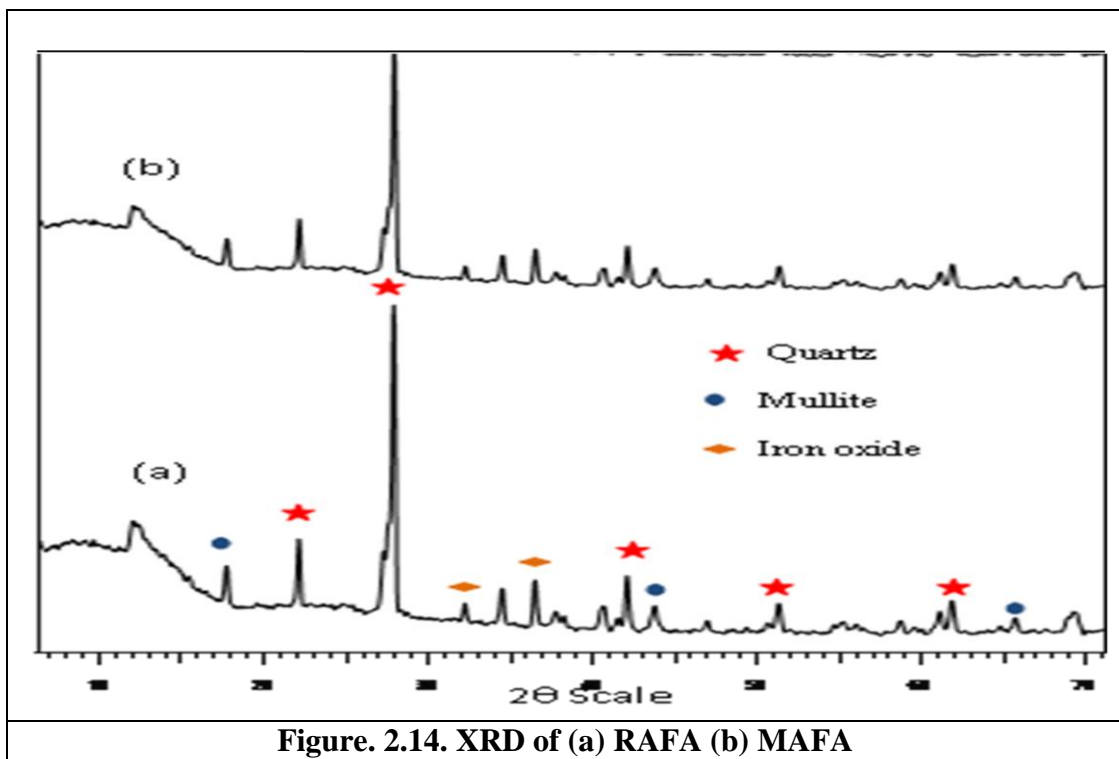


Figure. 2.14. XRD of (a) RAFA (b) MAFA

Table 2.10. XRD details of MAFA

Crystalline phases	2Theta	FA		MAFA-5h	
		Intensity Counts	Crystallite size (nm)	Intensity counts	Crystallite size (nm)
Mullite	~16	27.2	60	27.2	59
Quartz	~20	37.2	58	37.2	57
Quartz	~26	100	68	100	67
Calcite	~30	18.4	54	17.0	54
Hematite	~33	20.5	69	20.6	68
Magnetite	~35	21.0	56	20.4	55
Quartz	~39	18.4	26	18.1	25
Calcite	~40	20.5	50	20.9	49
Mullite	~42	17.8	36	17.5	28
Calcite	~50	17.3	54	16.2	53
Quartz	~54	12.1	33	10.7	29
Quartz	~60	17.9	32	17.8	18

2.5.3. Thermally Activated Fly Ash (TAFA)

Experimental Procedure

Thermocouple- controlled muffle furnace was used wherein RFA was calcined at heating rate of 15⁰C per minute to maximum temperatures of 500⁰C, with 4 hr holding time. Samples at maximum calcinations temperature 500⁰C, 700⁰C and 900⁰C were prepared

Characterization

FT-IR analysis of TAFA

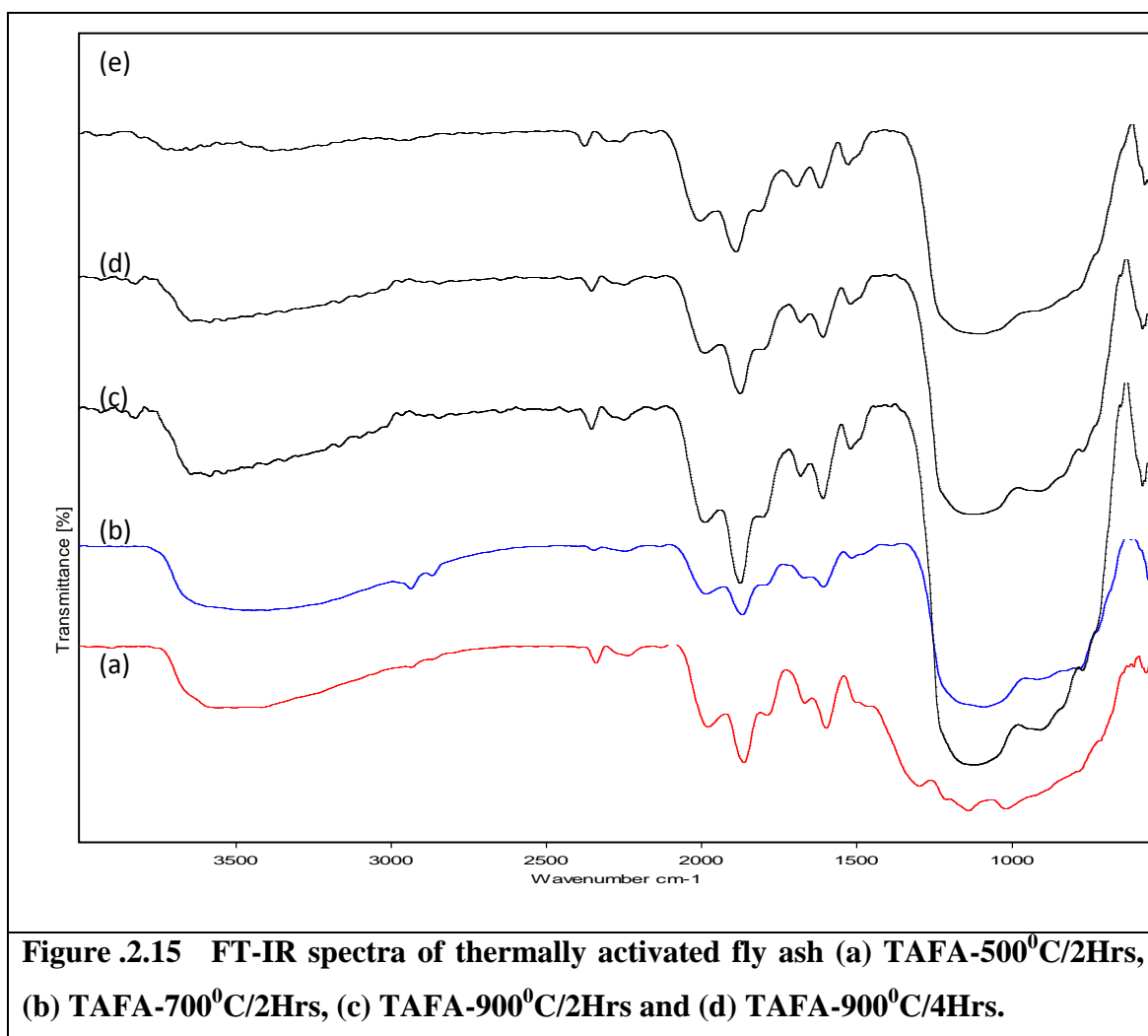
IR peak around 3600-3000 cm⁻¹ corresponds to the stretching frequency of OH functionality of Si-OH & that of water molecules adsorbed on the surface of FA. The broadening of peak is attributed to H-bonding of OH moiety. Bending frequency of

OH is revealed by the peaks around 1608, 1613 and 1680 cm^{-1} which undergo no changes after thermal activation of FA (**Table 2.11**).

The decrease in the broadness and intensity of peak at 3600-3000 cm^{-1} indicates the loss of molecular water during thermal activation. When FA undergo thermal activation upto 250°C there is loss of molecular water yet the crystalline OH persists up to 700°C. The Si-O-Si symmetric stretching frequency around 1100 cm^{-1} shifts to 1162 cm^{-1} , indication of this higher frequency shift is due to loss of molecular water. Peak around 2887 cm^{-1} is attributed to the C-H stretching of organic contamination in FA, the intensity of this band decreases when FA is thermally activated revealing the removal of organic contamination. (**Figure.2.15**)

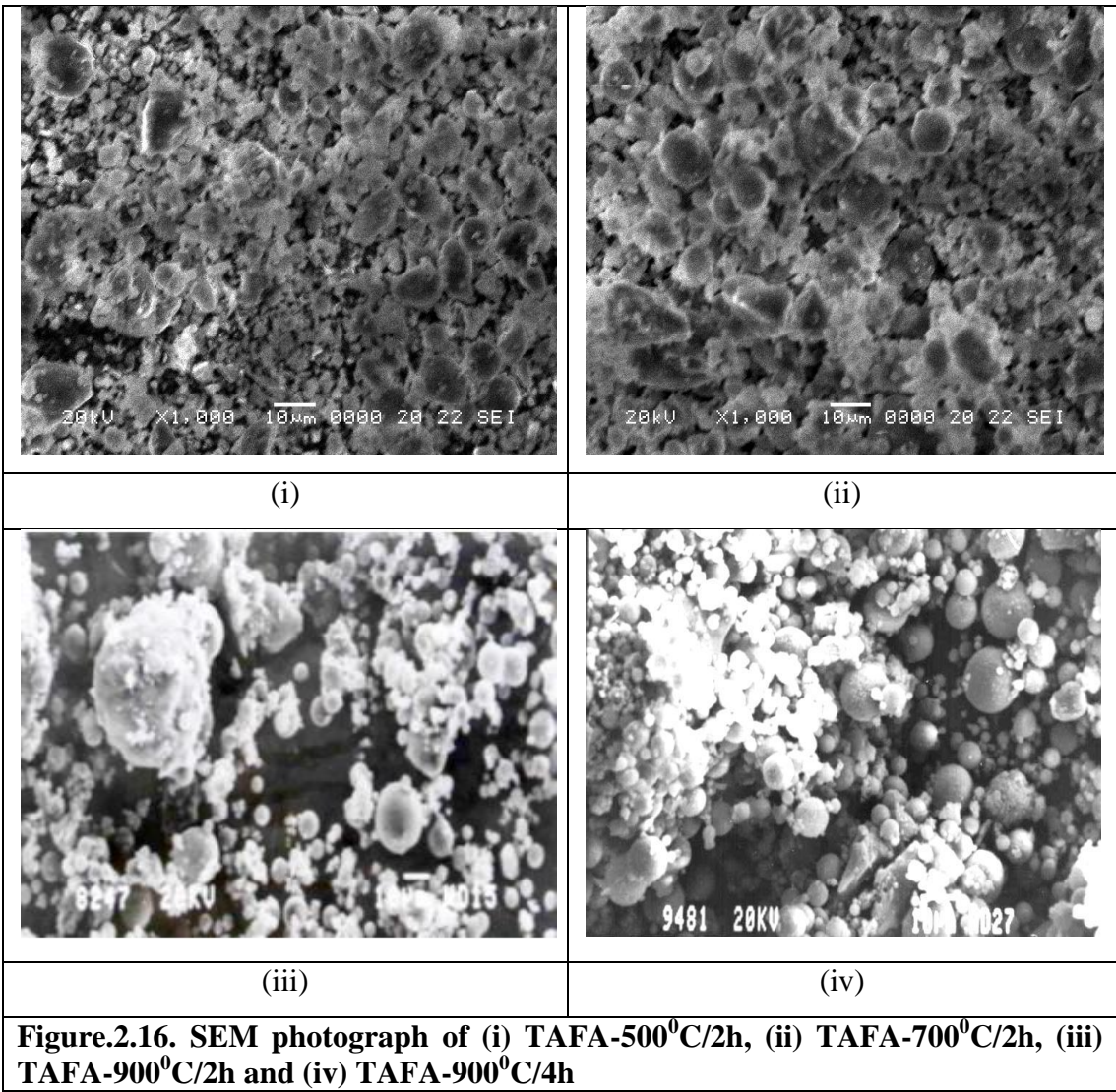
Table 2.11. IR stretching frequency of TAFA at different temperatures

S. No.	Chemical Functional groups/Vibration band	Characteristics absorption range, Wavelength (cm^{-1})				
		FA	TAFA (500°C/2h)	TAFA (700°C/2h)	TAFA (900°C/2h)	TAFA (900°C/4h)
1.	Surface-OH group of SiOH/Al ₂ O ₃ (Maxima.)	3632	3592	3590	3591	3590
2.	O-H Stretch (Alcoholic & water	3553	3155	3276	3327	3260
3.	C-H stretching vibration	2827	2887	2886	2890	2895
4.	v OH stretching	2343	2344	2341	2347	2345
5.	H-SiO ₃	2241	2240	2242	2246	2248
6.	=Si-H (monohydride)	1984	1984	1986	1980	1986
7.	Calcium Carbonate	1872	1872	1872	1873	1874
8.	H-O-H bending vibration	1681	1680	1682	1681	1680
9.	CaO	1524	-	-	-	-
10.	Si-O-Si asymmetric stretching	1100	1104	1112	1138	1140
11.	Si-O-Ca stretching	-	-	-	-	-
12.	Carbonate group	-	-	-	-	-
13.	Calcium oxide (CaO)	610	610	-	-	-
14.	C-OH,TWIST	570	570	-	-	-



SEM analysis of TAFA

When FA was subjected to thermal activation, carbonaceous and char were removed, which is also clear from the SEM images (Figure.2.16), this has happened, may be due to enhancement in the size of magnetic particles which are the result of transformation of hematite phase to magnetic phase.



XRD analysis of TAFA

It is revealed from XRD data that, on thermal activation of FA at high temperature quartz component of FA shows an increment in crystallinity and size of crystallite. Thermally activated FA major phases are mullite and quartz while the hematite and magnetite being the minor phases. **Table 2.12** shown below effect on crystallite size and intensity of various mineral phases upon thermal activation at different temperature and time duration. **Figure 2.17** shows XRD pattern of TAFA at various temperature and time duration.

Table 2.12: Effect of thermal activation on intensity of different crystalline phases for FA (XRD detail of TAFA)

Crystalline phases	2 θ	TAFA-500 ⁰ C/2h		TAFA-700 ⁰ C/2h		TAFA-900 ⁰ C/2h		TAFA-900 ⁰ C/4h	
		Intensity counts	Crystallite size (nm)	Intensity counts	Crystallite size (nm)	Intensity Counts	Crystallite size (nm)	Intensity Counts	Crystallite size (nm)
Mullite	~16	27.6	62	27.8	63	28.2	64	28.4	65
Quartz	~20	37.2	69	37.2	70	37.2	71	37.3	72
Quartz	~26	100	70	100	71	100	72	100	75
Calcite	~30	18.0	82	18.1	83	18.4	84	18.5	85
Hematite	~33	21.1	70	21.2	70	22.1	72	22.2	74
Magnetite	~35	20.5	55	20.2	54	20.4	54	19.5	53
Quartz	~39	19.2	24	19.5	26	19.5	24	19.6	25
Calcite	~40	23.8	52	23.9	53	24.0	53	24.0	54
Mullite	~42	16.8	28	16.8	28	16.6	26	16.7	29
Calcite	~50	18.1	60	18.2	61	18.6	62	18.8	68
Quartz	~54	12.2	46	12.3	47	12.4	48	12.5	49
Quartz	~60	17.9	33	18.1	34	18.1	35	18.1	36

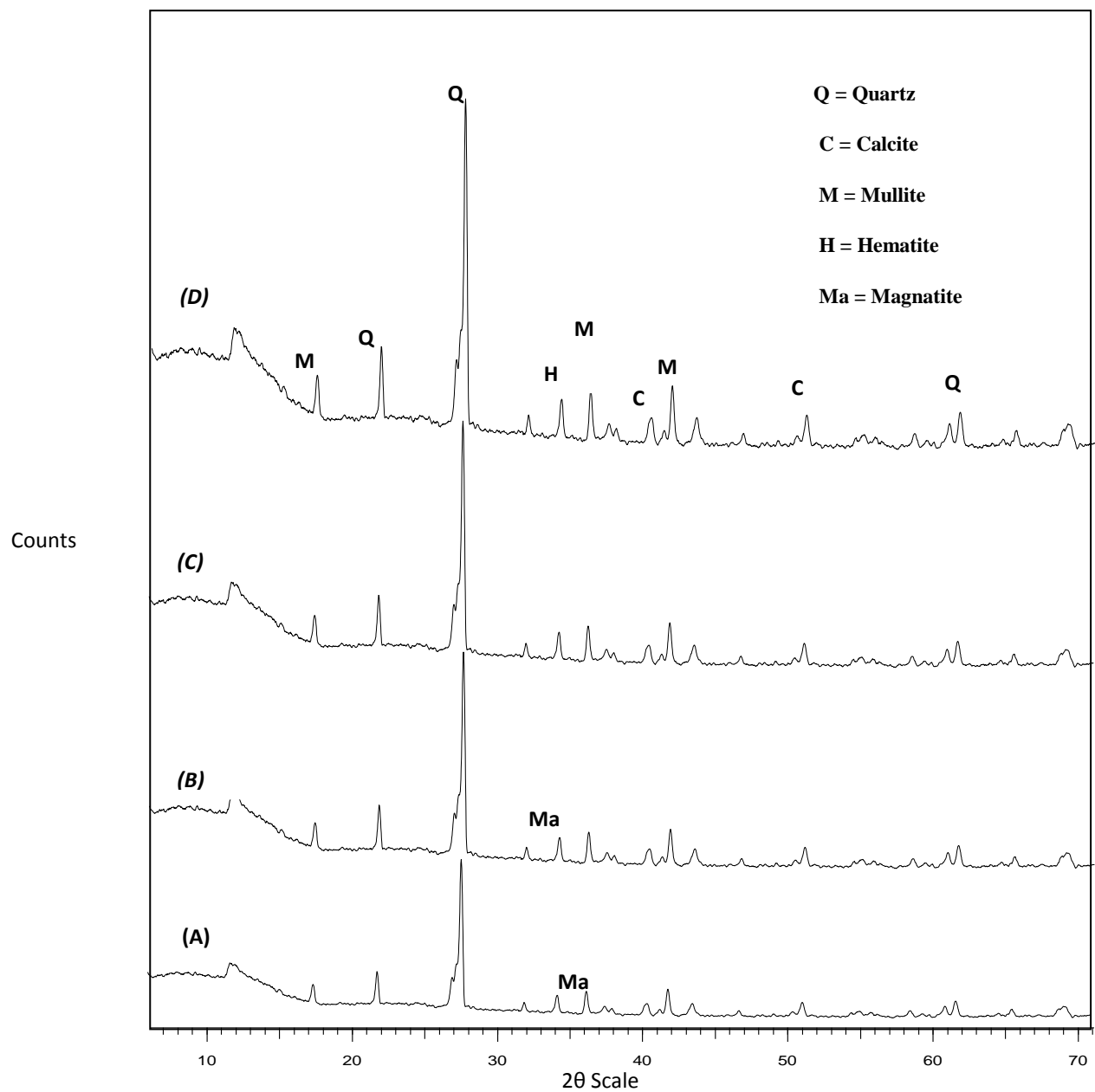


Figure.2.17 XRD (A) TFAA-500⁰C/2Hrs, (B) TFAA-700⁰C/2Hrs, (C) TFAA-900⁰C/2Hrs and (D) TFAA-500⁰C/4Hrs .

2.5.4. Chemically Activated Fly ash (CAFA)

Fly ash when subjected to alkali treatment forms silico-aluminate gel. The reaction occurring between the glassy component of FA and the alkali depends on the intrinsic factors viz. ash chemical composition, FA particle size and extrinsic factors viz. pH of the alkaline solution, curing time and temperature. During alkaline activation of FA the vitreous, amorphous and metastable structure of this alumina silicate material transforms into compact cementitious skeleton. Si-O-Si, Si-O-Al and Al-O-Al bonds of FA breaks releasing silicon and aluminium ions into the solution as soon as FA comes in contact with alkaline medium, forming higher number of Si-OH and Al-OH functionalities, which further condenses forming Si-O-Al, and Si-O-Si bonds forming zeolites precursor a 3-D alumino-silicate gel structure. If such gels are thermally activated than it forms zeolites of various shapes and sizes. An appropriate chemical treatment, followed by thermal can convert them into amorphous structure having OH functionalities adsorbed surfacially.

Experimental Procedure

In the present research work FA is chemically activated by treating it with conc. NaOH w/w 50% (FA:NaOH) for seven days , filtering it and after drying using this CAFA without calcinations UC-CAFA and calcining one batch of CAFA at 450⁰C for 5 hours to get calcined CL-CAFA as filler for preparing composites[46,47].

Characterization

FT-IR analysis of CAFA

A broad band in IR spectra of CAFA around 3400-3000c cm⁻¹represents OH group stretching frequency which is contributed by OH functionality of Si-OH and surface adsorbed water molecule. The hydroxyl functionalities are not solitary, but are strongly associated with inter molecular H-bonding, which is revealed by the broadness of the band.

FA after chemical activation shows intense band corresponding to OH group and variation in intensity of bands mainly corresponding to Si-O-Si bending (460 cm^{-1}), Z-O-Si (Z=Si, Al) asymmetric stretching at $1160, 1090, 913\text{ cm}^{-1}$ and peak at 798 cm^{-1} corresponds to the Si-O-Si symmetric stretching. CAFA's IR bands for vitreous phases of unreacted FA at 996 cm^{-1} , mullite at 1185 cm^{-1} and quartz at 1081 cm^{-1} are also shown in **Figure 2.18**.

SEM analysis of CAFA

SEM images of CAFA shows cenospheres which are spherical particles with diameter 840 nm to 6.95 micron meter . Particles are mainly hollow cenospheres, mineral aggregates and solid spheres with unburnt carbon and amorphous particles. Chemical activation of FA converts crystalline particles into amorphous which finally agglomerates as depicted in **Figure. 2.19**. Conversion of FA into amorphous state is revealed greatly by absence of spherical shaped FA particles.

XRD analysis of CAFA

XRD of CAFA when calcined at 450°C shows increment in amorphous phase and decline in crystalline domain as is revealed by XRD pattern. The chemical activation enhances the amount of quartz, calcite and mullite as depicted by comparing the intensity of peaks of CAFA and RAFA. CAFA crystallite size is 11 nm representing the nano crystalline phase after chemical treatment of FA (**Figure. 2.20**).

On the basis of various characterization results, it is clear that RAFA has OH – functionalities over its surface due to atmospheric moisture, the physio-sorbed moisture content is removed on heating, thermal activation gives stability of crystalline OH functionalities active for participation in the polymer synthesis, by increasing the crystallinity of the filler. mechanical activation on the other hand increases the amorphous contents, this results in the increase of OH functionalities by moisture absorption, which if desired may be removed by calcination.

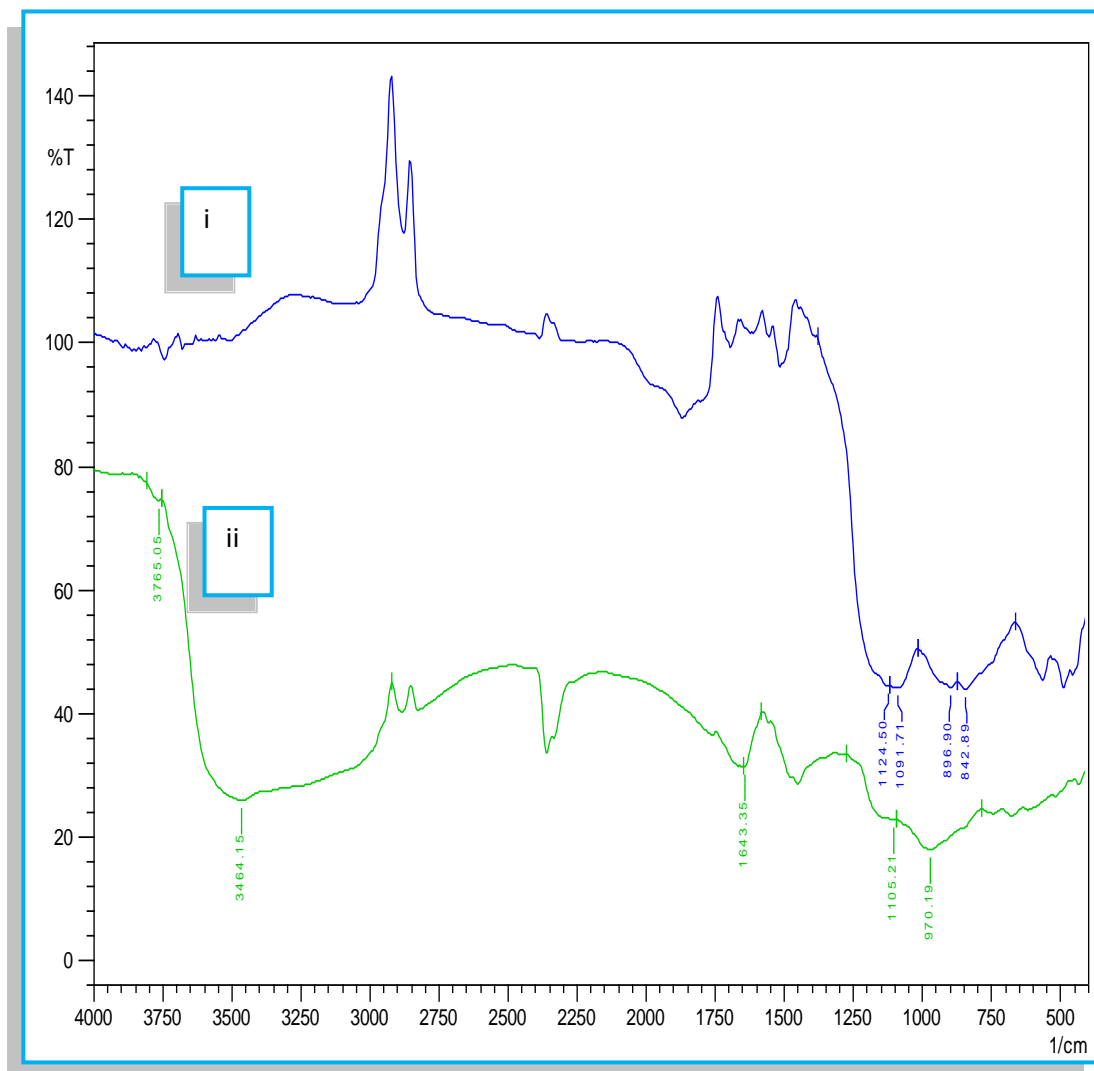


Figure. 2.18. FTIR spectrum of (i) RAFA (ii) CAFA

The decrease in particle size is obvious through mechanical activation which may results in more homogeneity and distorted particle structure of filler particles. However the calculation for polymeric ratio and filler is taken considering the aspect ratio unity. Chemical activation improves filler surface with chemisorbed OH functionalities suitable for PU and epoxy polymeric system. In the subsequent chapters the interesting results of role of filler activation and extent of OH

functionalization on physical nature and strength of different polymeric systems are presented.

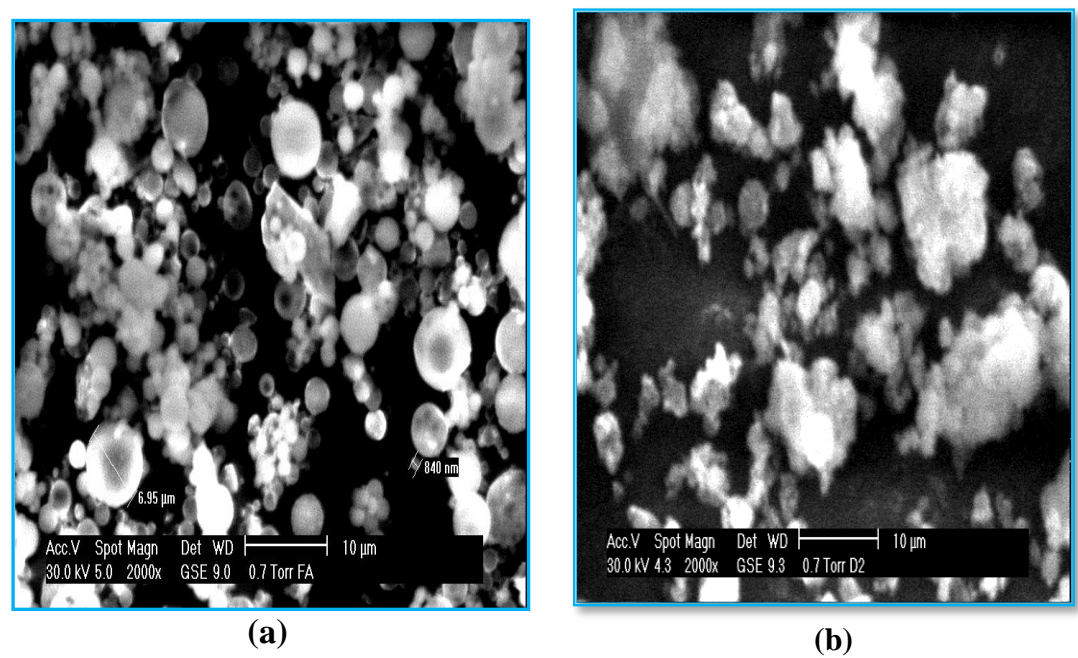


Figure. 2.19 SEM images of (a)RAFA and (b) CAFA

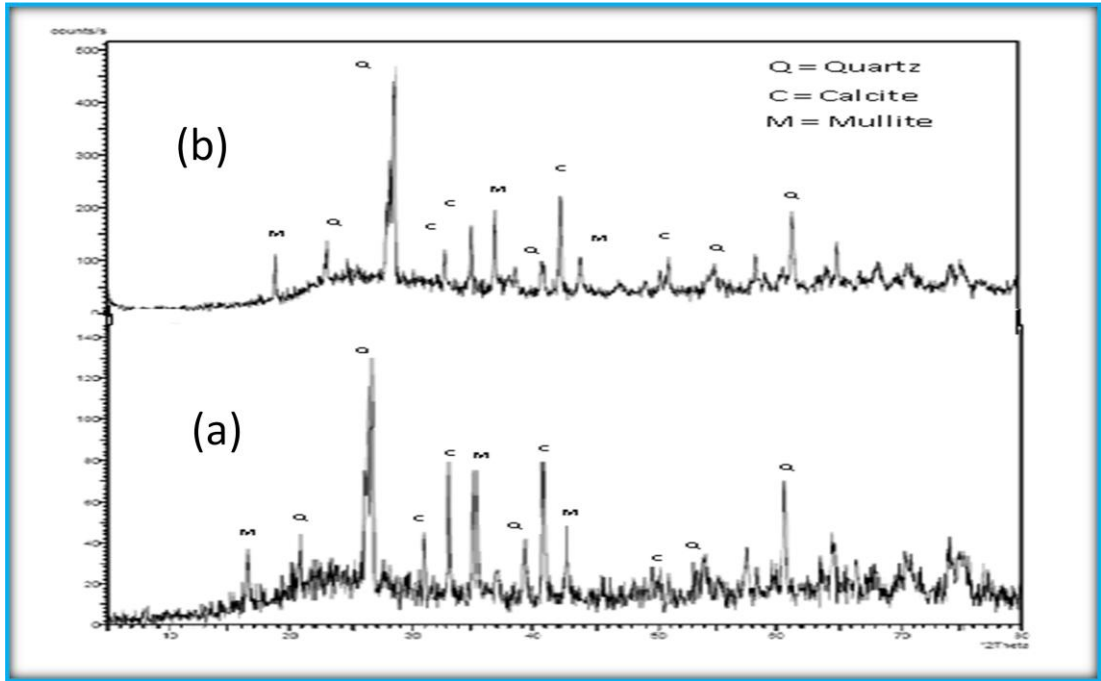


Figure. 2.20 X-ray diffraction pattern of (a) RAFA (b) CAFA

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**Preview of Monomer Molar Equivalency in
Polyurethane System:
A Model Study**

ABSTRACT

The chapter gives in detail the description of theoretical preview of PU-Polymerization. The concept of monomer mole ratio equivalency has been used for the PU system, wherein the monomer units taken were : Binder/chain extenders(CE), PEG-600 (polyethylene glycol) ; cross linkagers (CLA) as homogenous mixture of 1,4-butanediol(BD) and 1,1,1-trimethylol propane (TMP); curing agents(CRA); 2,4-toluene diisocyanates. For evaluating the extent of polymerization, NCO/OH (IR= index ratio) has been evaluated by using mole concept and is compared by using experimentally verified proposed model equations developed and used for determining the number of OH functionalities, for CE, BD, and TMP and evaluating number of NCO functionalities of curing agent TDI.

The ratio of binary components of CLA has not affected the extent of polymerization , rather the weight of CLA affected, that too was evaluated by the proposed model equations $\sum_n^{TMP} OH + \sum_n^{BD} OH = [W]CLA_{mix} \times 13 \times 10^{21}$. For IR values less than unity incomplete polymerization was noticed, while for IR unity effective/complete polymerization was seen. The extent of polymerization was experimentally verified by SEM study.

3.1 Introduction

By controlling different variables such as functionality, chemical compositions and molecular weight of different monomers a wide class of polymeric materials varying in physical properties can be designed [1-5]. PU is the class of versatile synthetic material prepared by the reaction of polyols and cross linking components [6-9] with curing agents [10-12]. The material finds uses as foams, elastomers, coating, sealers and adhesive based products. Some major applications of PU in the present century lie in the furniture, automotive, construction, thermal insulation and footwear sectors. With the growth of application of PU based product industries are always focused on improving the processibility, increase in the production rates, lowering in costs and minimum pollution. The formulation based on the innovation and more sophisticated applications, continued to develop every day and demand a better understanding of the structure property relation. The stoichiometric NCO/OH ratio referred as index or percentage is the key property to successfully produce the PU foams with the desired physical properties [13-15], several other chemicals including water, surfactants, catalyst, filler affects the reaction time, curing temperature and rate. In the present chapter an innovative method of estimation of OH and NCO functionalities [16-19] is developed through molar equivalency concept firstly the hypothetically experiments are designed to evaluate for calculation of IR using mole concept for every reactant used in synthesis of studied PU material. Model equations were developed for the said polymeric materials which have successfully evaluated the extent of polymerization, which were validated experimentally, the morphological structures were confirmed through scanning electron microscopic studies.

