Flexural and Impact Properties of High-Density Polyethylene/Linear Low-Density Polyethylene Blend

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SYNOPSIS

In this article, a study of flexural and impact properties of binary blends of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), over a full range of blending ratios, is presented. The property distinctions in the three ranges of composition (viz., HDPE-rich blend, LLDPE-rich blend, and the middle region) are remarkable and consistent with the different effects of cocrystallization in the respective concentration ranges. Furthermore, the analysis of flexural yield properties data, in terms of the Ree–Eyring equation, and the correlation of results with variation of x-ray crystallinity are presented, which suggests the existence of two types (i.e., mobile and immobile) of segments in the amorphous phase of the blend. The relative variation of these two types of amorphous phase in the three different composition ranges of the blend are discussed. The impact strength variation of this blend is also found to correlate with the variation of the fraction of amorphous phase in the blend. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

LLDPE has received wide commercial acceptance due to the easy alteration of its properties by changing the types of comonomer used (i.e., butene, pentene, octene, etc.) and/or their proportion in the polyethylene molecular chain. Recent reports about the ability of LLDPE to cocrystallize with a number of grades of polyethylene[1-4] open up an area of research where cocrystallization-induced property improvement is of value. Furthermore, the phenomenon of cocrystallization of LLDPE, with high-density polyethylene (HDPE), can be exploited industrially for engineering materials with properties suitable for various end-uses. In our previous publication,[4] some observations were reported regarding the variation of crystallite size, d-spacing and crystallinity due to the cocrystallization of the blend of LLDPE and HDPE as a function of blend composition. A subsequent study[5] of the tensile properties of this blend shows the trends of the variations of tensile properties with the blend composition being

accountable in terms of the variation of the cocrystalline phase.

In this article, we report the studies on flexural and impact properties of binary blends of HDPE and LLDPE over the entire range of blend composition.

EXPERIMENTAL

Materials

HDPE (Hostalene GF 7745F), a product of Polyolefin Industries Ltd., Bombay, having a melt flow index of 0.75 g/min, a density of 0.952 g/cc, and a melting temperature of 131°C, was used. LLDPE (Dowlex 2704E), a product of Dow Chemicals, was an octene-based copolymer, having a melt flow index of 1.00 g/min, a density of 0.924 g/cc, and a melting temperature of 126°C.

Sample Preparation

Tumble-mixed chips of HDPE and LLDPE were melt mixed in a single screw extruder with a temperature profile of 160, 200, and 210°C at the feed

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zone, at the compression zone, and at the die end, respectively. The extruded strands were cooled in water at 30°C and were chopped after 8 h maturation time. Test specimens were prepared by injection molding on a Windsor SP-30 injection molding machine at 300 Kg/cm² injection pressure, with 3 and 5 seconds of injection and cooling times, respectively, followed by cooling at ambient temperature. All the specimens were conditioned according to ASTM D 638. Tests were conducted at 23 ± 2°C. The sample geometries conformed to ASTM D 790 for flexural and ASTM D 256 for impact tests.

Measurements

Flexural measurements were made by the 3-point bending method on a universal testing machine (Instron 4202), at 100 mm span length, and crosshead

speeds 5, 25, 50, and 100 mm/min. Flexural stress and strain were calculated according to the standard relation[6] and flexural modulus was obtained from the initial slope of the stress–strain curve.

The Izod impact strength of notched samples was measured on suspended, hammer-type impact testing equipment FIE (042) and was expressed as the load required to break the sample.

Scanning electron micrographs were recorded on tensile fractured surfaces, using Stereoscan 360 Cambridge Instruments.

