

## ABSTRACT

High performance polymers such as polyimides, polyamides, polyesters, etc. are of considerable interest because of their excellent mechanical and high-temperature properties, but they exhibit very low solubility and high melting points which limit their widespread applications. There are several reports describing the approaches by making use of structurally modified monomers to improve the processability of high temperature polymers.

The main objective of the present research work is to design and synthesize processable high performance polymers such as polyesters, poly(ether-ester)s and phosphorous containing polyesters by making use of bifunctional monomers containing bulky “cardo” group or flexible alkyl chains. The other objective is to evaluate the applications of selected synthesized polymers as flame retardant materials.

Thus, our research effort was directed to design to improve the processability of polymers. Two bisphenol monomers namely 1,1-bis(4-hydroxyphenyl)cyclohexane (BPZ) and 1,1-bis(4-hydroxyphenyl)-4-methylcyclohexane (MBPZ) containing cardo cyclohexane moiety were synthesized by reacting cyclohexanone and 4-methyl cyclohexanone with phenol. A bisphenol monomer containing alkoxy spacer namely 1,1-bis(4-(3-hydroxypropoxy)phenyl)cyclohexane (BPPZ) was also synthesized by reacting BPZ with 3-bromo-1-propanol using anhydrous potassium carbonate catalyst in DMF medium. These bifunctional monomers provide the structural characteristics needed for the improvement of processability of polymer.

To optimize the polycondensation reaction, different parameters were considered. Based on the results, all the polyesters were synthesized by interfacial polycondensation technique using hexadecyltrimethylammonium bromide (HDTMAB) as a phase transfer catalyst in dichloromethane medium with good yield.

Two series of polyesters containing cyclohexane moiety as a cardo group were synthesized from respective bisphenol (BPZ and MBPZ) with various aliphatic and aromatic diacid chloride. A series of copolyesters containing cardo cyclohexane moiety were synthesized by reacting monomers BPZ/MBPZ and various proportion of BPA with adipoyl chloride. A series of new poly(ether ester)s was synthesized from BPPZ monomer with aliphatic and aromatic diacid chlorides. Phosphorous containing polyesters were synthesized by reacting BPA/BPZ/MBPZ with phenylphosphonic dichloride.

All the monomers and polymers were synthesized in good yield and the structure was confirmed by elemental analysis and spectroscopic techniques. The condensed phase characterization was carried out using DSC. The thermal degradation behaviour of polyesters was studied using thermogravimetric analyses. The polymers were obtained with moderate molecular weight and soluble in common organic solvents.

In the synthesized polyesters derived from BPZ and MBPZ, all the aromatic polyesters exhibited higher thermal stability than aliphatic polyesters. This may be due to higher crystallinity inside the hard domain. It was noticed that in all the aliphatic polyesters the thermal stability initially increased with increasing spacer length, but further increases in the spacer length led to decrease in the thermal stability. This may be due to the opposing effects of the decoupling function of the spacer and the flexibility of the spacer on the thermal stability. In copolyesters, the polymers containing higher percentage of BPA showed higher stability than the other. This may be

due to the introduction of bulky cyclic group in the main chain which reduces strong intermolecular interaction of stiff chain leading to chain separation. In poly(ether ester)s, despite the presence of cardo group, alkoxy spacer and ether linkage present along the polymer backbone exhibited high thermal stability with advantage of being soluble in most of the organic solvents. In phosphorous containing polyesters, BPA based polyester possess higher thermal stability than the other polyesters. However, the cyclohexane containing polyester S5P2 and S5P3 possess higher char yield than propane containing polyester S5P1. This may be due to higher number of carbon and stability of cyclic ring structure.

The DSC analysis results of BPZ based polyesters revealed that the aliphatic polyester which has lower number of methylene spacer showed glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ). Aliphatic polyesters which have a higher number of methylene spacer did not show  $T_g$  and  $T_m$ . No endothermic peaks were observed in aromatic polyesters. All the methyl substituted polyesters showed  $T_g$  due to the presence of methyl group in cyclohexane ring, which reduced the strong intermolecular interaction of stiff chain and enhanced amorphous nature. In copolyesters, the  $T_g$  value decreased with the increasing content of BPZ. The DSC data of the synthesized poly(ether-ester)s revealed that all the polymers possess  $T_g$ . The aliphatic poly(ether-ester)s showed the  $T_m$  due to the melting of microcrystalline units inside the hard domain. They displayed slightly enhanced crystallinity because of their rigid molecular structure due to the presence of alkoxy spacer and ether group. The absence of  $T_m$  and the presence of  $T_g$  in the DSC traces of polyesters indicated that synthesized phosphorous containing polymers were amorphous in nature. The incorporation of cyclohexane ring along the polymer backbone substantially decreased the  $T_g$  of BPZ based polyesters compared to the BPA based

polyester. The depression in  $T_g$  of cardo polyesters demonstrated the “plasticizing” ability of cyclohexane ring.

Application of phosphorous containing polyesters was evaluated in brief. The flame retardant behaviour was observed using LOI and UL94 vertical burning test. The obtained results confirmed that the synthesized phosphorous containing polyesters have the potential to serve as useful flame retarding additives for polymeric materials.

The tensile strength was measured using universal testing machine for phosphorus containing polyesters. The tensile strength results showed that the synthesized polyesters have a potential to be used as a plasticizer.

The thermal degradation kinetics study of synthesized polyesters was also carried out using TGA. Polyester with methyl substituent in cyclohexane exhibited higher activation energy for thermal degradation than unsubstituted polyester due to the introduction of methyl group into the polymer chain which stabilized the carbon free radical formed during degradation which led to higher thermal stability and higher activation energy.

Overall, polymer processability was improved by the incorporation of cardo cyclohexane ring via internal “plasticization”. The incorporation of alkoxy spacer and substituted cyclohexane “cardo” group resulted in poly(ether ester)s with improved solubility in common organic solvents and higher thermal properties. The introduction of phosphorus group into the polymer chain improved the flame retardant nature of synthesized phosphorus containing polyesters.