3.2 Evaluation of Weight of Curing Agent; conventional method

The amount of CRA required to achieve desired polymerization, depends not only on the total amount of OH functionalities of CLA and CE but also on the OH contributed from additives and fillers, thus for calculation required to achieve polymerization

in different PU-polymeric systems, the general formula used for calculation of amount of CRA, is studied to develop model equations for the present research investigation

The general method for evaluating the concentration of the curing agent for complete polymerization for PU system is adopted in previous studies is in equation1.

$$W_{\text{cur}} = \text{IR} [E W_{\text{cur}}] [\Sigma W_n / E W_n]. \dots\dots\dots (1)$$

Where, W_{cur} is weight of curing agent. $E W_{\text{cur}}$ is NCO Eq. wt of curing agent, W is weight of each liquid component, and $E W_n$ is OH Eq. wt for each liquid, IR is the index ratio which is the ratio of NCO and OH. In the equation 1 , wherein the weight of curing agent is evaluated for complete polymerization need to incorporate the equivalent weight of polyols and curing agents for which the hydroxyl number and % NCO contents respectively is required to be determined either volumetrically or potentiometrically. To understand the significance for the amount of curing agent in determining the extent of polymerization for the PU system previous method has been used to evaluate the amount of Isonate wherein it is acting as CRA and the mixture of Tepanol and Castor Oil as CLA and sartomer HTPB (hydroxyl terminated polybutadiene) as CE. The calculation for complete polymerization i.e. linking all the liquids to form a polymeric chain, indicating IR as ≈ 0.1 . The amount calculated for the different ingredients is as given in the **Table 3.1**

Table 3.1 Ingredients of a PU system

Ingredient	Chemical Used as	Grams	Eq.Wt.
Sartomer HTPB	CE	10	1190
Tepanol	CLA	0.4	211
Castor Oil	CLA	0.3	164
Isonate	CRA	W_{cur}	144

$$W_{\text{cur}} = (1.0) (144) [10/1190 + 0.4/211 + 0.3/164] = 1.75\text{g}.$$

If the amount of curing agent is less than 1.75gm it will definitely degrade the polymer quality with IR less than unity. Contrary curing agent weight more than 1.75 shall brittle the polymer with the variation in the mechanical properties with IR greater than unity. The above method cannot be applied successfully without determining the NCO and OH values through analytical techniques. Thus a quick assessment of polymerization on changing the additives is not possible.

3.3 Evaluation of Index Ratio for Polymerization: Monomer Molar Equivalency Method

During the present research work an innovative approach has been adopted for understanding the polymerization fundamentals through mole concept having least variation. The calculations are based on the monomer mole ratio equivalency concept for the theoretical preview of polymerization using (CE) PEG-600 (polyethylene glycol) as CE, homogenous mixture of 1,4-butanediol (BD) and 1,1,1-trimethylol propane (TMP) as CLA, 2,4-toluene diisocyanates as CRA. . Number of moles/ molecules for each monomer unit is based on the general equation: $[(w/M)fN_0]$ wherein $w = \text{wt. (g)}$, $M = \text{(mol. wt)}$, $f = \text{functionality}$, $N_0 = \text{Avagadro number}$. for ideal case of polymerization, with index ratio 1, number of moles/ molecules for all the monomer units having OH functionalities should be equal to the number of moles of curing agent with NCO functionality i.e $[(w/M)fN_0]_{\text{OH}} = [(w/M)fN_0]_{\text{NCO}}$.

3.4. Designed Theoretical Experimental Illustrations.

To apply monomer equivalency concept, to foretell the extent /quality of polymerization theoretical experiments were designed keeping ratio of PEG-600 and TDI constant as 3:2. The ratio and wt. of CLA components were varied and ΣOH and ΣNCO were calculated through molar equivalency. Results are tabulated in **Tables 3.2-3.4** (for experiment 1 to 3) to **Tables 3.5-3.7** (for experiment 4 to 6).

Designed Theoretical Experiment-1

The numbers of moles corresponding to BD and TMP in 1 gm of CLA are 0.005548 & 0.003726 respectively. The number of OH functionalities rendered by BD & TMP will be 0.011096 & 0.011178 respectively. 1 gm of CLA total OH contribution will be 13.4089×10^{21} , the number of OH functionality contribution by 3 gm of CE in PU system is 6.02×10^{21} . The total OH functionality contribution by the homogenous mixture of CE (3gm) and CLA (1gm) in PU mix $[\Sigma_{OH}^{CE+CLA}]$ is 19.428×10^{21} . curing of these polyols were done by 2 gm of TDI used as CRA, whose total NCO functionality contribution were 13.82×10^{21} . From the calculations the value of IR is 0.711, which clearly figures out the incomplete extent of polymerization of PU system in terms of molar equivalency of monomer units wherein number of OH functionalities of CE and CLA were surplus over the total number of NCO functionality contribution of CRA (**Table 3.2**).

Table 3.2. Monomer molar equivalency calculations for polyurethane, with BD: TMP ratio 1:1 and CLA wt.1gm

Parameters of monomers	BD (m.w.90.12)	TMP (m.w.134.17)	PEG-600 (m.w.600)	TDI (m.w.174.2)
functionality (f)				
RATIO by wt	1	1	3	2
Wt (g)	0.5	0.5	3	2
moles of monomers(w/M)	0.0055	0.0037	0.005	0.011
Moles of functional groups(f x moles)	0.0110 (OH)	0.0111 (OH)	0.010 (OH)	0.022 (NCO)
Number of functional groups (f x moles x N_0)	6.6×10^{21}	6.7×10^{21}	6.02×10^{21}	13.8×10^{21}
Total number of functional groups	19.4×10^{21} (OH)			13.8×10^{21} (NCO)

Index ratio of experiment 1; NCO/OH = **0.711**

BD+TMP=1 gm

Designed Theoretical Experiment-2

The numbers of moles corresponding to BD and TMP in 1 gm of CLA are 0.003695. & 0.0049636 respectively .The number of OH functionalities rendered by BD & TMP will be 0.00739 & 0.01489 respectively. 1 gm of CLA total OH contribution will be 13.4×10^{21} . The number of OH functionality contribution by 3 gm of CE in PU system is 6.02×10^{21} . The total OH functionality contribution by the homogenous mixture of CE (3gm) and CLA (1gm) in PU mix $[\Sigma_{OH}^{CE+CLA}]$ is 19.428×10^{21} . curing of these polyols were done by 2 gm of TDI used as CRA, whose total NCO functionality contribution were 13.82×10^{21} (**Table 3.3**). The NCO and OH functionalities should react in terms of molar equivalency for the complete extent of polymerization in PU system i.e the NCO: OH which is the IR should be unity. In this theoretical experiment IR is 0.711, which clearly figures out the incomplete extent of polymerization of PU system in terms of molar equivalency of monomer units wherein numbers of OH functionalities of CE& CLA were surplus over the total number of NCO functionality contribution of CRA.

Table 3.3 Monomer molar equivalency calculations for polyurethane, with BD: TMP ratio 1:2 and CLA wt.1gm

Parameters of monomers	BD (m.w.90.12)	TMP (m.w.134.17)	PEG-600 (m.w.600)	TDI (m.w.174.2)
functionality (f)		3	2	2
RATIO by wt	1	2	3	2
Wt (g)	0.33	0.66	3	2
moles of monomers(w/M)	0.0036	0.0049	0.005	0.011
Moles of functional groups(f x moles)	0.007 (OH)	0.014 (OH)	0.010 (OH)	0.022 (OH)
Number of functional groups (f x moles x N_0)	4.4×10^{21}	8.9×10^{21}	6.02×10^{21}	13.8×10^{21}
Total number of functional groups	19.42×10^{21} (OH)			13.8×10^{21} (NCO)

Index ratio of experiment 02; NCO/OH =**0.711**

BD+TMP=1 gm

Designed Theoretical Experiment-3

The numbers of moles corresponding to BD and TMP in 1 gm of CLA are 0.007397 & 0.00248 respectively the number of OH functionalities rendered by BD & TMP will be 0.014795 & 0.0074457 respectively 1 gm of CLA total OH contribution will be 13.3886×10^{21} . The number of OH functionality contribution by 3 gm of CE in PU system is 6.02×10^{21} The total OH functionality contribution by the homogenous mixture of CE (3gm) and CLA (1gm) in PU mix $[\Sigma_{OH}^{CE+CLA}]$ is 19.4086×10^{21} . curing of these polyols were done by 2 gm of TDI used as CRA, whose total NCO functionality contribution were 13.82×10^{21} (**Table 3.4**). The NCO and OH functionalities should react in terms of molar equivalency for the complete extent of polymerization in PU system i.e. the NCO: OH which is the IR should be unity [20-26]. In this experiment IR is $[13.82 \times 10^{21}] / [19.4086 \times 10^{21}] = 0.712$, which clearly figures out the incomplete extent of polymerization of PU system in terms of molar equivalency of monomer units wherein number of OH functionalities of CE & CLA were surplus over the total number of NCO functionality contribution of CRA.

Table 3.4 Monomer molar equivalency calculations for polyurethane, with BD: TMP ratio 2:1 and CLA wt.1gm

Parameters of monomers	BD (m.w.90.12)	TMP (m.w.134.17)	PEG-600 (m.w.600)	TDI (m.w.174.2)
Functionality (f)	2	3	2	2
RATIO by wt	2	1	3	2
Wt (g)	0.666	0.333	3	2
moles of monomers(w/M)	0.007	0.002	0.005	0.011
Moles of functional groups(f x moles)	0.014 (OH)	0.007 (OH)	0.010 (OH)	0.022 (OH)
Number of functional groups (f x moles x N_0)	8.9×10^{21}	4.4×10^{21}	6.02×10^{21}	13.8×10^{21}
Total number of functional groups	19.4×10^{21} (OH)			13.8×10^{21} (NCO)

Index ratio of experiment 3; NCO/OH =0.7

BD+TMP=1 gm

Designed Theoretical Experiment-4

The numbers of moles corresponding to BD and TMP in 0.5 gm of CLA are 0.0027. & 0.0018 respectively .The number of OH functionalities rendered by BD &TMP will be 0.0054 &0.0054 respectively (**Table 3.5**).1 gm of CLA total OH contribution will be 6.5016×10^{-21} . The number of OH functionality contribution by 3 gm of CE in PU system is 6.02×10^{-21} The total OH functionality contribution by the homogenous mixture of CE (3gm) and CLA (1gm) in PU mix $[\Sigma \text{OH}^{\text{CE+CLA}}]$ is 12.52×10^{-21} . curing of these polyols were done by 2 gm of TDI used as CRA, whose total NCO functionality contribution were 13.82×10^{-21} . The NCO and OH functionalities should react in terms of molar equivalency for the complete extent of polymerization in PU system i.e the NCO: OH which is the IR should be unity. In this experiment IR is 1.10, which clearly figures out the complete extent of polymerization of PU system in terms of molar equivalency of monomer units wherein numbers of OH functionalities of CE & CLA were equal to the total number of NCO functionality contribution of CRA.

Table 3.5 Monomer molar equivalency calculations for polyurethane, with BD: TMP ratio 1:1 and CLA wt.0.5gm

Parameters of monomers	BD (m.w.90.12)	TMP (m.w.134.17)	PEG-600 (m.w.600)	TDI (m.w.174.2)
Functionality (f)	2	3	2	2
RATIO by wt	1	1	3	2
Wt (g)	0.25	0.25	3	2
moles of monomers(w/M)	0.0027	0.0018	0.005	0.011
Moles of functional groups(f x moles)	0.0054(OH)	0.0054 (OH)	0.010 (OH)	0.022 (OH)
Number of functional groups (f x moles x N_0)	3.2×10^{21}	3.2×10^{21}	6.02×10^{21}	13.8×10^{21}
Total number of functional groups	12.5×10^{21} (OH)			13.8×10^{21} (NCO)

Index ratio of experiment 04; NCO/OH = **1.10**

BD+TMP=0.5 gm

Designed Theoretical Experiment-5

The numbers of moles corresponding to BD and TMP in 0.5 gm of CLA are 0.00184 & 0.00248 respectively (**Table 3.6**). the number of OH functionalities rendered by BD & TMP will be 0.00368 and 0.00744 respectively. 1 gm of CLA total OH contribution will be 6.7424×10^{-21} . The number of OH functionality contribution by 3 gm of CE in PU system is 6.02×10^{-21} . The total OH functionality contribution by the homogenous mixture of CE (3gm) and CLA (1gm) in PU mix $[\Sigma_{OH}^{CE+CLA}]$ is 12.713×10^{-21} . curing of these polyols were done by 2 gm of TDI used as CRA, whose total NCO functionality contribution were 13.82×10^{-21} . The NCO and OH functionalities should react in terms of molar equivalency for the complete extent of polymerization in PU system i.e. the NCO: OH which is the IR should be unity. In this theoretical experiment IR is $[13.82 \times 10^{-21}] / [12.713 \times 10^{-21}] = 1.08$, which clearly figures out the complete extent of polymerization of PU system in terms of molar equivalency of monomer units wherein number of OH functionalities of CE & CLA were equal to the total number of NCO functionality contribution of CRA.

Table 3.6 Monomer molar equivalency calculations for polyurethane, with BD: TMP ratio 1:2 and CLA wt.0.5gm

Parameters of monomers	BD (m.w.90.12)	TMP (m.w.134.17)	PEG-600 (m.w.600)	TDI (m.w.174.2)
Functionality (f)	2	3	2	2
RATIO by wt	1	2	3	2
Wt (g)	0.16	0.33	3	2
moles of monomers(w/M)	0.0018	0.0024	0.005	0.011
Moles of functional groups(f x moles)	0.0036 (OH)	0.0074 (OH)	0.010 (OH)	0.022 (NCO)
Number of functional groups (f x moles x N_0)	2.2×10^{21}	4.4×10^{21}	6.02×10^{21}	13.8×10^{21}
Total number of functional groups	12.7×10^{21} (OH)			13.8×10^{21} (NCO)

Index ratio for experiment 05; NCO/OH=1.08

BD+TMP=0.5 gm

Designed Theoretical Experiment-6

The numbers of moles corresponding to BD [30] and TMP in 0.5 gm of CLA are 0.0036 & 0.0012 respectively (**Table 3.7**). the number of OH functionalities rendered by BD & TMP will be 0.0072 & 0.0036 respectively 1 gm of CLA total OH contribution will be 6.7424×10^{21} . The number of OH functionality contribution by 3 gm of CE in PU system is 6.02×10^{21} The total OH functionality contribution by the homogenous mixture of CE (3gm) and CLA (1gm) in PU mix $[\Sigma_{OH}^{CE+CLA}]$ is 12.5216×10^{21} . curing of these polyols were done by 2 gm of TDI used as CRA, whose total NCO functionality contribution were 13.82×10^{21} . The NCO and OH functionalities should react in terms of molar equivalency for the complete extent of polymerization in PU system i.e the NCO: OH which is the IR should be unity. In this theoretical experiment IR is $[13.82 \times 10^{21}] / [12.5216 \times 10^{21}] = 1.10$, which clearly figures out the complete extent of polymerization of PU system in terms of molar equivalency of monomer units wherein number of OH functionalities of CE & CLA were equal to the total number of NCO functionality contribution of CRA..

Table 3.7 Monomer molar equivalency calculations for polyurethane, with BD: TMP ratio 2:1 and CLA wt.0.5gm

Parameters of monomers	BD (m.w.90.12)	TMP (m.w.134.17)	PEG-600 (m.w.600)	TDI (m.w.174.2)
Functionality (f)				
RATIO by wt	2	1	3	2
Wt (g)	03 gm		3	2
moles of monomers(w/M)	0.333	0.166	3	2
Moles of functional groups(f x moles)	0.0036	0.0012	0.005	0.011
Number of functional groups (f x moles x N_0)	0.0072(OH)	0.0036 (OH)	0.010 (OH)	0.022 (NCO)
Total number of functional groups	4.3×10^{21}	2.1×10^{21}	6.02×10^{21}	13.8×10^{21}
Functionality (f)	12.5×10^{21} (OH)			13.8×10^{21} (NCO)

Index ratio; NCO/OH of experiment 06=**1.10**

BD+TMP=0.5 gm

On calculating several numbers of sets of PEG-600/TDI ratio and variation in the ratio of BD and TMP in CLA, to forecast the polymerization extent, model equations are developed for calculating number of functional groups, wt. of TDI for known weight of CLA and CE, weight of TDI for desired IR ratio, as shown in the **Table 3.8**

Table 3.8 Proposed Model Equations for evaluating the total number of functional groups

Monomers	Functionality (f)	Proposed Models equation
PEG-600	2	$OH = 2W_{CE} \times 10^{-21}$
TDI	2	$NCO = [7W_{TD} - 0.1] \times 10^{-21}$
BD	2	$OH = 13W_{BD} \times 10^{-21}$
TMP	3	$OH = 13W_{TP} \times 10^{-21}$
IR(Index ratio)		$NCO/OH = [7W_{TD} - 0.1] / 2W_{CE} + 13W_{CLA}$
Wt. of Curing agents		$Wt = [2W_{CE} + 13W_{CLA} + 0.1] / 7 \text{ g}$ $\Sigma OH [CLA \& CE] = 2W_{CE} + 13W_{CLA} + 0.1$

W=wt. in gms.

3.5. Experimental Validation of Proposed Model Equations

To validate the proposed model equations several lab experiments were conducted to verify the inference drawn from the theoretical calculations using model equations and actual lab observations regarding polymerization status for the studied PU system. For comparison of the theoretical and the experimental works six different lab experiments were performed keeping the weight of the constituents similar to the theoretically designed experiments. Firstly the calculations were made by using the model equations and the physical lab verification was made through photographic image of PU and the SEM image of FA-r-PUC at the fixed filler amount 33.33%.

3.6. Results

Designed Lab Experiments -1

Lab experiment was conducted at CRA=2g, CE=3gm, BD: TMP ratio in CLA **1:1** and wt of CLA **1 gm**. (W=wt in gm) calculations were made (**Table 3.9**) by using model equations as per the table 3.8.

Tab 3.9. Results of calculation made using model equations for lab experiment 1

Model equations	weight of the components (gm)	Number of functional groups
$OH_{BD}=13W_{BD} \times 10^{-21}$	0.5	6.5×10^{-21}
$OH_{TMP}=13W_{TP} \times 10^{-21}$	0.5	6.5×10^{-21}
$OH_{CE}=2W_{CE} \times 10^{-21}$	3	6×10^{-21}
$OH_{CLA+CE}=[2n_{CE}+13n_{CLA}+0.1] \times 10^{-21}$	CE=3 CLA=1	19×10^{-21}
$NCO=[7W_{TD}-0.1] \times 10^{-21}$	2	13.9×10^{-21}
$IR=NCO/OH=[7W_{TD}-0.1]/2W_{CE}+13W_{CLA}$	IR=0.7	
Inference	Incomplete polymerization	

The inference drawn from the calculations made using model equations for lab experiment-1 is incomplete polymerization at IR=0.7 when lab experiment was conducted the observation on the status of polymerization is obtained and reported in the form of photographic image of PUM and SEM image of FA-r-PUC samples in **Figure 3.1A** and **B** respectively. This figure clearly shows incomplete polymerization at IR=0.07 with BD: TMP ratio in CLA 1:1 and wt. of CLA as 1 gm.

Designed Lab Experiments -2

Lab experiment was conducted at CRA=2g, CE=3gm, BD: TMP ratio in CLA **1:2** and wt of CLA **1 gm**.(W=wt in gm) calculations were made (**Table 3.10**) by using model equations as per the table 3.8.

Table 3.10. Results of calculation made using model equations for lab experiment -2

Model equations	weight of the components (gm)	number of functionalities
$OH_{BD}=13W_{BD} \times 10^{-21}$	0.33	4.2×10^{21}
$OH_{TMP}=13W_{TP} \times 10^{-21}$	0.66	8.5×10^{21}
$OH_{CE}=2W_{CE} \times 10^{-21}$	3	6×10^{21}
$OH_{CLA+CE}=[2n_{CE}+13n_{CLA}+0.1] \times 10^{-21}$	CE=3 CLA=1	18.7×10^{21}
$NCO=[7W_{TD}-0.1] \times 10^{-21}$	2	13.9×10^{21}
$NCO/OH=[7W_{TD}-0.1]/2W_{CE}+13W_{CLA}$	0.7	
Inference	Incomplete polymerization	

The inference drawn from the calculations made using model equations for lab experiment-2 is incomplete polymerization at IR=0.7 when lab experiment was conducted the observation on the status of polymerization is obtained and reported in the form of photographic image of PUM and SEM image of FA-r-PUC samples in **Figure 3.2C and D** respectively. This figure clearly shows incomplete polymerization at IR=0.07 with BD: TMP ratio in CLA 1:2 and wt. of CLA as 1 gm.

Designed Lab Experiments -3

Lab experiment was conducted at CRA=2g, CE=3gm, BD: TMP ratio in CLA **2:1** and wt of CLA **1 gm**. (W=wt in gm) calculations were made (**Table 3.11**) by using model equations as per the table 3.8.

Table 3.11. Results of calculation made using model equations for lab experiment -3

Model equations	weight of the components (gm)	number of functionalities
$OH_{BD}=13W_{BD} \times 10^{-21}$	0.66	8.5×10^{21}
$OH_{TMP}=13W_{TP} \times 10^{-21}$	0.33	4.2×10^{21}
$OH_{CE}=2W_{CE} \times 10^{-21}$	3	6×10^{21}
$OH_{CLA+CE}=[2n_{CE}+13n_{CLA}+0.1] \times 10^{-21}$	CE=3 CLA=1	18.7×10^{21}
$NCO=[7W_{TD}-0.1] \times 10^{-21}$	2	13.9×10^{21}
$NCO/OH=[7W_{TD}-0.1]/2W_{CE}+13W_{CLA}$	0.7	
Inference	Incomplete polymerization	

The inference drawn from the calculations made using model equations for lab experiment-3 is incomplete polymerization at IR=0.7 when lab experiment was conducted the observation on the status of polymerization is obtained and reported in the form of photographic image of PUM and SEM image of FA-r-PUC samples in **Figure 3.3E** and **F** respectively. This figure clearly shows incomplete polymerization at IR=0.07 with BD: TMP ratio in CLA 2:1 and wt. of CLA as 1 gm.

Designed Lab Experiments -4

Lab experiment was conducted at CRA=2g, CE=3gm, BD: TMP ratio in CLA **1:1** and wt of CLA **0.5 gm** (W=wt in gm) calculations were made (**Table 3.12**) by using model equations as per the table 3.8.

Table 3.12. Results of calculation made using model equations for lab experiment -4

Model equations	weight of the components (gm)	number of functionalities
$OH_{BD}=13W_{BD} \times 10^{-21}$	0.25	3.25×10^{21}
$OH_{TMP}=13W_{TP} \times 10^{-21}$	0.25	3.25×10^{21}
$OH_{CE}=2W_{CE} \times 10^{-21}$	3	6×10^{21}
$OH_{CLA+CE}=[2n_{CE}+13n_{CLA}+0.1] \times 10^{-21}$	CE=3 CLA=0.5	13.9×10^{21}
$NCO=[7n_{TD}-0.1] \times 10^{-21}$	2	13.9×10^{21}
$NCO/OH = [7W_{TD}0.1]/2W_{CE}+13 n_{CLA}$	1.1	
Inference	Complete polymerization	

The inference drawn from the calculations made using model equations for lab experiment -4 is complete polymerization at IR=1.1 when lab experiment was conducted the observation on the status of polymerization is obtained and reported in the form of photographic image of PUM and SEM image of FA-r-PUC samples in **Figure 3.4G** and **H** respectively. This figure clearly shows complete polymerization at IR=1.1with BD: TMP ratio in CLA 1:1and wt. of CLA as 0.5 gm.

Designed Lab Experiments -5

Lab experiment was conducted at CRA=2g, CE=3gm, BD: TMP ratio in CLA **1:2** and wt of CLA **0.5 gm**. (W=wt in gm) calculations were made (**Table 3.13**) by using model equations as per the table 3.8.

Table 3.13. Results of calculation made using model equations for lab experiment -5

Model equations	weight of the components (gm)	number of functionalities
$OH_{BD}=13W_{BD} \times 10^{-21}$	0.16	2.0×10^{21}
$OH_{TMP}=13W_{TP} \times 10^{-21}$	0.33	4.2×10^{21}
$OH_{CE}=2W_{CE} \times 10^{-21}$	3	6×10^{21}
$OH_{CLA+CE}=[2n_{CE}+13n_{CLA}+0.1] \times 10^{-21}$	CE=3 CLA=0.5	12.2×10^{21}
$NCO=[7W_{TD}-0.1] \times 10^{-21}$		13.9×10^{21}
$NCO/OH=[7W_{TD}-0.1]/2W_{CE}+13W_{CLA}$	1.1	
Inference	Complete polymerization	

The inference drawn from the calculations made using model equations for lab experiment -5 is complete polymerization at IR=1.1 when lab experiment was conducted the observation on the status of polymerization is obtained and reported in the form of photographic image of PUM and SEM image of FA-r-PUC samples in **Figure 3.5I** and **J** respectively. This figure clearly shows complete polymerization at IR=1.1 with BD: TMP ratio in CLA 1:2 and wt. of CLA as 0.5 gm.

Designed Lab Experiments -6

Lab experiment was conducted at CRA=2g, CE=3gm, BD: TMP ratio in CLA **2:1** and wt of CLA **0.5 gm** (W=wt in gm) calculations were made (**Table 3.14**) by using model equations as per the table 3.8.

Table 3.14. Results of calculation made using model equations for lab experiment -6

Model equations	weight of the components (gm)	number of functionalities
$OH_{BD}=13W_{BD} \times 10^{-21}$	0.33	4.2×10^{21}
$OH_{TMP}=13W_{TP} \times 10^{-21}$	0.16	2.0×10^{21}
$OH_{CE}=2W_{CE} \times 10^{-21}$	3	6×10^{21}
$OH_{CLA+CE}=[2n_{CE}+13n_{CLA}+0.1] \times 10^{-21}$	CE=3 CLA=0.5	12.2×10^{21}
$NCO=[7W_{TD}-0.1] \times 10^{-21}$	2	13.9×10^{21}
$NCO/OH=[7W_{TD}-0.1]/2W_{CE}+13W_{CLA}$	1.1	
Proposed inference	Complete polymerization	

The inference drawn from the calculations made using model equations for lab experiment -6 is complete polymerization at IR=1.1 when lab experiment was conducted the observation on the status of polymerization is obtained and reported in the form of photographic image of PUM and SEM image of FA-r-PUC samples in **Figure 3.6K** and **L** respectively. This figure clearly shows complete polymerization at IR=1.1 with BD: TMP ratio in CLA 2:1 and wt. of CLA as 0.5 gm.

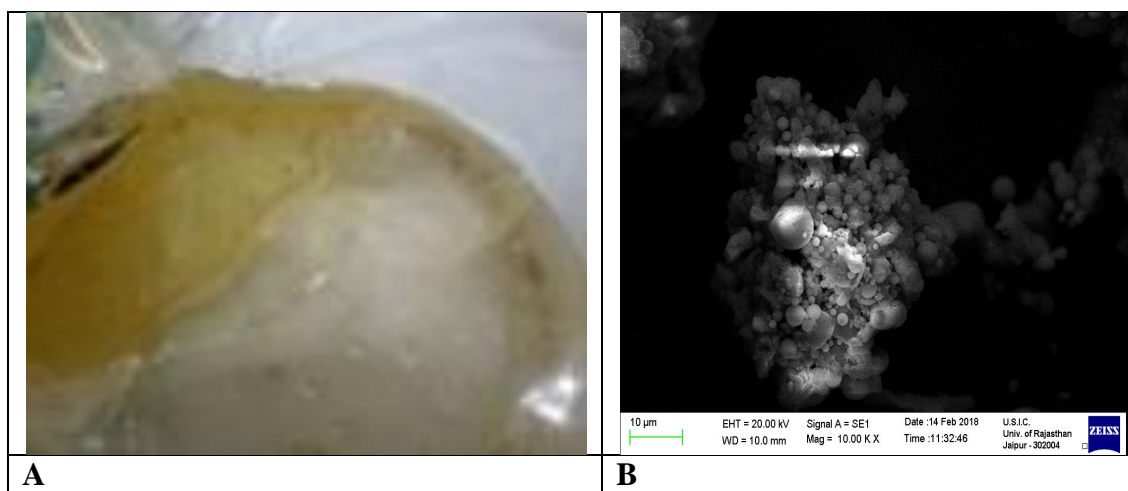


Figure.3.1 Photographic and SEM images of PUM and FA-r-PUC

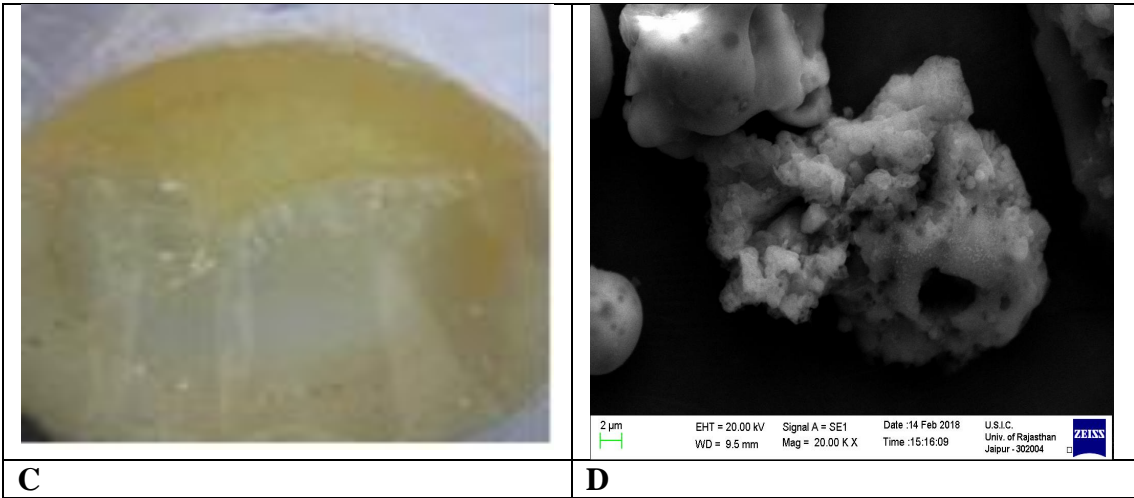


Figure.3.2 Photographic and SEM images of PUM and FA-r-PUC

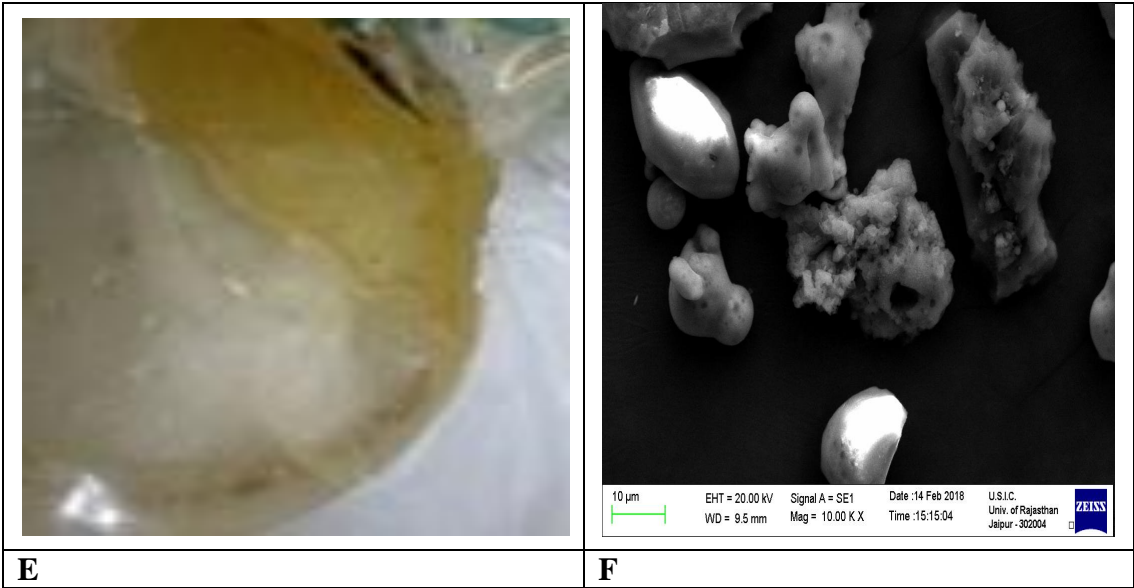


Figure.3.3 Photographic and SEM images of PUM and FA-r-PUC

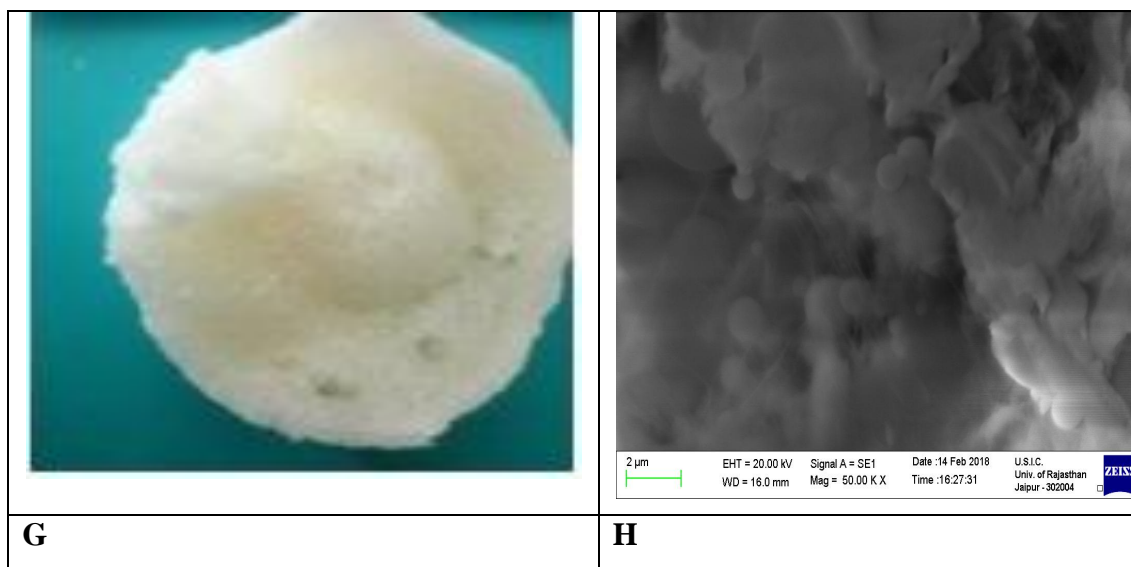


Figure.3.4 Photographic and SEM images of PUM and FA-r-PUC

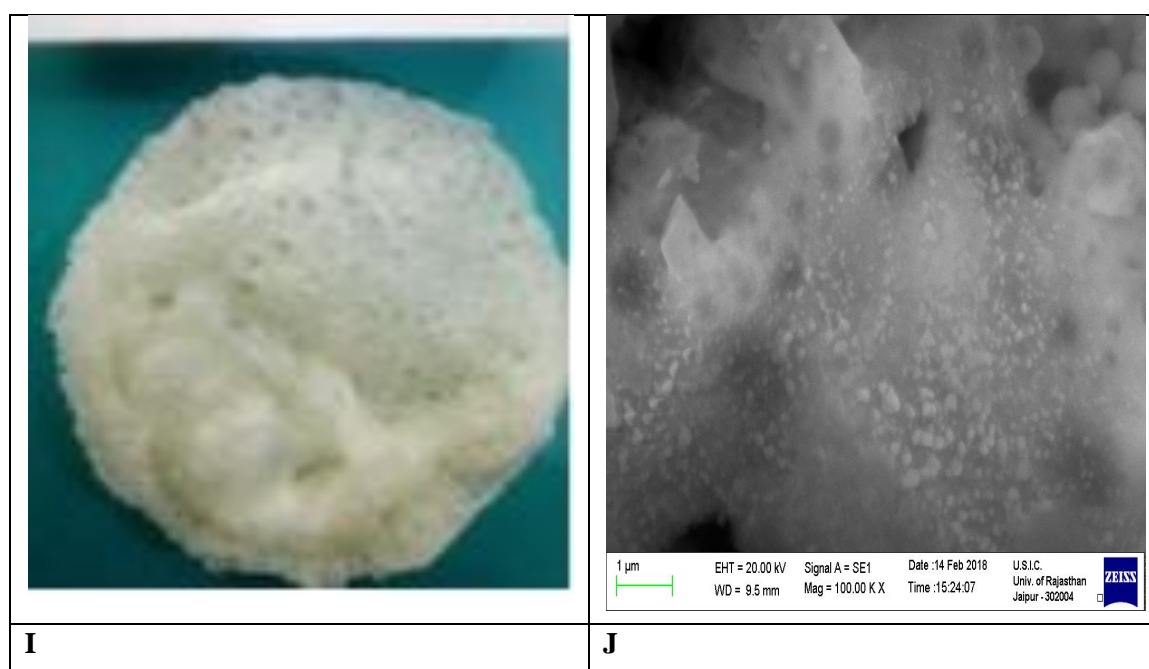


Figure.3.5 Photographic and SEM images of PUM and FA-r-PUC

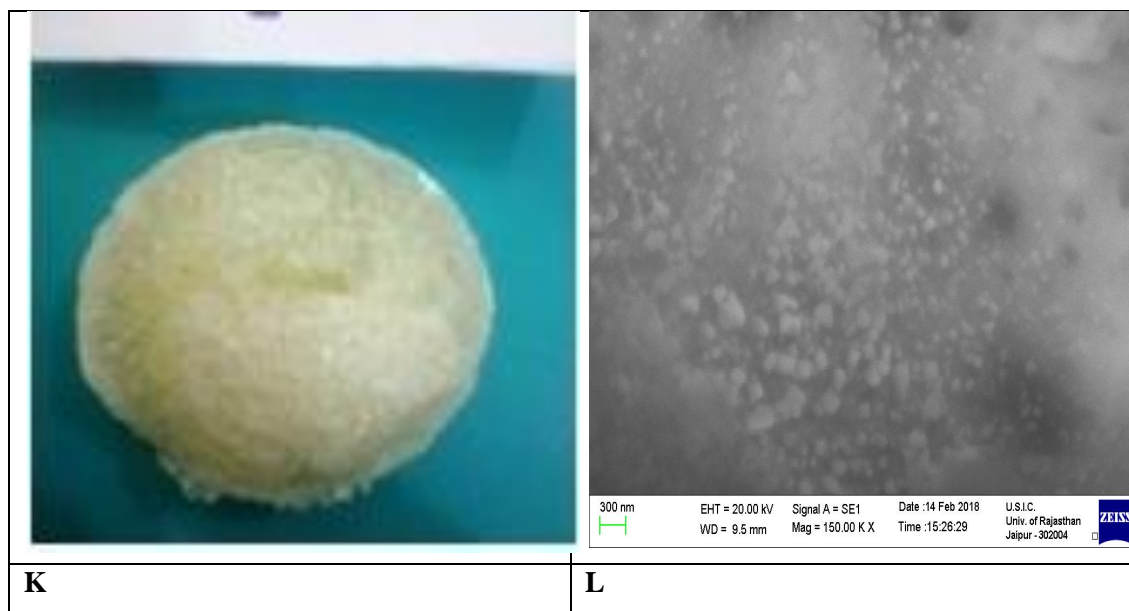


Figure.3.6 Photographic and SEM images of PUM and FA-r-PUC

3.7. Discussions

In the experiments 1,2 and 3 wherein 1 g of CLA was taken at all wt/wt ratio of BD and TMP (1:1,1:2 and 2:1) the OH [CLA&CE] functionalities $\geq \Sigma$ NCO functionalities i.e $[2W_{CE}+13W_{CLA}+0.1] 10^{21} \geq [7W_{TD}-0.1] 10^{21}$ for various ratios of BD and TMP of CLA. Incomplete polymerization with IR 0.7 evaluated by the proposed model for IR NCO/OH = $[7W_{TD}-0.1]/2W_{CE}+13W_{CLA}$ was supported by the SEM images also wherein non uniform distribution/clumping of FA was seen in PU matrix. In the experiments 4,5 and 6 wherein 0.5 g of CLA was taken at all wt/wt ratio of BD and TMP (1:1,1:2 and 2:1) the Σ NCO functionalities $\geq \Sigma$ OH [CLA&CE] functionalities i.e $[7W_{TD}-0.1] 10^{21} \geq [2W_{CE}+13W_{CLA}+0.1] 10^{21}$ for various ratios of BD and TMP of CLA. Complete polymerization with IR 1.1 evaluated by the proposed model for IR NCO/OH = $[7W_{TD}-0.1]/2W_{CE}+13W_{CLA}$ was supported by the SEM images wherein uniform distribution of FA was seen in PU matrix.

