CHAPTER 2
EXPERIMENTAL

This chapter deals with materials, testing equipments and experimental methods which are adopted for the present study. For the sake of convenience, this chapter has been divided into two parts namely, Part A and Part B. **Part A** covers the materials used in this research programme such as monomers, catalyst, solvent, fillers and other chemicals along with their chemistry, physical properties and testing equipments used to carry out this research work. Theory and techniques are briefly described in **Part B** for the characterization of dicarboxylic acid based chain extended PUs (CEPUs).

**PART A - Materials and equipments**

This section gives a brief description of the materials such as, polyol, diisocyanates, chain extenders, solvent, catalyst and testing equipment's that have been used to carry out this research work.

2.1 Materials

2.1.1 Polyols (Castor oil)

The essential components to prepare polyurethanes (PUs) are a long chain oligomeric polyol, a diisocyanate and low molecular weight chain extender. The polyol may be a polyether or an oligomer. Efforts have been made during the past few decades to replace these expensive polyols with low cost natural vegetable oils or other derivatives in the production of urethane products. Among the vegetable oils, castor oil (CO) possessing hydroxyl groups appear to be a good polyol for the synthesis of biobased polyurethane elastomers [1–9].

One of the most naturally occurring vegetable oils is castor oil [10–12], which not only has the advantage of possessing relatively high purity but is abundantly available in the forests of India. This oil is extracted from the beans of the plant
Ricinum Communis. This oil is widely used for the preparation of a variety of PUs [13-14]. Castor oil is composed essentially of triglycerides of hydroxy acids, recinoleic acid (89.4%), oleic acid (4.2%) and linoleic acid (3.3%) whose structure is given below:

\[
\begin{align*}
&\text{CH}_2\text{O}\text{CO}\text{(CH}_2\text{)}_{7}\text{CH}==\text{CH}\text{CH}_2\text{CH}==\text{CH}\text{(CH}_2\text{)}_{5}\text{CH}_3 \\
&\text{CH}_2\text{O}\text{CO}\text{(CH}_2\text{)}_{7}\text{CH}==\text{CH}\text{CH}_2\text{CH}==\text{CH}\text{(CH}_2\text{)}_{5}\text{CH}_3 \\
&\text{CH}_2\text{O}\text{CO}\text{(CH}_2\text{)}_{7}\text{CH}==\text{CH}\text{CH}_2\text{CH}==\text{CH}\text{(CH}_2\text{)}_{5}\text{CH}_3
\end{align*}
\]

**Figure 2.1. Chemical structure of castor oil**

Castor oil has a unique chemistry because it possesses both unsaturation and hydroxyl functional groups. The trifunctional nature of CO contributes toughness to the structure and the long fatty acid chain imparts flexibility. Due to its unusual structure, this oil is very versatile in its application. This oil has been known from primitive ages for its medicinal values. It plays an important role in the field of polymer chemistry. Castor oil reacts with polyfunctional isocyanates to form PUs that range from rigid form to elastomers [15-18]. The hydroxyl group of a castor oil can also impart plasticization in many polymer blends. Castor oil also undergoes many familiar organic reactions to form useful derivatives. Epoxidized, hydrogenated and hydroxylated castor oils are among the many derivatives. Epoxy derivatives are used to stabilize polyvinyl chloride (PVC) resins and hydroxylated oil yields quick-drying alkyd. The hydrogenated derivative oils are used as greases and paints for vehicles.

Some physico-chemical properties of castor oil calculated on the basis of ASTM methods is given in Table 2.1 [19]. Castor oil was obtained from the local market and used after drying.

### 2.1.2 Diisocyanates

In this research study, two diisocyanates such as toluene-2,4-diisocyanate (TDI) and hexamethylene diisocyanate (HDI) have been used. Each of the isocyanate functional groups can react with a hydroxyl group of castor oil to form a urethane
linkage. All diisocyanates are extensively used for the preparation of a wide variety of isocyanate resins like, PU paints, adhesives, etc. [20-24]. Some physico-chemical properties of different diisocyanates used in this study are briefly explained in the following paragraphs.

Table 2.1. Physico-chemical properties of castor oil
(As per ASTM specification D 960)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid number (mg/ KOH/g)</td>
<td>1.48</td>
</tr>
<tr>
<td>Acid value (max)</td>
<td>2.45</td>
</tr>
<tr>
<td>Clarity</td>
<td>Clear</td>
</tr>
<tr>
<td>Colour (Gardner), (max)</td>
<td>2.00</td>
</tr>
<tr>
<td>Hydroxyl number</td>
<td>160-162</td>
</tr>
<tr>
<td>Hydroxyl value (m eq/g) (mg/KOH/g)</td>
<td>2.80</td>
</tr>
<tr>
<td>Iodine value</td>
<td>84-88</td>
</tr>
<tr>
<td>Loss on heating (% max)</td>
<td>0.30</td>
</tr>
<tr>
<td>Refractive Index at 25 °C</td>
<td>1.477-1.478</td>
</tr>
<tr>
<td>Saponification value</td>
<td>176-184</td>
</tr>
<tr>
<td>Solubility in alcohol</td>
<td>Complete</td>
</tr>
<tr>
<td>Specific gravity at 25 °C</td>
<td>0.957-0.961</td>
</tr>
<tr>
<td>Unsaponificable (% max)</td>
<td>0.70</td>
</tr>
<tr>
<td>Viscosity (stokes) at room temperature</td>
<td>6.3-9.0</td>
</tr>
<tr>
<td>Molecular weight (M_n)</td>
<td>930</td>
</tr>
<tr>
<td>Water content (wt %)</td>
<td>0.21</td>
</tr>
<tr>
<td>Isocyanate equivalent</td>
<td>330</td>
</tr>
</tbody>
</table>

2.1.2.1 Toluene diisocyanate (TDI) or toluene-2, 4-diisocyanate: It is one of the aromatic diisocyanate, its boiling point is 251°C and its refractive index is 1.567. TDI is a toxic severe irritant sensitizer and moisture sensitive reagent. It has a molecular formula C₉H₆N₂O₂, its molecular weight is 174.16 and density is 1.22 g/cc at 20 °C. Chemical structure of TDI is;

