MICROSTRUCTURE-PROPERTY CORRELATIONS IN POLYOLEFIN LENDS

by

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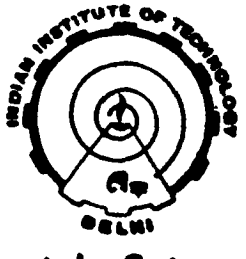

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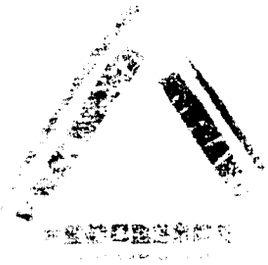

CERTIFICATE

This is to certify that the thesis entitled "MICROSTRUCTURE-PROPERTY CORRELATIONS IN POLYOLEFIN BLENDS" being submitted by Mr. H.S. Varma to the Indian Institute of Technology, Delhi, for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by him. Mr. H.S. Varma has worked under our guidance and supervision and has fulfilled the requirements for the submission of this 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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(Harendra Singh Varma)

ABSTRACT

The main objective of the present work was to study the effect of microstructure on properties of polyolefin blends. Considerable variation in physical structure of polymers (i.e. orientation, degree and character of crystallinity) takes place by variation in processing conditions such as temperature, retention times, external and internal forces etc. It was therefore considered of interest to investigate the effect of these variables on (a) flow behaviour (b) microstructure and (c) properties of polyolefin blends.

The polyolefin binary blends of PP/HDPE, PP/EPDM, HDPE/EPDM and ternary PP/HDPE/EPDM blends were investigated. Ethylene-propylene-diene terpolymer (EPDM) of two different grades viz., NORDEL-1560 and NORDEL-2760 from DuPont company were used as such. These rubbers have been designated as rubber A (Nordel-1560) and rubber B (Nordel-2760) respectively. The ethylene content of these two rubbers as determined by FTIR technique (ASTM D-3900) was found to be approximately 80%. The specific gravity and Mooney viscosity, ML (1+4) [121°C] were 0.85 and 60 $\pm$ 6 respectively for Nordel-1560. The binary and ternary blends were prepared by melt blending using a single screw extruder. The composition of PP/HDPE blends (PPE) was varied as 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70 and 20/80. These

polyolefin blends have been disignated as PPE and the HDPE content in these PPE blends is indicated by writing the appropriate subscript. For example PP/HDPE blends containing 10% and 25% (w/w) of HDPE have been designated as PPE_{10} and PPE_{25} respectively. The blends of PP with rubber A or B (PPA and PPB) and HDPE with rubber A or B (EA and EB) were also prepared by varying rubber content from 5, 10, 15, 20, 25 and 30% (w/w). The effect of higher rubber content on the properties of HDPE/rubber B (EB) blends was also studied by increasing the wt. % upto 60. The rubber content in these binary blends is indicated in a similar manner as described for PP/HDPE blends. In the preparation of ternary (PP/HDPE/rubber A or B) blends (PPEA or PPEB), PP/HDPE ratio was kept at 90/10 and the rubber content was varied from 5 to 25% (w/w).

Effect of temperature, shear stress and die geometry (L/D ratio) of capillary on the flow behaviour of polyolefin blends was investigated. Effect of rubber concentration on melt viscosity of PP and HDPE was studied at L/D 20 and at 180°, 200° and 215°C. A decrease in melt viscosity was observed on addition of an optimum concentration (5%) of rubber B to HDPE at 200°C and 215°C. However, at 180°C the viscosity increased with increasing rubber B content in EB blends. On the other hand addition of rubber B to PP resulted in an increase in melt viscosity at all rubber concentrations at 200°C. The melt elasticity

In the ternary PPEA and PPEB blends, at L/D 20 and L/D 33 and below a shear stress of 14×10^5 dynes/cm^2, a significant decrease in the melt viscosity of PPE_{10} blend was observed on addition of 5-10% of rubber A or B. On the basis of these results it could be deduced that rheological characteristics of a two or three phase polymer blend depended on the viscosity of the constituting polymers, deformability of droplets that may be present in the matrix polymer, die geometry (L/D ratio) of capillary and on the magnitude of temperature and shear stress. Etched surfaces of extrudates of PPB blends revealed that as the rubber B concentration increased from 5 to 30%, the number and size of rubbery inclusions increased. Addition of rubber A or B to PP resulted in a skin - core morphology of injection molded specimens. Addition of rubber A or B to HDPE resulted in a very fine dispersion of impact modifier in the HDPE matrix. In EA or EB blends there was no clear cut distinction between skin - core morphology in the injection molded specimens. On addition of rubber A or B to the binary PPE_{10} blend, composite rubber- HDPE particles within a PP matrix was indicated in the micrographs. This gave a very characteristic morphology to the ternary PPEA or PPEB blends where rubber A or B and HDPE had an affinity for each other and HDPE particles were surrounded by a rubber shell.