Evaluating IR, number of OH functionalities of CE, BD, TMP and number of NCO functionalities of CRA simultaneously by models and mole concept and validations

of the values by both the methods a comparative representation is presented in **Figure. 3.7-3.14** which clearly depicts that model equations described for the PU polymerization during the research work successfully can be used for similar systems of polymer matrix and composites with pre assessment of quality of polymeric products without wasting the materials.

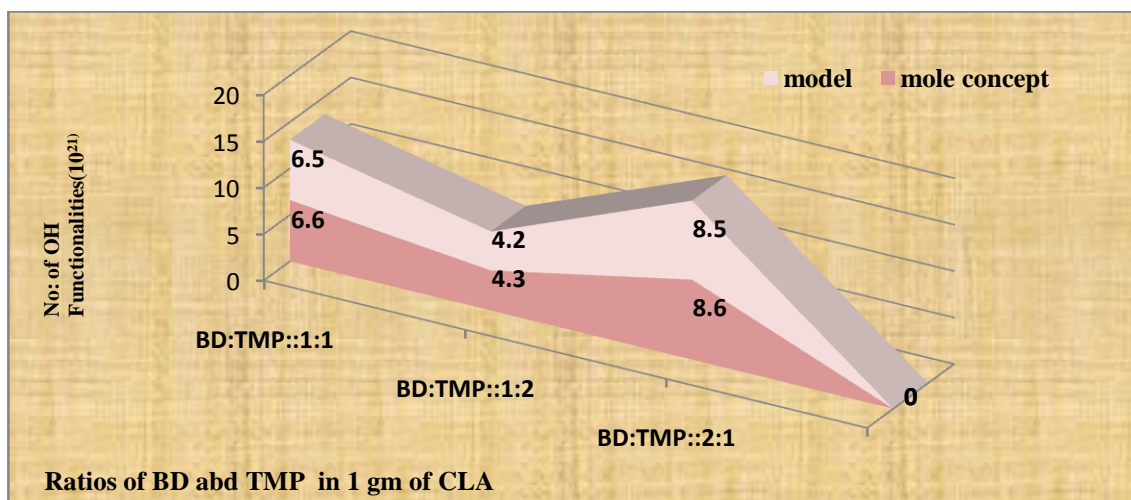


Figure.3.7 comparison of number of OH functionalities of BD in CLA (1gm) by mole concept and by model

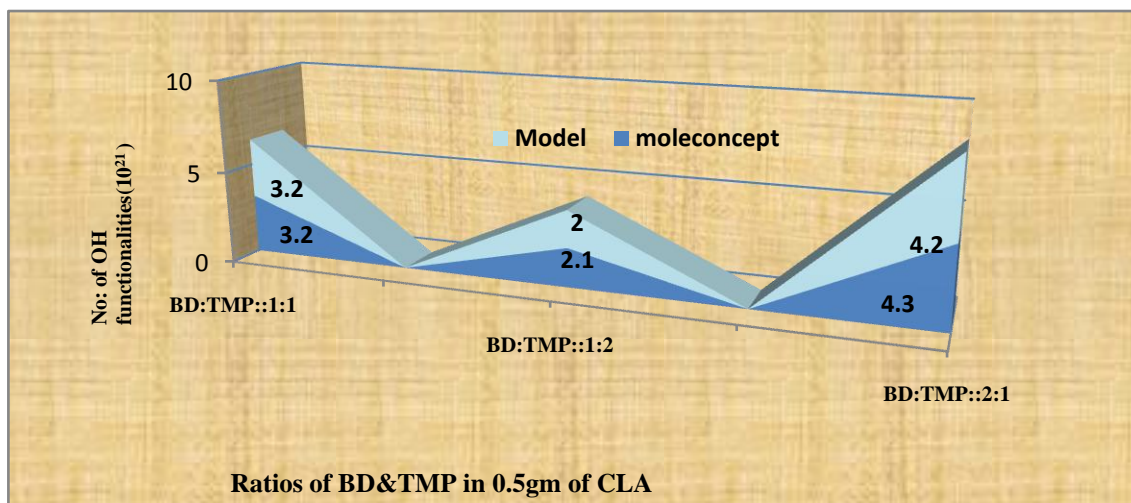


Figure.3.8 comparison of number of OH functionalities of BD in CLA (0.5gm) by mole concept and by model

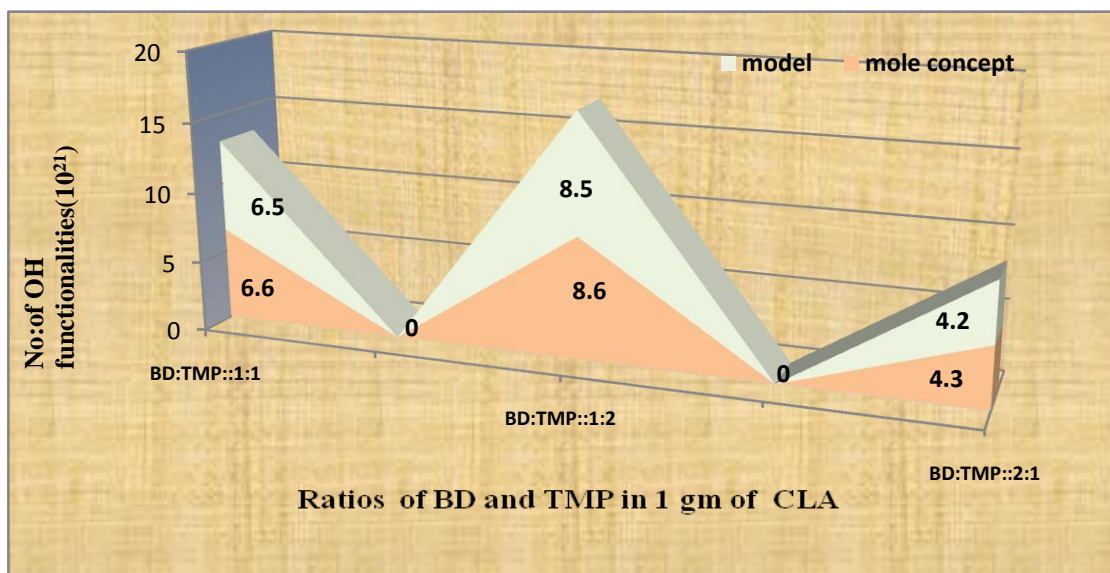


Figure.3.9 Comparison of number of OH functionalities of TMP in CLA (1gm) by mole concept and by model

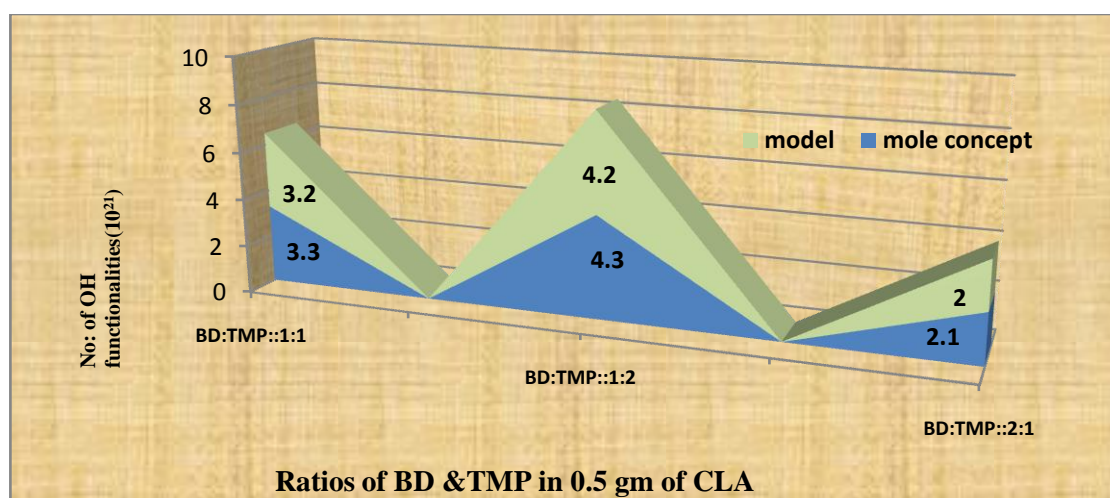


Figure.3.10 comparison of number of OH functionalities of TMP in CLA (0.5gm) by mole concept and by model

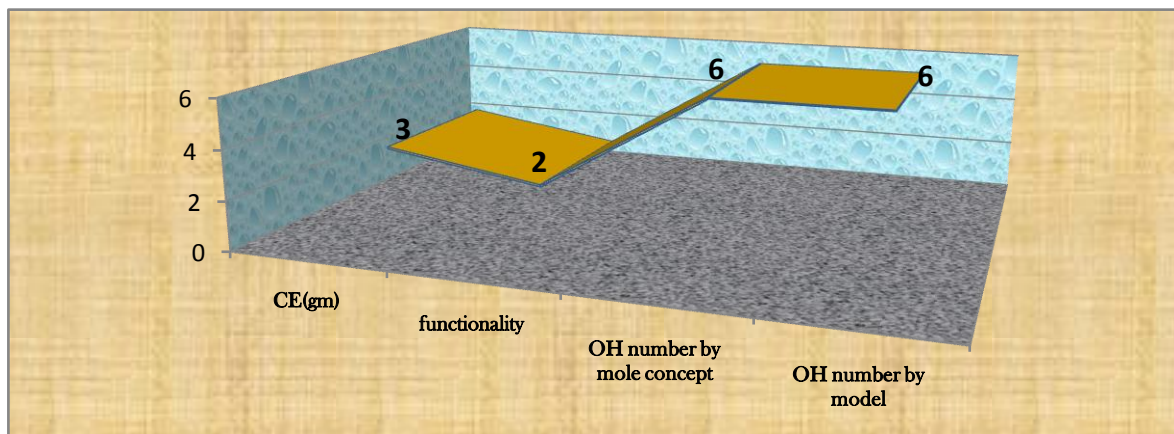


Figure.3.11 Number of OH (10^{21}) functionalities of CE by mole concept and by model

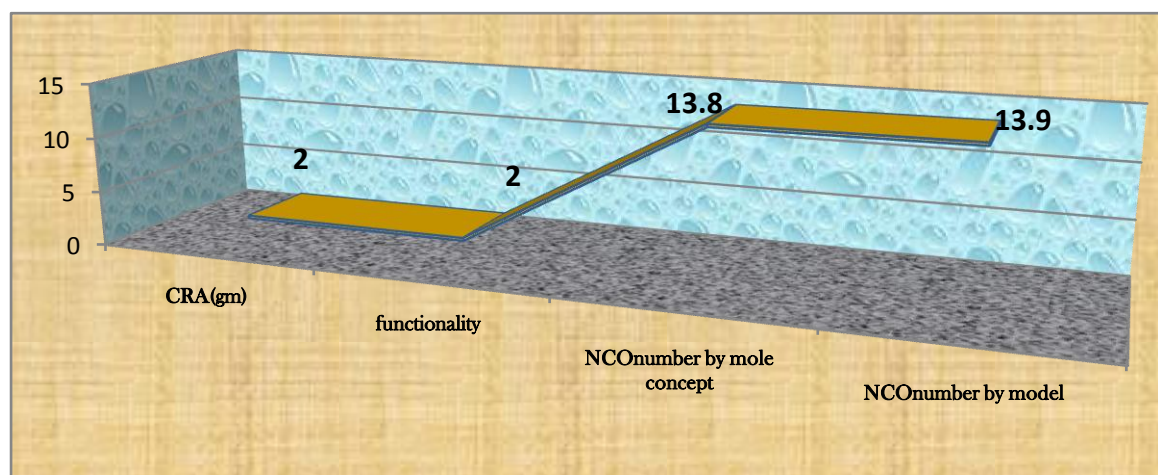


Figure.3.12 Number of NCO (10^{21}) functionalities of TDI by mole concept and by model

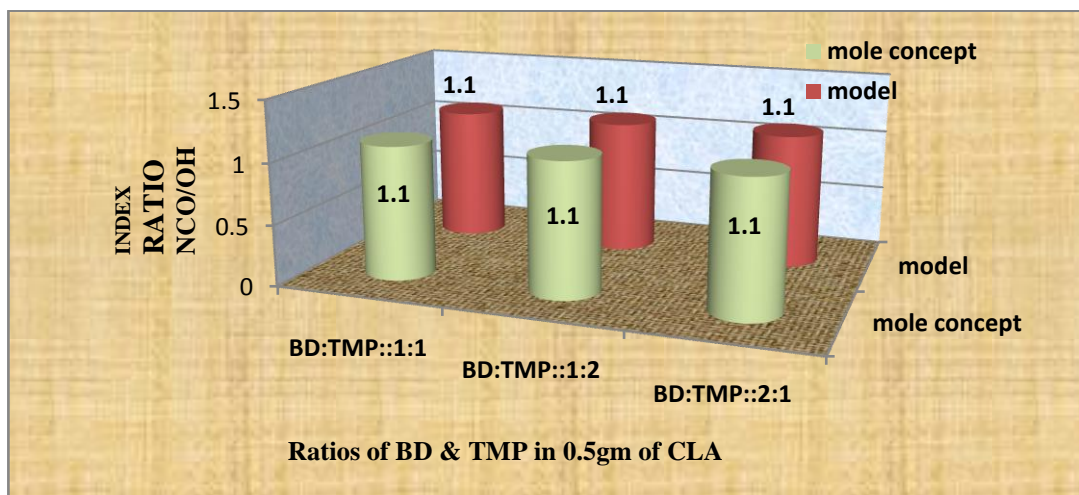


Figure.3.13. Comparison of Index Ratio (NCO/OH) for PUC when 0.5 gm of CLA taken at constant wt/wt ratio of CE&CRA3:2 by model & mole concept.

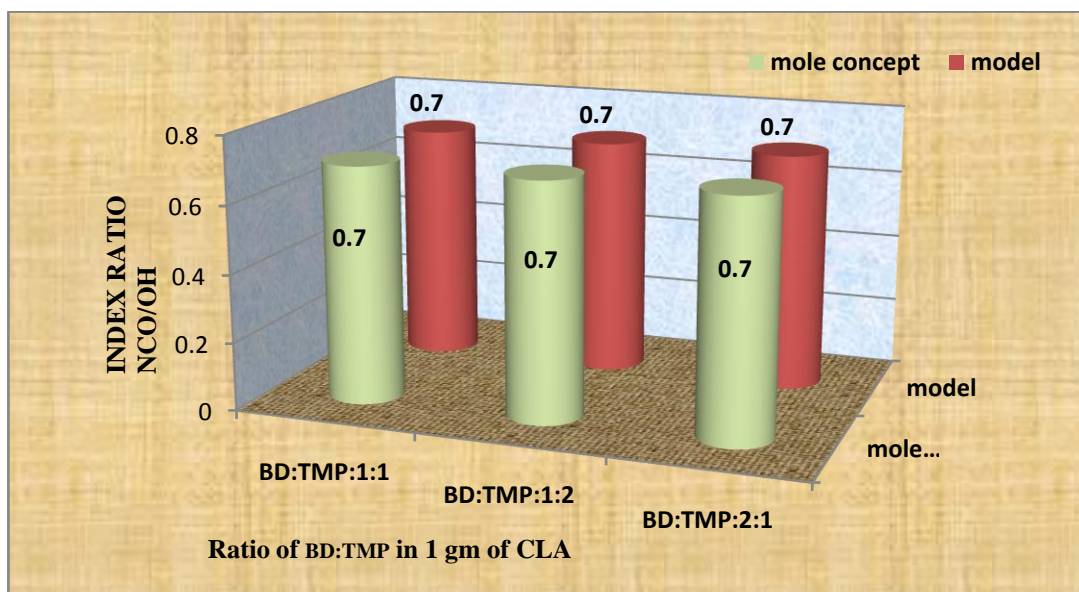


Figure.3.14. Comparison of Index Ratio (NCO/OH) for PUC when 1 gm of CLA taken at constant wt/wt ratio of CE&CRA3:2 by model & mole concept.

In experiments for IR values 0.7 incomplete polymerization was seen while for IR value as 1.1, complete polymerization was noticed. PU synthesis having OH contribution from CE, CLA and NCO contribution from CRA evaluated by proposed models were in good agreement with the mole concept method. IR values evaluated by the mole concept and the models were in great approximation. The present research work also envisages on the independency of the ratio of components of CLA on the extent of polymerization but solely shows dependency on the weight of CLA taken in the mixture: $\sum_n^{TMP} OH + \sum_n^{BD} OH = [W]_{mix} \times 13 \times 10^{21}$, general form for any ratio of BD and TMP when taken as homogenous mixture

$$\sum_n^{TMP} OH + \sum_n^{BD} OH = [(B/B+T) + (T/B+T)] W \times 13 \times 10^{21}$$

$$\sum_n^{TMP} OH + \sum_n^{BD} OH = [W]_{mix} \times 13 \times 10^{21}$$

B=BD and T=TMP

Thus the Extent of polymerization is not the function of ratio of binary components of CLA. The Polyols of CLA i.e BD and TMP were taken in the ratio 2:1 (w/w) it was found that incomplete polymerization takes place when 16.66% (w/w) CLA was taken however CLA with 9.09% (w/w) results in the formation of the PU matrix and composite thereof, this composition was suitable for the FA-reinforced composite synthesis provided the ratio by mass of CE: CRA:: 3: 2. The ratio of Polyols of CLA (BD & TMP) was reversed in the second experiment with w/w ratio of BD:TMP:: 1:2, it was found that no polymerization takes place when 16.66% CLA was used, however CLA at 9.09% results in the synthesis of the PU at the same ratio by mass of CE: CRA:: 3: 2. In the third experiment the ratio of Polyols of CLA i.e BD: TMP:: 1:1 (w/w) was taken, it was found that the synthesis of the PU-polymerization take place with the CLA weight percent as 9.09% whilst incomplete polymerization with the CLA 16.66% was noticed. The same matrix was used for the synthesis of the FA-reinforced composite, provided the ratio by mass of CE: CRA:: 3: 2.

3.8. Conclusion

For PU synthesis using mole concept based model equations developed for BD and TMP of CLA, shows that, the extent of polymerization is independent of the ratio of components of the CLA but depends on the amount of CLA added to CE. The OH and NCO value calculated by using the mole concept is in match with the one evaluated by using the developed proposed models equations. The IR values evaluated for deciding the extent of polymerization were in great agreement with values through mole concept and by the proposed models. The models proposed for this PU system is time effective and a good mathematical tool for predicting the extent of polymerization. However the proposed models for the PU system approved useful for the monomers units uniform in terms of functionalities i.e polyols having only OH functionalities and isocyanates possessing only NCO functionalities. In case of Pre polymers wherein heterogeneous functionalities exists in each component of polymeric system knowledge of ratio of functionalities for the evaluation of OH and NCO numbers is needed before calculating wt of CRA and IR for complete polymerization and deciding the amount of monomers for complete polymerization for the desired quantity product in cost effective way.

3.9. References

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**Synthesis and Properties of Cross Linked
Polyurethane Matrix using
Butane-1, 4-Diol and 1, 1,1Trimethylol
Propane as Cross Linker**

ABSTRACT

The chapter presents the effect of variation in w/w ratios of binary components of CLA possessing different functionalities on the mechanical properties of the polyurethane matrix (PUM). PUM has been prepared using polyol PEG-600 as CE ,homogenous mixture of butane -1,4-diol (BD) and 1,1,1 trimethylol Propane(TMP) ,as CLA . The mechanical properties of PUM are reported to be solely dependent on the internal microphasic geometry of hard segment (HS) domain and the soft segment (SS) domain of the matrix rather than on the extent of polymerization. The appropriate model structures are proposed for role of HS and SS in establishing the properties of the PU composite.

4.1 Introduction

Excellent strength makes polyurethane system (PUs) a class of cellular plastics as a best utility material for industrial and domestic purposes. Flexible characteristic of PUs depends on the cell and the matrix structure. For load bearing applications, high density PUs are used while for purposes like packaging, insulation and supports low density PUs are useful. Looking to the PUs wide range of applications of PUs, so various methods have been developed for improvising the properties of PUs, either by chemical modification of matrix or by chemical and physical modifications of fillers used in making filler reinforced polyurethane composites. . The chemical nature of CLA and CE and affects the physical and chemical properties of PUs [1-4]. CLA component's functionalities and the w/w ratios of the components in binary/ternary CLA mixtures thereof, considerably influence the mechanical properties of PUs [5-6]. The reaction between CRA and CE is exothermic in nature mixture becomes viscous and eventually forms solid mass, by the formation of carbamate/ urethane links [7].

The present chapter describes in detail, the effect of w/w ratios of the components of CLA with functionalities two (BD) and three (TMP) on the mechanical properties like tensile strength, modulus, % elongation, break point and hardness of PUM [8-12]. As per the detailed description of Chapter 3, it was concluded that the extent of polymerization was not dependent on the w/w ratio variations of binary components of CLA but was solely dependent on the gross weight of CLA taken irrespective of the w/w ratios, so the variation in the mechanical properties with the variation of w/w ratios of binary components of CLA cannot be attributed to the extent of polymerization. The variation in the mechanical properties of PUM is attributed to the factors which are mainly affecting the non polar SS [13, 14] and polar HS [15-18] domain's microphasic segregation or their miscibility in the PUM. The experiments conducted with different w/w ratios of binary components of CLA were done with constant index ratio 1.64.

4.2 Experimental Details

For ensuring the complete polymerization, polyol and isocyanates weight ratio selected is 1:1 which corresponds to IR as 1.64. 7 gm of PEG-600 as CE was mixed with 1.66 gm CLA, a homogenous mixture of butane -1,4-diol (BD) acting as a chain linker and 1,1,1 trimethylol Propane(TMP) an aliphatic triol acting as chain cross linker . The two different w/w ratios of TMP and BD were 2:1 and 1:2 while weight of the CLA remained constant. 8.35 gm of TDI was used as curing agent and mixed with mixture of CE and CLA prepared in the previous step. AL-40 silicon spray was used as the mold releasing for easy release of the sample after curing. The method for PUM sample preparation as per the ASTM standards has already been given in Chapter 2. With selection of weight ratio as 1:1 for the polyols and the curing agents for the PU system. The index ratio evaluated by the model equation (1)

$$\text{Index ratio} = \text{NCO/OH} = [7n_{\text{TD}} - 0.1] / 2n_{\text{CE}} + 13 n_{\text{CLA}} \dots\dots\dots(1)$$

Putting weight of all components in gms

$$\text{Index ratio} = [7 \times 8.35 - 0.1] / [2 \times 7 + 13 \times 1.66] = \mathbf{1.64}.$$

The matrix with the binary component BD and TMP in the w/w ratio of 2: 1 is designated as PUM-A while the one with 1:2 has been designated as PUM-B. The mechanical properties of all the samples were evaluated by UTM, sample dimensions are given in **Table 4.1**. All experiments of PUM and FA-r-PUC were conducted with IR as 1.64.

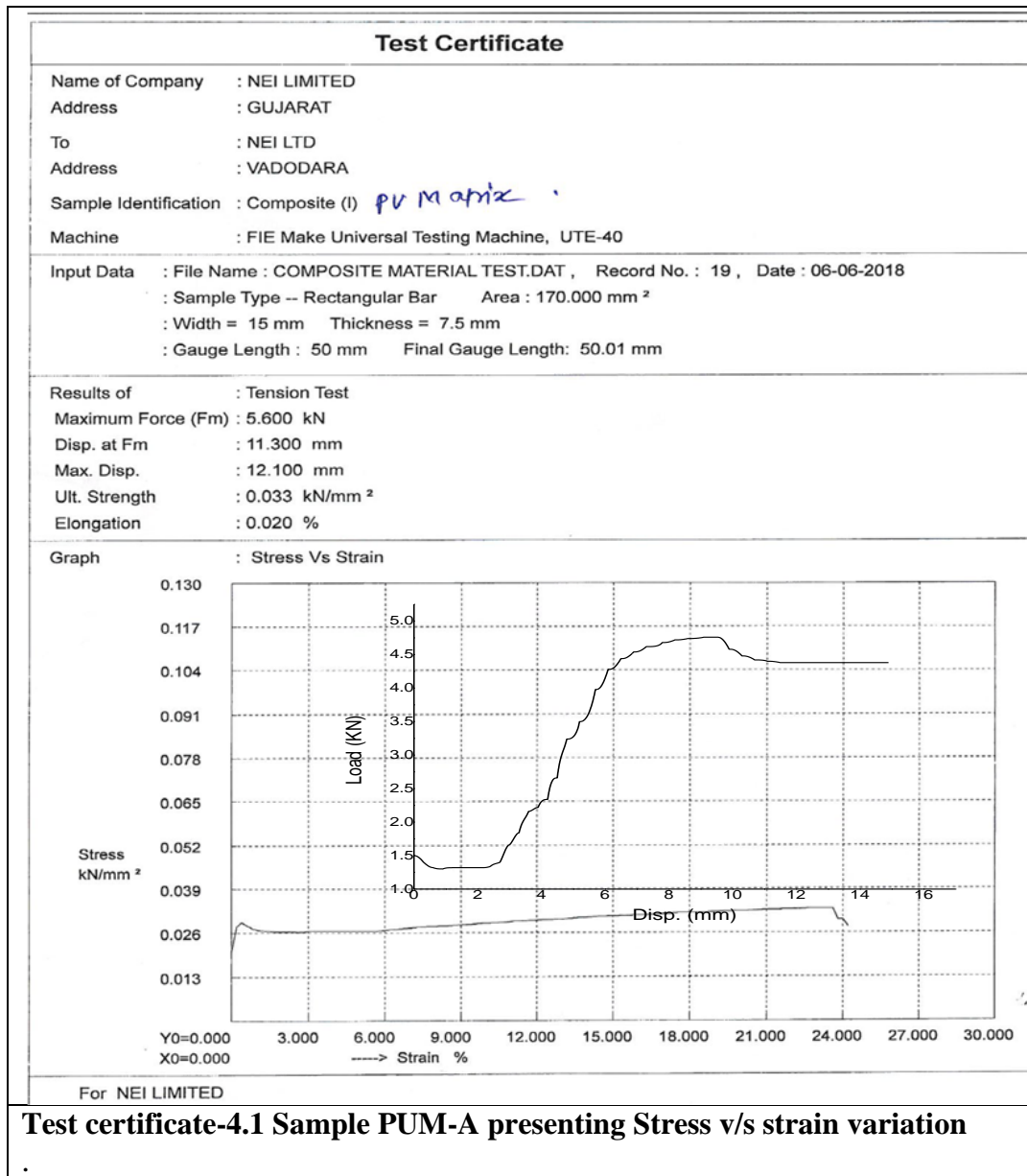
Table 4.1 Sample dimension for evaluation of mechanical properties using UTM

S.No:	Sample Dimension	values
1	Sample type	ASTM D638 Type I
2	Area	200mm ²
3	Width	15mm
4	Thickness	7.5mm
5	Gauze length	50mm
6	Final gauze length	50.01

4.3 Results and Discussion

4.3.1 Mechanical Properties of PUM

The mechanical properties evaluated by UTM for the sample PUM-A and PUM-B are described in **Table 4.2**. The load v/s displacement graphs are shown in the **test certificates 4.1 and 4.2**. A comparison of mechanical properties of PUM A and B are represented in **Figure. 4.1**.



Test Certificate	
Name of Company	: NEI LIMITED
Address	: GUJARAT
To	: NEI LTD
Address	: VADODARA
Sample Identification	: Composite (I) <i>B matrix (2:1)</i>
Machine	: FIE Make Universal Testing Machine, UTE-40
Input Data	: File Name : COMPOSITE MATERIAL TEST.DAT , Record No. : 30 , Date : 08-06-2018
	: Sample Type -- Rectangular Bar Area : 200.000 mm ²
	: Width = 15 mm Thickness = 7.5 mm
	: Gauge Length : 50 mm Final Gauge Length: 50.01 mm
Results of	: Tension Test
Maximum Force (Fm)	: 4.780 kN
Disp. at Fm	: 8.500 mm
Max. Disp.	: 12.400 mm
Ult. Strength	: 0.024 kN/mm ²
Elongation	: 0.020 %
Graph	: Stress Vs Strain
<p>The graph displays two data series. The primary series plots Load (kN) on the y-axis (0 to 5.0) against Displacement (mm) on the x-axis (0 to 30.000). The load curve rises sharply to about 4.5 kN at 2 mm displacement, then levels off with a slight peak around 8.5 mm before declining. A secondary series plots Stress (kN/mm²) on the y-axis (0.012 to 0.120) against Strain (%) on the x-axis (0.000 to 30.000). This stress curve is a nearly horizontal line at approximately 0.024 kN/mm².</p>	
For NEI LIMITED	

Test certificate-4.2 Sample PUM-B presenting Stress v/s strain variation

Table 4.2 Results of mechanical properties of PUM samples

S.No:	Mechanical Properties	PUM-A values	PUM-B values
1	Tensile strength	33MPA	24MPA
2	Young modulus	16.5 GPA	12 GPA
3	Hardness	76 HRE	64 HRE
4	% Elongation	0.020	0.020
5	Break point	33	24
6	Force(max)	5.600 KN	4.780 KN
7	Displacement at F(max)	11.300 mm	8.500 mm
8	Maximum Displacement	12.100 mm	12.40 mm
9.	Ultimate strength	0.033 KN/mm2	0.024 KN/mm2

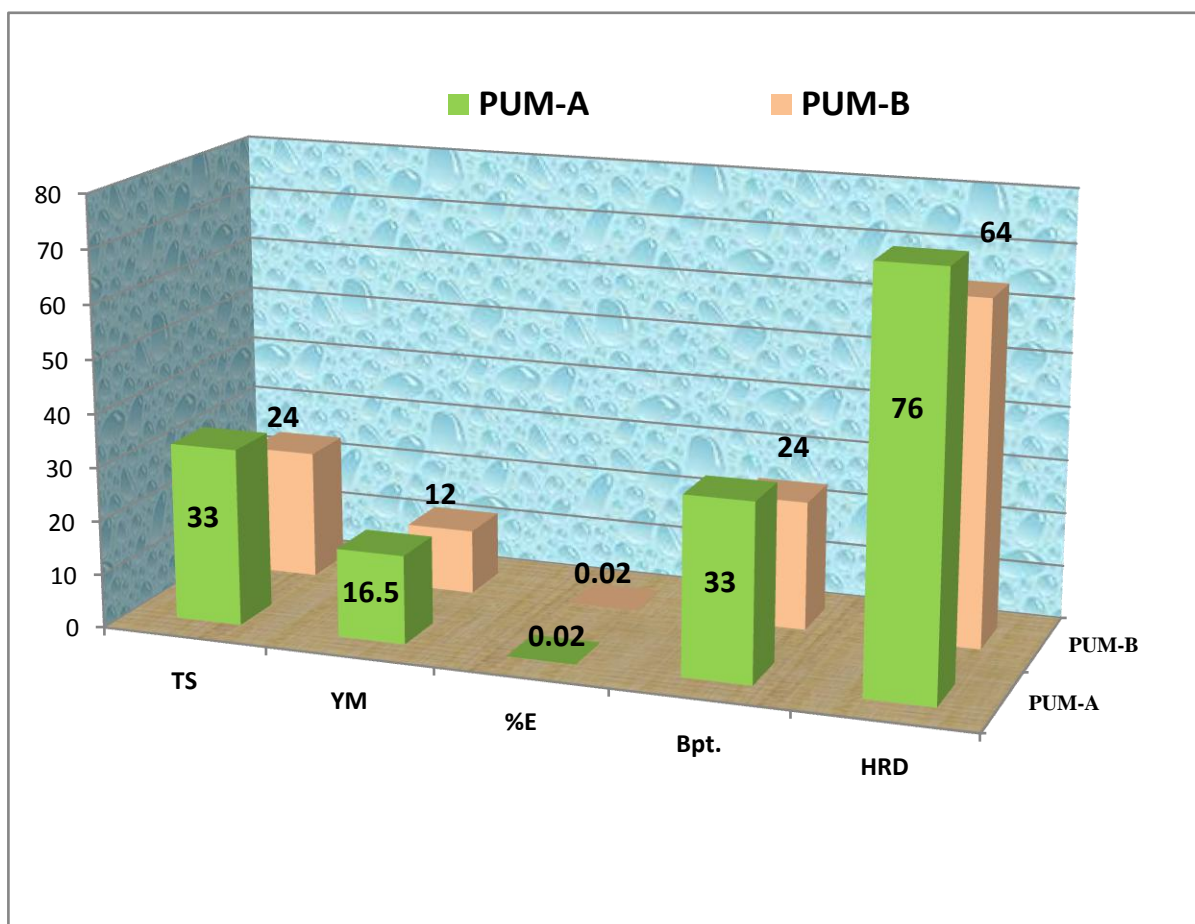


Figure.4.1 Comparative graph of mechanical properties of PUMs

4.3.2 Role of BD and TMP in Properties of PUM

BD is a short chain bi functional component of the CLA mixture and act as chain linker by forming carbamate/ Urethane links with the isocyanates functionalities of the CRA. TMP being tri functional component act as cross linker of the PU polymeric chain by carbamate links and provides a three dimensional network to the PU polymeric system. The role of BD and TMP as CLA is shown in the **Figure.4.2** and **Figure 4.3** respectively. Understanding of role of BD and TMP is necessary to determine the microphasic segregation and miscibility of hard segment and soft segment domain of PUs.

