SYNTHESIS AND STRUCTURE PROPERTY RELATIONSHIP IN POLYESTERS AND COPOLYESTERS

BY

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TO

MY

GURU AND PARENTS

CERTIFICATE

This is to certify that the thesis entitled "Synthesis and Structure-Property Relationship in Polyesters and Copolyesters," being submitted by Mr. Satya Narain Garg, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in the Department of Textile Technology, is a record of bonafide research work carried out by him. Mr. Satya Narain Garg has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

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

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PREFACE

The work reported in this thesis is mainly related to polyethylene terephthalate and its copolymers. However, the chapter 4 is on polybutylene terephthalate. In all there are six chapters. The first two chapters, which form the major part of this thesis, have been devoted to the synthesis, characterization, study of crystallization kinetics, light scattering, and fibre properties of polyethylene terephthalate and polybutylene terephthalate block copolymers. The third chapter deals with the study of crystallization behaviour of polyester-polyamide block copolymers. A study of morphology and properties of polybutylene terephthalate crystallized from amorphous glassy state has been reported in chapter 4 while the fifth chapter has been devoted to the study of stress-induced crystallization of polyethylene terephthalate. The sixth chapter concludes the work reported in these five chapters and provides suggestions for future work.

ABSTRACT

The block copolymers of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) were synthesized in order to improve the crystallization rate of PET for its use in moulding applications. Block copolymers were prepared by end group coupling of the preformed oligomers of PET and PBT. These polymers were characterized by viscosity, differential thermal analysis, differential scanning calorimetry and thermogravimetric analysis. The glass transition temperature, melting temperature, crystallization temperature, initial decomposition temperature, integral procedural decomposition temperature, and energy of activation of thermal decomposition decreased with the increase in the PBT content. The heat of crystallization and heat of fusion first increased and then decreased with the increase in PBT content.

The rates of crystallization of these polymers were measured by observing changes in mass density as a function of time. The rate of crystallization first increased upto 3.5 wt.% PBT content and then decreased

with the increase in PBT content. The crystallization behaviour was analyzed by Avrami equation. Avrami plots for PET homopolymer and the block copolymer containing 1.0% Wt. PBT were different from those obtained for block copolymers containing 2-20 wt.% PBT. This was attributed to the difference in the rates of crystallization. The values of Avrami constant for block copolymers containing 2-20 wt.% PBT were found to be in 1.1-1.2 range. Two values of Avrami constant were obtained for PET homopolymer and block copolymer containing 1 wt.% PBT. In the initial stages of crystallization value was about 0.9 in the later stages it was about 2.5. Explanation for deviation from predicted values is given.

Light scattering studies were carried out in order to observe the role of PBT in the crystallization of block copolymers. In the initial stages of crystallization of the block copolymer, a four lobe light scattering pattern with lobes along the polarizer directions was observed which is typical of PBT at similar crystallization condition. This indicates that PBT component crystallizes first. These types of pattern changed to the four lobe

pattern with lobes at 45° to the polarizer directions in the later stages of crystallization which is typical of PET. Thus, it has been proposed that in a block copolymer of PET and PBT, PBT crystallizes first and then acts as nuclei for the PET component to crystallize. The spherulite size increased as a function of time while the ultimate spherulite size decreased with an increase in PBT content.

Fibres from these block copolymers were melt spun. These fibres showed good mechanical properties comparable to that of PET homopolymer fibre. The decrease in tensile strength with the incorporation of PBT was not very significant. Fibres from block copolymers containing 3.5 and 5.0 wt.% PBT could not be drawn as they were highly crystalline. The drawn block copolymer fibres showed lower crystallinity and orientation compared to that of drawn PET homocopolymer fibre.

The effect of incorporation of amorphous polyamide on the crystallization behaviour of polyester was studied in a commercial polyester-polyamide block copolymer. The polyamide component was a reaction

product of a C_{36} dicarboxylic acid and hexamethylene diamine. The crystallization rate of the copolymer was found to be lower than that of PET. It was proposed that polyamide part does participate in spherulite formation during crystallization as evidenced by polarizing microscopy.

In another short study PBT was crystallized from its amorphous glassy state. The morphology and properties were studied by X-ray diffraction technique, density measurements, tensile testing, and small angle light scattering. The samples remained transparent after crystallization was over. No superstructure was observed by polarizing microscopy and light scattering. Tensile strength and crystallinity increased with the temperature of crystallization.

The effect of stress-induced crystallization of PET on the superstructure produced and other properties were studied by stretching the PET films at different rates to different draw ratios at 80°C. A semi-automatic structure was fabricated for this purpose. These samples were characterized by light scattering, birefringence, X-ray diffraction and

crystallinity measurements. Light scattering studies showed that the superstructure produced on stretching was rod-like. At low draw ratios, these rods were preferentially oriented perpendicular to the stretching direction while at high draw ratios they were oriented in the direction of stretching. Annealing at constant length did not change the superstructure produced upon drawing. The orientation and crystallinity were higher in the samples stretched at higher rate of drawing.

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