![Figure 2.2. Structure of toluene diisocyanate](image)
2.1.2.2 Hexamethylene diisocyanate (HDI) or 1, 6-diisocyanato hexane: It is an aliphatic diisocyanate, has a molecular formula \( \text{C}_8\text{H}_{12}\text{N}_2\text{O}_2 \) and its molecular weight is 168 g. Its density is 1.040 g/cc at 20 ºC and refractive index is 1.4525. It is highly toxic, severe irritant sensitizer and moisture sensitive, but it is less reactive compared to TDI. The chemical structure of HDI is:

\[
\text{O} = \text{C} = \text{N}-(\text{CH}_2)_6 - \text{N} = \text{C} = \text{O}
\]

**Figure 2.3. Structure of hexamethylene diisocyanate**

Aliphatic diisocyanates are used in special applications, such as enamel coatings which are resistant to abrasion and degradation from ultraviolet light. These properties are particularly desirable in, for instance, the exterior paint applied to aircraft. Diisocyanates are stable compounds and are stored in an air tight polythene ware at 4 ºC. TDI and HDI of Fluka, USA make were used for this research investigation.

**Chemistry of isocyanates:** All the diisocyanates are more or less toxic by nature. 2, 4- toluene diisocyanate is an asymmetrical molecule and thus has two isocyanate groups of different reactivity. The 4-position is approximately four times more reactive than the 2-position. However, since both isocyanate groups are attached to the same aromatic ring, reaction of one isocyanate group will cause a change in the reactivity of the second isocyanate group [25]. HDI is a symmetrical molecule and thus has two isocyanate groups of equal reactivity.

**[Precautions:** Isocyanates are toxic materials and care should be exercised in their use. Their main effect is on the respiratory system and as a result people exposed to them may suffer from sore throats and bronchial spasms. Isocyanates may also affect the skin and the eyes. The respiratory effects of the isocyanates are directly related to their volatility].

The effects of the nature of diisocyanates on the properties of dicarboxylic acid based chain extended PUs has been reported in the forth-coming chapters. The comparisons of properties are also highlighted.
2.1.3 Chain extenders (dicarboxylic acids)

The different types of dicarboxylic acids such as, saturated and unsaturated, aliphatic and aromatic, and cis and trans form have been used for the synthesis of chain extended PUs (CEPUs) in order to probe their influence on the performance of PUs.

2.1.3.1 Maleic acid: The IUPAC name of maleic acid (MA) is cis-butenedioic acid. It is an unsaturated dicarboxylic acid. The molecule consists of an ethylene group flanked by two carboxylic acid groups. Its molecular formula is C₄H₄O₄ and molecular weight is 116.1 g. The physical properties of MA are white solid, soluble in water and melting point is 130 – 139 °C. Maleic acid is derived from maleic anhydride by hydrolysis. The chemical structure of MA is shown in Figure 2.4.

2.1.3.2 Glutaric acid: The IUPAC name of glutaric acid (GA) is pentanedioic acid. Its molecular formula is C₅H₈O₄ and molecular weight is 132.12 g. It is a white crystalline solid and melting point is 95 to 98 °C. It is a relatively "linear" dicarboxylic acid. It is water-soluble only to a few percent at room temperature. The water-solubility of GA is over 50%. Glutaric acid itself has been used in the production of polymers such as polyester polyols and polyamides. Chemical structure of GA is shown in Figure 2.4.

2.1.3.3 Citric acid: 2-Hydroxypropane-1, 2, 3-tricarboxylic acid is the IUPAC name of citric acid (CA) and it is a weak organic acid. Its molecular formula is C₆H₈O₇ and molecular weight is 210.14 g. It is a white crystalline solid and melting point is 153 °C. The chemical structure of CA is shown in Figure 2.4. Citric acid shows the properties of carboxylic acids and alcohol. Citric acid is used as one of the active ingredients in the production of anti-viral tissues. In biochemistry it is important as an intermediate in the CA cycle and therefore occurs in the metabolism of almost all living things. It also serves as an environmental cleaning agent and acts as an antioxidant. Citric acid exists in a variety of fruits and vegetables, most notably citrus fruits. At room temperature, CA is a white crystalline powder. It can exist either in an anhydrous (water-free) form or as a monohydrate. The monohydrate can be converted into the anhydrous form by heating it above 74 °C. Citric acid is one of a series of
compounds involved in the physiological oxidation of fats, proteins and carbohydrates to carbon dioxide and water.

2.1.3.4 Phthalic acid: The IUPAC name of phthalic acid (PA) is benzene-1, 2-dicarboxylic acid. It is an aromatic dicarboxylic acid with formula C₆H₄(COOH)₂ and molecular weight is 166.14 g (Figure 2.4). It forms white crystals, melting at 210 °C with decomposition into water and phthalic anhydride. Phthalic acid is one of three isomers of benzene dicarboxylic acid, the others being isophthalic acid and terephthalic acid. Sometimes the term "phthalic acid" is used to refer to this family of isomers, but in the singular "phthalic acid", refers exclusively to the ortho- isomer. Phthalic acid is used mainly in the form of an anhydride to produce other chemicals such as dyes, perfumes, saccharin, phthalates and many others. PA (and anhydride) is extensively used in the color industries.

2.1.3.5 Tartaric acid: The IUPAC name of tartaric acid (TA) is 2, 3-dihydroxy butanedioic acid. It is a white crystalline organic acid (L-tartaric). It occurs naturally in many plants, particularly grapes, bananas and tamarinds and is one of the main acids found in wine. It is added to other foods to give a sour taste and is used as an antioxidant. Salts of TA are known as tartrates and are a dihydroxy derivative of succinic acid. Its molecular formula is C₄H₆O₆ and molecular weight is 150 g (Figure 2.4). It is a white crystalline solid and its melting point is 171-174 °C.