The most important conclusions from the micrographs of PPE_{10} blend was the very strong influence of HDPE in reducing the average spheulite size of PP. Addition

of rubber B to PP resulted in an increase in the average spherulite size up to 10%. In PPB blends the rubber was dispersed in droplet like domains both in the intra spherulitic as well as inter spherulitic regions. EB blends containing upto 40% of rubber B showed little change in the crystalline structure of HDPE except for the increased sharpness or perfection of crystalline structure.

In the DSC scan of PPE_{10} blend, presence of two distinct endothermic transitions corresponding to the melting peaks of HDPE and PP were observed, thereby indicating incompatibility of PP and HDPE homopolymers. Addition of low percentages of HDPE or rubber B to PP resulted only in a marginal change in T_c and T_m. However increasing the percentages of rubber in binary blends of PP resulted in a decrease in T_m. Addition of 5% of rubber B to HDPE resulted in an increase in T_m, T_c, the rate of crystallization and nucleation of HDPE. The higher T_m and T_c's of EB blends could be explained on the basis of the ability of EPDM copolymers to dissolve and extract from HDPE most of the defective chains to give more perfect crystallites. Further increase in rubber content (10 to 40% (w/w)) in the EB blends resulted in a decrease in T_m and T_c but still these were higher than the pure HDPE homopolymer. Results of x-ray diffraction measurements indicate that % apparent degree of crystallinity (X_c) of PPE_{10} blend was marginally higher than PP. A slight

increase in the % X_c was observed by addition of rubber B to HDPE upto 25%. Further increase of rubber content resulted in a decrease in overall crystallinity. In PPA, PPB and ternary PPEA blends increase in rubber content led to a decrease in % X_c.

The Young's modulus and Izod impact strength of PPE_{10} blend was higher than that calculated by the rule of mixtures, showing thereby a synergistic effect. Addition of HDPE to PP result in a decrease in tensile strength (at yield) and the decrease was proportional to the HDPE content. The elongation at break also decreased by addition of HDPE upto 50%. Further increase in HDPE resulted in an increase in Elongation at break in PPE blends. Incorporation of rubber A or B in HDPE or PP up to 30% resulted in a significant increase in impact strength. Increase in rubber content to more than 50% in the binary EB blends resulted in thermoplastic elastomers. Percent elongation at break increased on increasing the rubber content in PP or HDPE/rubber blends. Tensile yield strenth and Young's modulus decreased upon incorporation of rubber in PP up to 30%. About 22 and 15% increase in tensile yield strength was observed by addition of 5 and 10% of rubber B to HDPE respectively.

In DMA scan of PPE_{10} blend three well defined loss modulus maxima at -124°, -110° and 32°C were observed. The

main glass transition peaks γ -transition in HDPE (-92°C) and β -transition (25°C) shift away from each other thereby indicating the incompatibility of PP and HDPE. PPA and PPB blends were also found to be incompatible.

In both EA and EB blends containing lower percentages of rubber i.e., up to $\sim$ 10%, an increase of α-peak temperature of pure HDPE homopolymer was observed indicating that HDPE lamellae thickness might have increased at these compositions. Increase of rubber A or B content to 30% decreased the α-peak temperature indicating a decrease in the HDPE lamellae thickness. The broadening and somewhat splitting of the main T_g peak of HDPE (γ-transition) in EA or EB blends indicated some mixed phase formation.

In DMA scans of PPEA or PPEB blends an increase in the width (broadening) of main T_g relaxations of PP, HDPE and rubber A or B was observed which is an evidence for the existence of some mixed phase formation in PPEA or PPEB blends. Thus, incorporation of rubber A or B to an incompatible binary PPE_{10} matrix resulted in improved adhesion and miscibility between PP and HDPE components.

Effect of exposure of PP, PPE_{10} and PPEA blends to uv light on structural changes in the polymers was investigated using FT-IR technique. An increase in carbonyl

content due to photo-oxidation was observed in all polymer samples. However, the extent of such an oxidation was highest in PPE_{10} blend, followed by PP and ternary blends containing 5-10% of rubber A were found to be the most stable. A mechanism has been proposed to account for these observations.

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