Blend of High-Density Polyethylene and a Linear Low-Density Polyethylene with Compositional-Invariant Mechanical Properties

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ABSTRACT : This article presents the tensile properties and morphological characteristics of binary blends of the high-density polyethylene (HDPE) and a linear low-density polyethylene (LLDPE). Two constituents were melt blended in a single-screw extruder. Injection-molded specimens were evaluated for their mechanical properties by employing a Universal tensile tester and the morphological characteristics evaluated by using a differential scanning calorimeter and X-ray diffractometer. It is interesting to observe that the mechanical properties remained invariant in the 10–90% LLDPE content. More specifically, the yield and breaking stresses of these blends are around 80% of the corresponding values of HDPE. The yield elongation and elongation-at-break are around 65% to corresponding values of HDPE and the modulus is 50% away. Furthermore, the melting endotherms and the crystallization exotherms of these blends are singlet in nature. They cluster around the corresponding thermal traces of HDPE. This singlet characteristic in thermal traces entails cocrystallization between these two constituting components. The clustering of thermal traces of blends near HDPE meant HDPE-type of crystallites were formed. Being nearly similar crystallites of blends to that of HDPE indicates nearness in mechanical properties are observed. The X-ray diffraction data also corroborate these observations. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2604–2608, 2002

Keywords: high-density polyethylene; mechanical properties of polyethylene; polyethylene blend; property-morphology correlation

INTRODUCTION

Blending of polymers most often result in the alteration of properties.[1–3] In a binary system, the mechanical properties of blends generally vary between the properties of two pure polymers. It is also common to encounter the properties of a blend that may be quite better or inferior than both the polymers. If the properties of blends remain constant at least for some composition range, it provides a greater dependence of properties in designing a blend. These blends could be exploited toward economical advantages.[4,5] Such blends of high-density polyethylene (HDPE) and a linear low-density polyethylene (LLDPE) are presented here which show almost constant mechanical properties irrespective of their composition, particularly in the range of 10–90% LLDPE. Furthermore, the properties of these blends are close to the superior constituent (i.e., the HDPE). The reasons for their maintenance of mechanical

Table I   Characteristic Properties of HDPE and LLDPE

Properties	HDPE	LLDPE
Intrinsic viscosity (dL/g, in decalin at 115°C)	1.100	1.597
Melt flow index (g/10 min)	0.75	0.75
Density (g/mL)	0.952	0.921
Melting temperature (°C)	131.0	126.7
Crystallization temperature (°C)	114.2	107.8
Tensile yield strength (MPa)	24.5	10.0
Number of CH3 per 100 carbon atoms	1.81	3.11

properties to the near viscinity of HDPE are explored.

EXPERIMENTAL

Materials

HDPE (Hostalen GF 7745F) used was a product of Polyolefin Industries Ltd., Bombay, India. A haxene-based commercial-grade LLDPE obtained from the local market was used for this study. Some important characteristic properties of these two polymers are listed in Table I.

Sample Preparation

Thoroughly tumble-mixed HDPE and LLDPE granules in appropriated compositions were melt mixed in a single-screw extruder (Betol 1820, L/D ratio = 17) with a screw speed of 22 rpm. The temperature profile was kept at 160°C at the feed zone, 200°C at the compression zone, and 210°C at the metering zone and die end. The extruded strands were cooled in water at 30°C and subsequently granulated after allowing a maturation time of 8 h. Tensile specimens were prepared by injection-molding techniques (Windsor SP-30, India) from these granulated blends and pure polymers at 300 kg/cm^2 injection pressure, 3 and 5 s of injection and cooling times, respectively, maintaining an identical temperature profile to that of blending extruder. The injection-molded specimens were powdered to carry out differential scanning calorimeter (DSC) and X-ray diffraction experiments.

Measurements

Tensile Properties

The tensile measurements were made on a Universal testing machine (Instron 4202, USA) at a gauge length of 50 mm and cross-head speed of 5 mm/min. An average of five data points is reported here as the data for a particular blend composition.

Thermal Properties

The crystallization exotherm and melting endotherm were recorded on a DSC (Perkin–Elmer, DSC-7 system, USA) at heating and cooling rates of 10°C/mm in a nitrogen blanket. About 10 mg of powdered sample was used in all the cases. The samples were first run through a heating cycle from ambient temperature to 160°C. After allowing an elapse time of 2 min at 160°C, the samples were run through a cooling cycle. The heating and cooling traces reported here were the curves that normalized against the sample weight. The peak temperature of the crystallization exotherm is defined as the crystallization temperature and the slope at the hither temperature side of the curve, representative of the rate of crystallization. The degree of crystallization is calculated from the heat of crystallization, taking the heat of crystallization for 100% crystalline and polyethylene as 65 cal/g.