2.1.3.6 Itaconic acid: The IUPAC name of itaconic acid (IA) is methylene succinic acid. It is a white crystalline powder that is soluble in water, ethanol and acetone. Its molecular formula is C₅H₆O₄ and molecular weight is 130.09 g. It is a white crystalline solid and melting point is 171-174 °C. Chemical structure of IA is shown in Figure 2.4. The uses of IA are; (a) bond for teeth: bond for teeth made by itaconic acid, acrylic acid and high bond metallic oxide has good anti-pressure and physiological applicability and (b) specialized lens: polymer which contains IA has special luster and transparency, and is fit for making synthetic cut stone and special lens. The chemical structure of all dicarboxylic acid chain extenders is shown in Figure 2.4. All dicarboxylic acids obtained from Fluka were used to prepare CEPUs.
2.1.4 Catalyst - Dibutyl tin dilaurate (DBTL) is a colorless, pungent smelling liquid. It has density of 1.05 g/cc at 20 °C. It has –COO– functional group and is used as a catalyst for PU synthesis. Structural formula of DBTL is given below;

2.1.5 Starch

Starch is composed of carbon, hydrogen and oxygen in the ratio of 6:10:5 (C₆H₁₀O₅)n, placing it in the class of carbohydrate organic compounds. Starch consists of two components namely amylose (water soluble component) and amylopectin (water insoluble) [26]. Amylose is a linear polymer chain of α-D glucose units, linked in the 1,4- positions. The partial structure of amylose is shown in Figure 2.6. Amylopectin has a branched chain structure and is also composed of α-D-glucose...
unit. The chains of $\alpha$-D-glucose units are linked with 1,4- linkages, but chains branch off with branching taking place at every 24-30 glucose units through 1,6- linkages.

![Chemical structure of amylose](image)

**Figure 2.6. Chemical structure of amylose**

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch origin</td>
<td>Maize</td>
</tr>
<tr>
<td>Amylopectin (%)</td>
<td>70</td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>pH of water slurry</td>
<td>5 - 6</td>
</tr>
<tr>
<td>Bulk density (g/ml)</td>
<td>0.07</td>
</tr>
<tr>
<td>Glass transition temperature (°C)</td>
<td>158</td>
</tr>
</tbody>
</table>

**Table 2.2. Typical properties of starch**

Depending on the variety, commercial starch contains small amounts of proteins, fatty minerals, phosphorus containing materials or phosphate ester groups and traces of inorganic materials. Starch is found to be naturally occurring organic filler. It consists of spherical or ellipsoidal grains ranging in particle size from 3 to 100 $\mu$. They are generally insoluble in cold water, alcohol and ether and also form a jelly with hot water. Its specific gravity is 1.499-1.513. Starch is produced from different sources like corn, potatoes and rice. Some of the typical properties of starch is given in Table 2.2.

Recently starch has been proposed as filler for rendering plastics as biodegradable. Advantages of using starch as filler are; naturally occurring and readily available, cost reduction with improved physical and chemical properties and improved processability, is subjected to ‘biological and oxidative attack’ rendering
the plastics bio-degradable and biodegradation with non-toxic by-products. The corn starch (60 mesh) was obtained from Sd fine-chem Ltd., Mumbai.

2.1.6 Zeolite (AlPO₄-5)

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves". The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels. These are conventionally defined by the ring size of the aperture, for example, the term "8-ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminum) atoms and 8 oxygen atoms. These rings are not always perfectly symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many zeolites are not cylindrical. In this research work the pre size of the zeolite filler used is about 7.3 Å [27] (Figure 2.7).

Zeolite-based oxygen concentrator systems are widely used to produce medical-grade oxygen. The zeolite is used as a molecular sieve to create purified oxygen from air due to its ability to trap impurities, in a process involving the adsorption of nitrogen, leaving highly purified oxygen and up to 5% argon. It is also used for extracting cholesterol for serum cholesterol analysis. Synthetic zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic
cracking and hydro-cracking. Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening and other applications. In chemistry, zeolites are used as traps for molecules to separate molecules (only molecules of certain sizes and shapes can pass through) as traps for molecules, so they can be analyzed. Zeolites have the potential of providing precise and specific separation of gases including the removal of $\text{H}_2\text{O}$, $\text{CO}_2$ and $\text{SO}_2$ from low-grade natural gas streams.

Figure 2.7. Structure of AlPO$_4$-Zeolite
Hydrophobic zeolites are commonly synthesized either by direct synthesis or by thermochemical framework modification of hydrophilic zeolites through dealumination procedures [28-29]. The surface properties of zeolites have also been modified by silylation to produce hydrophobic zeolites [30]. Recently, hydrophobic zeolites which have the ability to remove volatile organic compounds have also been reported [31]. More importantly, some other workers have recently published the results of their work on the application of zeolites for oil-absorption from oil-water mixtures [32, 33-36].

Some researchers from Spain have recently reported their work on synthesis of zeolites from fly ash at pilot scale and the applications of these materials in waste water treatment technology [37]. Geopolymers which are amorphous to semi-crystalline three-dimensional silico-aluminate structures, similar to aluminosilicate zeolitic structures, have surface areas of 1 to 2 orders of magnitude higher than that of zeolites and high thermal stability (up to 1000–1200 °C) [38].

2.1.7 Silk fiber

Silk fibers can be obtained from reeling of cocoons [39]. The domesticated silkworm’s (B. mori) based silk fibers are about 10–25 μm in diameter and consist of two proteins; a light chain and heavy chain which are present in a 1:1 ratio and are linked by a single disulfide bond [40]. Silk is composed of protein chains with amino acids as their building blocks. These proteins are coated with a family of hydrophilic proteins called sericins [40-41]. The disulfide linkage between the heavy chain and the light chain holds the fibroin together and glycopectine, is noncovalently linked to these proteins [42]. Fibroin is the core protein of the silk filament and it is stretchable.

