EFFECT OF STRUCTURE ON THE PROPERTIES OF POLY (ETHYLENE TEREPHTHALATE)— POLY (ALKYLENE TEREPHTHALATE) COPOLYESTERS

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CERTIFICATE

This is to certify that the thesis entitled "EFFECT OF STRUCTURE ON THE PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE)-POLY(ALKYLENE TEREPHTHALATE) COPOLYESTERS" submitted by Radha Agarwal to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy is a record of bonafide research work carried out by her. Radha Agarwal has worked under our guidance and supervision and has fulfilled the requirements for the submission of the thesis, which to our knowledge has reached the 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 investigations deal with the study of the effect of alkylene groups on the properties of poly(alkylene terephthalate) homopolyesters and copolyesters. The copolyesters were prepared by melt condensation of low and high molecular weight PET with low molecular weight poly(hexamethylene terephthalate)(PHT), poly(octamethylene terephthalate)(POT) and poly(decamethylene terephthalate)(PDT).

PET and PHT having $[\eta]$ ranging from 0.18-0.60 dl/g and 0.2-0.4 dl/g respectively (in phenol-tetrachloroethane at 35°C) were prepared by changing the time of polycondensation from 1.5-4 h. The $[\eta]$ of POT and PDT was 0.2 (after 2.5 h of melt fusion) and 0.18 dl/g (after 4 h of polycondensation) respectively. Copolyesters having following % mole fractions of PHT or POT were prepared - sample EH_1 or EO_1 (7.92), EH_2 or EO_2 (20.54), EH_3 or EO_3 (34.02), EH_4 or EO_4 (43.64), EH_5 or EO_5 (53.72), EH_6 or EO_6 (74.78) and EH_7 or EO_7 (87.5). PET-PDT copolyesters were prepared by changing the % mole fraction of PDT from 2 (ED_1), 5 (ED_2), 10 (ED_3) and 20 (ED_4). Altogether 18 copolyester samples were prepared.

Melt fusion of PHT ($[\eta]$ = 0.3 dl/g), POT ($[\eta]$ = 0.2 dl/g) and PDT($[\eta]$ = 0.18 dl/g), with commercial PET

($[\eta]$ = 0.62 dl/g, $\bar{M}_v$ = 14000) was also done. Three such copolyester samples were prepared by blending PET with 5 mole % of PHT, POT and PDT and these have been designated as FH_1, FO_1 and FD_1 respectively. Melt-blending of PET with 7 mole % of PHT or POT (sample FH_2 or FO_2) and 10 mole % of PHT (sample FH_3) was also carried out. Seven samples were thus obtained by melt fusion of high molecular weight PET with oligomeric PHT, POT and PDT. The various polymer samples were characterised by IR and NMR spectroscopy.

Intrinsic viscosity of copolyesters was higher than homopolyesters. The conditions of melt fusion were optimised by varying the duration of reaction. Maximum $[\eta]$ in phenol:TCE was obtained after 3 h of polycondensation at 265°C. Therefore, the copolyesters were prepared by carrying out the reaction for 3 h.

Density of copolyesters decreased with an increase in % mole fraction of PHT/POT/PDT in the PET backbone.

Isothermal crystallization was done at 80°C for different times and rate of crystallization was followed by small angle light scattering (SALS). A characteristic usual type of pattern typical of spherulite, with lobes at 45° to the polarizer direction, which is normally observed in PET, was observed in PHT, POT and PDT also. Spherulitic patterns were observed after quenching, 1 sec, 5 sec, and 1 min in PDT, POT, PHT and PET respectively which indicate the following rate of crystallization.

$$\text{PDT} > \text{POT} > \text{PHT} > \text{PET}$$

The spherulite radius increased as the time of crystallization increased. A comparison of ultimate spherulite radius of PET-PHT copolymers with PET-POT copolymers indicates that for the same composition the spherulite radius was larger in PET-POT copolymers.

A decrease in the T_g, T_c and T_m was observed with the increase in number of methylene groups in the PET backbone. In the samples containing 20 mole % to 70 mole % of comonomers two endothermic transitions (T_m) were observed. The higher T_m value is attributed to the PET block and lower for PHT/POT blocks. In copolyesters having 20 mole % to 87.5% of comonomer two exothermic peaks were observed in the cooling curves. The high temperature peak may be attributed to crystallization of PET and the peak at lower temperature to blocks of PHT/POT/PDT. Some information regarding the crystallization was also obtained by the slope of crystallization curves. Incorporation of flexible segments in PET reduced the onset temperature of crystallization exotherm.

Thermal stability of polymer was evaluated by dynamic thermogravimetry. An increase in the number of methylene groups resulted in a decrease in IDT, T_g, T_{max} and IPDT. This may be attributed to the higher flexibility of the backbone.

Seven copolyester samples (FH_1, FH_2, FH_3, FO_1, FO_2, FD_1) were spun into fibres using a bench scale spinning and drawing unit. Fibres obtained were drawn to different draw ratios (3,4 and 5:DR) at 100°C. Heat setting of 5:DR fibres was done at 135°C for 30 min in an air oven under taut conditions. A decrease in the initial modulus and an increase in % elongation was observed with the increase in the number of methylene groups in the PET backbone.

DSC studies of copolyester fibres indicated a decrease in T_g, T_c and T_m on increasing the number of methylene groups in PET backbone. In heat-set fibres endothermic and exothermic transitions associated with T_g and T_c were absent.

A decrease in the density and birefringence was observed on increasing number of methylene groups in PET backbone. X-ray diffraction pattern of copolyesters was similar to that of PET. Percentage crystallinity, Herman's orientation factor and amorphous orientation was found to be lower than that of PET in 5:DR heat-set copolyester fibres.

Higher moisture regain was observed at 65% and 84% relative humidity. The dyeing was carried out using disperse dye (Cibacet Orange 2R) without using a carrier at 110°C. Better dyeability in copolyester fibres was observed compared to PET. Initial rate of dyeing was very high in copolyesters than in PET. Good correlation between % crystallinity and modulus, elongation-at-break and diffusion coefficient was observed.

These studies thus indicate that chemical structure and fine structure of copolymers affect the various useful properties of fibres.

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