X-ray Diffraction

The X-ray diffraction measurement was carried out on a Rigaku diffractometer, Japan, using Ni-filtered Cu K$_\alpha$ radiation at a scanning speed of 5% in the 2θ range of 5–40°. The d-spacing and crystallite size were calculated as per the procedure described in ref. 6.
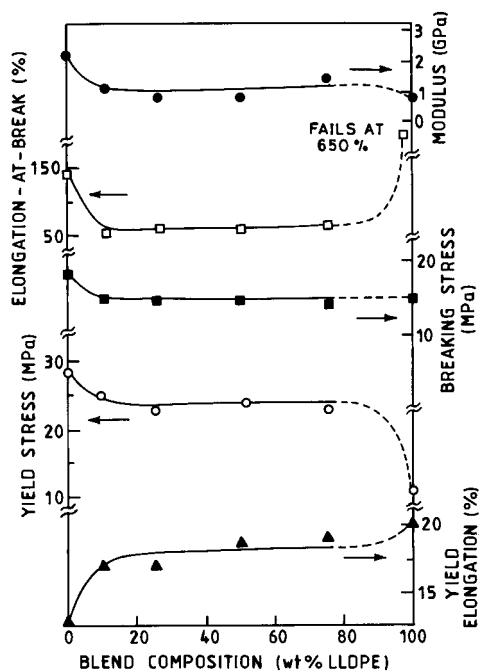
RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the variation of yield strength, yield elongation, breaking stress, elongation-at-break, and modulus with blend composition. It is clearly discernible from Figure 1 that these properties rapidly attain plateaus around 10% LLDPE content, followed by maintaining them at that level up to 90% of LLDPE content. A sharp change in properties is assumed in the 90–100% LLDPE-containing range by obeying the behavior of the 0–10% LLDPE-containing blend and is represented by a dotted line. Quantitatively, the field stress and breaking stress of these blends attain a plateau at 80% of HDPE values, which are 24.5 and 11.5 MPa, respectively. The plateaus yield
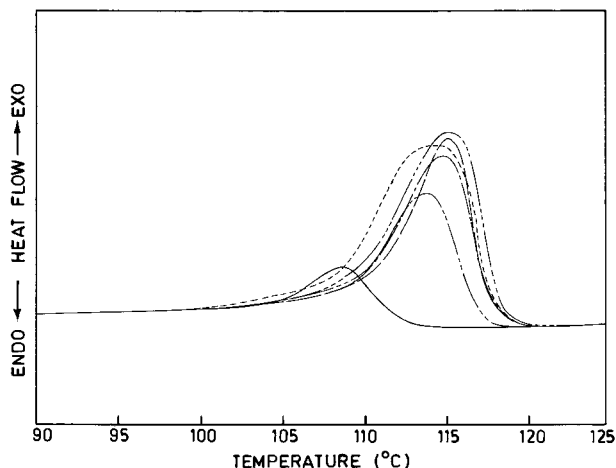
elongation and elongation-at-break are at about 65% of HDPE values where the corresponding values are 12.5 and 140%, respectively. The plateau modulus is just 50% away from HDPE modulus. Although these mechanical properties of blends are quite close to that of HDPE, a distinct nearness could be seen by comparing the elongation-at-break of these blends to that of HDPE and LLDPE. The elongation-at-break of LLDPE is furthest at 92% away, whereas it is just 65% from HDPE.

DSC Study

The crystallization exotherm (CE) of blends and their parent components are shown in Figure 2. The shape and size of these CE are unique and they all are singlet in nature. The CE of LLDPE is the smallest and is a distance apart in the temperature axis from CE of blends and that of HDPE. The CE of blends varies in close proximity to the CE of HDPE, although their size varies systematically with the increase in LLDPE content. The melting endotherms (ME) qualitatively present similar features to that of CEs except that the ME of LLDPE is a bit broad and possesses a hump in it. This hump perhaps arises out of the presence of defective crystallites. The incorporation of HDPE in the blend helps prevent the formation of such crystallites.


Figure 2 Crystallization exotherms of HDPE/LLDPE at various compositions (wt % LLDPE): - - - (0%), - - · · · - - (10%), − − − (25%), − · − · − (50%), − · · − · · (80%), — (100%).