The polypeptide chains of fibroin are conformational by unstable and frequently assume a helical configuration or aggregate side by side to form a sheet like structure. The hydrogen bond between C=O and N-H groups takes place in polypeptide chains. Silk fibroin is purified from sericins by boiling silk cocoons in an alkaline solution. Twenty-five to thirty percent of the silk cocoon mass is sericin, which is removed during the de-gumming process (Figure 2.8). Silk fibroin (SF), extracted from Bombix mori silk fibre is a highly promising protein for its structural properties.
Degumming of silk fiber: The fibroin filaments of cocoon silk are naturally gummed together with the protein sericin, on account of which silk fibres loses its brightness and softness. Removal of sericin is a pre-requisite before any subsequent processing as it hindrance to proper absorption of finishing agents. Degumming of silk fiber is the function of pH, temperature and time of alkali treatment. The procedure of degumming involves the boiling of silk fiber for about 1 h in an aqueous solution of 0.5% Na₂CO₃ followed by washing with distilled water and drying for 24 h at 40 °C. The dried fiber was cut into 5 mm length prior to use. This treatment will give a weight loss of about 21±1% [43].

![Degumming process of silk fiber](image)

Figure 2.8. Degumming process of silk fiber

The mechanical properties of silk fibers are given in Table 2.3. Silk Fibroin (B. mori silkworm) was obtained as a gift sample from Department of Sericulture, University of Mysore, Mysore.

Table 2.3. Mechanical properties of silk fiber (B. mori) [44]

<table>
<thead>
<tr>
<th>Silk fiber</th>
<th>Modulus (GPa)</th>
<th>UTS (MPa)</th>
<th>Strain (%) at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. mori silk (with sericin)</td>
<td>5–12</td>
<td>500</td>
<td>19</td>
</tr>
<tr>
<td>B. mori silk (without sericin)</td>
<td>15–17</td>
<td>610–690</td>
<td>4–16</td>
</tr>
</tbody>
</table>

2.2 Equipments

The following equipments are used for the preparation and characterization of chain extended polyurethanes and its composites.

2.2.1 Density

Densities of CEPU and its composites are measured using Mettler electronic balance, Toledo, Switzerland, model AG 204 with a weighing accuracy of ± 0.0001 g according to ASTM 792-86.
2.2.2 Resilience

Resilience is measured as the ratio of rebound height to drop height of a metal plunger of prescribed weight and shape which is allowed to fall on the specimen. It is a function of both dynamic modulus and internal friction of specimens. Resilience of the specimens was recorded as per ASTM D 2632 - 88 method using Rebound resilience tester, New Delhi, India.

2.2.3 Universal testing machine (UTM)

The tensile behaviors of CEPUs and their composites were carried-out as per ASTM D 638 using 4302 model universal testing machine (UTM), H 50 KM, 50KN, Hounsfield, UK with an accuracy of ± 2 MPa. A minimum of five samples were tested at room temperature for each dicarboxylic acids based CEPUs and average values are reported. The microprocessor UTM machine is used with all the attachments for the measurement of tensile behavior of CEPUs and its composites.

2.2.4 Surface hardness tester

Hand operated durometer was used to measure the surface hardness of the prepared CEPUs. There are two types of surface hardness tester. The relative hardness value scale lies in the range 0-100 shore A (for elastomers). Values of more than 90 are however considered unreliable and hence, beyond this range shore D (for plastics) tester is used.

2.2.5 Fourier transform infrared (FTIR) spectroscopy

IR spectra of CEPUs were recorded using FTIR (Japan made JASCO model FT-IR 4100) spectroscopy. The thin transparent CEPU films were used to record the IR spectra at a resolution of 2 cm⁻¹ and 32 scans. The IR spectra were recorded in the wave number range 4000-400 cm⁻¹. The obtained IR data of different CEPUs are interpreted in the forth coming chapters.

2.2.6 Hazemeter

The optical properties such as total percent transmittance, total diffuse and haze were measured using Suga test Hazemeter (model 206, Japan). The haze behavior of dust and grease free CEPUs films have been recorded as per ASTM D-1003-61 method.
2.2.7 Thermoanalytical techniques

All calorimetric measurements were made by differential scanning calorimetry (DSC) (model DSC-Q 200, USA) of DuPont TA, Instrument. The DSC runs were recorded at a heating rate of 10 ºC /min under nitrogen gas purge. The temperature range of the instruments is -200 to 600 ºC. The DSC instrument was calibrated using pure indium metal. All the measurements were carried out with an accuracy of ± 0.01 ºC. The temperature range of the instrument is from ambient to 1200 ºC.

The thermal stability of all CEPUs and their composites was analyzed by using thermogravimetric analyzer (TGA) (model TGA-Q 50, USA), DuPont TA Instrument. The TGA studies have been carried out from ambient to 800 ºC at a heating rate of 20 ºC/min and the weight loss with respect to temperature was recorded.

The dynamic mechanical properties of PUs were carried out with dynamic mechanical analyzer (DMA) (model Q 800, USA). The DMA equipment consists of a probe mechanically connecting the entities such as a force transducer to control the force applied to the sample, an oscillatory applied force (or applied strain), a position transducer to measure the displacement and a temperature – controlled sample specimen. There is a provision for the sample mounting and deforming in a defined manner viz., compression, and tension and bending geometries by the equipment probe and surrounded by a furnace and monitored by a thermocouple along with suitable measuring systems. The operational range of instrument is from -200 to 600 ºC.