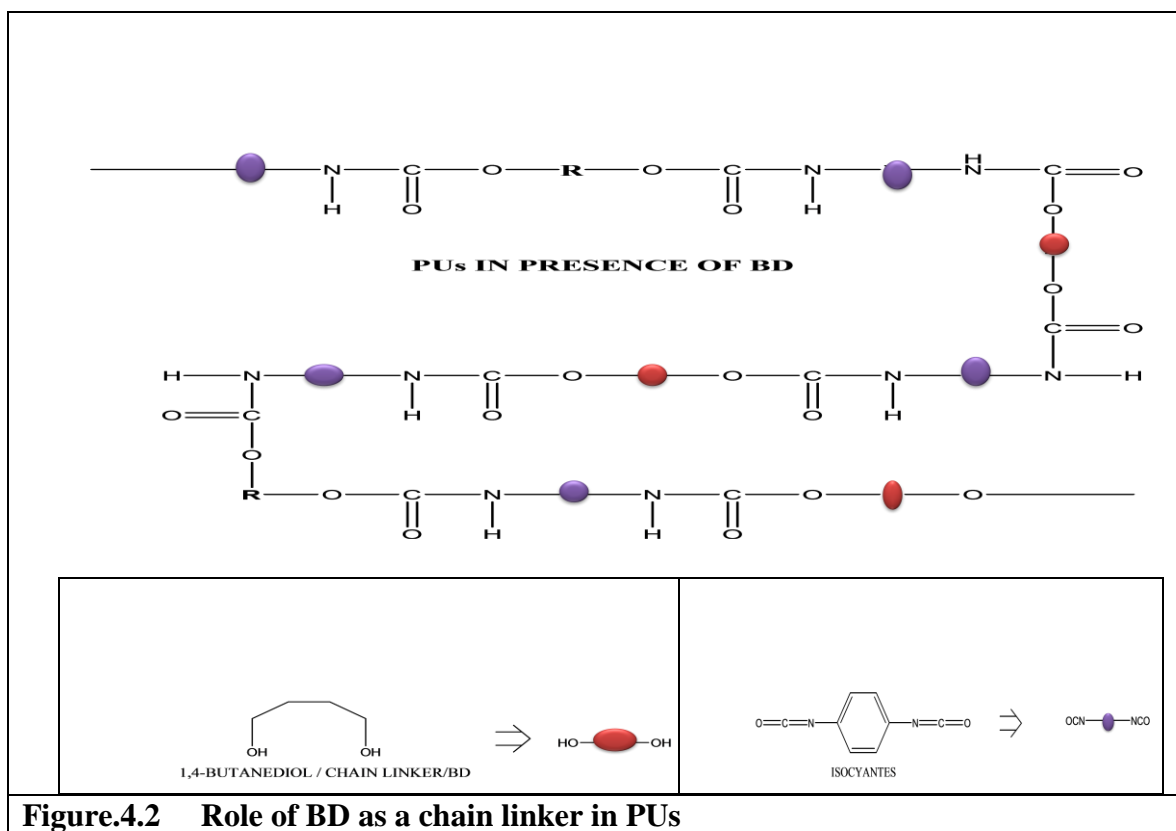


Figure.4.2 Role of BD as a chain linker in PUs

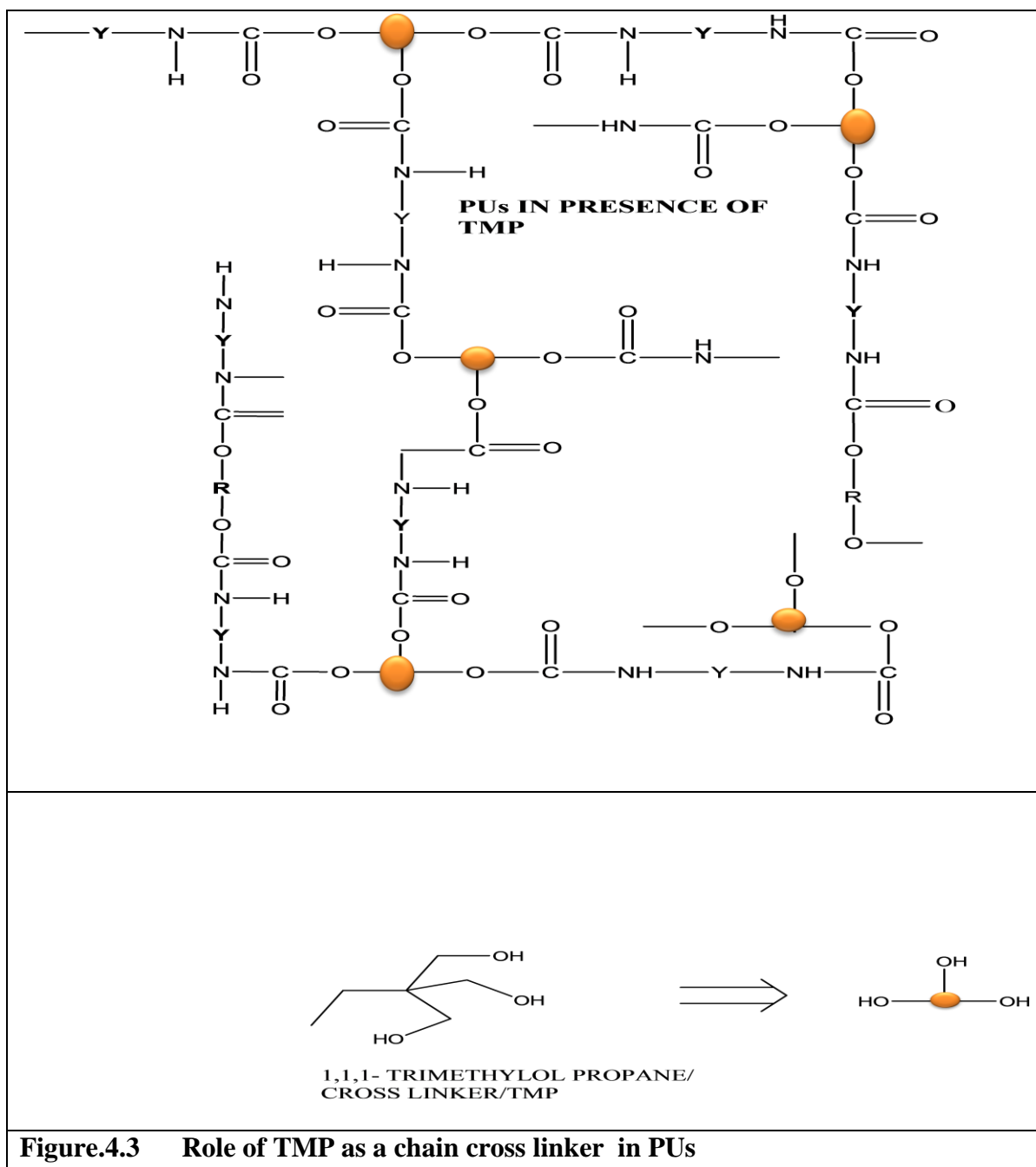
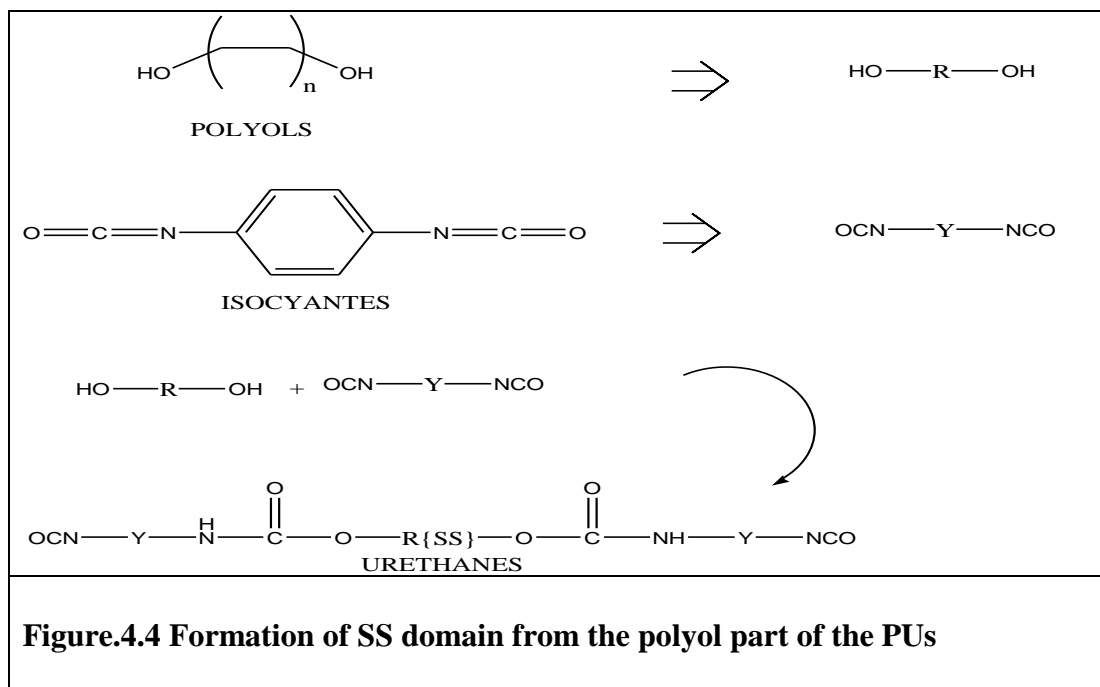
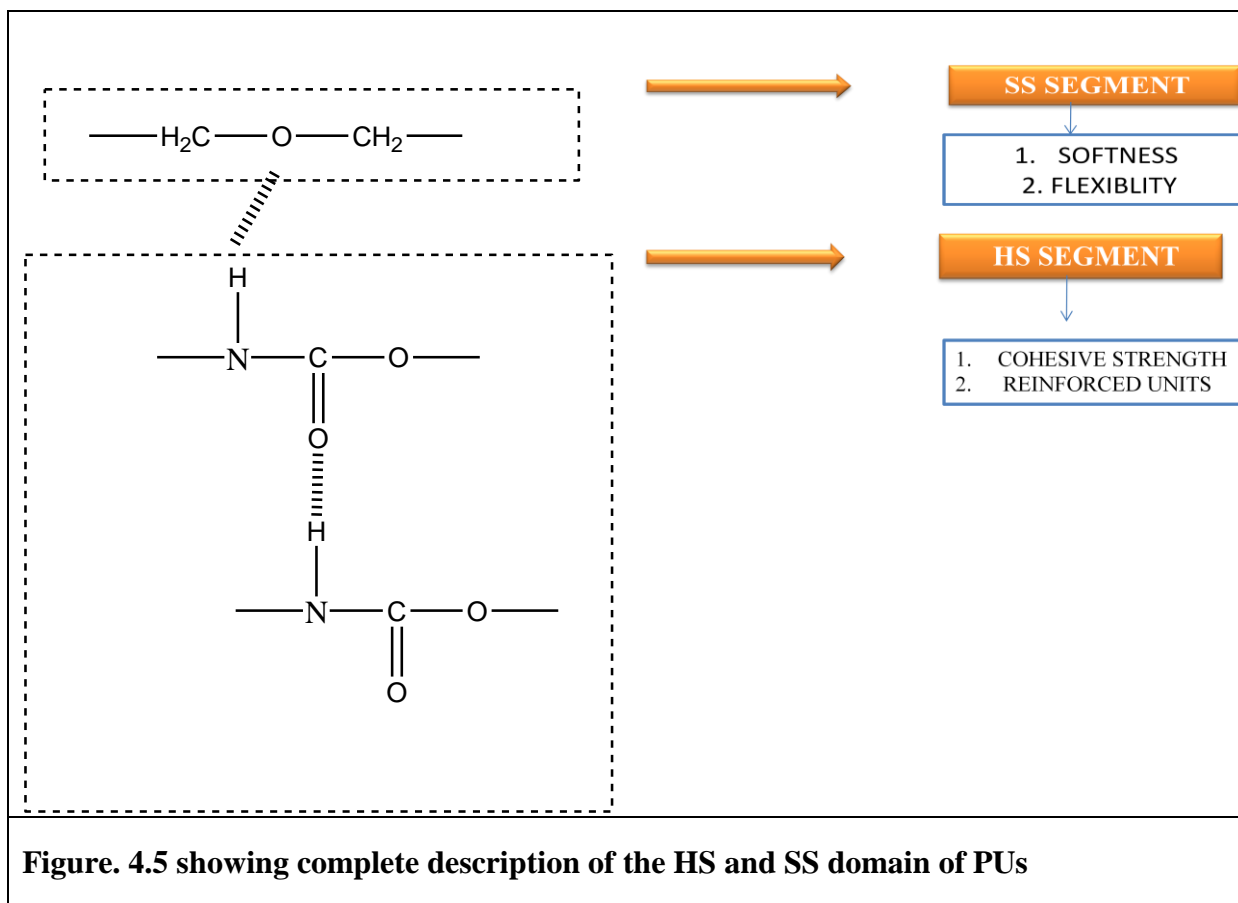


Figure.4.3 Role of TMP as a chain cross linker in PUs

The hard segment (HS) and soft segment (SS) domains of PU microphasic structure are made up of different polymeric bonding. The SS domain is mainly attributed from the polyol component while HS domain contribution is from isocyanate functionalities (**Figure.4.4**).



SS domain provides the softness and flexibility to PUs while the HS domain augments the cohesive strength of PUs and intrinsic reinforcement to the PUs [19-22]. The H- bonding between the H atoms of the carbamate link with the oxygen atom of the carbonyl of the carbamate link form the HS in PUs. With the enhancement of this H- bonding between two carbamate links amplifies the HS domain thus affect the properties of the PUs. The HS and SS domain of PUs is shown in **Figure.4.5**.



Cohesive strength and the intrinsic reinforcement attribution to PUs by HS and the microphase segregation of HS and SS domain of PUs can be adjusted by the selection of components of CLA i.e with components of varying functionalities and their varying w/w concentration ratios.

4.3.3 Effect of w/w Ratio Variations of the Binary Components of CLA on Mechanical Properties of PUMs.

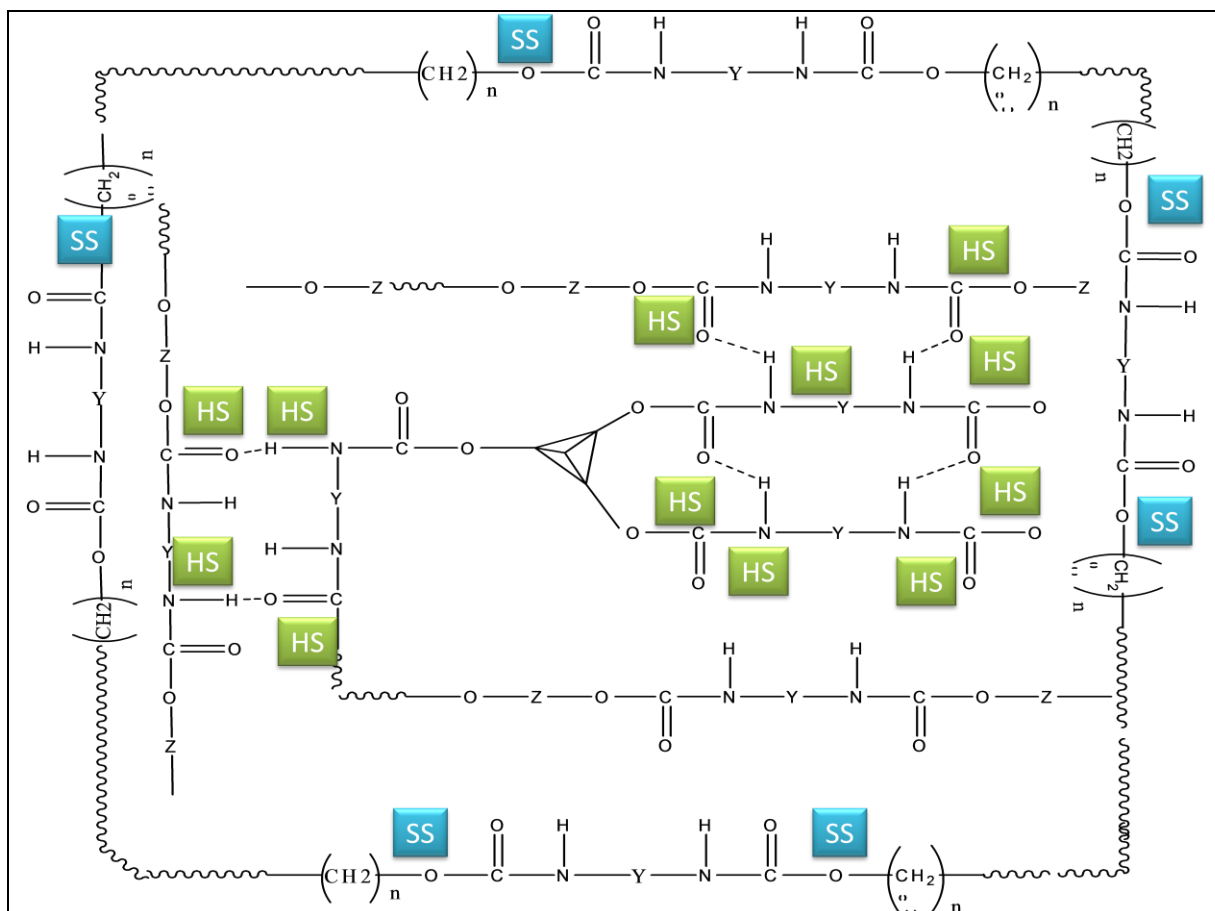
BD: TMP ratio 2:1

Short chain diols BD enhances the immiscibility of polar HS and non polar SS domain and leads to phase segregation, as it promotes the association of HS domain

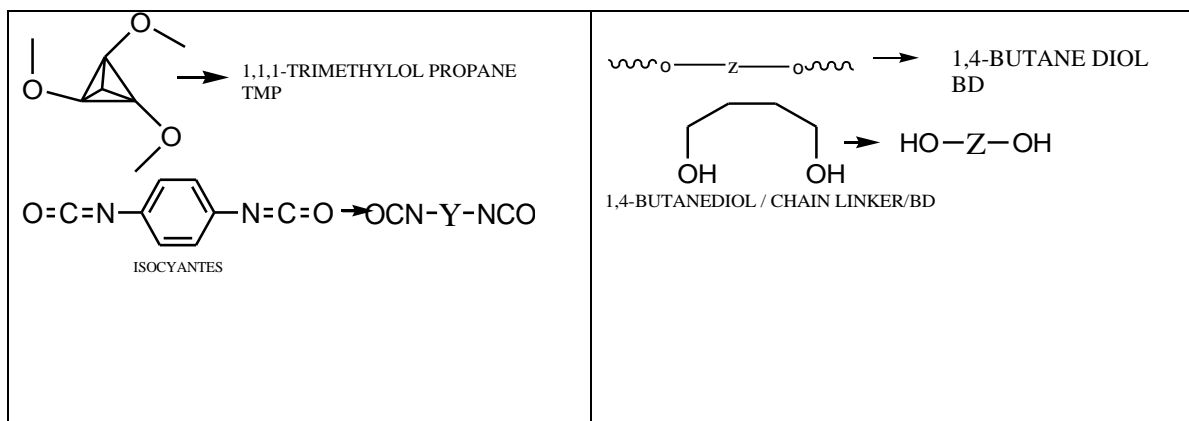
by forming H- bonding within the HS domain itself, however the H- bonding between HS and SS domains are considerably reduced due to intertwining diols which being less steric structured compared to TMP causes more engagement with the isocyanate moieties of CRA forming carbamate links [23, 24]. When the concentration of this short chain less steric structured diol (acting as a chain linker of CLA) concentration is increased compared to sterically more hindered triol TMP, the change in microphasic internal arrangement occurs which is shown in the **PU model 1** of matrix PUM-A. When BD component increases from 33% (BD: TMP:: 1:2 PUM-B) to 66% (BD: TMP:: 2:1 PUM-A) the phase segregation enhances between the HS and SS domains [25-29], making cohesive impact and self reinforcement aspect of HS domain to increase considerably and making tensile strength and young modulus to increase from 24 MPa to 33 MPa and 120 GPa to 165 GPa respectively during the present research work

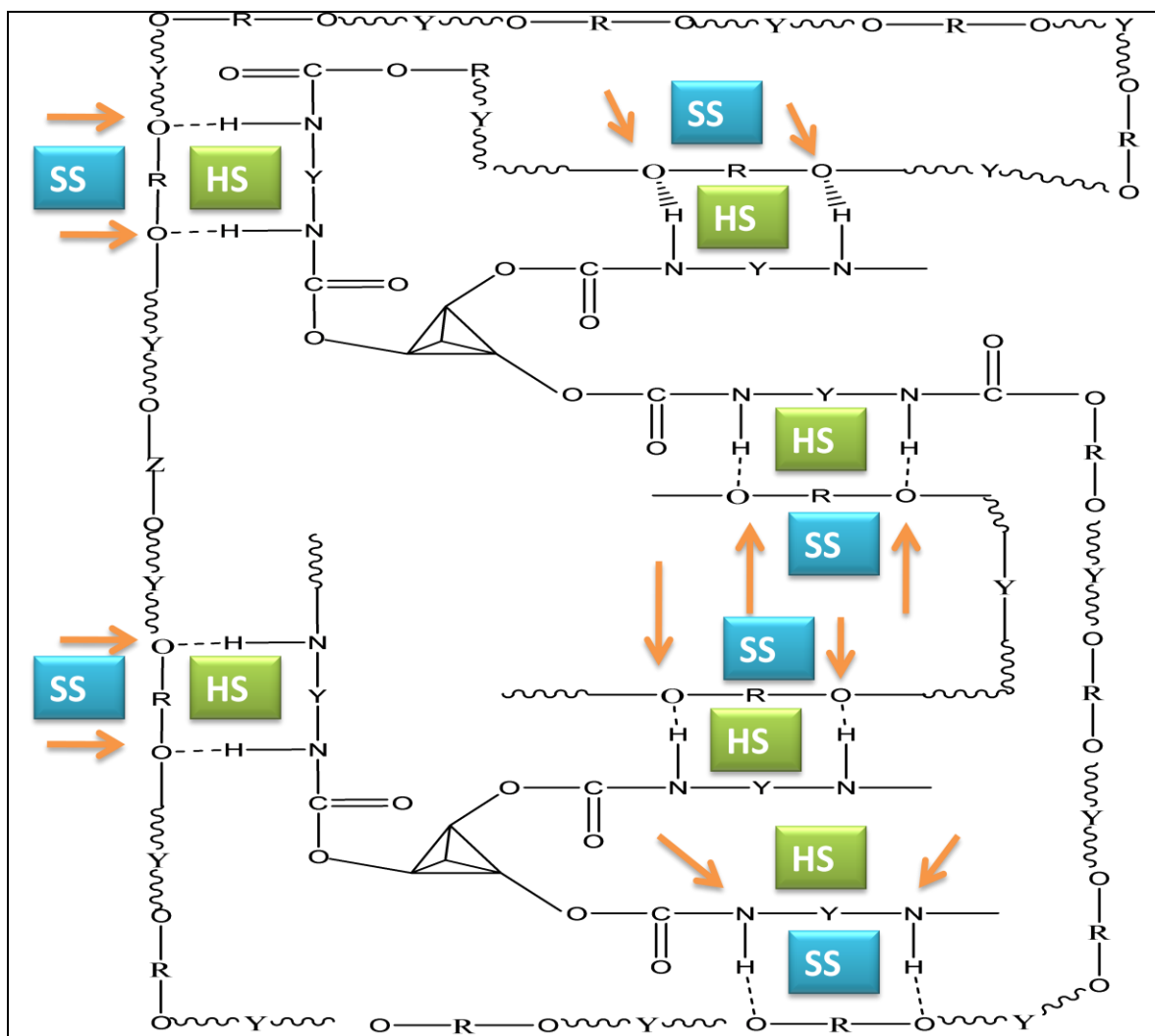
BD: TMP ratio 1:2

TMP is a branched chain cross linking component of CLA whose w/w concentration ratio when increased from 33% (BD:TMP:: 2:1 PUM-A) to 66% (BD:TMP:: 1:2 PUM-B) shows decreased mechanical properties viz. tensile strength decreases from 33 MPa to 24 MPa and young modulus also decreases from 165 GPa to 120 GPa . This decline in the mechanical properties of PUM-B is attributed to the structural aspect of triol being a branched cross linker when its concentration increases from 33 % to 66 % has more probability to interact with the isocyanate moieties of the CRA forming the carbamate links , that too increases the proximity of HS and SS domains making exhaustive H- bonding between the polar HS and Non polar SS domains of PUs, which decreases the extent of microphasic segregation between HS and SS domains of PUs as shown in **PU model 2**. This declines the cohesive impact and intrinsic reinforcement of HS domain making the mechanical properties to go to lower level as depicted from the results.

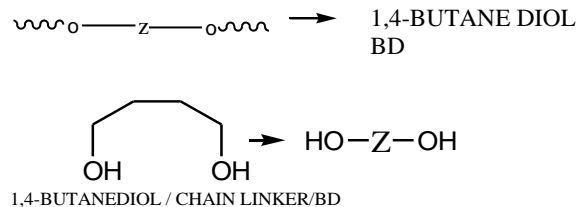
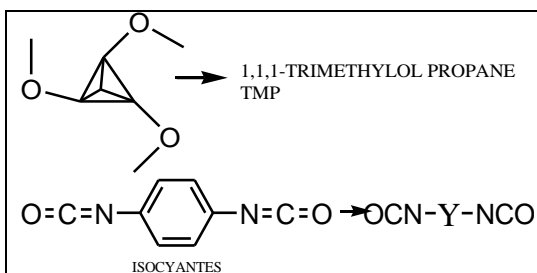


PU Model 1. The effect of **TMP & BD ratio 1:2** on the HS and SS segments of PUS , increasing microphasic segregation





PU Model 2. The effect of **TMP & BD ratio 2:1** on the HS and SS segments of PUS , reducing microphasic segregation



4.3.4 Effect of w/w Ratio of TMP and BD on Hardness of PUs

The increased w/w concentration ratio of BD causes the augmentation in the cohesive impact/strength of the PUs as it essentially increases the proximity of the HS domains and ultimately enhances the exhaustive H- bonding within HS domains, which makes the microphasic structure more compact and hard as revealed by the result for PUM-A with 76 HRE hardness, however with increase in w/w concentration ratio of TMP causes the proximity of HS and SS domain of PUs thereby decreasing the cohesive impact /strength due to exhaustive H- bonding between HS and SS domains. This revealed by the results for PUM-B with 64 HRE hardness. (Figure.4.6)

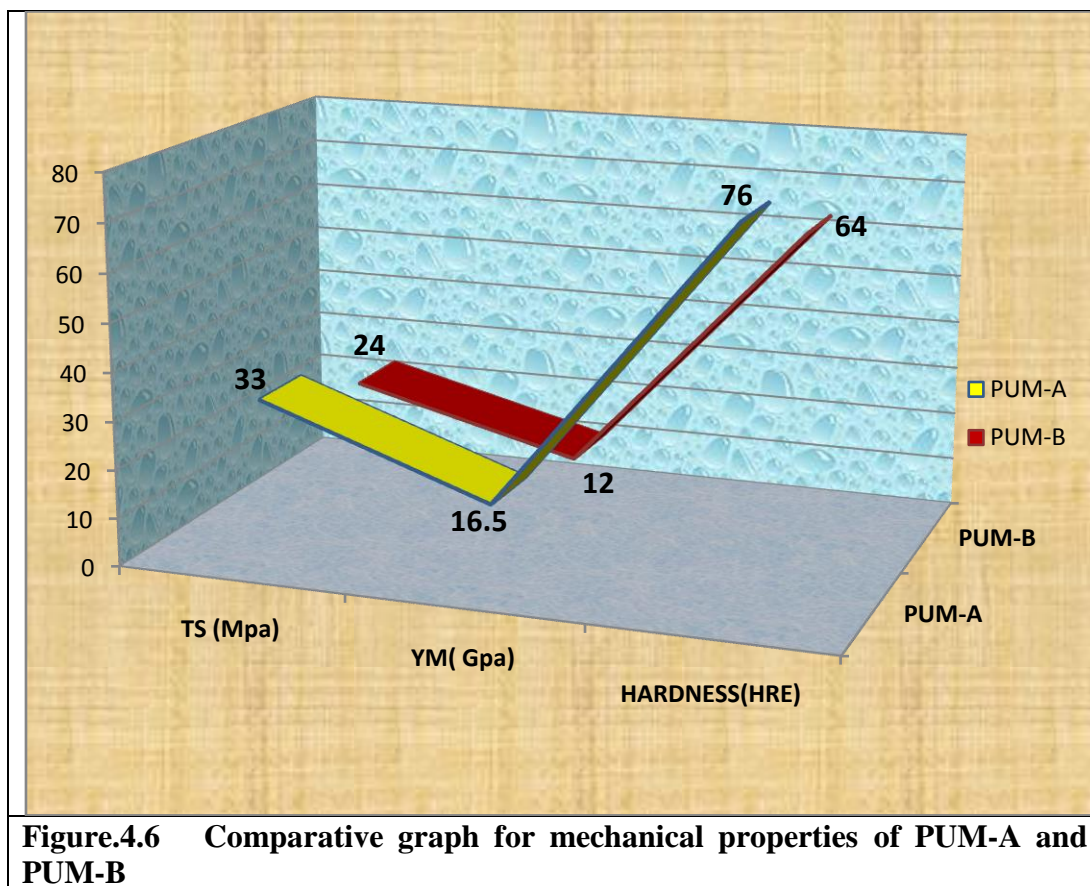


Figure.4.6 Comparative graph for mechanical properties of PUM-A and PUM-B

4.4 Conclusion

With the increase in concentration of chain linker with trifunctionality component (TMP), the mutual miscibility of two phases increases because of the proximity of moieties of HS and SS domains augments the exhaustive H- bonding between HS and SS domains reducing the phase segregation. This ultimately reduces the cohesive strength / cohesive impact of the PUs thus declines the intrinsic reinforcement potential of HS domains. This results in enhancement of the phase miscibility of HS and SS domains along with degradation of self reinforcement potential of HS units and decrease in the mechanical properties of the PUs.

When concentration of chain linker component of CLA having small chain and less steric structure i.e. BD is increased it leads to segregation of the two phases declining the H-bonding interaction between HS and SS domains as a result their mutual miscibility decreases. This makes the H- bonding to be more pronounced between the HS domains themselves leading to association of HS and increasing the cohesive impact and self reinforcement unit aspect of HS to be more enhanced which is revealed by the mechanical properties of PUM-B.

4.5 References

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**Effect of Surface Functionalized FA on
Mechanical Properties of FA Reinforced
Polyurethane Composites**

ABSTRACT

This chapter describes the effect of raw and surface functionalized FA (chemically activated FA; CAFA, thermally activated FA; TAFA) on the mechanical properties of FA reinforced polyurethane composites (PUC). The cross linkagers with different functionalities and in different w/w component ratios affected the mechanical properties of PUM thus PUC were synthesized using two types of PUM viz. PUM-A (BD: TMP:: 2:1) & PUM-B(BD:TMP::1:2). Mechanical properties viz. Tensile strength and Young's modulus of PUM-A and PUM-B as evaluated by UTM, were found greater than raw and surface functionalized FA reinforced PUCs. Surface adhered and chemically bonded hydroxyl moieties of filler FA attributed in lowering the mechanical properties of PUC. This signifies exhaustive interaction of HS and SS domains of PUC, which resulted in lowering the intrinsic reinforcement potential and cohesive strength of HS domain, which caused lowering of mechanical properties of raw and surface functionalized FA reinforced PUC in comparison to PUM. The extent of HS and SS domain interaction and its correlation with variation in the functionality of fillers has been experimentally verified by stretching frequency of carbonyl group of carbamate links in PUs in their IR studies. OH functionality of FA is reported to form carbamate links with NCO group of CRA as revealed by the increase in the stretching frequency of carbonyl of carbamate links (proximity of HS and SS domains in PUs) with decrease in intensity of NCO of CRA.

5.1 Introduction

FA is silico-aluminate material has unique property of porosity and its particle size which can support various functional moieties making it perfect filler over the utilization of other conventional fillers like kaolin, mica, glass etc. [1-7]. Present chapter focuses on the use of surface functionalized FA i.e. chemically activated FA; CAFA and thermally activated FA; TAFA in developing surface functionalized FA reinforced PUC (SF-FA-r-PUC).

The matrix used for preparation of PUC has variation in w/w ratios of binary components of CLA i.e. PUM-A and PUM-B. SF-FA-r-PUCs were evaluated for their mechanical properties viz. TS, YM and hardness by UTM and Rockwell hardness tester respectively. The properties were compared for PUM-A and PUM –B [8-11]. The results are explained by correlating internal microphasic geometry of PUC and PUM w.r.t to distribution of HS and SS domains by using CAFA and TAFA as filler in making PUC [12-14]. The increase in the IR frequency of carbonyl group of urethane linkage for SF-FA-r-PUC suggests the exhaustive interaction of HS and SS domain of PUC [15] with increase of surface hydroxyl moieties on FA. Variation in mechanical properties of PUC was not attributed to the extent of polymerization as the constant weight of CLA was used in all experiments. As explained in Chapter 3 extent of polymerization is not the function of ratio of binary components of CLA. Experiments are conducted at higher index ratio i.e.1.64 [16].