The variations in quantitative CE parameters [i.e., crystallization temperature (T_c), half-width, rate of crystallization (R_c), and crystallinity against blend composition] are shown in Figure 3. The T_c and R_c maintain almost constant values up to the 90% LLDPE content, followed by a sharp drop. However, the crystallinity shows an

**Figure 1** Plot of various tensile properties as a function of LLDPE content.
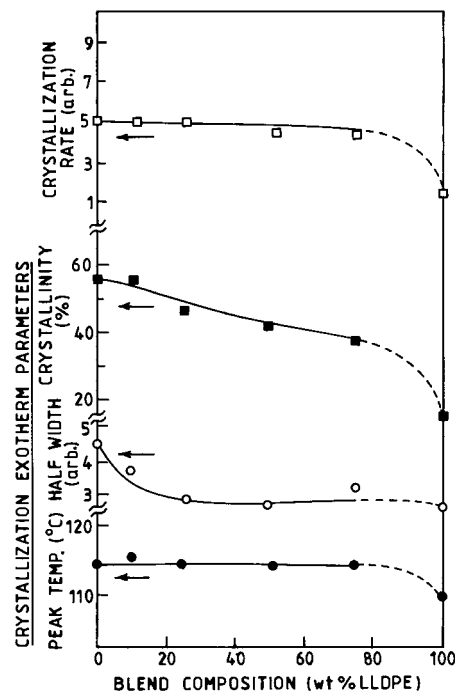
Figure 3 Plot of various crystallization parameters as a function of LLDPE content.

approximately linear decrease with the increase in the LLDPE content.

The effects of LLDPE in the blends of HDPE as discernible from the CE parameters are as follows. It reduces the crystal size distribution of HDPE and attains the crystal size distribution of LLDPE (i.e., half-width maintains LLDPE value throughout the composition). The average size of the crystallites of HDPE is maintained (i.e., the T_c remains constant all through the composition). However, the crystallinity reduces considerably with the increase in LLDPE content. Thus, the total number of crystallites decreases in the blends with the increase in LLDPE content.

The rate of crystallization is invariable up to 90% LLDPE content (see Fig. 4) and a sharp drop of it is seen thereafter. The close proximity to the rate of crystallization to the HDPE means that the HDPE type of crystallization dominates in the blend. The faster growing crystallites of HDPE-trapping nuclei of LLDPE,[7] constituting HDPE-like polyethylene segments in their growth process, could well explain the formation of HDPE-type crystallites. As these crystallites are formed because of an unperturbed segment of ethylene sequence (i.e., HDPE-like segments) free from crystalline difects, no hump is seen in the melting endotherm of blends. Furthermore, these crystallites are made up of similar compositions due to the picking up of similar chain segments for their formation. Therefore, these blends show similar mechanical properties irrespective of their composition.
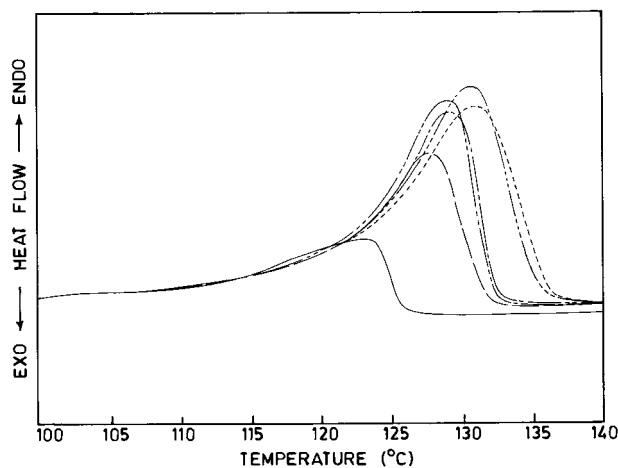
Figure 4 Melting endotherms of HDPE/LLDPE at various compositions (wt % LLDPE): - - - (0%), - - ·· · - - (10%), − ·· − (25%), − · − (50%), − − − (80%), — (100%).
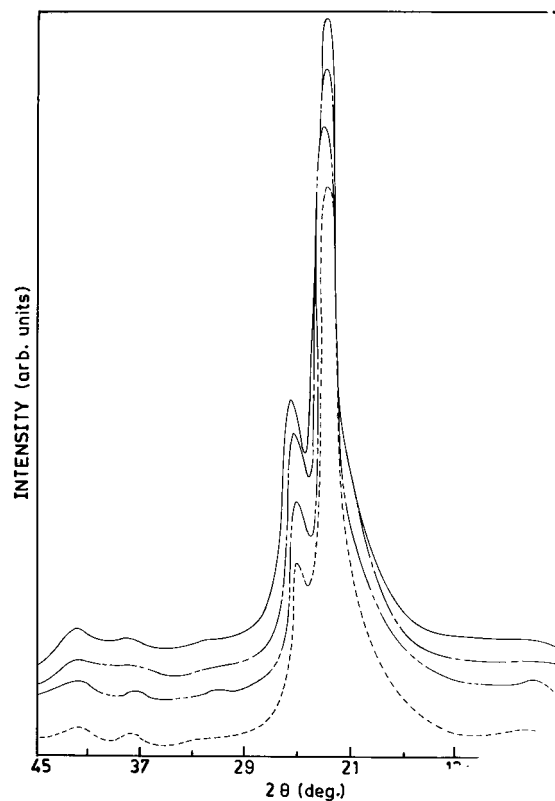