2.2.8 Wide angle X-ray scattering spectroscopy (WAXS)

X-ray data for the CEPUs and their composites were recorded by Philips PW 1140 diffractometer with [35 mA, 30 KV] Bragg Brentano Geometry (fine focus setting) using Germanium monochromated radiation of Cu Kα (λ = 1.5418A°), 2θ ranges from 5 to 50° at intervals of 0.02° using a curved position sensitive detector (CPSD) in the transmission mode. These patterns were indexed using TREOR procedure. The intensity was corrected for Lorentz-polarization factors and also instrumental broadening using Stoke’s deconvolution method [45].
2.2.9 Positron annihilation lifetime spectra

The Positron annihilation lifetime spectral (PALS) measurements were carried out with a fast-fast coincidence system consisting of BaF$_2$ scintillators coupled to XP2020/Q photo multipliers as detectors. A 17 µCi$^{22}$Na deposited on a pure kapton foil of 0.0127 mm thickness was used as the positron source. The standard source sample sandwich geometry (sample on either side of the source) was employed for positron lifetime measurements. More details of the experimental procedure can be found elsewhere [46-48]. Positron lifetime spectra with more than $10^6$ counts were recorded for each sample. The instrumental time resolution and source correction terms were obtained from the measured spectrum of a medium of known lifetime (well annealed aluminum) fitted with a computer program RESOLUTION [49]. The resolution function was resolved into three Gaussians with a resultant time resolution of 220 ps. The lifetime spectra were analyzed using the program PATFIT-88 with source and background corrections [49].

2.2.10 Scanning electron microscopy

The morphology of the CEPUs and their composites were analyzed using scanning electron microscopy (SEM) on a JEOL equipment model JSM-5300 with 10 kV of voltage acceleration. The micrographs of CEPUs were recorded from cryofractured surfaces of the specimen after coating with a thin layer of gold.

PART B - Theory and techniques

Prepared CEPUs have been characterized by physical, chemical, mechanical and analytical techniques. Physical methods such as density, surface hardness and percentage swelling were used to characterize PUs. Analytical instruments such as FTIR spectroscopy, hazemeter, DSC, TGA and DMA are used to characterize CEPUs and their composites. The microcrystalline parameters and morphological behaviour of CEPUs and their composites were evaluated by wide angle X-ray scattering (WAXS) diffractometer and scanning electron microscopy (SEM) respectively.
The following paragraphs provide a brief theory, techniques and experimental procedure adopted for each of the above methods.

2.3 Physical methods

The following physical methods are used to evaluate the physical properties such as density, chemical interaction, dimensional stability and other properties of CEPUs and filled CEPUs.

2.3.1 Density

Density of CEPU specimens were measured according to ASTM D 792-86 (displacement) method using Metler Toledo electronic balance. This technique is applicable for solid samples such as film, sheet or powder. The accuracy of density obtained by this method is ± 0.0001 g/cc. The Metler electronic balance should be standardized as per standard before using the PUs specimen.

2.3.2 Resilience

Resilience of polymer sample was determined as the ratio of metal plunger of prescribed weight and shape which is allowed to fall on the PU specimen. It is also a function of both dynamic modulus and internal friction of solid specimen.

2.3.3 Swelling behavior

Procedure to measure percent swelling of CEPUs in organic solvents is briefly explained as follows: a known weight of \( w_1 \) dried CEPU was immersed in different solvents until a state of equilibrium was attained at room temperature. When material swells, weight of the swollen material is noted \( w_2 \). The percentage of swelling was calculated by the relation [50]:

\[
\text{Percentage swelling} = \frac{W_2 - W_1}{W_1} \times 100
\]

(1)

2.3.4 Surface hardness

Surface hardness test of a polymer was performed as per ASTM D 785 using Shore A (elastomer) and Shore D (plastic) durometers (Techno instruments Co.,
Hardness is the property of a material showing resistance to surface indentation. The CEPU specimens were kept under the indenture of shore A and shore D testers and the deflection on the scale was noted. The indentation value reflects the resistance to local deformation, which is a complex property, which is related to modulus, strength, elasticity, plasticity and dimensional stability. It also gives an idea about the degree of crosslinking. A minimum of six readings were noted down for each sample at different positions and an average value was recorded.

### 2.4 Mechanical properties

The mechanical properties have been carried out using universal testing machine (UTM). The following paragraph briefly describes the procedure adopted for measuring the mechanical properties of CEPU’s and their composites.

Tensile properties such as tensile strength, percentage elongation at break and tensile modulus were determined according to ASTM D 638 using Houns Field H 50 KM, 50 KN UTM, UK for dumb-bell shaped specimens. The specimens from the flexible sheets were prepared with the help of a punching die, whereas from the rigid sheets, dumb-bell shaped specimens were prepared by cutting 165 mm long and 14 mm wide rectangular pieces and then shaping them by filing. The edges of the specimens were conditioned as per the standard before testing. A gauge length of 25 mm full scale, cross head speed of 1 cm/min and load of 100 kg was adopted. A minimum of six samples were tested at room temperature for each composition and an average value was taken. Mathematical expressions used to calculate the tensile behavior are as follows;

\[
\text{Tensile strength} = \frac{\text{Load at break}}{\text{Cross sectional area}} \tag{2}
\]

\[
\text{Percentage Elongation at break} = \text{Strain} \times 100 \tag{3}
\]

Tensile modulus = Slope of straight line portion of the stress versus strain curve \tag{4}
2.5 Chemical resistivity

The chemical resistivity test was carried out as per ASTM D 543-87 specification. Evaluation of CEPUs for special applications involving corrosive conditions should be based on the particular reagents and concentration to be encountered. The limitations of the results obtained from this test method should be recognized. The choice of types and concentration of reagents, duration of immersion, the test and properties to be reported are necessarily arbitrary. In this investigation, the PU specimens were exposed to different chemical environments such as 10% CH₃COOH, 10% HCl, 5% H₂O₂, 10% KMnO₄, CCl₄, acetone, benzene and distilled water [51].

Test procedure: The dried samples of the required dimensions (10 mm x 30 mm x 3 mm) were weighed accurately. The specimens were placed in appropriate containers along with the chemical reagents used and the specimens were immersed in reagents for 7 days in the laboratory atmosphere. The specimens were suspended so as to avoid any contact with the wall or bottom of the container. After 7 days the specimens are removed individually from the chemical reagent, and gently wiped with tissue paper and reweighed. The difference in weights was calculated and the percentage change in weight was found out which in turn gave an idea about resistance of the PU specimens to various chemical reagents.