5.2 Experimental Details

5.2.1 Composite Formulation.

Raw fly ash percent loading was done at 5%, 10%, 20%, 37% and 64%, thus wt of filler was varied from 2 gm to 20 gm to achieve the maximum loading. The variation in surfacial properties of fly ash was achieved by chemical activation, thermal activation and the combination of chemical and thermal activation together. A constant weight of 10 gm of filler was selected to evaluate the change in

the mechanical properties with surface functionalization of the filler. Following terms are used in mentioning the different fillers and composites in the text.

Type of fly ash filler	Abbreviation	Polyurethane composites
Raw fly ash	RAFA	R-PUC
Calcined fly ash	CLFA	CL-PUC
Uncalcined fly ash	UCFA	UC-PUC
Thermally activated fly ash	TAFA	T-PUC

Two categories of PUCs i.e. PUC-A with BD: TMP ratio 2:1 while PUC-B with BD: TMP ratio 1:2 have been synthesized.

For preparing the composite, 10gm of filler was thoroughly mixed with 7 gm of PEG-600 and CLA 1.66gm to which 8.33 gm of TDI was added under constant stirring, the composite slurry was poured in the molds to prepare the samples of uniform dimensions (area -200 mm², width, 15mm; thickness, 7.5mm; gauge length, 50mm. The description and working details of UTM machine are already described in Chapter 2.

5.3 Results and Discussion

5.3.1 Spectroscopic Characterization of PUC

The PUC formed after the reaction of OH functionality of CE and CLA with NCO functionalities of the CRA is characterized by the formation of urethane links – NHCOO- indicated by the IR peaks for N-H stretching band around 3393cm⁻¹ and C=O stretching around 1711 cm⁻¹. The peak around 2240-2260 cm⁻¹ indicates the excess of NCO content of CRA at IR>1 i.e. 1.64 in the present case.

Spectroscopic analysis of PUCs by IR spectra given in **Figures 5.1 to 5.4** significantly reveal that variations in the concentration ratio of binary components of CLA as well as different types of FA used in designing the PUCs, are not reflected significantly in the IR spectra of PUC-A and PUC-B (overlapping spectral zones of

PUC-A and PUC-B) . The observed change in each case is in the intensities of different peaks only.

As OH functionalities (bonded OH on FA) are more for R-PUC-A/B, CL-PUC-A/B, UC-PUC-A/B, the intensity of NCO peak around 2240cm⁻¹ to 2280 cm⁻¹ was highly reduced indicating the reaction between NCO of CRA and OH of FA, forming FA-carbamate links (**Scheme 5.1**) with less concentration of unreacted CRA, as shown in the IR spectra (Figure. 5.1 to Figure.5.3)

As OH functionalities (bonded OH on FA) were decreased in T-PUC-A/B, the intensity of NCO peak of CRA was highly pronounced 2240cm⁻¹ to 2280 cm⁻¹ as shown in the Figure.5.4.

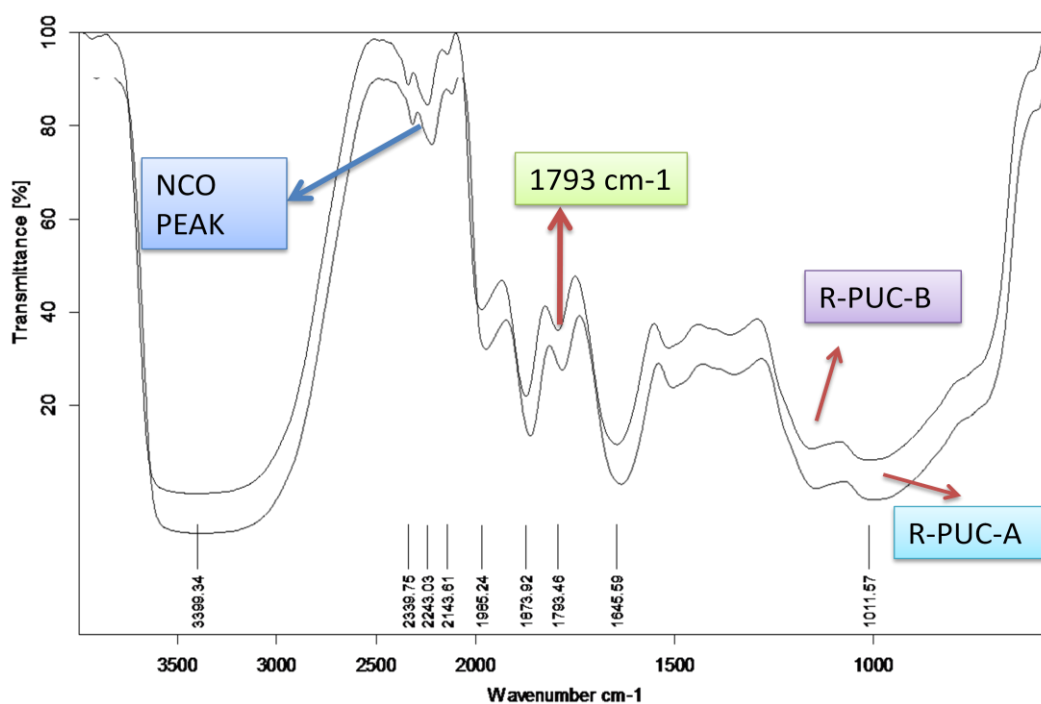


Figure.5.1. IR spectra of R-PUC-A and R-PUC-B

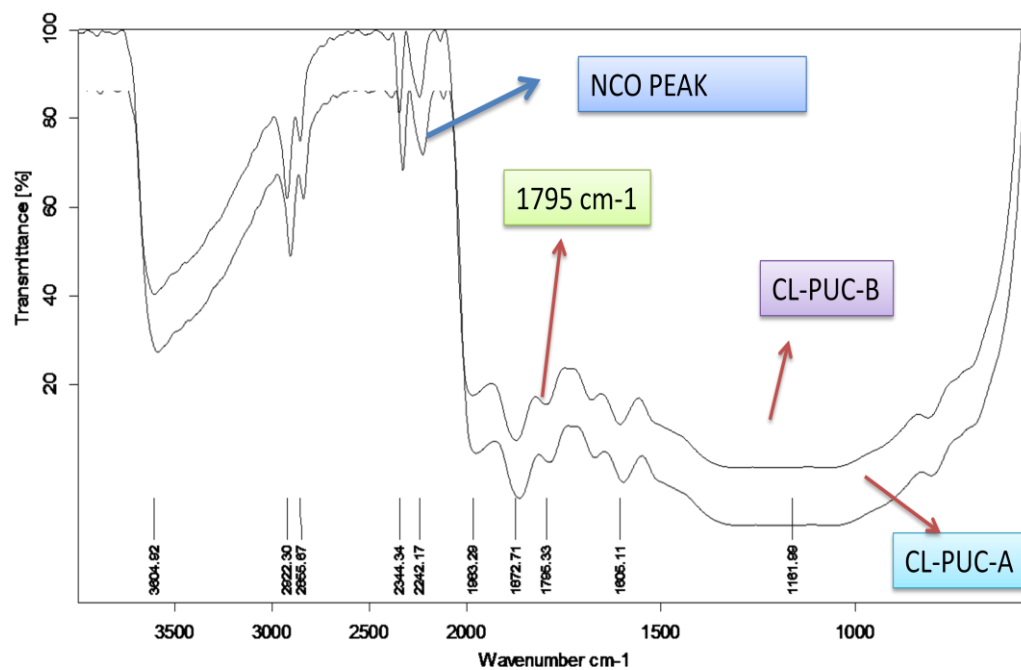


Figure.5.2. IR spectra of CL-PUC-A and CL-PUC-B

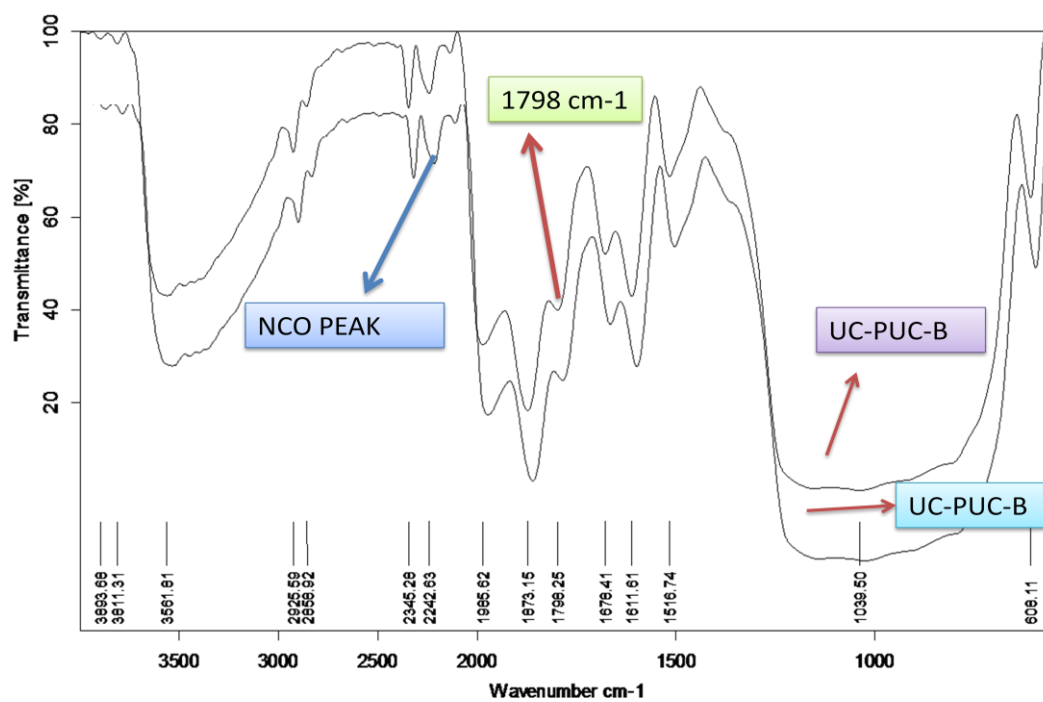


Figure.5.3. IR spectra of UC-PUC-B and UC-PUC-A

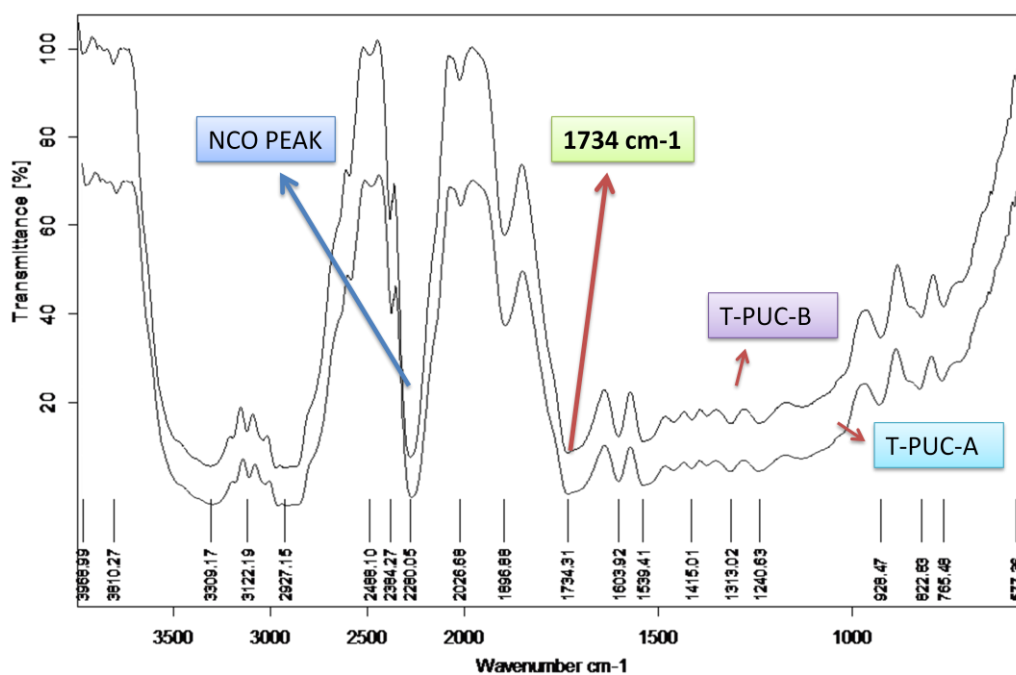
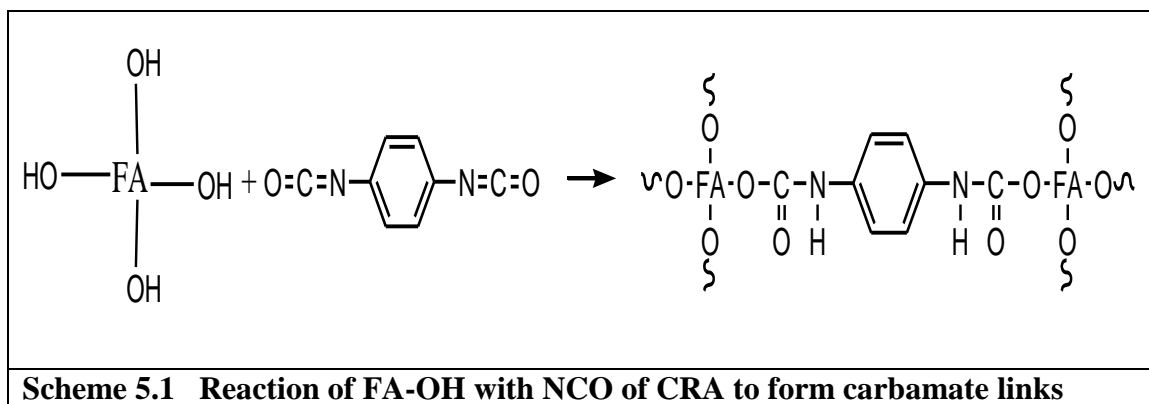


Figure.5.4. IR spectra of T-PUC-A and T-PUC-B



The decrease in the stretching frequency of the carbonyl group attributes to the formation of the carbamate links between NCO groups of CRA and OH functionalities of FA. All the above mentioned facts from IR spectroscopic data of PUCs clearly indicates that FA-OH is not directly involved significantly in the H-bonding with HS domain or in reducing their associations.

5.3.2 Effect of HS and SS Domains Interaction on Carbonyl Frequency of Urethane Links

The urethane bond links polyol groups with isocyanate functionalities in PUs. As the interaction among HS and SS domain increases, the exhaustive H-bonding occurs between N-H of urethane with ethereal oxygen of PUs (**Figure.5.5**) as a consequence stretching of C=O increases in compare to the C=O stretching frequency involved in making H-bonding when HS domains associates within themselves. This is confirmed by revealed by IR data table for C=O stretching frequency of various SF-FA-r- PUC (**Table 5.1**).

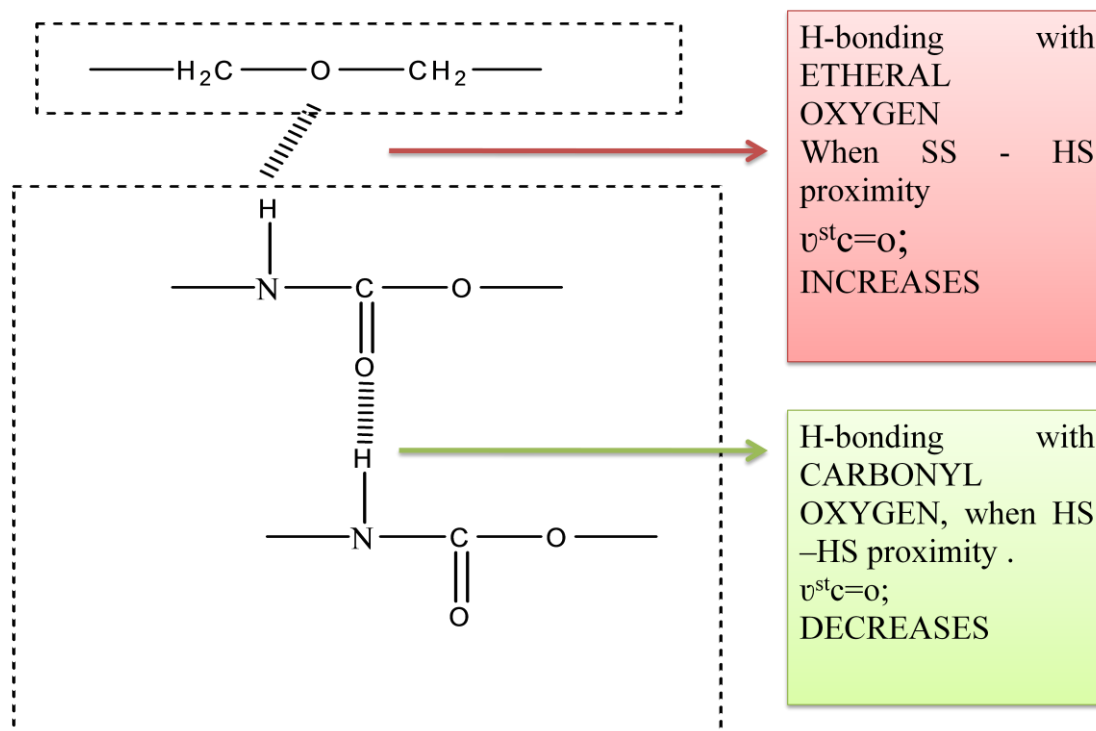


Figure 5.5 HS and SS domains of the PU system

Table 5.1 Stretching frequency of various SF-FA-r- PUC.

Type of Composite	ν^{st} C=O of urethane link in FA-r-PUC
T-PUC	1734 cm-1
UC-PUC	1798 cm-1
CL-PUC	1795 cm-1
R-PUC	1793 cm-1

As OH moieties concentration increases on SF-FA-r-PUC , tendency of HS and SS domains proximity increases both in PUC-A and PUC-B which leads to increase in stretching of C=O in carbamate links . However, when TAFA is used in designing PUC, concentration of OH moieties is less on FA surface due to high temperature heating which results in slightly increase of association of HS domains thus ν^{st} C=O frequency decreases i.e. 1734 cm-1 , which essentially signifies the H-Bonding between N-H of one carbamate unit with C=O of another carbamate unit.

5.4 Mechanical Properties of PUCs

The samples of PUCs using raw and OH functionalized FA with matrix of type PUM-A and PUM-B were designed as per the ASTM standards [17] and evaluated for their mechanical properties. The results have been presented in **Tables 5.2 and 5.3** for PUC and PUC B respectively. The load (KN) v/s displacement (mm) graphs of different type of composites of PUC-A and PUC-B are given in the **Test certificates 5.1 to 5.8.**

Table 5.2. Values of mechanical properties of different types of PUC-A

S.No	Mechanical Properties	R-PUC-A	UC-PUC-A	CL- PUC-A	T-PUC-A
1.	Tensile strength	24 MPA	11MPA	22MPA	26 MPA
2.	Young modulus	12 GPA	5.5 GPA	11 GPA	13 GPA
3.	Hardness	102HRE	118 HRE	101 HRE	90 HRE
4.	% Elongation	0.02	0.02	0.02	0.02
5.	Break point	24	22	22	26
6.	Force(max)	4.800 KN	4.760 KN	4.420 KN	5.120 KN
7.	Displacement at F(max)	8.700 mm	11.700 mm	8.500 mm	0.100 mm
8.	Maximum Displacement	16.600 mm	17.4 mm	16.00 mm	13.700 mm
9.	Ultimate strength	0.024 KN/mm ²	0.011 KN/mm ²	0.022 KN/mm ²	0.026 KN/mm ²

Table 5.3. Values of mechanical properties of different types of PUC-B

S.No:	Mechanical Properties	R-PUC-B	UC-PUC-B	CL-PUC-B	T-PUC-B
1.	Tensile strength	13 MPA	8 MPA	12 MPA	16 MPA
2.	Young modulus	6.5 GPA	4 GPA	6 GPA	8 GPA
3.	Hardness	101 HRE	125HRE	121 HRE	84 HRE
4.	% Elongation	0.02	0.02	0.02	0.02
5.	Break point	13	8	12	16
6.	Force(max)	4.760 KN	1.680 KN	4.600 KN	4.640 KN
7.	Displacement at F(max)	9.100 mm	5.300 mm	11.000 mm	6.300 mm
8.	Maximum Displacement	35.400 mm	10.000 mm	22.00 mm	15.200 mm
9.	Ultimate strength	0.013 KN/mm ²	0.008 KN/mm ²	0.012 KN/mm ²	0.016 KN/mm ²

Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : VADODARA

Sample Identification : Composite (I)

AT 10 C1:17

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT , Record No. : 22 , Date : 06-06-2018

: Sample Type -- Rectangular Bar Area : 200.000 mm²

: Width = 15 mm Thickness = 7.5 mm

: Gauge Length : 50 mm Final Gauge Length: 50.01 mm

Results of : Tension Test

Maximum Force (F_m) : 4.800 kN

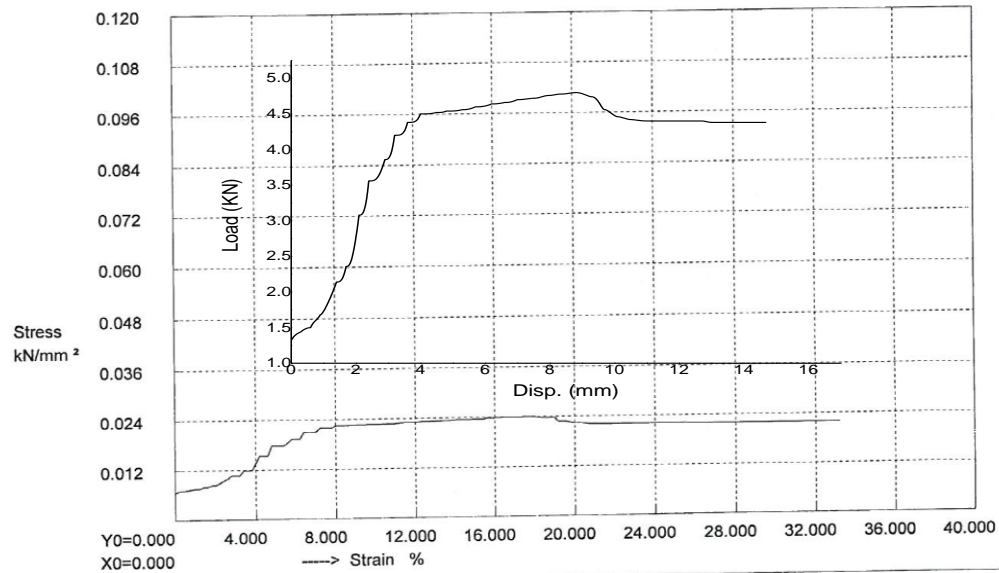
Disp. at F_m : 8.700 mm

Max. Disp. : 16.600 mm

Ult. Strength : 0.024 kN/mm² A

Elongation : 0.020 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate 5.1 For the sample R-PUC-A presenting Stress v/s strain variation

Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : VADODARA

Sample Identification : Composite (I) *CANC*

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT , Record No. : 16 , Date : 06-06-2018

: Sample Type -- Rectangular Bar Area : 450.000 mm²

: Width = 15 mm Thickness = 7.5 mm

: Gauge Length : 50 mm Final Gauge Length: 50.01 mm

Results of : Tension Test

Maximum Force (Fm) : 4.760 kN

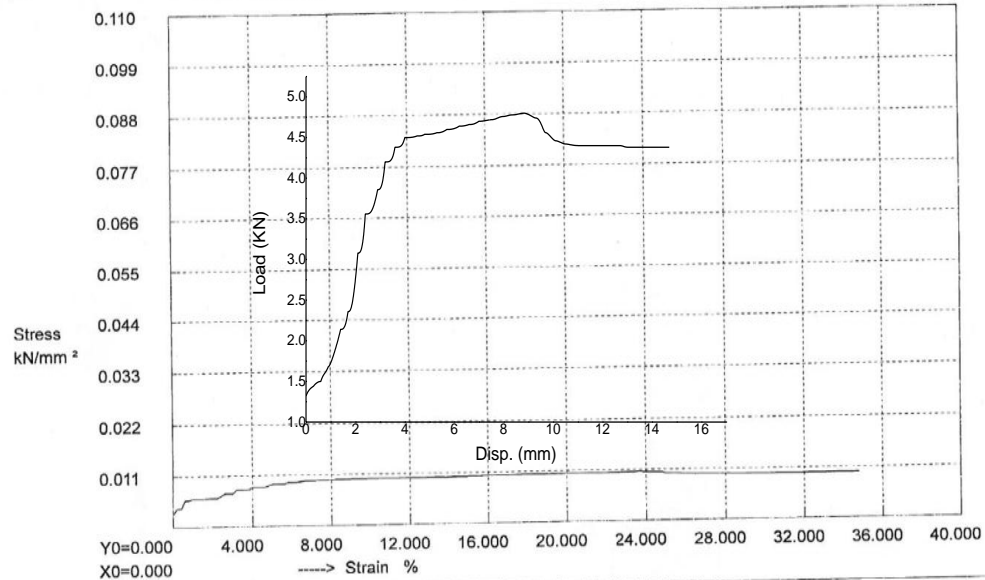
Disp. at Fm : 11.700 mm

Max. Disp. : 17.400 mm

Ult. Strength : 0.011 kN/mm²

Elongation : 0.020 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate 5.2 For the sample UC-PUC-A presenting stress v/s strain variation

Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : VADODARA

Sample Identification : Composite (I) CT10(1:2)

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT , Record No. : 23 , Date : 06-06-2018

: Sample Type -- Rectangular Bar Area : 200.000 mm²

: Width = 15 mm Thickness = 7.5 mm

: Gauge Length : 50 mm Final Gauge Length: 50.01 mm

Results of : Tension Test

Maximum Force (Fm) : 4.420 kN

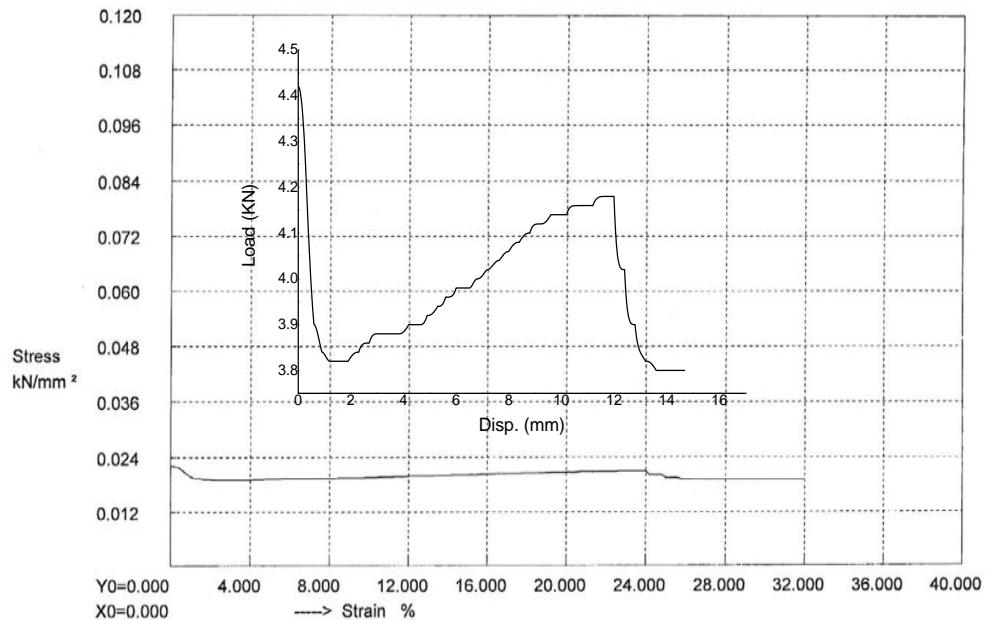
Disp. at Fm : 0.000 mm

Max. Disp. : 16.000 mm

Ult. Strength : 0.022 kN/mm²

Elongation : 0.020 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate 5.3 For the sample CL-PUC-A presenting stress v/s strain variation

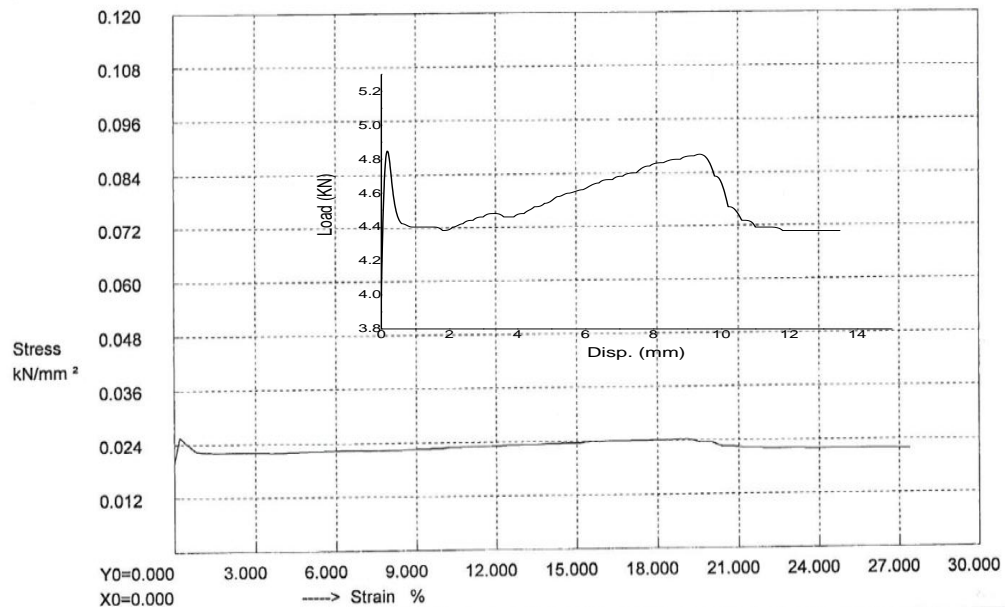
Test Certificate

Name of Company : NEI LIMITED
Address : GUJARAT
To : NEI LTD
Address : VADODARA
Sample Identification : Composite (I) *A2(NC)*
Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT, Record No. : 29, Date : 06-06-2018
: Sample Type -- Rectangular Bar Area : 200.000 mm²
: Width = 15 mm Thickness = 7.5 mm
: Gauge Length : 50 mm Final Gauge Length: 50.01 mm

Results of : Tension Test
Maximum Force (F_m) : 5.120 kN
Disp. at F_m : 0.100 mm
Max. Disp. : 13.700 mm
Ult. Strength : 0.026 kN/mm²
Elongation : 0.020 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate 5.4 For the sample T-PUC-A presenting Stress v/s strain variation

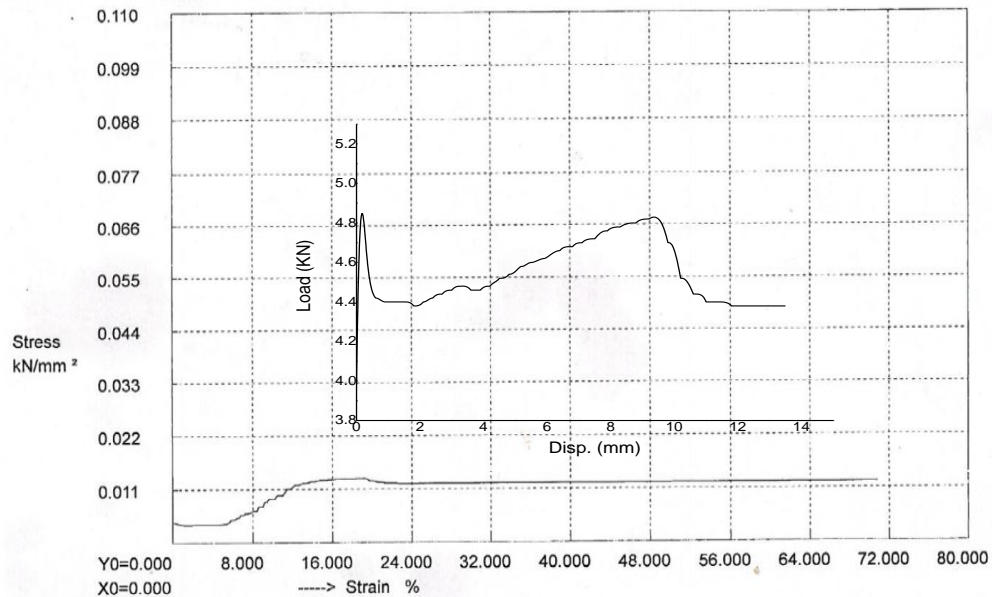
Test Certificate

Name of Company : NEI LIMITED
 Address : GUJARAT
 To : NEI LTD
 Address : VADODARA
 Sample Identification : Composite (A) C 2 M
 Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT, Record No. : 10, Date : 28-05-2018
 : Sample Type -- Rectangular Bar Area : 360.000 mm²
 : Width = 15 mm Thickness = 7.5 mm
 : Gauge Length : 50 mm Final Gauge Length: 50.1 mm

Results of : Tension Test
 Maximum Force (Fm) : 4.760 kN
 Disp. at Fm : 9.100 mm
 Max. Disp. : 35.400 mm
 Ult. Strength : 0.013 kN/mm²
 Elongation : 0.200 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate-5.5 For the sample R-PUC-B presenting stress v/s strain variation

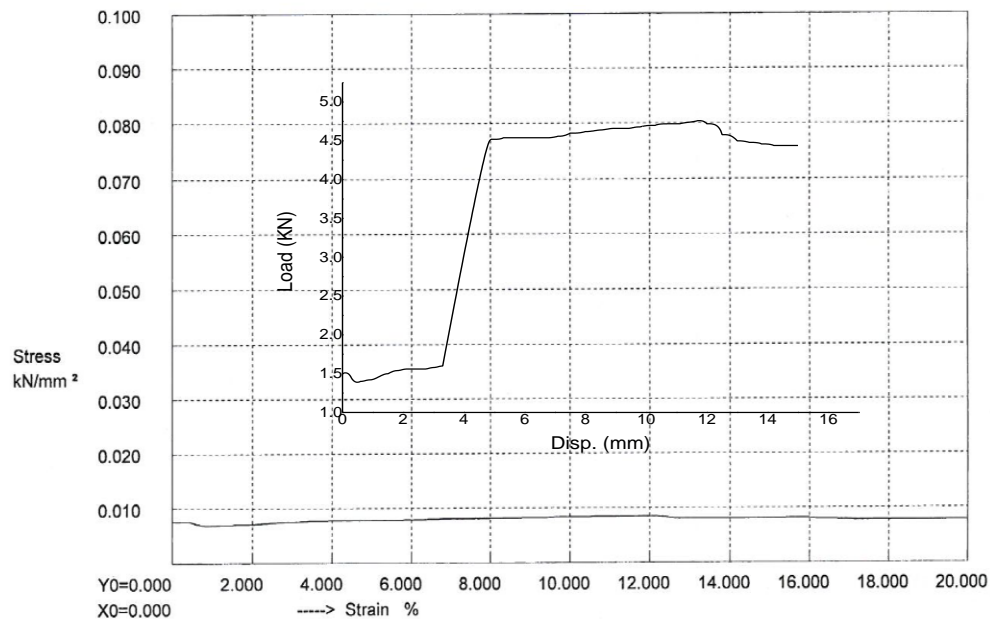
Test Certificate

Name of Company : NEI LIMITED
Address : GUJARAT
To : NEI LTD
Address : VADODARA
Sample Identification : Composite (B2M)
Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT, Record No. : 12, Date : 06-06-2018
: Sample Type -- Rectangular Bar Area : 200.000 mm²
: Width = 15 mm Thickness = 7.5 mm
: Gauge Length : 50 mm Final Gauge Length: 50.01 mm

