CHAPTER 8
SUMMARY

This chapter summarizes the results of the present research investigation. The objective of this research work was the preparation and characterization of dicarboxylic acids based chain extended polyurethanes (CEPUs) using naturally occurring castor oil as polyol. By incorporating different proportions of filler or fiber into CEPUs, a wide spectrum of physical mechanical and thermal properties has been achieved. Scope for future work, which is a fall out of this investigation, is presented in section 8.2.

Polyurethanes are a living science and are a global network for research, development and production. Fast-growing demand can only be met by developing a wide variety of newer PUs. In this research investigation a series of castor oil (CO) based CEPUs have been prepared using different diisocyanates (toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI)) with six dicarboxylic acids such as maleic acid (MA), glutaric acid (GA), citric acid (CA), phthalic acid (PA), tartaric acid (TA) and itaconic acid (IA) as chain extenders.

8.1 An overview of this research investigation

Recently CEPUs have been investigated by many researchers. However, relatively little systematic characterization has been reported on dicarboxylic acids based CEPUs using castor oil as the polyol in chain extension process. In this work, the dicarboxylic acid based CEPUs were obtained using the prepolymer method, which involved the preparation of an isocyanate-terminated prepolymer, which was chain-extended after addition of chain extender (dicarboxylic acids). From this research investigation it is understood that,

- CEPU, consists of alternating sequences of soft and hard segments. The soft segment, which is in a viscous or rubbery state, provides elastomeric character
for the polymer, whereas the hard segment, which is in a glassy or semicrystalline state, provides dimensional stability by acting as a thermally reversible and multifunctional crosslink and also as reinforcing filler.

- A wide spectrum of physical properties and morphologies has been observed, depending upon the composition and the chemical architecture of the hard and soft segments
- CEPU can be tailor-made and present many of the features related to conventional applications. Dicarboxylic acid based CEPU can be used alone or reinforced with other materials (filler and fiber). There are many technological advantages in using the CEPU or CEPU/composites including low cost, excellent performance and good applicability.

CEPU has been reported to show a greater tendency for phase separation than PU (without chain extender). Introduction of dicarboxylic acid groups in the PU significantly increases the phase separation, yielding products of superior properties. The mechanical properties of CEPU are directly related to the nature of the hard-segment domains, which are extensively hydrogen-bonded with the neighboring chains. The mechanical behavior of PUs is basically different from that of chemically crosslinked products. Applied mechanical stress causes orientation which leads to disruption and reformation of hydrogen bonds in an energetically more favorable position. Consequently, TDI based CEPU shows high values for both tensile strength and elongation. Depending on the introduction of chain extender such as linear (GA), branched (IA), aromatic (PA) and distinctly different geometrical structure (trans-trans, and cis-cis chain extenders (TA and MA)) CEPU have been synthesized for a variety of end uses.

The properties of the dicarboxylic acids based CEPU depend upon the nature of the chain extenders. The polyurethanes used in this study were synthesized by polycondensation reactions described in chapter 3. The obtained tough and transparent CEPU obtained have been examined for mechanical, thermal, chemical, optical and morphological behaviors. FTIR spectra confirmed that almost all diisocyanate groups reacted during polymerization. No unwanted by-products are given off because the raw materials react completely.
CEPUs are widely used in various industries because of their excellent physico-mechanical properties. However, for some specific uses, some mechanical properties, e.g., strength and toughness of conventional elastomer materials, are not adequately high. Various approaches have been developed to improve such properties. One of the most effective and simple method is the incorporation of micro or nano fillers or functional fillers or fibres into PU matrix.

A series of CEPU/starch biodegradable composites have been prepared with varying amounts of starch content. The result of these investigations have shown that the starch acts as hard segment in these PUs. Hence, the prepared biocomposites exhibited a significant improvement in mechanical and thermal behaviour. However, water ageing reduces the mechanical behaviour of the composites. This result indicates that these composites are water sensitive. The PU/starch composites are biodegradable in nature.

This research work covers the fabrication and characterization of CEPU/zeolite composites. The results show that zeolite had good interactions with the polymer matrix. Taken together, these results suggest that the mechanical properties of the PU are improved upon the incorporation of zeolite without altering the chemical structure of the CEPU. The mechanical characterization of the composites is in accordance with their morphology and show superior properties in comparison with the neat CEPU. We believe that these findings widen the potential application range of PU products.