2.6 Heat aging

Heat aging test has been conducted as per the specification of ASTM D 3045 method. For heat aging, the specimens were placed in a hot air oven at the required temperature (90 °C). The annealing time began at the time of the specimens being placed in the oven and allowed for different durations. The effects of heat ageing on the mechanical behaviors/change in weight of the CEPUs and its composites have been reported in forth coming chapters.

2.7 Fourier Transform Infrared (FTIR) spectroscopy

FTIR is a well established analytical tool that is widely used in the characterization of monomers, reactants, polymers and final products. It has recently been used to study the chemical structure of the polymer film. Many scientists extensively used IR spectroscopy for characterizing the CEPUs and IPNs of PUs [52-57]. FTIR detects the characteristic vibrational frequencies of the molecules to
determine the molecular structure. When exposed to infrared radiation, a molecule selectively absorbs infrared frequencies that match those of its allowed vibrational modes. It thus provides detailed information about the chemical bonding and molecular structure. The majority of the FTIR instruments cover the wave number range from 4000 to 400 cm$^{-1}$. The technique involves the passage of a beam of electromagnetic radiation through the surface of the sample. The samples are in the form of thin transparent films. The FTIR spectra of the synthesized PU films in our investigations were recorded between 4000-600 cm$^{-1}$.

2.8 Optical properties

Light transmission, haze and clarity are the optical properties of much interest. Haze and loss of clarity indicates discontinuities or irregularities within or at the surface of the material and these could be due to impurities, minute bubbles or voids, surface roughness or regions of different refractive indices.

Light transmission and haze

Light transmission may be defined as the percentage of light transmitted without deviation and absorption. The haze is the percentage of incident light which is transmitted with more than a certain specified angular (2.5°) deviation by forward setting. Both properties vary with the geometry of the optical measuring system used, which must be carefully specified.

ASTM D 1003 allows several different instruments, all based on the use of an integrating sphere. One is based on spherical hazemeter, which is pivotable about a vertical axis through the entrance port, where the specimen is placed. When the sphere is rotated slightly so that the incident light hits the opposite highly reflecting wall of the sphere (which forms a reflectance standard) adjacent to the exit port, a measurement with and without specimen gives a measure of the total transmittance.

The three properties of interest are;

Total transmittance \[ (T_t) = \frac{(T_1 - T_2)}{T_1} \] (5)

Diffuse transmittance \[ (T_d) = \frac{(T_4 - T_3)(T_2/T_1)}{T_1} \] (6)

Haze \[ = \frac{T_d}{T_t} \times 100 \] (7)
where, $T_1$, $T_2$, $T_3$ and $T_4$ represent the incident light, total light transmitted by the specimen, the light scattered by the instrument and the light scattered by the specimen respectively. The optical properties were recorded for dust and grease free thin films of CEPUs [58-59].

2.9 Thermoanalytical techniques

Thermal analysis is one of the most powerful techniques available for understanding thermo-physical properties of materials. Among several thermal techniques available for such studies, DSC, TGA and DMA continue to dominate. A comprehensive coverage of this important field of thermal characterization of polymers including theory and instrumentation was given by Turi [60]. A brief coverage of DSC, TGA and DMA techniques are highlighted in the following paragraphs.

2.9.1 Differential scanning calorimeter

DSC was introduced commercially during the early 1960’s and it has been found to provide a convenient and useful method for monitoring the course of exothermic reactions including those involved in the crosslinking of the CEPUs. Its main advantages are; (i) the modest requirements in terms of sample size, of the order of milligrams, and (ii) it can provide quantitative data on overall reaction kinetics with relative speed and ease.

In addition, it can be used to measure the thermal transitions such as glass transition temperature ($T_g$), crystalline melt ($T_m$) and curing temperature range which is associated with the nature of polymer (amorphous/crystalline), impurities present in the samples, degree of crosslinking or state of cure of the polymers. The interpretation of the results does however, require a critical approach, which is not always sufficiently evident in the published work [60-65].

One of the major applications of DSC is the measurement of transition temperatures such as $T_g$, $T_m$ and $T_{\text{cryst}}$ [66-67]. In the absence of endothermic or exothermic reactions, the DSC heat flow output is proportional to the sample heat capacity and $T_g$ may be determined from the characteristic discontinuity in heat capacity. The $T_g$ of crosslinked polymer in general shows an increase with increasing
degree of crosslinking and provides a useful index of the degree of cure. The temperature (extrapolated) at which a steep-jump in specific heat capacity occurs is taken as the $T_g$ of the specimen.

Techniques: The DSC cell was operated with a flow of dry oxygen-free nitrogen. The temperature scale of the instrument was calibrated with high purity indium as a melting point standard (156.6 °C), while the heat flow calibration was done with a high purity alpha alumina disc supplied by the company as a calorimetric standard. In this investigation, all calorimetric measurements were made by dynamic DSC scans. About 6-8 mg of sample was taken in an aluminium pan for dynamic (constant rate of rise in temperature) DSC studies. The dynamic DSC scans recorded in the temperature range -50 to 200 °C at a heating rate of 10 °C/min. An empty aluminium pan was used as the reference material.

2.9.2 Thermogravimetric Analyzer

TGA is finding increasing utility in the investigation of pyrolysis and thermal degradation behaviour of solids [68-73]. In addition to that, both qualitative and quantitative analysis is also possible. When a sample is subjected to TGA analysis, the decomposition occurs at a very slow rate until a critical temperature is reached. Then the pyrolysis rate increases very rapidly to maximum, after which, as the sample disappears, the rate of weight loss drops more rapidly. Such behaviour is the characteristic of a large number of decomposition processes, including many polymer pyrolysis.

Thermal Stability: The relative thermal stability of the CEPUs and its composites were evaluated by comparing decomposition temperatures at various percent weight losses. The oxidation index (OI) was calculated based upon the weight of carbonaceous char (CR) as related by the empirical equation;

$$OI \times 100 = 17.4 \times 0.4 \times CR$$

Techniques: The TGA module was operated with a flow of dry oxygen free nitrogen. The temperature scale of the instrument was calibrated with high purity calcium oxalate ($CaC_2O_4 \cdot H_2O$). The sample size taken in each analysis is around 8-10 mg. The
TGA scans are recorded at a constant heating rate in the temperature range ambient to 800 °C. Thermal analysis was carried out at a heating rate of 20 °C/min in static nitrogen atmosphere. The results of TGA data are given in respective places in concerned chapters. For thermal analysis, completely polymerized and dried PU products are taken.