Results of : Tension Test
Maximum Force (F_m) : 1.680 kN
Disp. at F_m : 5.300 mm
Max. Disp. : 10.000 mm
Ult. Strength : 0.008 kN/mm²
Elongation : 0.020 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate-5.6 For the sample UC-PUC-B presenting stress v/s strain variation

Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : VADODARA

Sample Identification : Composite (I) B2MC

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT, Record No. : 15, Date : 06-06-2018

: Sample Type -- Rectangular Bar Area : 374.000 mm²

: Width = 15 mm Thickness = 7.5 mm

: Gauge Length : 50 mm Final Gauge Length: 50.01 mm

Results of : Tension Test

Maximum Force (F_m) : 4.600 kN

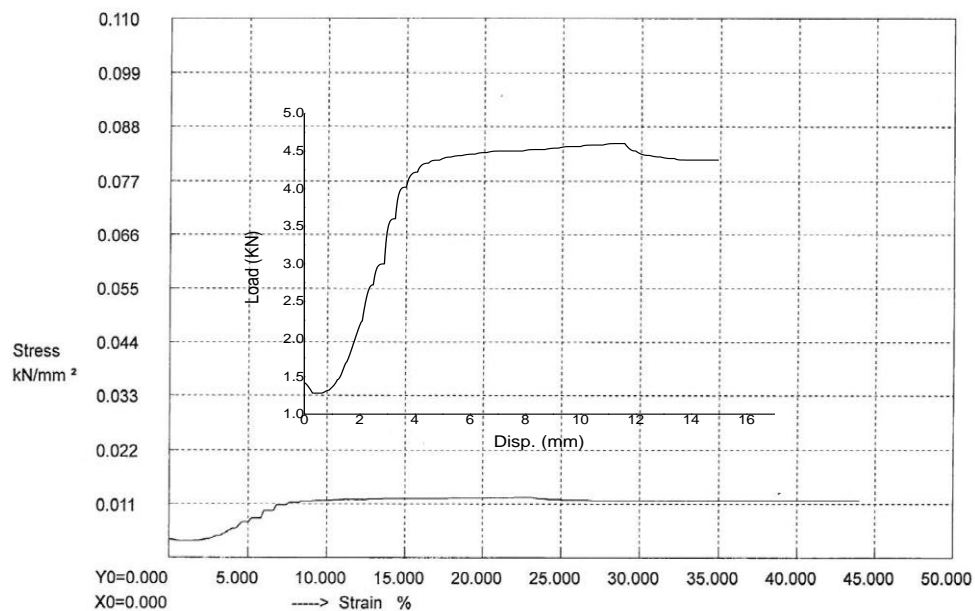
Disp. at F_m : 11.000 mm

Max. Disp. : 22.000 mm

Ult. Strength : 0.012 kN/mm²

Elongation : 0.020 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate 5.7 For the sample CL-PUC-B presenting Stress v/s strain variation

Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : VADODARA

Sample Identification : Composite (I) BT-10 (2:1)

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT , Record No. : 13 , Date : 06-06-2018

: Sample Type -- Rectangular Bar Area : 294.000 mm²

: Width = 15 mm Thickness = 7.5 mm

: Gauge Length : 50 mm Final Gauge Length: 50.01 mm

Results of : Tension Test

Maximum Force (F_m) : 4.640 kN

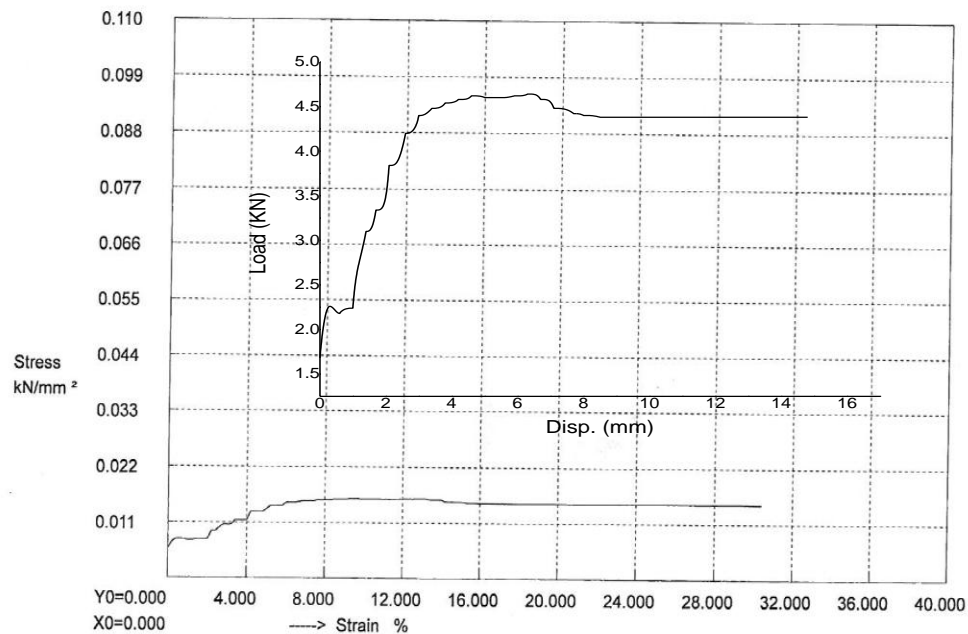
Disp. at F_m : 6.300 mm

Max. Disp. : 15.200 mm

Ult. Strength : 0.016 kN/mm²

Elongation : 0.020 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate 5.8 For the sample T-PUC-B presenting Stress v/s strain variation

5.4.1 Effect of SF- FA on HS and SS Domain of PUM-A and PUM-B

HS and SS domains in PUM have been explained in Chapter 4. Wherein it has been clearly defined that with proximity of HS and SS domain in PUs intrinsic reinforcement potential of HS domain declines and the interphase segregation at microphasic level decreases reducing the cohesive impact and so the mechanical properties of the PUs. As the RAFA is added to PUM to design R-PUC its mechanical properties decreases and this decrease is attributed to the adhered OH moieties on FA surface which forms urethane/carbamates links with polyols, chain linkers, and cross linkers of CLA augmenting the proximity of HS domains with SS domains. The same effect was observed with binary component of CLA with higher functionality of TMP. As the concentration of OH functionalities is augmented on RAFA by chemical activation (UCFA and CAFA), it leads to enhanced proximity of HS domains with SS domains.[18-22]. The scanning electron microscopic structures of UC-PUC shown in **Figure.5.6** and CL- PUC shown in **Figure. 5.7** clearly show that chemically surface functionalized filler particles are imbedded strongly in the resin structures. For illustrating clearly the model structures for T-PUC and UC-PUC are given in **Figures. 5.8** and **Figure 5.9** respectively which show different linkages and interactions among SS and HS domains.

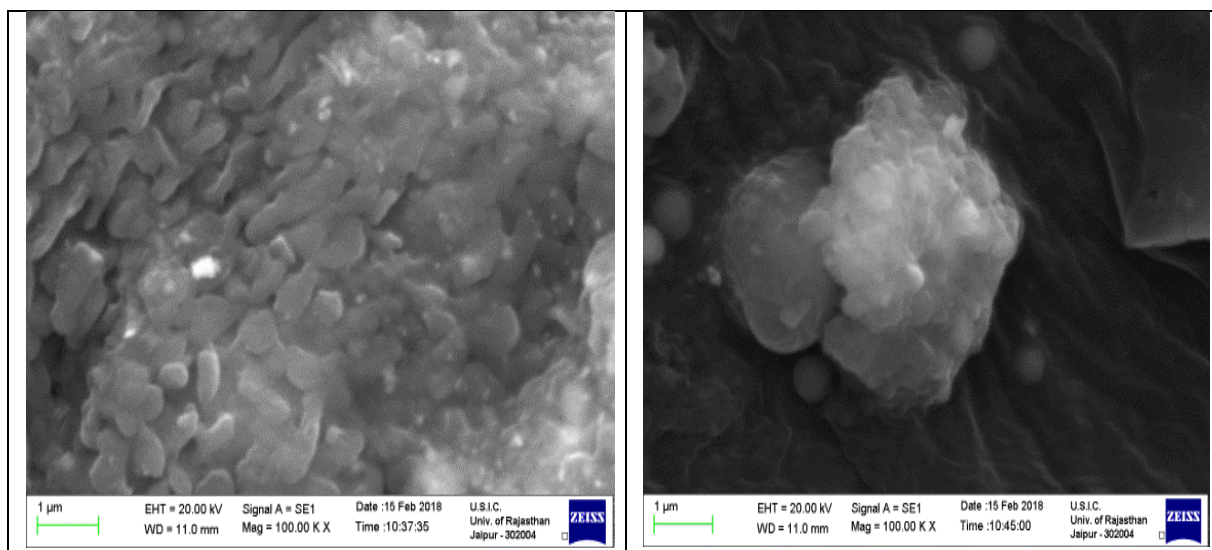


Figure.5.6 SEM image showing proximity of HS domains with SS domains in UC-PUC

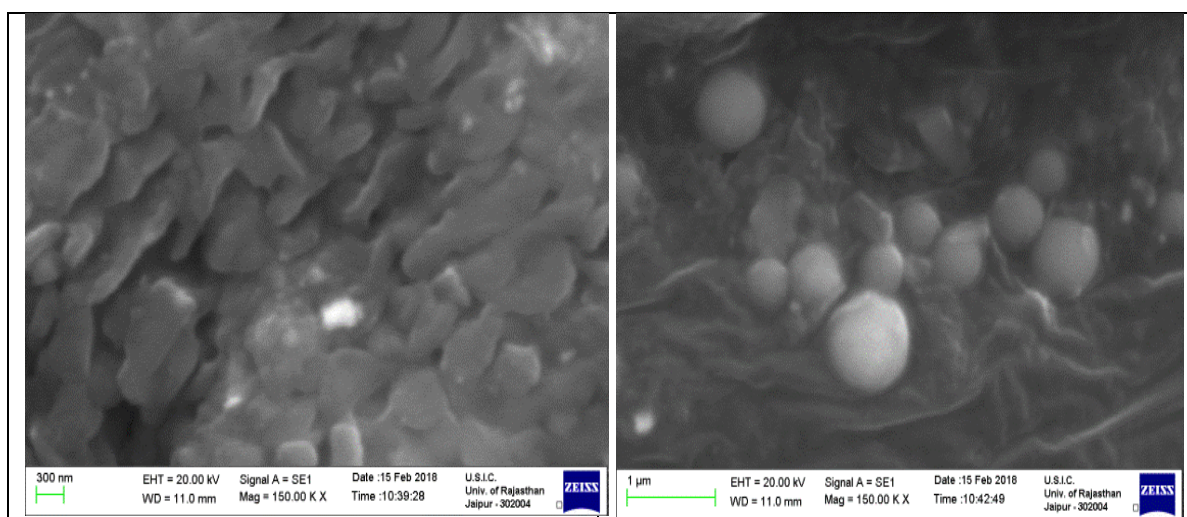
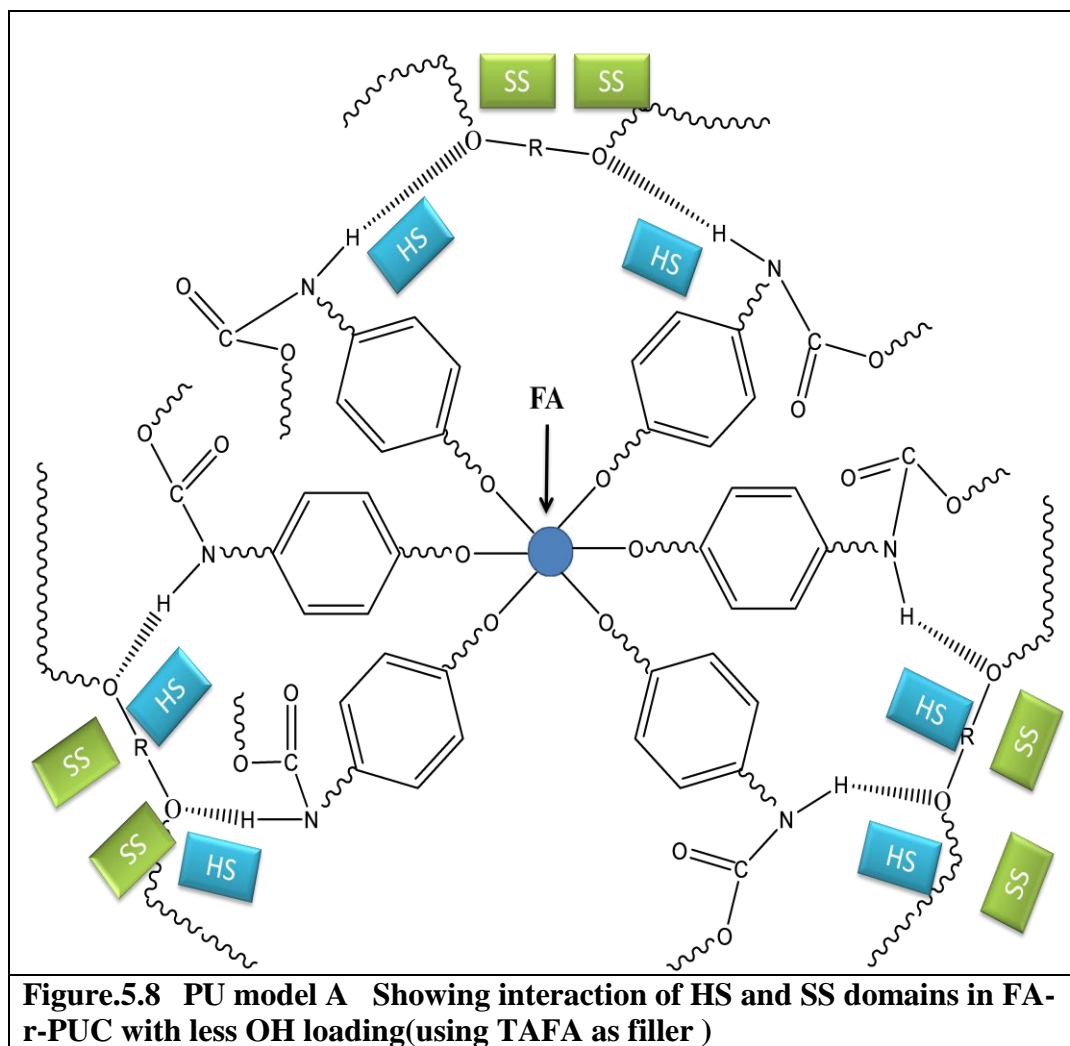


Figure.5.7 SEM image showing proximity of HS domains with SS domains in CL-PUC



As discussed earlier on thermal treatment surface adhered OH concentration declines in the filler leading to separate the HS and SS domains and improving the cohesive impact and self reinforcement of HS domains which ultimately enhances the mechanical properties. The values of YM and TS greater for T-PUC as compared to R-PUC, CL-PUC and UC-PUC.

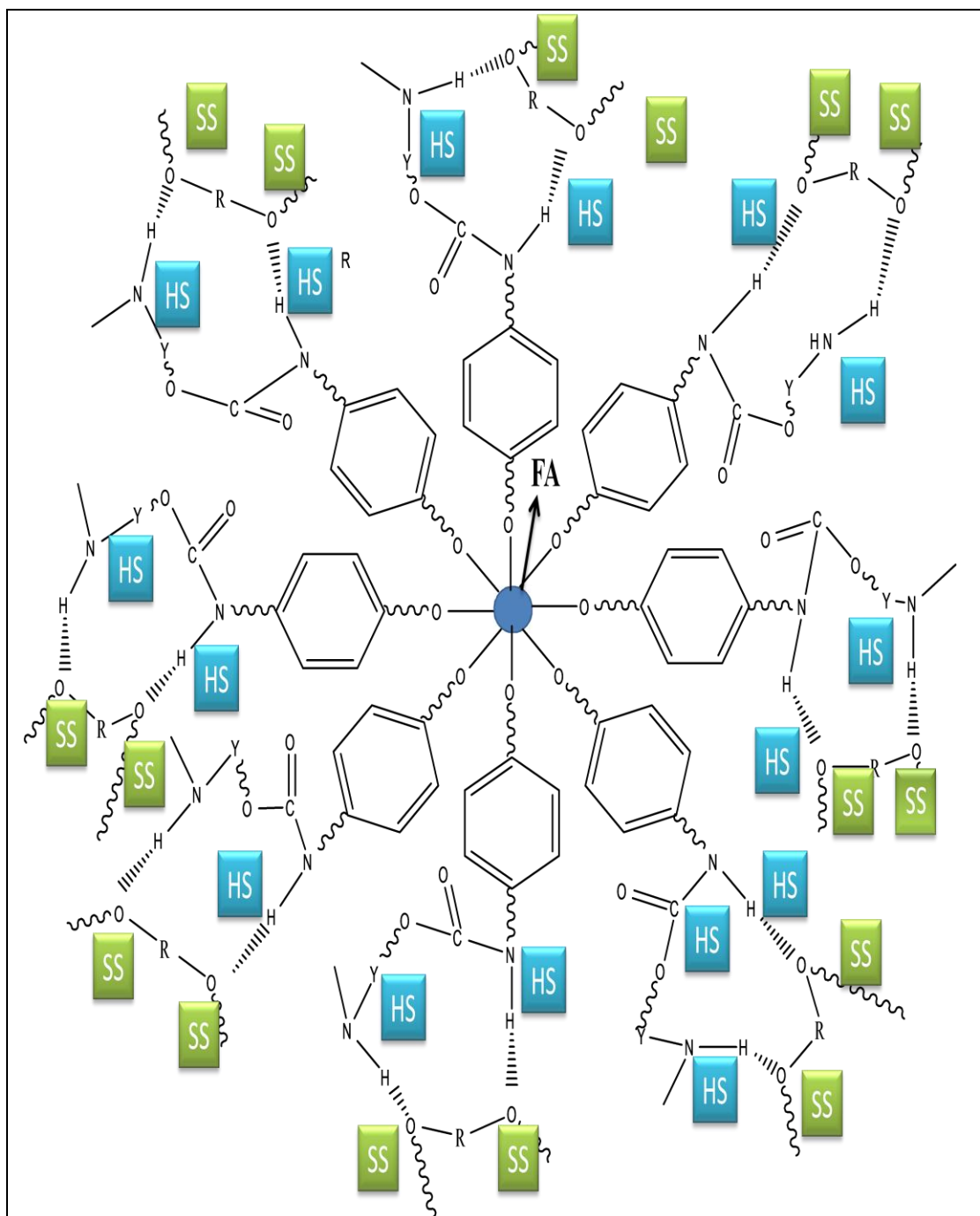


Figure.5.9 PU model B Showing interaction of HS and SS domains in FA-r-PUC with more OH loading (using RAFA, CLFA and UCFA as fillers)

A comparison is shown graphically in **Figure. 5.10** and **Figure.5.11** for PUC-A and PUC-B. The order of mechanical properties of PUM and PUCs as observed in the present case is-

PUM-A > T-PUC-A > R-PUC-A > CL-PUC-A > UC-PUC-A
PUM-B > T-PUC-B > R-PUC-B > CL-PUC-B > UC-PUC-B

5.4.2. Correlation of Mechanical Properties of PUC with Carbonyl Frequency of Urethane Links

With increase in the association among HS and SS domains, microphasic segregation of domains decreases which declines self cohesive impact of HS thus reduces mechanical properties [23-27]. The microphasic rearrangement is revealed by the increase in the st. C=O frequency of carbamate links in various PUCs at constant Wt % of filler taken as 37.05% in all PUCs in the present work to control the defects generated by filler particles on HS and SS domains. Results are shown in **Figure. 5.12** also confirmed by IR spectra shown in in Figures. 5.1 to 5.4. From the graphical representation of the correlation between the carbonyl stretching frequency of carbamate group and the mechanical properties of PUCs containing different types of the filler FA, it is confirmed that as the number of OH functionalities increases on FA, number of carbamate links with NCO of CRA increases which leads to enhanced HS and SS interaction leading to decline in the mechanical properties. On synthesizing the polymer composites at constant index ratio, with increase in the number of OH functionality on the surface of the filler the intensity of the NCO peak in the IR spectra of PUC is also decreases. The above finding is summarized in **Scheme 5.2**.

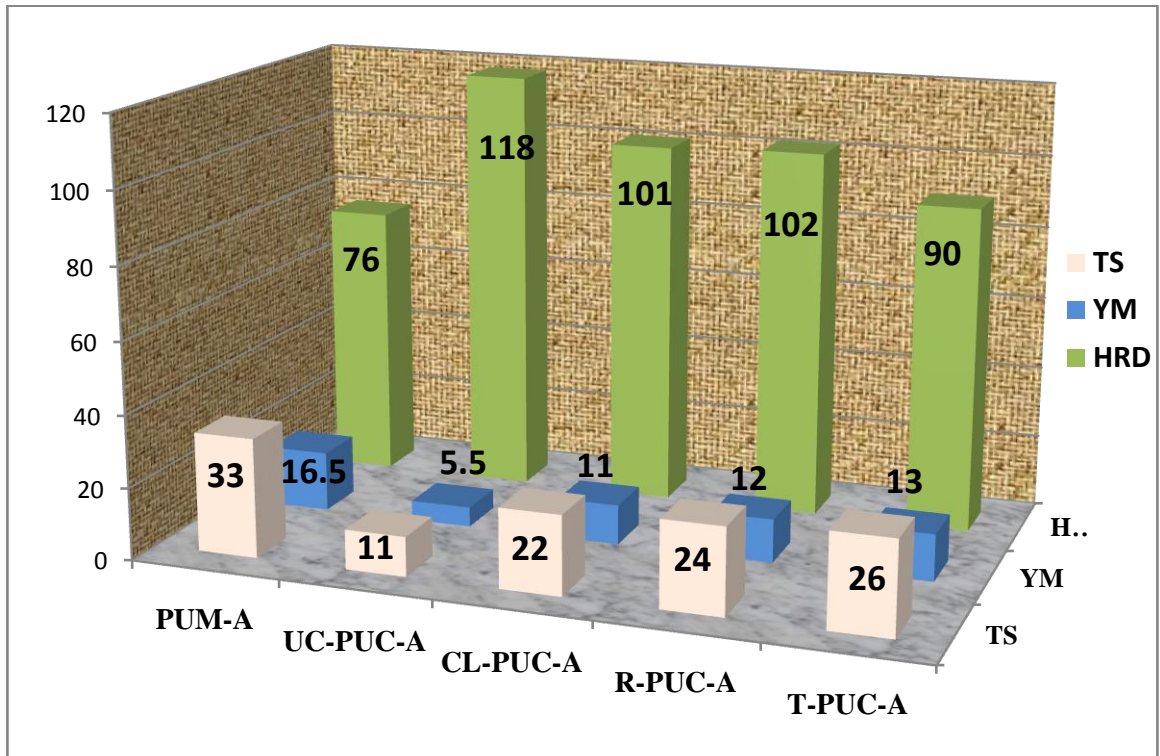


Figure 5.10. Mechanical properties comparison of PUM-A and PUC-A

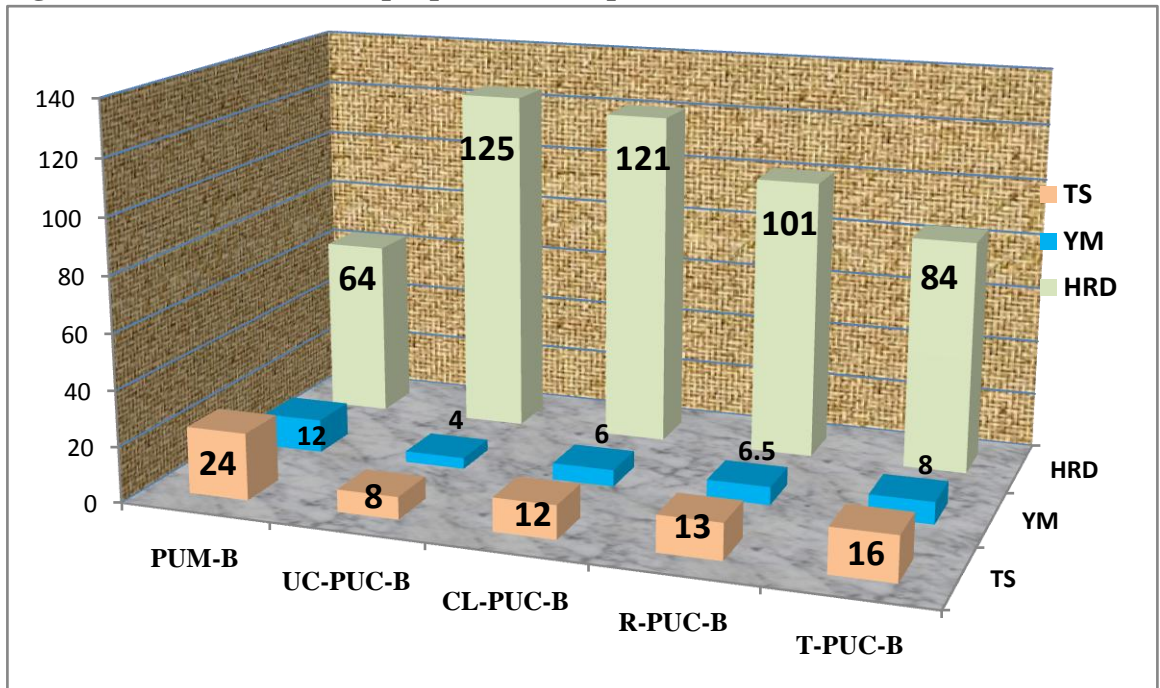
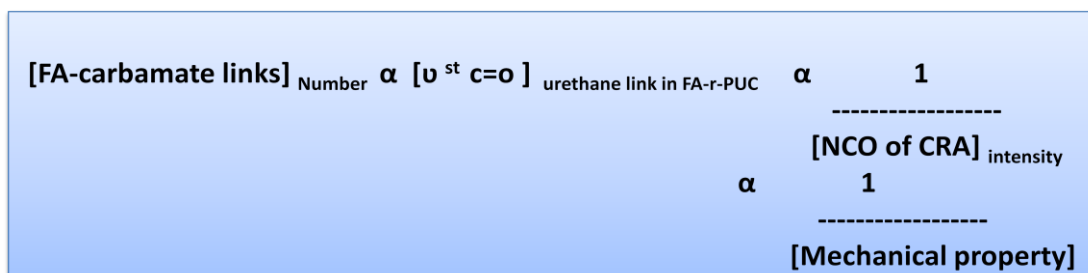
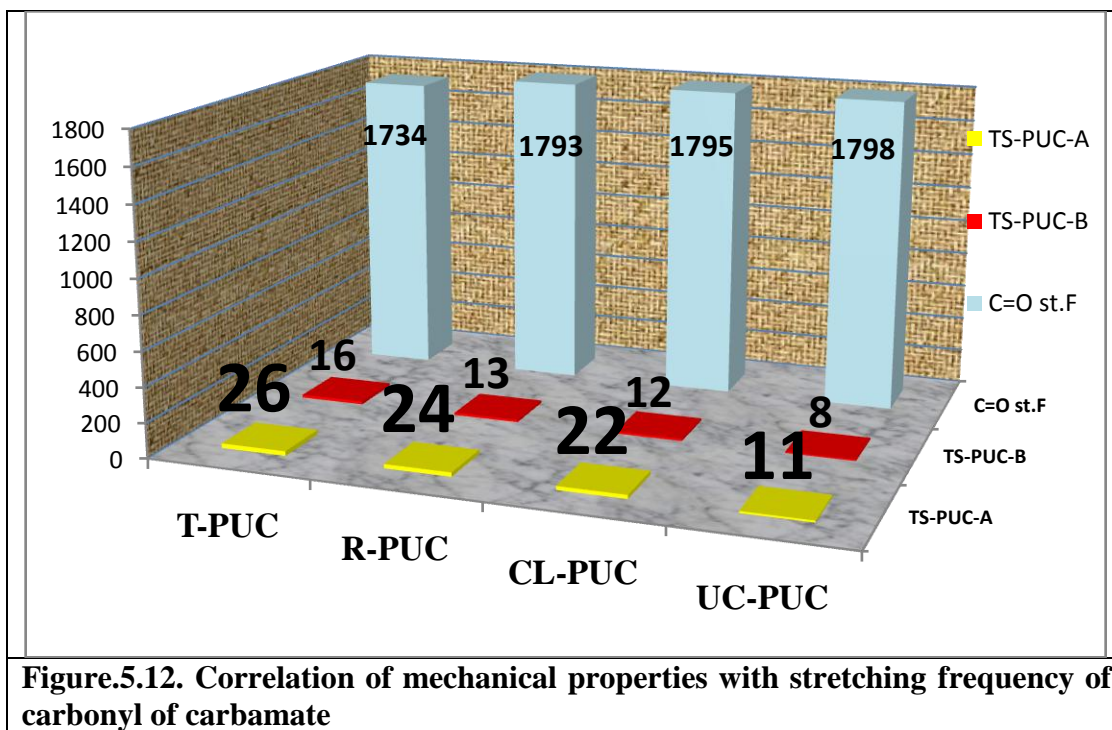


Figure.5.11. Mechanical properties comparison of PUM-B and PUC-B



Scheme 5.2 Correlation between mechanical properties with intensity of NCO peaks in PUC.

5.4.3 Hardness of PUM and PUC

PUC formulation decreases mechanical properties in comparison to PUM in terms of TS and YM but in terms of hardness PUC has enhanced values over PUM due to inorganic filler entrapment [28-31]. A comparison of values of hardness of different types of PUCs and PUMs are already presented in Figures.5. 10 and 5.11.

5.5 Conclusion

Mechanical properties viz. TS YM etc of PUM are more for PUM as compared to FA-r-PUC. Surface functionalized fillers with OH moieties used in raw form or chemically activated reduces the mechanical properties of composites even when PUC is synthesized at higher index ratio (revealed by the presence of NCO stretching frequency around 2240 cm^{-1} in all SF-FA-r-PUC i.e $\text{NCO/OH} = 1.64$) as this leads to removal segregation of HS and SS domain at microphasic level. The achieved microphasic rearrangement thus reduces the intrinsic cohesive reinforcement impact of HS domain. Filler reinforced PUC formulation with better mechanical properties can be designed by thermal treatment of filler bearing surface adhered OH moieties. Internal microphasic rearrangement of HS and SS domains clearly revealed by $\nu_{\text{st c=O}}$ of carbamate links which signifies that for higher mechanical properties of PUCs possess lower $\nu_{\text{st c=O}}$ while with lower mechanical properties PUCs possess higher $\nu_{\text{st c=O}}$ of carbamate links.

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**A Comparative Study of Mechanical and
Thermal Properties of Raw and Surface
Functionalized Fly Ash Reinforced
Epoxy Composites**

ABSTRACT

This chapter describes the comparative study of mechanical properties mainly TS and YM of raw and surface functionalized FA reinforced epoxy composites. Mechanically activated fly ash reinforced epoxy composites shows two and half times increment in the modulus without sacrificing the tensile strength at 33.64% loading efficiency of fly ash. OH functionalized (calcined and non calcined) fly ash reinforced composites show higher YM but a decrease in magnitude of TS as compared to epoxy matrix. The thermal stability of EPM and EPCs are evaluated knowing T_g through DSC technique. Among all sorts of FA-r-EPC best thermal stability (higher T_g value) exhibited by R-EPC but TS is decreased Surface modification of filler (mechanically/ thermally/ chemically) pertains variation on crystalline or amorphous domains of raw filler. OH moieties loaded FA i.e. CAFA reinforced EPC shows better mechanical properties compared to TAFA reinforced EPC. Mechanical properties of particulate-polymer composites depend on various parameters viz. interface adhesion, particle loading, particle size etc. The variations of the properties on varying different parameters are explained by various phenomenological and semi-empirical models.

6.1 Introduction

Epoxy composites due to their light weight and excellent load bearing capacity serve as the best polymeric material in the today's world. Chemical combination of epoxy monomers with hardeners gives a cross linked polymer network in which the extent of cross linking depends primarily on ratio of resin and hardener, pressure, temperature and mixing techniques [1]. In epoxy cured polymers using an amine as a hardener, a soft unreacted / partially reacted material is dispersed in hard microgel phase. As the concentration of amine is increased the hard microgel phase augments. The extent of cross linking i.e. approximate quantification of hard microgel phase is usually measured by IR absorbance technique wherein effective crosslinking gives increased absorbance for OH groups and a decrease in intensity of epoxide bonds peaks. The stiffness and strength of the polymer matrix depends on the extent of crosslinking which further can be improvised by adding various inorganic particulate fillers such as micro/ nano SiO_2 , glass, CaCO_3 , Al_2O_3 , $\text{Mg}(\text{OH})_2$, etc. [2-7] Nano filler reinforced epoxy composites show improved stiffness / modulus as compared to cured epoxy matrix [8-12]. The tensile strength of the filler reinforced epoxy composites depends on the transfer of stress between filler particles and the matrix [13-16]. The effectiveness of stress transfer mechanism depends on the extent of bonding of filler particulate with the matrix. The inorganic particulate filler improves hardness and stiffness of the composites. [17-21]

Present chapter incorporates the comparative results of mechanical properties of raw and surface functionalized fly ash reinforced epoxy composites synthesized during the work. Fly ash particulate size, surfacial properties, thermal, mechanical and chemical activation affected the mechanical properties of FA reinforced epoxy composites at constant percent loading [22-28]. The mechanical properties are compared and explained by the phenomenological and semi empirical models in an innovative way.

6.2 Experimental Details

The terms used for the different types of FA and their composites formed thereof are as under.

S.No:	Type of FA	Type of EPC
1	RAFA	R- EPC
2	CLFA	CL- EPC
3	UCFA	UC- EPC
4	TAFA	T- EPC
5	MAFA	M-EPC

6.2.1. Epoxy Matrix/Composite Formulation [EPM/EPC]

For ensuring the complete extent of polymerization, Epoxy matrix was prepared by using epoxy resin DGEBA (LY561) and Amine based hardener TETA, (HY 951) in 1:1 w/w ratio, the mixture of resin and hardener were homogenized uniformly, later casted in mold fabricated as per the ASTM D638 Type IV standard described in detail in Chapter 2. Samples designed are with dimensions as area 96.60mm², width 14mm, thickness 7mm, and gauge length 50 mm. for designing FA reinforced EPC, resin is first mixed with FA and then hardener is added following the procedure described earlier.

Filler used in designing the EPC were RAFA, CAFA (calcined and uncalcined) MAFA and TAFA. The mechanical, thermal and chemical activation techniques and procedures for preparations of fillers are given in Chapter 2. Samples of EPC with surface functionalized FA and RAFA were with filler loading at four different weigh % i.e. 20.22%, 28.86%, 33.64% and 37.83%. The samples selected for comparative study were with constant weight percent of 33.64% and with constant weight percent of resin and hardener as 33.17% each. Curing was done at room temperature.