Silk fibroin, from the silkworm, has excellent properties such as excellent surface character, biocompatibility and high specific strength. Studies have been conducted to investigate the development and characterization of CEPU/silk fiber composites. This research work has focused on silk-based biocomposites and the mechanical, thermal and morphological characterizations have been reviewed. It has been demonstrated that the properties of the CEPUs enhanced significantly after incorporation of short silk fibre. Further analyses on the strengthening mechanism indicates that such improved mechanical properties are attributed to good interfacial interaction between the PU and silk fibre.
The molecular transport behaviour of various organic solvents and gases through CEPU membranes is of great importance, because they are widely used for various barrier applications. These transport studies become of utmost importance while designing barrier material or tubes for transporting liquids and gases. Alkane and aromatic solvents have been chosen as probe molecules as these have diverse applications in process industries and in manufacture of perfumes, dyes, bulk drug formulations, etc. In this research work the sorption (S), diffusion (D) and permeation (P) coefficients of \( n \)-alkanes and aromatic penetrants through CEPU membranes at different temperatures (25-60 °C) have been investigated. The effects of the nature of chain extender, penetrant size and temperature on the transport properties were studied. The results of this study indicate that diffusion coefficients and permeation coefficients increase with an increase in the size of penetrants and temperature. Molecular transport is found to follow the Fickian behaviour in all cases over the investigated temperature range. The activation energies for diffusion and permeation and thermodynamic parameters have been estimated. Molecular transport behavior with organic probe molecules plays a very important role in establishing the structure-property relationships of CEPUs. There is ample scope to make use of PU membranes in controlled delivery of drug or pesticides or in the disposal of nuclear waste. The CEPUs and their composites exhibit excellent resistance to long-term immersion in water, seawater and alkaline solutions as well as good resistance to ketones.

8.2 Scope for future work

Increasing concerns about the environment and sustainability are fueling a growing worldwide research effort devoted to understanding and using renewable resources. The aim is to reduce the dependence on fossil fuels, which are rapidly being exhausted and to develop innovative technologies and competitive industrial products. Vegetable oils are abundant and cheap renewable resources which represent a major potential alternative source of raw materials suitable to developing newer eco-friendly products. Depleting oil resources and dependence on other nations for oil has led to concerns over the price of raw materials used to manufacture PUs. Hence, naturally occurring renewable oils such as soybean, palm oil and modified oils have been successfully used as a replacement for synthetic polyols in the production of new series PUs components.
PUs as specialty chemicals explores conventional CEPU and its composites - emphasizing formulations, as versatile structures that can be used for specific design objectives in environmental and engineering applications. Present investigation on CEPU's and their composites is also the first in its field to provide useful wealth of scientific data to material engineers for commercial exploitation of CEPU's.

There is ample scope for extension of this research investigation because of its vast nature and due to the fact that a variety of compositions and properties have been covered. PU can be fabricated for wide variety of applications from automobile to medical science. These CEPU's and its composites are used to manufacture, for example, insulated building panels, mattresses and upholstered furniture, car seats, domestic refrigerators and freezers, truck bodies, footwear and coatings.

During recent decades, there has been a tremendous growth in the use of green composites in various fields of application, ranging from aerospace, automotive parts, boats to recreation equipment, office products, biomedical devices, etc. It is important to tailor their properties by adjusting fibre loading and architecture and fibre–matrix interface, by modifying matrix, and by hybridizing to meet different requirements. Thus composites of CEPU can be prepared by using different natural fibers such as sisal, jute, hemp, etc.

Typical research areas are; (i) green composites by using raw materials from renewable resources, (ii) biodegradable composites, nano composites (iii) coating / adhesives applications, (iv) foaming and (v) elastomer for low temperature applications, etc.

The focus in present day technology is on nano-fillers and function filters to fulfill the upcoming challenges. An investigation using nano-fillers at low volume fraction level (phr) may offer many new challenges in the field of engineering applications. Similarly nano-fillers at medium to high phr values and functional fillers like conducting fillers, magnetic fillers and antimicrobial additives can open up many new challenges in the field of PU technology.