2.9.3 Dynamic mechanical analyzer

This technique is generally used for the qualitative characterization of viscoelastic properties of polymers. In this test, the ability of materials to store and/or dissipate mechanical energy imparted on deformation is being measured. These tests can be performed over a wide range of rates, frequency and temperature as well as time for relaxation studies. In addition to the static force applied to the sample, there is an oscillatory applied force (or applied strain). This result is the ability to measure modulus (which is the ratio of stress, which is normalized force, per unit strain, which is normalized displacement). From each cycle, the DMA calculates both the modulus and the phase, i.e., the response delay caused by viscoelastic changes taking place in the sample. From these fundamental measurements the storage and loss modulus, compliance and viscosity can be calculated. These parameters can be calculated as a function of applied stress-strain and frequency as well as temperatures. The modulus information obtained from dynamic mechanical testing is very useful for researchers, manufacturers and users of polymers in structural applications. Recently many scientists have characterized the segmented PU elastomers by DMA [74-75].

Techniques: A dynamic mechanical analyzer, DMA 2980 of TA Instrument was used for testing of prepared CEPUs. Rectangular samples having a size of about 17.9 X 4.5 X 1.5 mm were tested in the single cantilever mode to measure the storage modulus ($G'$), the loss modulus ($E''$) and the phase angle as expressed by tan δ. All data were obtained using a frequency of 1, 5 and 10 Hz. Samples were cooled from room temperature to -100 °C, kept isothermally at this temperature for 5 min to equilibrate subsequently. DMA thermograms were recorded in the temperature range -100 to 200 °C at a heating rate of 2 °C/min, under nitrogen gas purge. The $T_g$ was taken at the temperature of the maximum in the loss modulus curve.
2.10 Wide angle X-ray spectroscopy

A thorough survey of literature shows that structure-property-relationships of dicarboxylic acid based chain extended PUs and their composites have not been studied by wide angle X-ray spectroscopy (WAXS). The formations of CEPUs are associated with crystal imperfections. Among the other imperfections, the crystal size and lattice strain is important. Here, the X-ray profile broadening analysis was employed to determine these microstructural imperfection parameters and hence, to obtain the structure-property correlation on the basis of X-ray profile and physical measurements [76-78]. The purpose of X-ray analysis carried out here is to relate the changes in microstructural parameters, to the physical macro changes like hardness and tensile behavior which has been done by earlier investigations in the case of man-made polymer fibers and IPNs [79-81]. In this study the degree of crystallinity has been estimated, since the estimation of crystallite size and lattice strain are more fundamental as they determine the degree of broadening of the X-ray profiles in polymer samples.

In most of the polymer samples the increase in hardness or tenacity is associated with increase in crystal size and this aspect has been investigated for the PU samples using wide angle X-ray scattering method.

X-ray pattern recording and analysis

In general theories for X-ray profile analysis of polymer samples has been adopted [82-84]. Two distinct kinds of structure lines of broadening occurs simultaneously and they are; (i) size broadening, caused by a finite size of region in the specimen, diffracting incoherently with respect to each other and (ii) strain broadening due to varying displacement of the atoms/molecules with respect to their reference positions. Normally specimen size broadening is very small and it will be ignored here.

There are various techniques of separating the broadening due to the crystal size and lattice strain from the given X-ray reflection profile. They are, (i) integral breadth and (ii) Fourier technique of Warren- Averbach [82]. But these methods are required to get the X-ray reflection from the same set of Bragg planes. This has been made order since many polymers do give only one order of X-ray reflection. Hence,
the well established single order method adjusted by Somashekar and Somashekarappa [83] has been used which use one dimensional paracrystalline model of Hosemann’s. Here, the X-ray profile for various values of (<N>) and (g) and then matched parameters with the experimental profile to obtain reliable microstructural parameters.

Crystal imperfection parameters like crystal size (<N>) and lattice strain/distortion (g) are obtained by matching the simulated and experimental profiles. Simulation of an intensity profile was carried out on the basis of Hosemann’s one-dimension linear paracrystalline model and the following equations used for this purpose [83];

The scattered intensity is;

\[ I(s) = I_{N-1}(s) + I_1^N(s) \]  \hspace{1cm} (9)

where, \( I_{N-1}(s) \) is computed using,

\[ I_N(s) = 2 \Re \left[ \frac{(1 - I^{N+1})}{(1 - I)} + \frac{I_N}{d(1 - I)^2} \{I_N^N(N(1 - I) + 1) - I \} \right]^{-1} \]  \hspace{1cm} (10)

With \( \nu = 2a^2s + d \) and \( I = I_1(s) = \exp(-a^2s^2 + ids) \) and the modified intensity (\( I^1N(s) \)) for the probability peak centered is given by [68];

\[ I^1_{N}(s) = \frac{2a_N}{D(\pi)^{1/2}} \exp(iDs) \left[ 1 - a_N S \{2D(a_Ns) + i(\pi)^{1/2} \exp(-a_N^2s^2) \} \right] \]  \hspace{1cm} (11)

where, \( a^2_N = N\omega^2/2 \), \( \omega \) is the standard deviation of nearest neighbor probability function and \( D(a_Ns) \) [85]. Dawson’s integral or the error function with purely complex argument and can be easily computed. \(<N>\) is the number of unit cell counted in a direction perpendicular to the (hkl) Bragg plane, \( g \) is the lattice strain given by \( \Delta d/d = \omega/d \). The experimental profile between \( s_o \) and \( s_o + s_o/2 \) (or \( s_o \) and \( s_o + B.2d \)). If there is a truncation of the profile \( B < 1 \) is matched with the corresponding simulated order of reflection between calculated and experimental normalized intensity values. SIMPLEX a multidimensional algorithm [85] is used for minimization.
Using this procedure, the values of the crystal size and lattice strain were obtained for X-ray reflection at various 2θ angles and here dhkl is the perpendicular distance from the origin to the hkl plane, \( \omega \) is the standard deviation of the probability distribution associated with the distortion of the lattice and it is related to the strain by \( g^2 = (\omega/d)^2 \). Here, \( s \) is \( 2\pi (\sin\theta)/\lambda \) and \( s_0 \) is the scattering vector corresponding to the peak of the X-ray profile. Here, the surface-weighted (D_{sur}) or volume weighted (D_{vol}) crystal size is given by the integral [86];