6.3. Results and Discussion

6.3.1 Spectroscopic Characterization of EPM and EPC

IR spectra of EPM and EPC are presented in **Figure 6.1(A and B)**. EPM is characterized by the disappearance of the sharp peak around 3200-3600 cm^{-1} of the amine group and the appearance of the broad OH peak around 3200-3600 cm^{-1} signifies the formation of the crosslinking between the epoxy resin and the hardener. The comparison of IR spectra of EPM and EPC (Figure 6.1) shows the overlapping spectral zone of EPM and EPC which essentially signifies the chemical non bondage of Si of FA with N of TETA as the peak corresponding to Si-N is missing (850cm^{-1} to 900 cm^{-1}). The peaks at 915 cm^{-1} and 831 cm^{-1} attributes to the C-O stretching frequency and C-O-C group of oxirane respectively. As both the peaks are present in the EPM also and reflects the unreacted molecules of epoxy resin. Peaks are given in the **Table 6.1**.

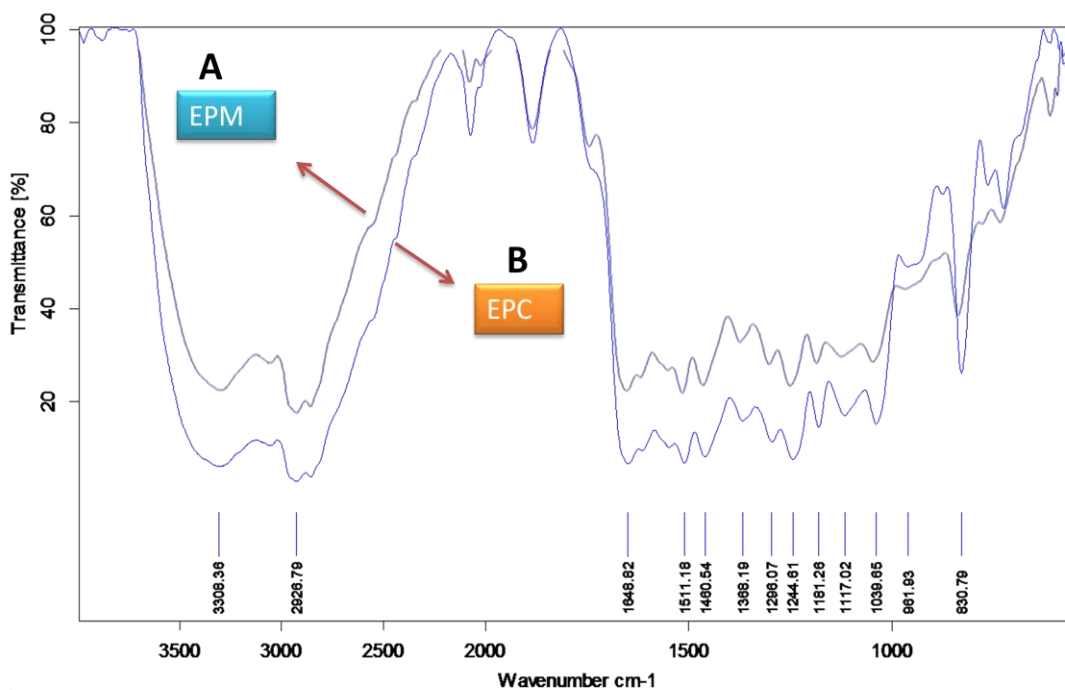


Figure 6.1(A and B) IR spectra of EPC and EPM

Table.6.1. IR frequencies of EPM and EPC

S.No:	IR frequencies in EPC (cm ⁻¹)	IR frequencies in EPM(cm ⁻¹)	Groups corresponding to frequencies
1	3297	3308	N-H
2	3063	3059	O-H
3	2925	2926	-CH ₂ - & -CH ₃ - Asymm.
4	2857	2859	-CH ₂ - & -CH ₃ - Symm.
5	2072	2069	Overtones of C-H of benzene ring
6	2016	2014	
7	1810	1811	
8	1741	1740	
9	1648	1648	C=C benzene Ring stretching
10	1511	1511	
11	1460	1460	-CH ₂ - bending
12	1368	1368	-CH ₃ -bending
13	1297	1296	
14	1245	1244	-C-C-O-C st.
15	1180	1181	
16	1117	1117	C-N st.
17	1041	1039	-C-O-C-
18	915	915	C-O st. OF Oxirane.
19	831	830	c-o-c st of oxirane
20	726	724	 O.O.P Out of plane bending
21	604	603	
22	572	570	C-N & N-H Bending.

6.3.2 SEM Analysis of EPM and EPC

Analysis of SEM images of EPM **Figure 6.2** and EPC **Figure 6.3** at 100Kx and 150Kx reveals the uniform distribution of FA in EPM.

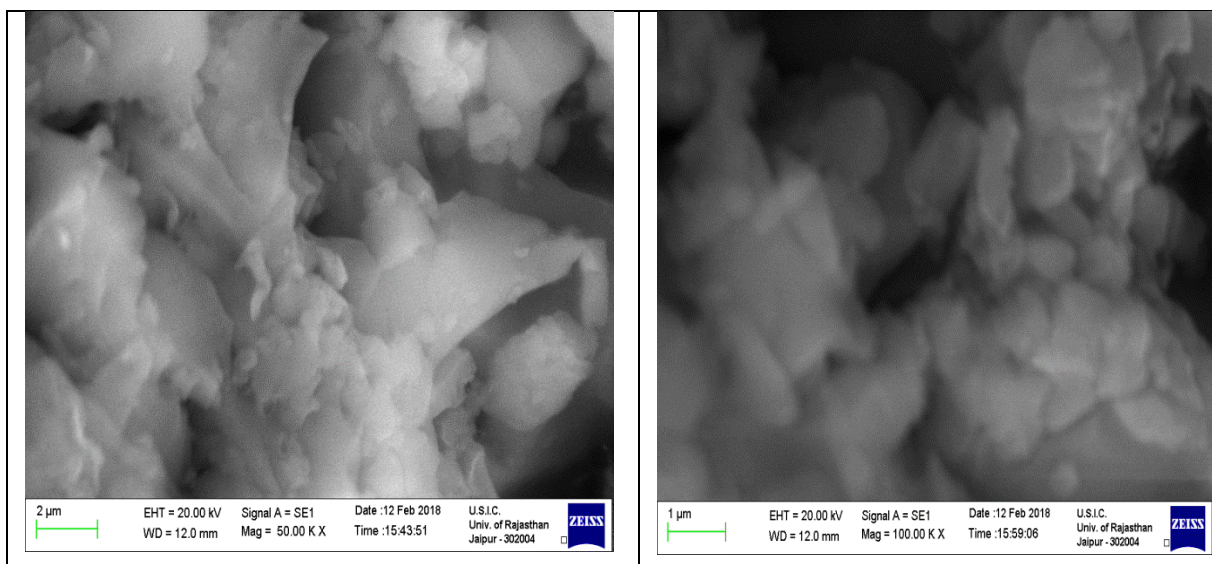


Figure.6.2 SEM image of EPM

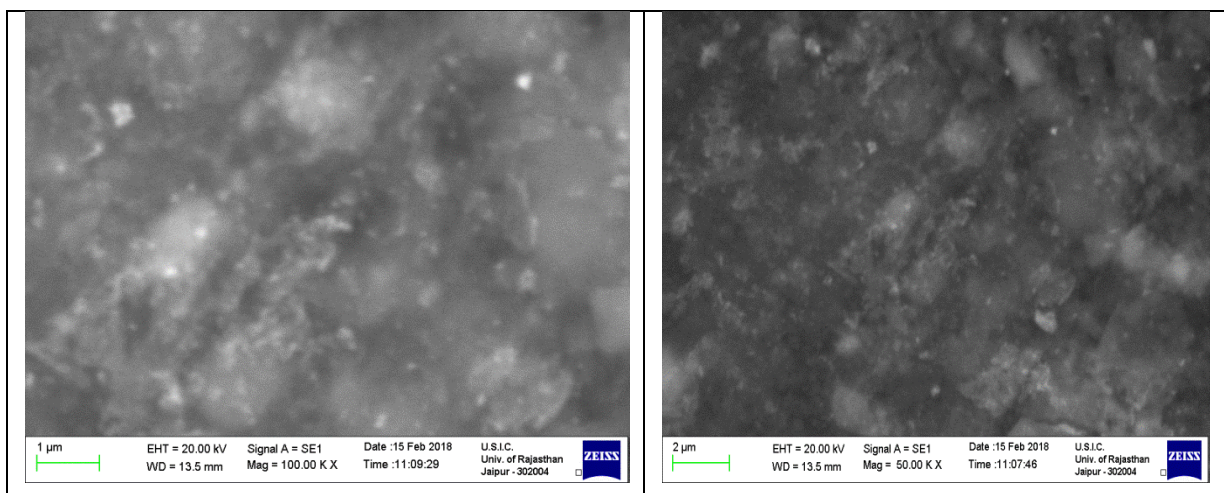
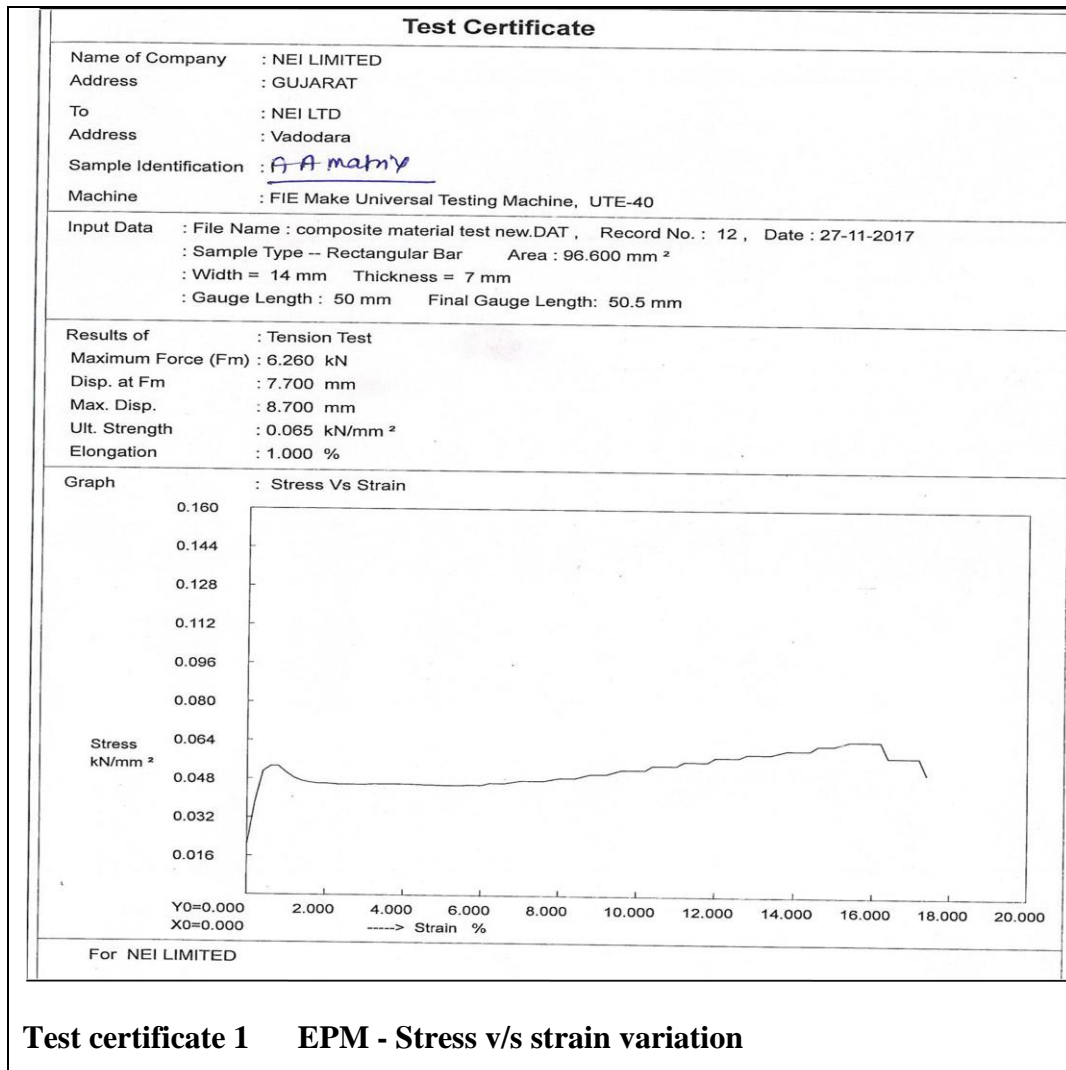


Figure.6.3 SEM image of EPC Showing uniform distribution of FA in EPM

6.3.3 Mechanical Properties of EPM and EPC

Mechanical properties of EPM and different types of EPC samples were analyzed by UTM. The evaluated properties are given in the **Table 6.2** and their graphical representation of stress and strain is given in the **Test certificates 1 to 6**.



Test Certificate	
Name of Company	: NEI LIMITED
Address	: GUJARAT
To	: NEI LTD
Address	: Vadodara
Sample Identification	: F
Machine	: FIE Make Universal Testing Machine, UTE-40
Input Data	: File Name : composite material test new.DAT , Record No. : 16 , Date : 27-11-2017 : Sample Type -- Rectangular Bar Area : 98.000 mm ² : Width = 14 mm Thickness = 7 mm : Gauge Length : 50 mm Final Gauge Length: 50.2 mm
Results of	: Tension Test
Maximum Force (Fm)	: 5.720 kN
Disp. at Fm	: 3.400 mm
Max. Disp.	: 4.800 mm
Ult. Strength	: 0.058 kN/mm ²
Elongation	: 0.400 %
Graph	: Stress Vs Strain
<p>Stress kN/mm²</p> <p>Y0=0.000 X0=0.000</p> <p>-----> Strain %</p>	
For NEI LIMITED	

Test certificate 2 R-EPC - Stress v/s strain variation

Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : VADODARA

Sample Identification : Composite (B) 602

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT, Record No. : 2, Date : 23-12-2017

: Sample Type -- Rectangular Bar Area : 98.000 mm²

: Width = 15 mm Thickness = 7.5 mm

: Gauge Length : 50 mm Final Gauge Length: 50.2 mm

Results of : Tension Test

Maximum Force (F_m) : 6.320 kN

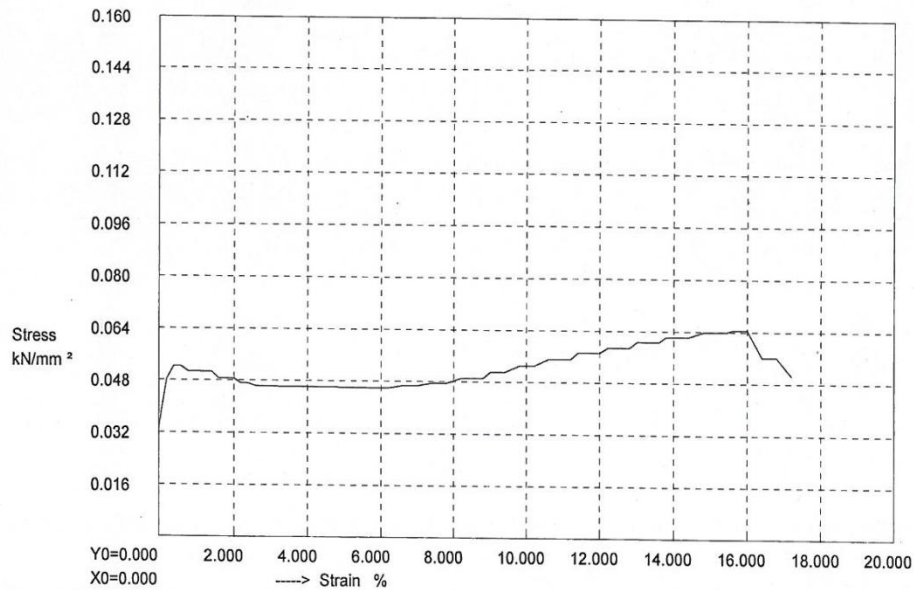
Disp. at F_m : 7.800 mm

Max. Disp. : 8.600 mm

Ult. Strength : 0.064 kN/mm²

Elongation : 0.400 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate 3 CL-EPC - Stress v/s strain variation

Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : Vadodara

Sample Identification : **N**

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : composite material test new.DAT , Record No. : 20 , Date : 21-12-2017

: Sample Type -- Rectangular Bar Area : 98.000 mm²

: Width = 14 mm Thickness = 7 mm

: Gauge Length : 50 mm Final Gauge Length: 50.2 mm

Results of : Tension Test

Maximum Force (F_m) : 5.900 kN

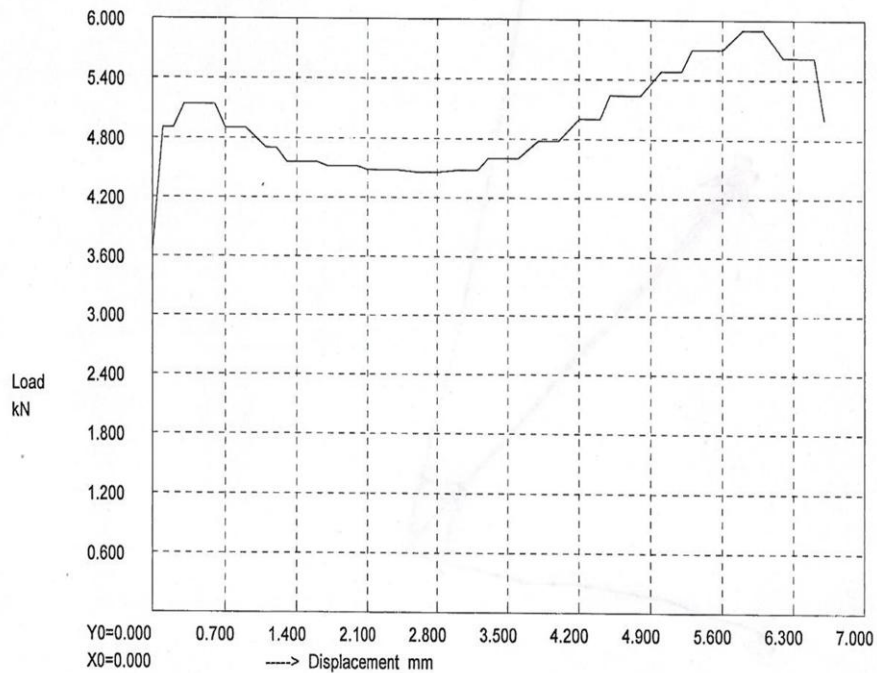
Disp. at F_m : 5.800 mm

Max. Disp. : 6.600 mm

Ult. Strength : 0.060 kN/mm²

Elongation : 0.400 %

Graph : Load Vs Displacement



For NEI LIMITED

Test certificate 4 UC-EPC - Stress v/s strain variation


Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : Vadodara

Sample Identification : 

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : composite material test new.DAT , Record No. : 18 , Date : 27-11-2017

: Sample Type -- Rectangular Bar Area : 98.000 mm²

: Width = 14 mm Thickness = 7 mm

: Gauge Length : 50 mm Final Gauge Length: 50.2 mm

Results of : Tension Test

Maximum Force (Fm) : 5.560 kN

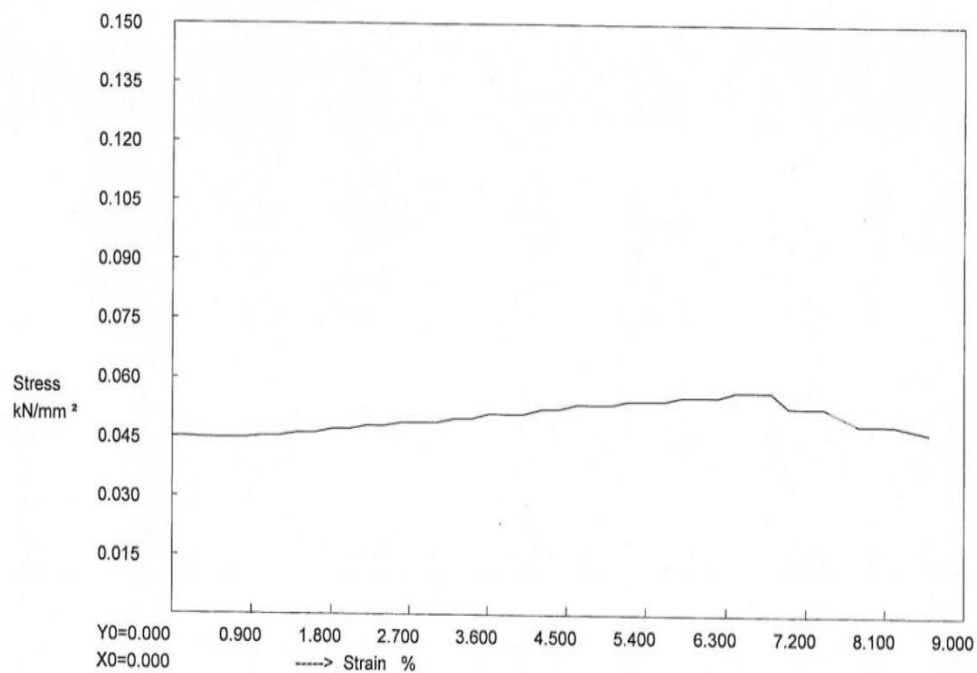
Disp. at Fm : 3.200 mm

Max. Disp. : 4.300 mm

Ult. Strength : 0.057 kN/mm²

Elongation : 0.400 %

Graph : Stress Vs Strain



For NEI LIMITED

Test certificate 5 T-EPC-Stress v/s strain variation.

Test Certificate

Name of Company : NEI LIMITED

Address : GUJARAT

To : NEI LTD

Address : VADODARA

Sample Identification : Composite (I) FAME 5

Machine : FIE Make Universal Testing Machine, UTE-40

Input Data : File Name : COMPOSITE MATERIAL TEST.DAT, Record No. : 8, Date : 23-12-2017

: Sample Type -- Rectangular Bar Area : 90.000 mm²

: Width = 15 mm Thickness = 7.5 mm

: Gauge Length : 50 mm Final Gauge Length: 50.2 mm

Results of : Tension Test

Maximum Force (Fm) : 6.020 kN

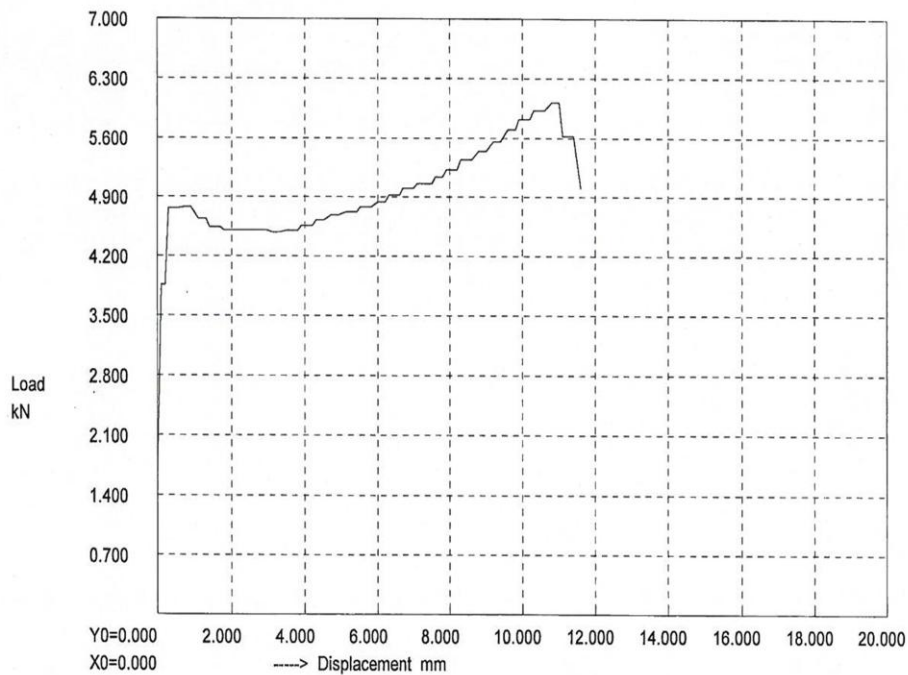
Disp. at Fm : 10.800 mm

Max. Disp. : 11.600 mm

Ult. Strength : 0.067 kN/mm²

Elongation : 0.400 %

Graph : Load Vs Displacement



For NEI LIMITED

Test certificate 6 M-EPC - Stress v/s strain variation.

Table 6.2 Mechanical properties of EPM and different types of EPCs

	Mechanical Properties	EPM	R-EPC	CL-EPC	UC-EPC	T-EPC	M-EPC
1	Tensile strength	65 MPa	58 MPa	64 MPa	60 MPa	57 MPa	67 MPa
2	Young modulus	6.5 GPa	14.5 GPa	16 GPa	15 GPa	14.25GPa	16.7GPa
3	% Elongation	1	0.4	0.4	0.4	0.4	0.4
4	Break point	65	58	64	64	57	67
5	Force(max)	6.260 KN	5.720 KN	6.320 KN	5.90 KN	5.560 KN	6.020 KN
6	Disp.at F(max)	7.70 mm	3.40 mm	7.80 mm	5.800 mm	3.20mm	10.8 mm
7	Maximum Displacement	8.700 mm	4.800 mm	8.600 mm	6.600 mm	4.300 mm	11.600 mm
8	Ultimate strength	0.065 KN/mm ²	0.058 KN/mm ²	0.064 KN/mm ²	0.06 KN/mm ²	0.057 KN/mm ²	0.067 KN/mm ²

6.3.4. Results of Reinforcement of RAFA and Surface Functionalized FA on TS and YM of EPM

Results of variation in the mechanical properties of the EPCs on the reinforcement of RAFA and other fly ash samples are given in **Figure. 6.4**. Among surface functionalized EPC, M-EPC(TS 67MPa & YM 16.7 GPa) has the best mechanical properties in term of TS and YM as compared to EPM (TS 65MPa & YM 6.5 GPa) while T-EPC loses mechanical properties in terms of TS; 57 MPa but gains in terms of YM 14.25 GPa.

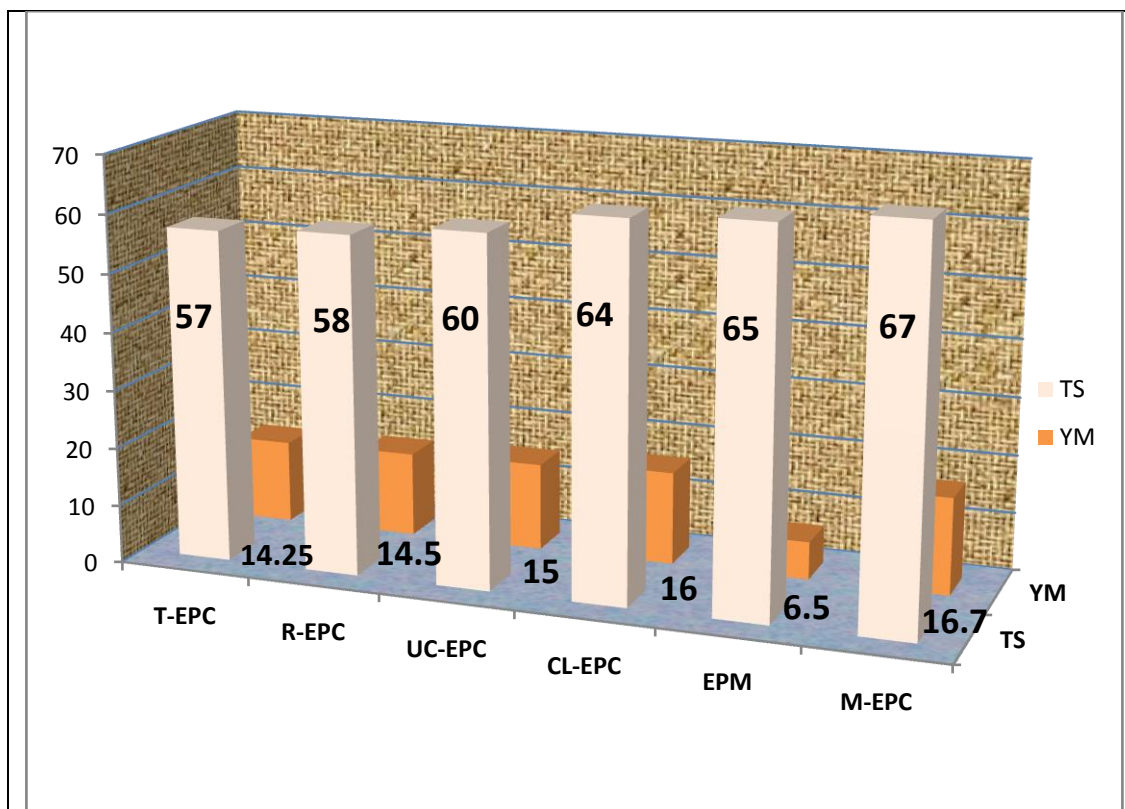


Figure6.4. Graphical representation of the mechanical properties of EPM and EPCs

6.3.5 Effect of Reinforcement of RAFA on TS of EPM

Under uni-axial loading, tensile strength of composite is the maximum magnitude of stress which the composite material can sustain [29, 30]. The strength of composite having filler of size micro and nano size depends on the efficiency of transfer of stress between filler and matrix. The composite strength depends mainly on certain factors viz filler loading, filler size, interfacial strength between matrix and filler, greater is the effectiveness of stress transfer mechanism between filler and matrix more will be the strength of the composite material [31, 32] Filler RAFA was used in designing EPC .The TS of EPC depends on interfacial strength as all other factors were kept constant in study. TS mainly depend on interfacial adhesion between filler and matrix. For ineffectively bondage /adhesion of micro sized filler FA to matrix it

shows continuity in debonding with the matrix , as is revealed by the decrease in TS of EPM from 65MPa to 58 Mpa of EPC.

By assumption that filler poor bondage to the matrix makes stress transfer between matrix and filler inefficient and that the stress transfer solely depends on effective sectional area of matrix the model expressing tensile strength is, as given by the **equation 6.1**.

$$\sigma_c = \sigma_m (1 - V_p) \dots\dots\dots 6.1$$

Where

σ_c = tensile strength of fly ash reinforced epoxy composites

σ_m = tensile strength of epoxy matrix.

V_p = particle volume fraction.

The equation is mainly for the less effectively bonded particulate fillers. There is increment in the value of particle volume fraction with increase in loading making tensile strength of the composite to show decreasing trend with loading [33].

6.3.6 Effect of Reinforcement RAFA on YM of EPM

Modulus of filler reinforced EPC depends on elastic properties of filler, matrix, particle loading and the aspect ratio of filler. Aspect ratio of a filler is the ratio of width to height of particulate, which in case of spherical shaped filler FA is unity, so YM of EPC will depends on elastic properties of filler and matrix and wt% of particle loading .Inorganic filler FA used has higher modulus as compared to EPM so the adding FA to EPM shall increase YM of EPC.As per the Einstein model for predicting modulus of rigid particulate reinforced composites following **equation 6.2** is followed.

$$E_c = E_p (1 + 2.5) V_p \dots\dots\dots 6.2$$

Where

E_c = YM of EPC

E_p = YM of EPM

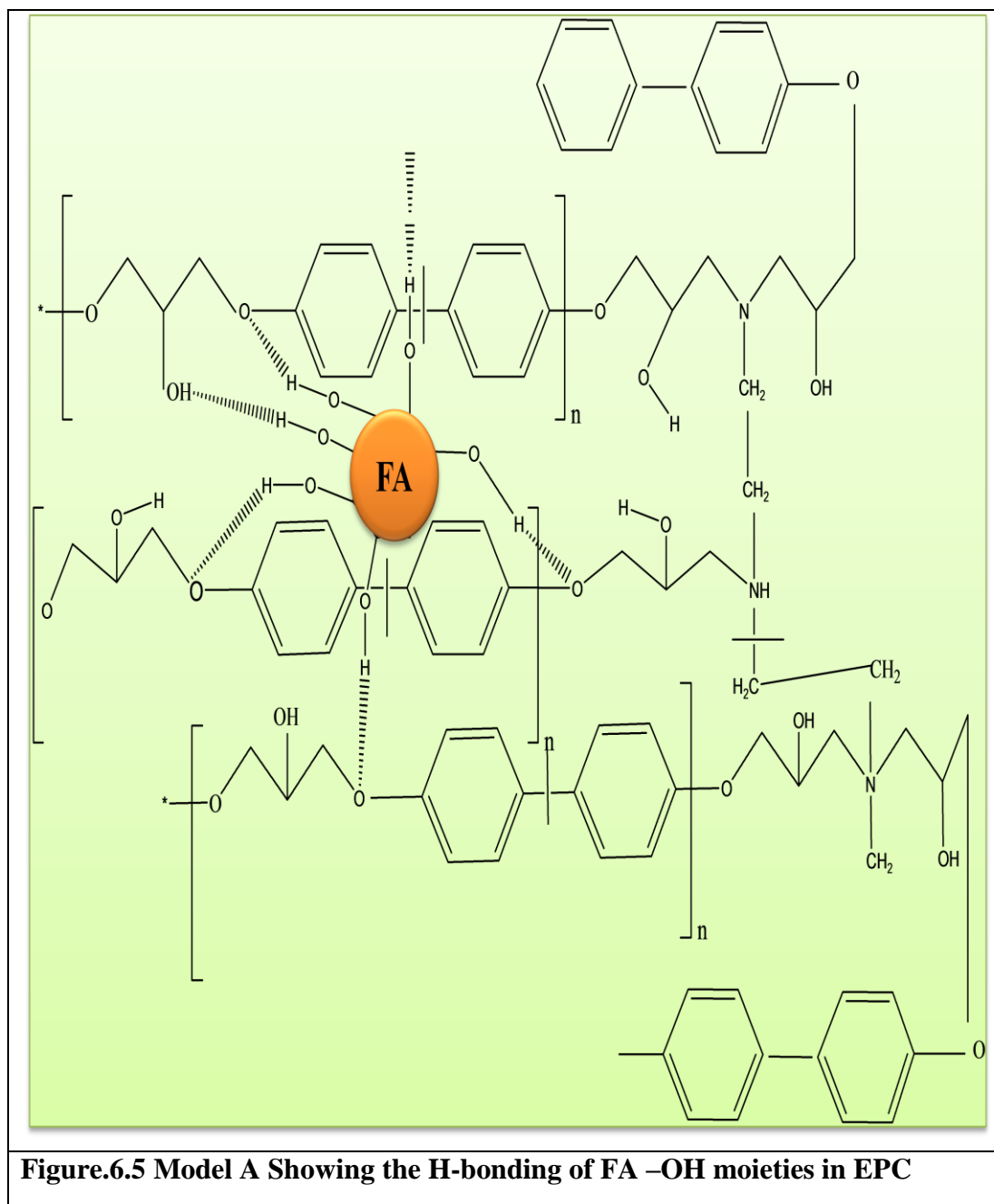
V_p = Particle volume fraction

The model is valid for rigid spheres wherein uniform dispersion is there for filler in matrix. The increase in modulus as per the Einstein model foretells increase in modulus of EPM with loading of filler FA i.e. higher value of V_p with filler loading.

6.3.7 Comparison of TS and YM of UC-EPC and CL-EPC with R-EPC

As tensile strength of composites depends on the transfer mechanism of stress from matrix to filler, more the adherence of filler with matrix better and efficient shall be the stress transfer mechanism. As the filler CAL-FA and UCAL-FA both are chemically activated for loading OH functionalities, results in better interaction of filler with matrix by H-bonding (**Figure 6.5 model A**) which augments the TS magnitude for both composites (CL-EPC; TS 64MPa & UC-EPC; TS 60 MPa) as compared to R-EPC (TS 58 MPa). As calcined FA has solely chemically bonded OH moieties, while loosely adhered surfacial OH moieties are removed during calcinations, and the aggregation of FA due to intense H-bonding is considerably reduced, imparting better stress transfer mechanism from matrix to filler, so TS of CL-EPC is more than UC-EPC by 4 MPa units. In homogenous EPM w.r.t microphasic internal structure addition of filler RFA increases modulus but its magnitude is more pronounced in case of CL-EPC and UC-EPC as compared to R-

EPC, because inter particle H-bonding enhances the reinforcement and increases reluctance of matrix for deformation against the stress.



