STUDIES ON STRUCTURE, MORPHOLOGY AND FIBRILLATION BEHAVIOUR OF HIGH-DENSITY POLYETHYLENE AND BLENDED TAPES

by

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.....to my beloved parents

CERTIFICATE

This is to certify that the thesis entitled "**STUDIES ON STRUCTURE, MORPHOLOGY AND FIBRILLATION BEHAVIOUR OF HIGH-DENSITY POLYETHYLENE AND BLENDED TAPES**" being submitted by **Mr. S. Mahajan**, 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. Mahajan has worked under my guidance and supervision and 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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(S. Mahajan)

ABSTRACT

The studies reported in this thesis have been made on uniaxially oriented tapes produced from high-density polyethylene (HDPE), polypropylene (PP), and blends of HDPE with various types of ethylene copolymers. These include high molecular weight polyethylene (HMWPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), ethylene-vinylacetate (EVA), ethylene-propylene-diene terpolymer (EPDM), and ethylene- propylene block copolymers (EP_bC). The study of drawn tapes is mainly concerned with the inter-relationships between structure, morphology and properties with special emphasis on fibrillation behaviour. The tapes used for these studies were produced on a single stage extrusion-stretching-winding unit at 10 m/min. These tapes were uniaxially stretched to various draw ratios and at different temperatures. Structure and morphology of these tapes are studied, which include (i) characterization of crystalline and amorphous phase morphology, (ii) thermal shrinkage behaviour of tapes at elevated temperatures, (iii) static mechanical and dynamic mechanical behaviour, and (iv) tearing strength and fibrillation tendency.

The study led to some interesting insights into the interaction between fibrillation behaviour and structure of amorphous phase particularly the strong dependence of fibrillation tendency on molecular orientation and fraction of amorphous phase. To gain an understanding of this phenomenon at gross morphological level, the structure and morphology of both crystalline and amorphous phases were characterized in terms of fine structure of crystallites, crystallite orientation, amorphous phase orientation and fraction of amorphous phase with the help of small-angle X- ray scattering (SAXS), polarizing microscopy, and wide-angle X-ray diffraction (WAXD). Some additional aspects relating to gross fibrillar structure of oriented tapes were also studied. These include,

determination of void parameters such as, void dimensions in equatorial and meridional directions, volume fraction of voids and void number density per unit volume of tape with the help of combination of SAXS, density, and differential scanning calorimetry (DSC) analyses. The fibrillation process and fracture surface morphology of drawn tapes were also studied with the help of scanning electron microscopy (SEM). Combining results of these studies with the morphology of crystalline and amorphous phases of oriented tapes, an effort has been made to understand the nature of crack initiation, crack propagation and final fracture of oriented tapes in tearing, as well as, in combined tension-twist mode.

A summary of the principal features of the investigations made and the main findings are given below.

The influence of molecular structure of ethylene copolymers on crystallization behaviour, structure- morphology and mechanical properties of HDPE/ethylene copolymer blends of 90:10 blend composition have been investigated. The tensile drawing study of undrawn tapes show an enhanced strain hardening and a consistent reduction in natural, as well as, maximum draw ratio with increase in molecular irregularity of different ethylene copolymers. It is observed that blends are partially miscible in amorphous phase. Ethylene components of copolymer form cocrystalline phase with HDPE. The lateral crystallite thicknesses, crystallinity and amorphous phase orientation of blends consistently decreases with increase in molecular irregularity of ethylene copolymers. This relates to large scale change in crystallization and drawing behaviour of HDPE in the blends. It is stipulated that molecular network exerts an important influence on physical and mechanical properties of undrawn and drawn tapes.

The oriented tapes prepared from HDPE/PP and HDPE/EP_bC are incompatible at higher blend composition range. This is supported by the presence of two β-relaxation

peaks each of PE and PP in the dynamic mechanical spectra of these blends. The two peaks however, merge into a very broad, single relaxation peak at low blend compositions (9 and 18% blends), indicating partial miscibility and compatibility of blend components. Variation of blend composition significantly affects the melting and crystallization temperature, crystallinity, crystallite dimensions, crystallite and amorphous phase orientation of blend components, which in turn, affects the mechanical properties of undrawn and drawn tapes. A relatively simple method to estimate the amorphous phase orientation of blends is also proposed.

The tear energy (G_c) required to propagate a tear along the direction of molecular orientation show a direct relation with amorphous phase orientation, fraction of amorphous phase, void size in meridional direction and volume fraction of voids. The decrease in G_c with increase in molecular orientation and crystallinity of tapes is due to the formation of large number of axially elongated voids at interfibrillar regions and decrease of viscous flow occurring in the vicinity of propagating crack tip. Large increase (15 to 45%) in G_c, was obtained for HDPE blended tapes containing about 10% EVA, EPDM and EP_bC. This is related to the extensive interfibrillar molecular network, improved interfibrillar adhesion and an increase in fraction of amorphous phase.

The fibrillation behaviour (axial splitting tendency) of drawn tapes was characterized by combined tension-twist fibrillation test. This is a new test proposed for determination of fibrillation strength. It was found that increase in amorphous phase orientation and crystallinity of tapes systematically decrease the fibrillation strength and fibrillation toughness as a consequence of deterioration in interfibrillar adhesion and formation of large number of axially elongated voids at interfibrillar regions. General models to explain this phenomenon via microcrack formation, interfibrillar shearing process and failure are proposed.

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