\[
<D>_{S,V} = \frac{\int L P_{SV}(L) dL}{L \int P_{SV}(L) dL}
\]

and

\[
P_s(L) \alpha [\delta^2 A_s(n) / \delta L^2]
\]

and the volume-weighted column-length distribution function is given by;

\[
P_v(L) \alpha L [\delta^2 A_s(n) / \delta L^2], L = n dhkl, \text{ } n \text{ is the harmonic number [83].}
\]

### 2.11 Positron annihilation lifetime spectra (PALS)

All lifetime measurements were performed at room temperature. All spectra were resolved into three lifetime components as it gave better \( \chi^2 \) values and standard deviations compared to two and four component analysis. Therefore three lifetime analysis results are reported here. Generally, the attribution of the resolved three positron lifetime components to various states of positron annihilation is as follows. The first short-lived component \( \tau_1 \) with intensity \( I_1 \) is attributed to p-Ps and free positron annihilation. The intermediate lifetime component \( \tau_2 \) with intensity \( I_2 \) is considered to be caused mainly by the annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline-amorphous (c-a) inter-phase. The longest lived component \( \tau_3 \) with intensity \( I_3 \) is due to pick off annihilation of o-Ps in the free volume sites present in the amorphous regions of the polymer matrix [87-88].

In polymers, of the three lifetime components, the o-Ps pick-off lifetime (\( \tau_3 \)) and its intensity (\( I_3 \)) are of importance, because \( \tau_3 \) is related to the free volume hole size and \( I_3 \) to the relative number density of free volume holes in the material, because the chain mobility and chain conformations under stress depends on the size and available free volume content (fractional free volume) of the material. Hence, it
becomes pertinent to focus on only these two parameters of positron lifetime. The \( \alpha \)-Ps lifetime \( \tau_3 \) is related to the free volume hole size by a simple relation developed by Nakanishi et al [89] based on the theoretical models originally proposed by Tao [90], for molecular liquids and later by Eldrup et al [91]. In this model, the Positronium atom was assumed to be localized in a spherical potential well having an infinite potential barrier of radius \( R_0 \) with an electron layer in the region \( R < r < R_0 \). The relation between \( \tau_3 \) and the radius \( R \) of the free volume cavity is thus;

\[
(\tau_3)^{-1} = 2 \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right] \tag{14}
\]

where, \( R_0 = R + \delta R \) and \( \delta R \) is a fitting parameter. By fitting equation (14) with measured \( \tau_3 \) values for known hole sizes in porous materials like zeolites, a value of \( \delta R = 0.1657 \) nm was obtained. With this value of \( \delta R \), the free volume radius \( R \) has been calculated from equation (14) and the average size of the free volume hole \( V_f \) is evaluated as \( V_f = (4/3)\pi R^3 \). The fractional free volume (\( F_v \)) or the free volume content can be estimated as;

\[
F_v = CV_f I_3 \tag{15}
\]

where, \( C \) is a constant whose value is taken as \( 0.0018 \text{Å}^{-3} \) [46].

2.12 Scanning electron microscopy

The cryofractured specimen’s morphology of the various CEPUs are well documented in the literature [92-97]. The combination of rubbery and glassy polymer networks gives interesting scanning electron microscopy (SEM) photomicrographs. Since morphology plays a major role in affecting PUs performance, it has been extensively studied using SEM.

Since its commercial introduction in the early sixties, the SEM has been used in a number of situations requiring greater resolution than the light optical microscopes. Here, a fine beam of electrons is scanned (focused) on the surface of an opaque sample to which a light conducting film has been applied by evaporation. An image of the surface of the sample can be obtained from the intensity of the secondary electrons. A fixed energy electron beam is scanned across the surface of the sample.
The results appear on the read out device as a visual image of the surface of the sample. The resulting image has a great depth of field and a remarkable three-dimensional appearance. The results are similar to those obtained from an optical microscope except that the magnification is considerably greater in SEM. Conventional SEM images are formed by scanning a focused beam of electrons across the surface of a PU specimen and detecting the secondary electrons that are ejected by the specimen.

The morphology of PU composites was studied using a scanning electron micrograph (SEM). The micrographs of the composites were taken on Jeol (JSM-5300) with probe microanalysis Sl. No. 320 after gold (100Å) coating. The magnification is displayed on the respective microphotographs of the samples.

2.13 Soil degradation behavior

Biodegradation of all the PUs were studied by the soil burial method [98]. For this purpose plastic containers of about 200 cm$^3$ capacity were filled with soil. Circular polymer samples of about 0.4 g weight were placed in the containers at a depth of about 5 cm. The soil was kept moist by sprinkling water at regular time intervals. The excess water was drained through the hole at the bottom of the container. The containers were stored at about 30 to 35 °C. The degradation of the samples was studied at regular time intervals of 15 days by removing the samples carefully from the soil and washing them gently with distilled water to remove the soil adhering on the surface. The samples were dried at 60 °C under vacuum until the constant weight was obtained. Weight loss of the polymer with respect to time was recorded.
2.14 References

31. X.S. Zhao, Q. Ma
44. N. Tammanna and Sonwalker Hand book of silk technology, Wiley Eastern Ltd.
67. M.J. Richardson and N.G. Savill, Polymer, 16 (1975) 753.
97. Y.S. Lipatov, V.V. Shilov, Y.P. Gomza, V.S.Skorodzievsky, A.I.Ustinov and