6.3.8 Comparison of TS and YM of M-EPC with R-EPC

Study of mechanical properties reveals that particle size considerably affects mechanical properties, as per the proposed model **equation 6.3**.

$$\sigma_c = \sigma_m + K_p (V_p) d_p^{-1/2} \dots\dots\dots 6.3$$

Where

σ_c = TS of EPC

σ_m = TS of EPM

V_p = Particle volume fraction

d_p = mean particle size

As the particle size is decreased there is a significant increase in TS of composites i.e from 58 MPa in R-EPC it increases to 67 MPa in M-EPC, with the same number of OH functionalities as on RAFA. In the MAFA mean particle size is less due to milling, it adheres more effectively with the matrix through H-bonding and makes the stress transfer mechanism excellent as compared to all other EPCs. As the mean particle size decreases in M-EPC it creates pronounced possibility of inter particle /inter filler interaction by H-bonding thus enhances the reluctance of matrix for deformation i.e. high modulus as compared to all other EPCs.

6.3.9 Comparison of TS and YM of T-EPC with R-EPC

T-EPC shows low TS (57 MPa) and YM (14.25 GPa) as compared to R-EPC having TS (58 MPa) and YM (14.50 GPa). This is attributed to lesser extent of interaction of TAFA-OH functionalities with matrix through H-bonding, making stress transfer mechanism less efficient compared to R-EPC revealed by less value of TS in T-EPC by 1 GPa unit. Owing to slightly lesser inter filler interaction through H-bonding in T-EPC, it results in decrease in YM to a slightly lesser extent.

6.4 Comparative Study of Thermal Properties of EPM and EPCs

Thermal stability of polymers/composites is evaluated by their glass transition temperature T_g whose determination is an important parameter for determining the end use of polymer. T_g is the temperature before which polymer's physical properties are like of plastic material while after that polymer material transforms into glassy state [34, 35]. Factors affecting the T_g values are mainly corresponding to the polymer chain stiffness/stiffening causing groups whose decrease in flexibility decreases the T_g and vice versa. Stronger inter molecular forces also increases T_g values. At T_g there is conversion of hard / brittle glassy state to viscous rubbery state so T_g lies before T_m (melting point). Augmentation of crystallinity in material is revealed by higher T_g values while amorphous state is revealed by low T_g values. T_g were evaluated for EPM, R-EPC, CL-EPC, UC-EPC, T-EPC and M-EPC by DSC technique. The graphs are shown in **Figures 6.6 to 6.11**. The comparative values of T_g of EPM and EPCs are given in **Figure.6.12**.

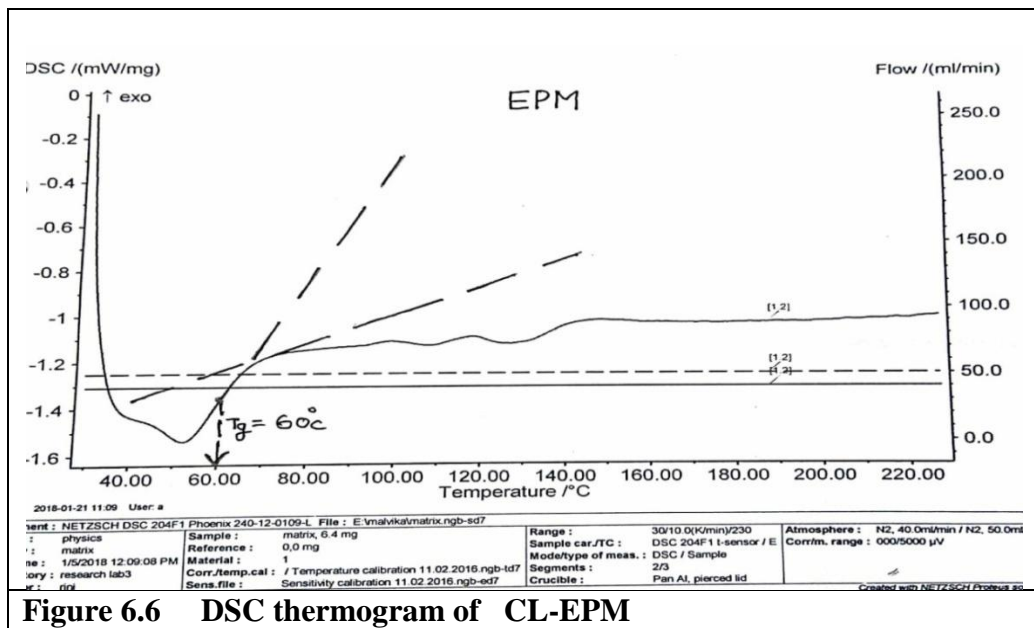


Figure 6.6 DSC thermogram of CL-EPM

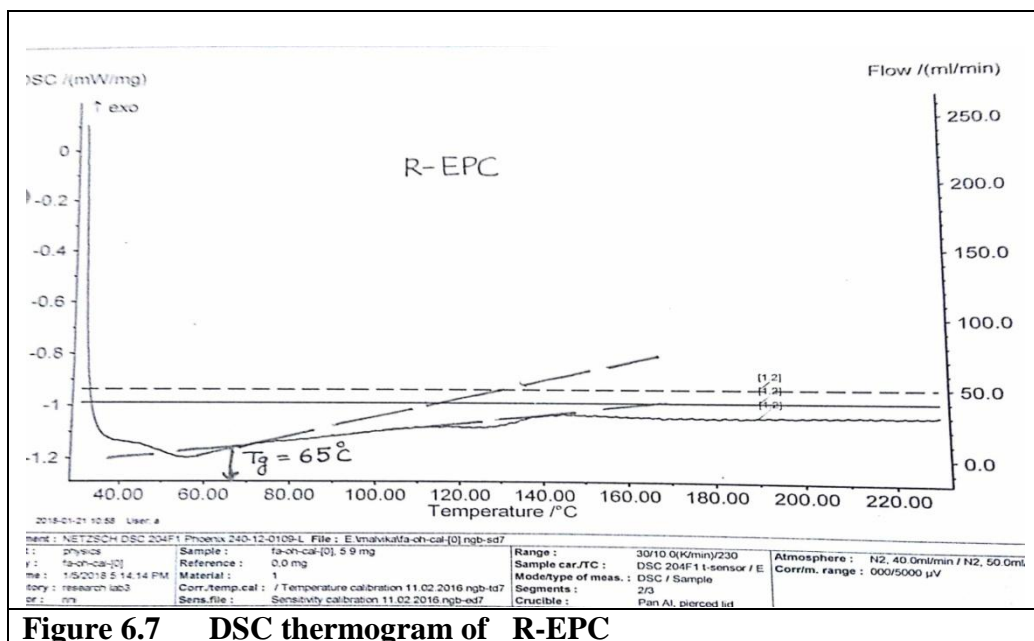


Figure 6.7 DSC thermogram of R-EPC

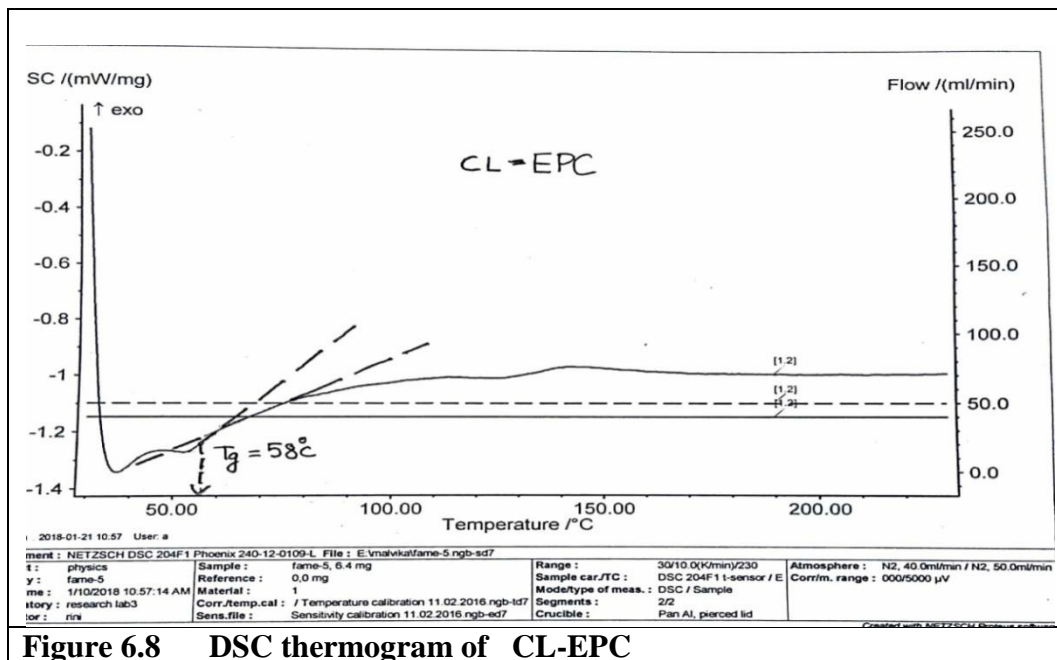


Figure 6.8 DSC thermogram of CL-EPC

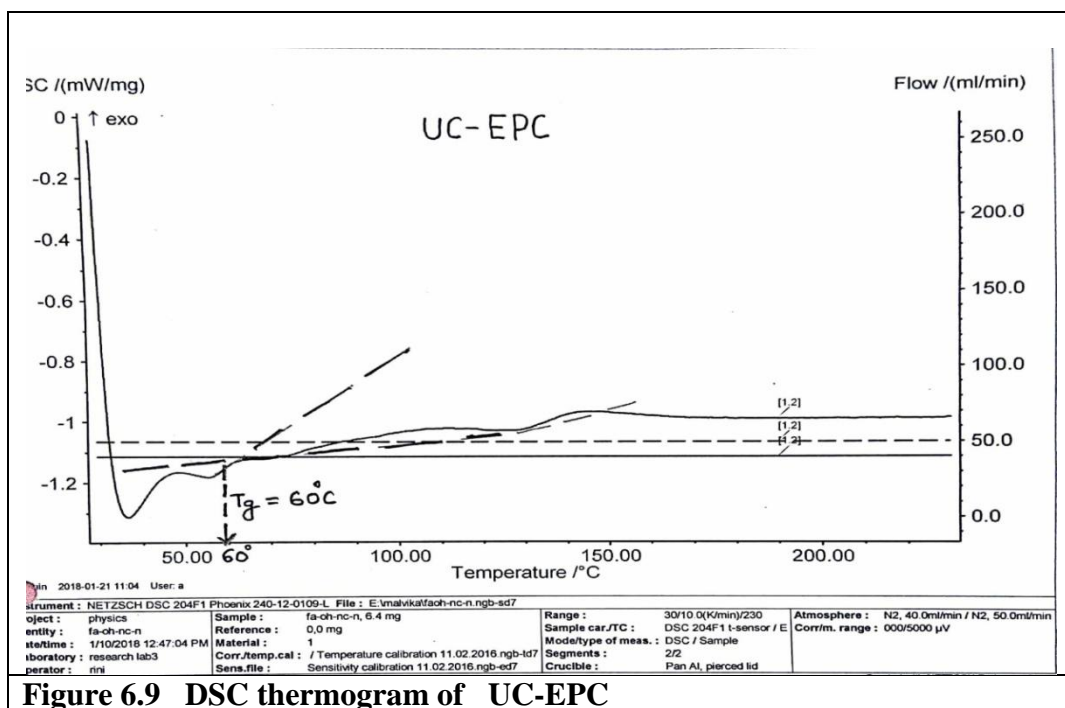


Figure 6.9 DSC thermogram of UC-EPC

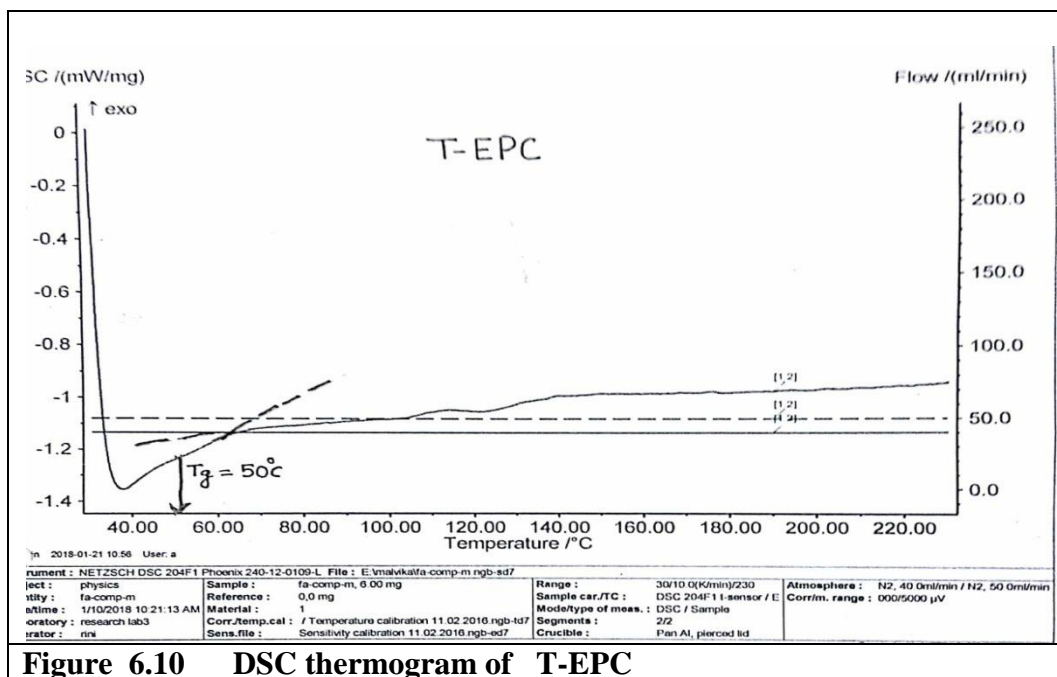


Figure 6.10 DSC thermogram of T-EPC

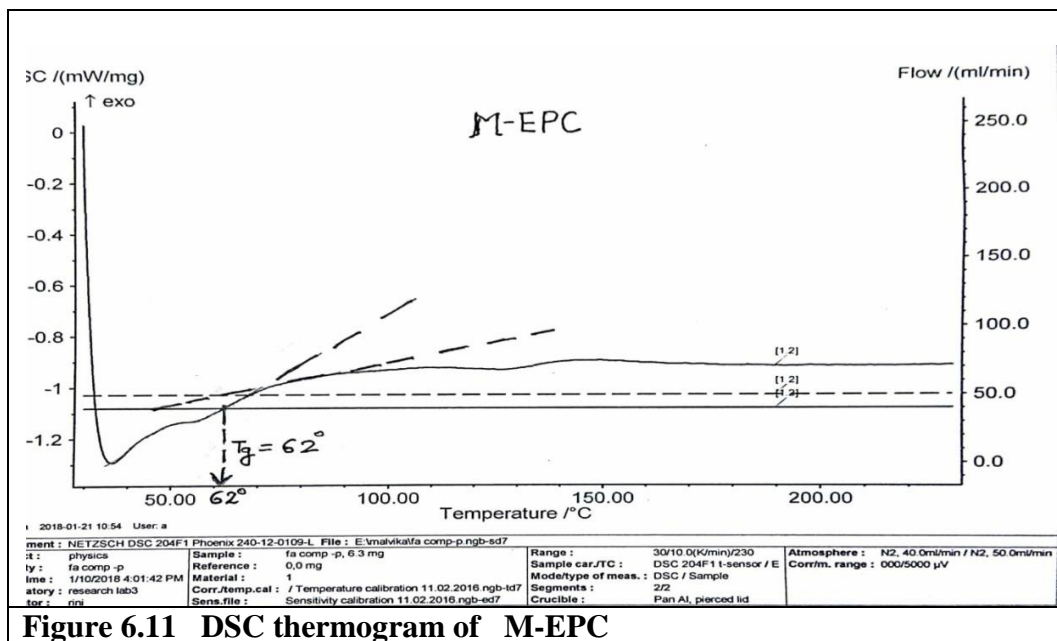


Figure 6.11 DSC thermogram of M-EPC

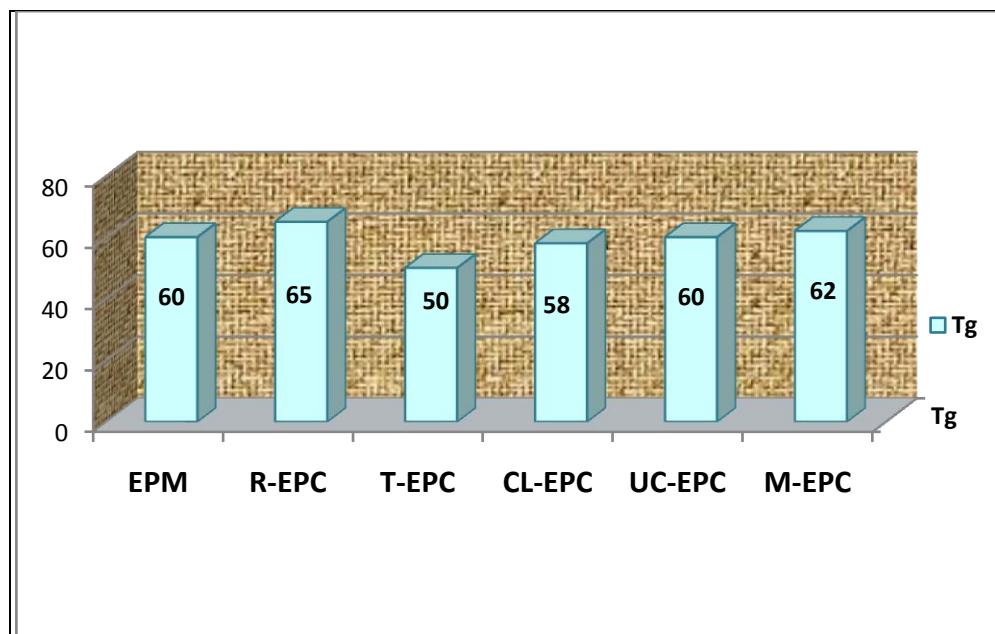


Figure.6.12. Comparison of Tg of EPM and EPCs

The comparative study of Tg values of EPM and EPCs as shown in the Figure 6.12. Clearly reveals that:

- (a) For R-EPC , Tg is more as compared to EPM as addition of filler RFA in designing FA reinforced epoxy composites increases the crystallinity as shown in XRD diffractogram detailed description in chapter 2(2.6.3.1. *C XRD Analysis of RAFA*) as revealed by high Tg value (65°C) compared to EPM (60°C).
- (b) OH loaded FA i.e CAFA possess more amorphous domains detailed description in chapter 2(2.6.3.4.C *XRD analysis of CAFA*) as crystallinity of FA decreases and amorphous domains becomes more significant on chemical activation Tg value (CL-EPC Tg; 58°C and UC-EPC Tg; 60°C) decreases as compared to R-EPC(Tg; 65°C).
- (c) For T-EPC –Tg value(50°C) is low as compared to R-EPC(65°C) owing to the removal of the carbonaceous and char material , detailed description in chapter 2(2.6.3.3. A *FT-IR analysis of TAFA*) which provides free space for movement of polymeric chains along with that lesser OH functionalities reduces inter particle interaction attributed by lower Tg values.

- (d) For M-EPC-Tg value (62°C) is more compared to UC-EPC and CL-EPC as mean particle size decrease, detailed description is in Chapter 2(2.6.3.2. *C XRD analysis of MAFA*) but crystallinity still persists prominently than CAFA.

6.5 Comparison of the Mechanical Properties of EPC and PUC Reinforced with RAFA and Surface Functionalized FA

The variation in the mechanical properties of the composites with variation in the properties of the filler has been the part of the research work, but how does different matrix i.e. PUM and EPC behaves differently towards the same modified filler with similar loading % of filler is also the part of study.

Matrices having heterogeneous internal bondages of the functional groups (HS and SS domains of PUM) create segregation at microphasic level which makes them to behave differently as compared to those matrices having homogenous internal bondages of functional groups with no internal segregation at microphasic level, when reacted with same surface modified filler in designing of composites, this differential behaviour of matrices at microphasic level makes them to behave differentially with same filler and with similar % loading ,when their composites are designed.

The mechanical properties of filler reinforced epoxy composites depends on the transfer of stress between filler particles and the matrix. This stress transfer mechanism and its effectiveness depend on the extent of bonding of filler particulate with the matrix. The inorganic particulate fillers improvise the hardness and the stiffness of the composites.

As the concentration of OH moieties increases on FA, tendency of HS and SS domains proximity increases both in PUC-A and PUC-B. As the HS and SS domain association increases, microphasic segregation of domains decreases which declines self cohesive impact of HS and reduces the mechanical properties of the FAreinforced PUC.It is clear from the study of mechanical properties of EPC and

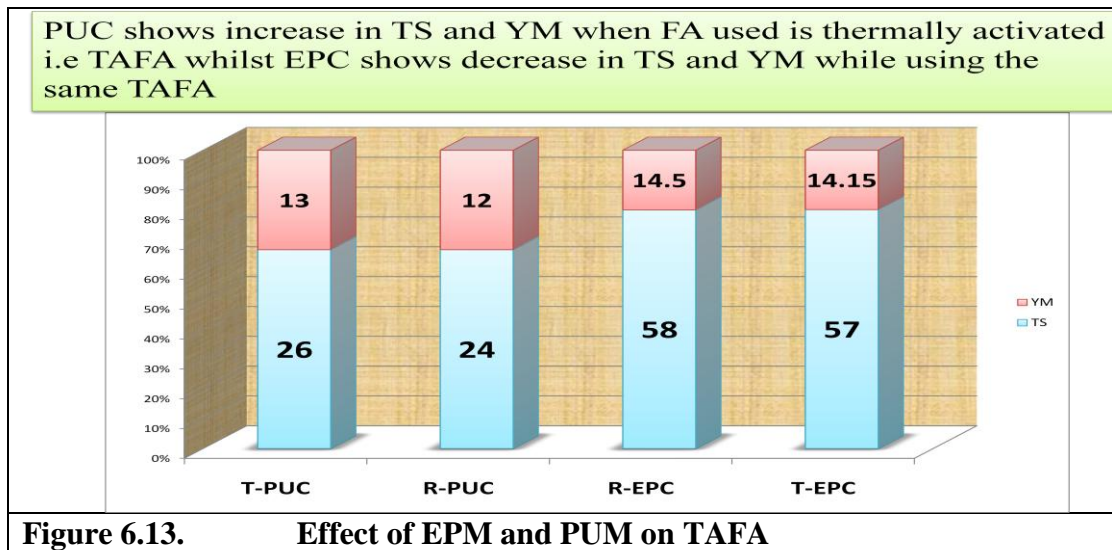
PUC that the increment in OH functionality of filler FA on one hand increases the adherence of filler with matrix thereby increasing the stress transfer mechanism effective in epoxy based composites and improvises their mechanical properties, whilst the same augmentation of OH functionality on filler FA decreases the microphasic segregation and reducing the intrinsic reinforcement thereby decreasing the mechanical properties of the polyurethane based composites.

6.6 Results for the EPC and PUC

1. PUC shows increase in TS and YM when FA used is thermally activated i.e TAFA [Chapter 5(5.3.3)] while EPC shows decrease in TS and YM while using the same TAFA shown in **Figure 6.13**.

T-PUC	TS	26 MPa
T-PUC	YM	13 GPa
R-PUC	TS	24 MPa
R-PUC	YM	12 GPa

T-EPC	TS	57 MPa
T- EPC	YM	14.15 GPa
R- EPC	TS	58 MPa
R- EPC	YM	14.5 GPa



2. PUC shows decrease in TS and YM when FA used is chemically activated UC-CAFA [Chapter 5] whilst EPC using same UC-CAFA shows increase in TS and YM [Chapter 6] shown in **Figure6.14**.

UC-PUC	TS	11 MPa
UC-PUC	YM	5.5 GPa
R-PUC	TS	24 MPa
R-PUC	YM	12 GPa

UC -EPC	TS	60 MPa
UC - EPC	YM	15GPa
R - EPC	TS	58 MPa
R - EPC	YM	5GPa

•PUC shows decrease in TS & YM when FA used is chemically activated UC-CAFA whilst EPC using same UC-CAFA shows increase in TS and YM

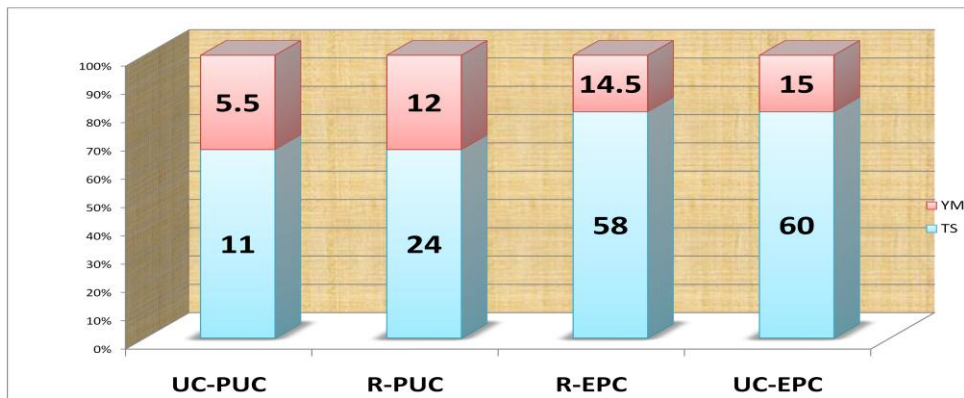


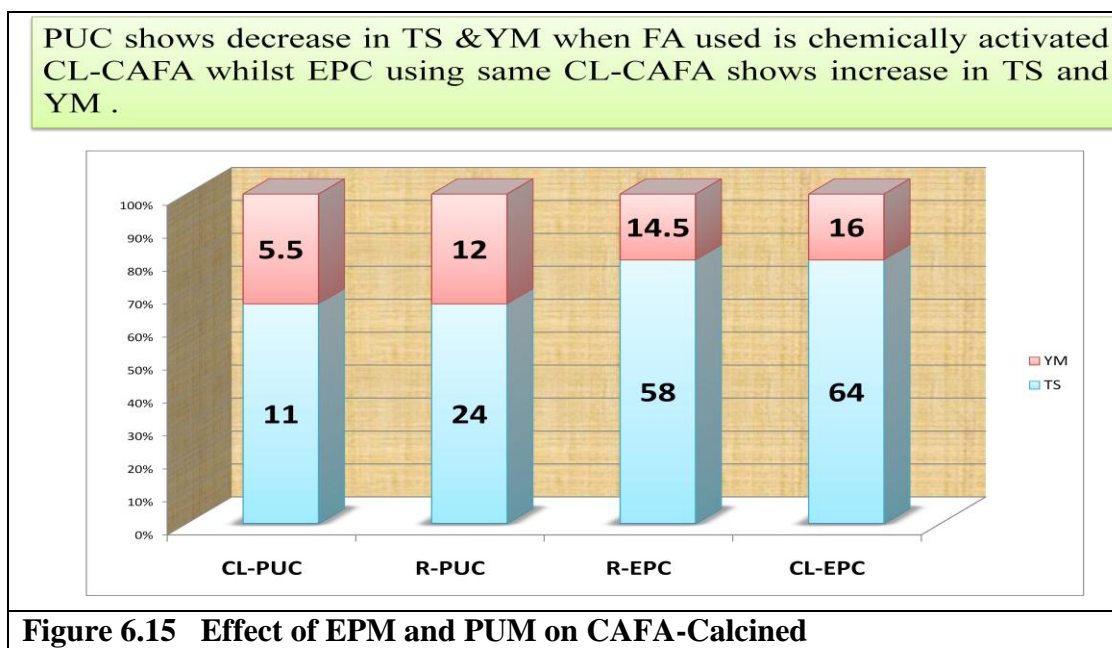
Figure 6.14 Effect of EPM and PUM on CAFA-Uncalcined

3. PUC shows decrease in TS and YM when FA used is chemically activated CL-CAFA [Chapter 5] while EPC using same CL-CAFA shows increase in TS and YM [Chapter 6] A comparison is shown in **Figure 6.15**.

CL-PUC	TS	22 MPa
CL-PUC	YM	11 GPa
R-PUC	TS	24 MPa
R-PUC	YM	12 GPa

CL -EPC	TS	64 MPa
CL - EPC	YM	16GPa
R - EPC	TS	58 MPa
R - EPC	YM	14.5GPa

Augmentation of OH groups (surface adhered or chemically bonded) on filler decreases mechanical properties of PUC[36] while in EPC it causes increase in mechanical properties Matrices showing heterogeneity in internal bondages of the functional groups (HS and SS domains of PUM) i.e having segregation at microphasic level behaves differently as compared to those matrices having homogeneity in internal bondages of functional groups with no internal segregation at microphasic level w.r.t surface modified filler in designing of composites[37-39].



PUM-A and PUM-B shows higher YM as compared to EPM because of the exhaustive cross linkages, making the matrix to show more reluctance for deformation as compared to the EPM. EPM acts **synergistically** for surface functionalized FA w.r.t mechanical properties whilst PUM acts **antagonistically** for surface functionalized FA in terms of mechanical properties [40-44].

6.7 Conclusion

Mechanical properties of particulate-polymer composites depend on various parameters viz. interface adhesion, particle loading, particle size. The variations of

these properties can be explained by various phenomenological and semi-empirical models but none single equation is there which is equivocally applicable to all particulate composites under all conditions. The proposed models can predict the variation in a particular property against any specific parameter. Among FA-r-EPC best thermal stability (higher Tg value) exhibited by R-EPC but TS decreases, however M-EPC gains 2.5 times modulus magnitude with 2GPa unit increment in tensile strength with higher Tg as compared to EPM , approves to be the best composite preparation of the epoxy system in terms of mechanical properties and thermal stability.

T-EPC shows least thermal stability with Tg-50°C but has TS and YM more than R-EPC. CL-EPC and UC-EPC has better mechanical properties (TS & YM) compared to R-EPC. Surface modification of filler (mechanically/ thermally/ chemically) pertains variation on crystalline or amorphous domains of raw filler, than that can be evaluated in terms of Tg values. Filler to be used in making composites with higher thermal stability should be modified in a way wherein augmentation of crystallinity persists. FA surface functionalized with OH moieties in CAFA reinforced EPC shows better mechanical properties compared to TAFA reinforced EPC. Observations are summarized in **Table6.3**.

Table 6.3 Selection of FA-r- EPCs for different uses

TS(low)	YM(high)	Compared to EPM	R-EPC UC-EPC CL-EPC T-EPC
TS(high)	YM(high)	Compared to EPM	M-EPC
TS(high)	YM(high)	Compared to R-EPC	UC-EPC CL-EPC M-EPC
TS(low)	YM(high)	Compared to R-EPC	T-EPC
Tg (high)		Compared to EPM	R-EPC M-EPC
Tg (low)		Compared to EPM	CL-EPC T-EPC
Tg (equal to)		EPM	UC-EPC
Tg (high)		Compared to R-EPC	NONE

The filler surface properties and the matrix microphasic structure both need to be taken into consideration, before laying out the flow chart of designing filler reinforced composite material.

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Articles developed by FA-r-EPC synthesized during present work.



FA-r-EPC – Marker Board



FA-r-EPC- Mosaic Tiles

FA-r-EPC composite pipe brackets



FA-r-EPC-bangle

Articles developed by FA-r-PUC synthesized during present work.



Leak proof FA-r-PUC



PUM showing cut resistancy



PUM cork material






FA-r-PUC Pin holders

List of Publications

1. Patents:

- (i) Patent entitled “ A method for synthesizing polythene coated solid hybrid filler has been published”

  	
Application Details	
APPLICATION NUMBER	201811010844
APPLICATION TYPE	ORDINARY APPLICATION
DATE OF FILING	23/03/2018
APPLICANT NAME	1 . ASHU RANI 2 . ANKIT SHARMA
TITLE OF INVENTION	A METHOD FOR SYNTHESIZING POLYTHENE COATED SOLID HYBRID FILLER
FIELD OF INVENTION	POLYMER TECHNOLOGY
E-MAIL (As Per Record)	ip@legasis.in
ADDITIONAL-EMAIL (As Per Record)	ip@legasis.in
E-MAIL (UPDATED Online)	

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2. Research Publications:

- (i) Ankit Sharma*, S.K. Sharma and Ashu Rani “**Study of Ratio Variation of Binary Components of Cross Linking Agent on Extent of Polymerization and Mechanical Properties of Polyurethane Composites**”, *Asian Journal of Chemistry*; Vol. 31, No. 11 (2019), 2537-2542
- (ii) Sushil Kumar Sharma, Ankit Sharma “**Bio-transformation of prochiral ketones to pharmaceutically used chiral alcohols by Baker’s Yeast**”*Int.J.Inn.Research In Sci.,Engg.& Tech.*2016 5 (12) 20660-20663.

3. Presentation in Conference/Symposium/Workshop/Seminar

- (i) Poster Presentation on “**Component ratio analysis of bonding agent by HPLC and effect of dilution on retention time of BD and TMP**” at National Symposium on “Modern Trends in Chemistry”-MTC-2013

organised by Department of Chemistry, M S University of Baroda, Gujarat at March 21-23, 2013.

- (ii) Oral Presentation on **“Ratio analysis of components of LA for Polyurethane composites”** at National Conference on “Innovations in Composites for General Purpose to High End Applications” organised by University of School of Basic & Applied Sciences, Guru Gobind Singh Indraprastha University, Dwarka, New Delhi at Feb., 17-18, 2015.
- (iii) Poster Presentation on **“Eco-friendly reduction of pro-chiral carbonyl compounds to chiral alcohols by Baker’s Yeast”** at UGC-Sponsored National Conference on “Modern Trends in Chemical Sciences” organised by Department of Chemistry, Mohan Lal Sukhadia University, Udaipur at Jan. 30-31, 2016.
- (iv) Poster Presentation on **“Baker’s yeast mediated synthesis of some bioactive chiral alcohols”** at National Seminar on “Recent Trends in Chemical Research” organised by Department of Chemistry, Jai Narayan Vyas University, Jodhpur. at Feb. 5-7, 2016.
- (v) Poster Presentation on **“Component analysis of CLA of PU matrix by HPLC”** at International Conference on “Frontiers at the Chemistry-Allied Sciences Interface” organised by Department of Chemistry, University of Rajasthan, Jaipur at April 25-26, 2016.
- (vi) Poster Presentation on **“Prakratik strot ki kasoti par hamari jeevan sheli”** at National hindi vigyan conference, organised by vigyan bharti, University of Rajasthan, Jaipur at Dec 16-17, 2016.

4. Books:

- (i) B.Sc. Organic Chemistry-Part I, **Ankit Sharma, Sushil Kumar Sharma**, Pragti Prakashan, Meerut. 2018
- (ii) B.Sc. Organic Chemistry-Part II, **Ankit Sharma, Sushil Kumar Sharma**, Pragti Prakashan, Meerut. (In Press). 2020