Figure 5 X-ray diffraction pattern of HDPE (—), LL-DPE (− − −), 25% (− · −), and 50% (− ·· −) LLDPE-containing blends.

X-ray Study

Figure 5 presents the X-ray diffraction pattern of HDPE, LLDPE, and two of their blends with 25 and 50% LLDPE contents to avoid overcrowding of curves. These curves show similar features with two strong and sharp reflections at $2\Theta = 21.4°$ and $2\Theta = 24°$ corresponding to (110) and (200) planes, respectively. The shoulder at $2\theta = 19°$ is not seen in the diffraction pattern of HDPE in this case, which was reported earlier.[8]

The d-spacing and crystallite size are plotted in Figure 6 against blend composition. The d-spacings slightly increased on the addition of LLDPE and maintained their value up to 90% LLDPE control. A break in the d-spacings in the 90–100% range of LLDPE could be clearly seen from Figure 6. Such a feature is also apparent from the plot of crystallite size against blend composition, although an increase in crystallite size is noted. The maintenance of d-spacings and crystallite size of the HDPE level despite the increased addition of LLDPE many be viewed as the participation of those polyethylene segments of LLDPE which
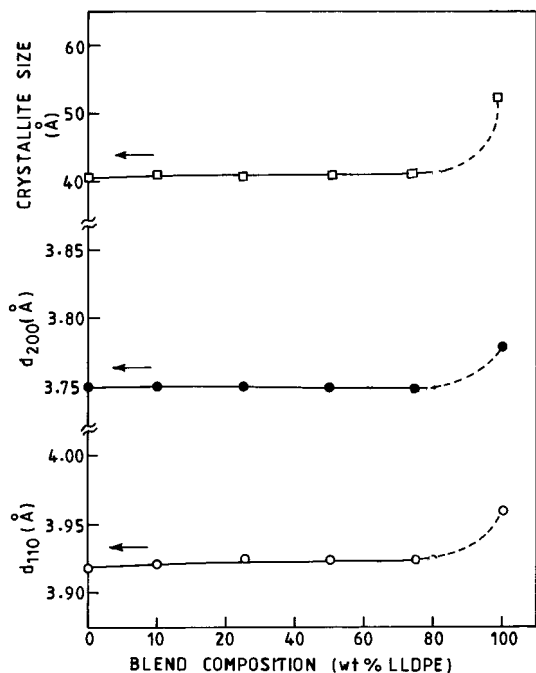
Figure 6 Plot of d-spacing and crystallite size as a function of LLDPE content.

tightly conform in the HDPE polyethylene chain segment undergoing crystallization.

CONCLUSION

The blends of HDPE and LLDPE show strikingly close mechanical properties of mechanically superior constituent HDPE. The yield stress and breaking stress of blends attain 80% of the respective values of HDPE around 10% LLDPE content and maintain that value up to the extent of 90% LLDPE content, followed by a sharp drop. Such plateaus are seen for most of the mechanical properties in the 0–90% LLDPE content. The plateaus of yield elongation and elongation-at-break are about 65% of the HDPE value, whereas the plateau modulus is just 50% away.

The crystallization exotherm and X-ray diffraction characteristics suitably explain the nearness of mechanical properties to the HDPE of blends for the major composition range.

It is observed that the HDPE type of crystallites with almost similar composition irrespective of the blend composition is responsible for manifesting composition-invariant mechanical properties. The faster rate of crystallization and higher crystallization temperature are perhaps conducive to forming HDPE-type crystallites in the blend. The faster growing HDPE crystallites trapped unperturbed polyethylene chain segments of LLDPE and formed HDPE-type crystallites. The composition of HDPE-type crystallites remain the same all through the composition because of the fact that only linear chain segments participate in crystallization and do not manifest compositional-dependent mechanical properties. Probably the crystalline defects in LLDPE get eliminated because of the formation of HDPE-type crystallites forming at a higher temperature, which prefer selecting linear ethylene sequences. Consequently, the melting endotherm of blends are free of hump.

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