STRUCTURE-PROPERTY RELATIONSHIPS IN COPOLYESTERS

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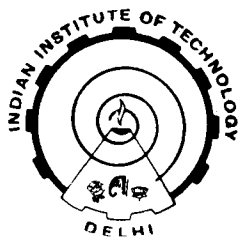
DOCTOR OF PHILOSOPHY



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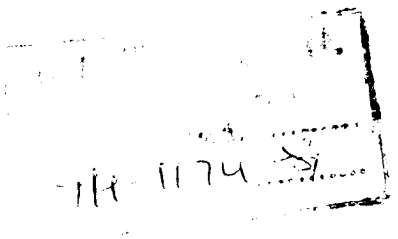
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CERTIFICATE

This is to certify that the thesis entitled "STRUCTURE-PROPERTY RELATIONSHIPS IN COPOLYESTERS" being submitted by Mr. Yuvraj Singh Negi to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Polymer Chemistry, is a record of bonafide research work carried out by him. Mr. Yuvraj Singh Negi has worked under our guidance and supervision and has fulfilled the requirement for the submission of this thesis, which to our knowledge, has requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The present investigation deals with the Synthesis, Characterisation and Structure-property Relationships in Copolyesters. Structural modification of poly(ethylene terephthalate) has been investigated by incorporation of 1,6-hexamethylene terephthalate and 1,8-octamethylene terephthalate units in a random manner.

Crystallisation properties of polyesters depend to a great extent on the carbon content of the glycol. Melting point, crystallisation rates and crystallinity are expected to change by incorporation of these polymethylene units in the backbone.

Melt condensation process has been adopted for synthesizing the copolyesters. Several copolyester samples were obtained by changing mole % of 1,6-hexanediol with respect to ethylene glycol from 0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 50, 80 and 100% and these samples have been named as PET, H_1, H_2, H_3, H_4, H_5, H_6, H_7, H_8, H_9, H_{10} and H_{11} respectively. Four copolyesters were obtained from a monomer feed containing 2.5 (D_1), 5 (D_2), 7.5(D_3) and 10(D_4) mole % of 1,8-octanediol with respect to ethylene glycol.

Characterisation of polymers was done by determining melting point, solution viscosity, end group analysis, ir spectroscopy, ^{1}H-NMR and ^{13}C-NMR spectroscopy and thermogravimetric analysis methods.

Melting point of copolyesters decreased with increasing mole % of hexamethylene or octamethylene in the PET backbone. An eutectic point was observed in PET were replaced by hexamethylene groups. Characteristic ir absorption bands associated with various groups in copolyesters were observed. In the ^{1}H-NMR and ^{13}C-NMR spectra, additional signals characteristics of the third comonomer were noted. Intrinsic viscosity of the polymers was determined at 30° and 35°C in m-cresol and phenol:tetrachloroethane mixture (3:5 v/v). Higher values were obtained in phenol:tetrachloroethane solvents. Carboxyl equivalent weight was determined by titration with alkali. Lower values were observed in copolymers. End group analysis and viscosity measurements indicated a decrease in molecular weight of copolyesters.

Thermal stability of copolymers was evaluated by dynamic thermogravimetry in air atmosphere. An increase in the concentration of flexibilising hexamethylene or octamethylene groups resulted in a decrease in relative

thermal stability as assessed by initial decomposition temperature, integral procedural decomposition temperature and final decomposition temperature.

For spinning and drawing of the copolyesters, a bench scale spinning and drawing unit was used. Fibres obtained at room temperature were drawn to different draw ratios (3,4 and 5:DR). The temperature of drawing varied according to the crystallisation temperature of polymers. Heat-setting of 5:DR fibres was done at 135°C for 30 min. in air oven. A decrease in mechanical strength and initial modulus was observed in copolyesters and extensibility on the other hand, was enhanced.

Glass transition (T_g), crystallisation temperature (T_c) and melting point (T_m) were studied by DTA using quenched fibre samples. A decrease in T_g, T_c and T_m was observed on increasing the hexamethylene content in polyester backbone. Heat of fusion (ΔH_f) values for 5:DR and heat set fibre was evaluated from the melting endotherm of DSC traces. Higher ΔH_f values were obtained in case of the heat set fibres.

A decrease in storage modulus $|E'|$, loss modulus $|E''|$ and tan δ_{max} values was observed on increasing the hexamethylene units in the backbone. A decrease in density and optical birefringence in copolyesters was observed. X-ray diffraction pattern of copolyesters was similar to that of the PET. This study shows the incorporation of hexamethylene groups in the amorphous matrix. Percent crystallinity was found to be lower than PET in 5:DR fibres.

The moisture regain of the copolyester fibre was determined by vacuum desiccator method. Copolyester fibres showed higher moisture regain than PET fibres. The addition of hexamethylene units modifies the amorphous regions of PET fibres which enhances the hydrophilicity of the fibres and is responsible for high moisture absorption.

The dyeing was carried out using C.I. Disperse Red-17, C.I. Disperse Yellow and C.I. Disperse Brown without carrier in beaker dyeing machine. High dyeability was obtained with copolyesters than the homopolyester fibre. This may be due to higher moisture regain of the fibres. As a consequence more fibre swelling at the dyeing temperature would be possible. This would facilitate dye penetration in the fibres. The dye fading on fibres was found to be of the same magnitude as that of PET.

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