RESULTS AND DISCUSSION

Flexural Properties

Figure 1 shows the typical flexural stress–strain curves of these samples at a constant crosshead
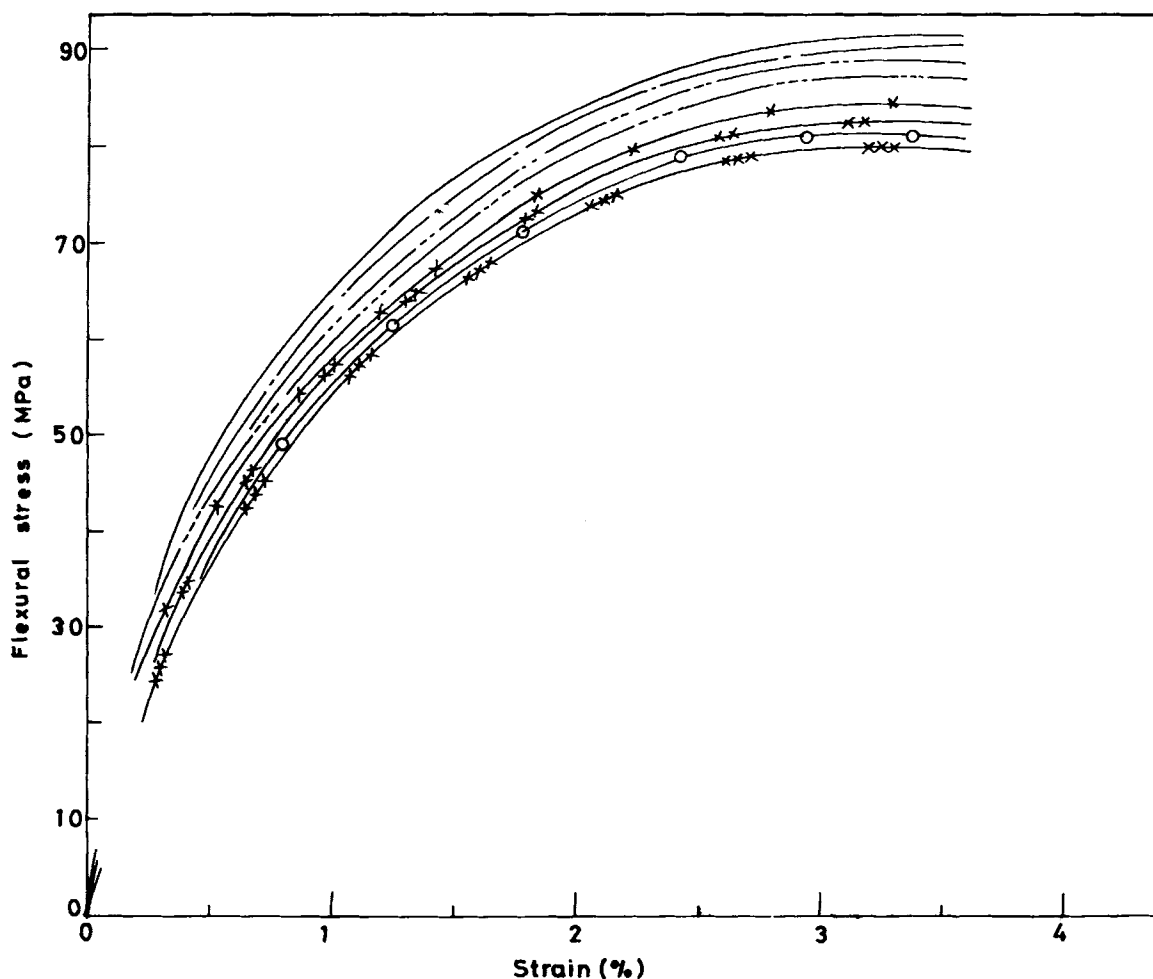
Figure 1   Flexural stress–strain curves of HDPE/LLDPE blend at various LLDPE contents (wt %): (——) 0, (— - —) 10, (— - - —) 25, (— - - - —) 35, (— X —) 50, (— XX —) 70, (— O —) 80, (— XXX —) 100.

speed 100 mm/min. The flexural strengths at yield of HDPE and LLDPE are 90 and 79.5 MPa, respectively, and that of the blend lies within these two extreme values. All the samples show yield at 2.6 to 3.4% strain.

The variations of flexural strength, at yield and modulus with blend composition, are shown in Figure 2. The variation of flexural strength, at yield with LLDPE content of the blend, is sigmoidal, implying a greater effect on the flexural yielding when the two polymers are in sufficiently large proportion, and not when any one of them is in the minority.

Flexural modulus, on the other hand, shows a rapid decrease when the LLDPE content of the blend increases from 0 to 50%, followed by a slight but continuous increase of the flexural modulus with increasing LLDPE content from 50 to 100%.

In previously reported studies of crystallization behavior[4] and tensile properties[5] of this blend, three regions of composition were identified, where the properties showed distinguishable behaviors. These three regions represent: "HDPE-rich" blend (0–30% LLDPE content), "LLDPE-rich" blend (70–100% LLDPE content), and the "middle region" of blend
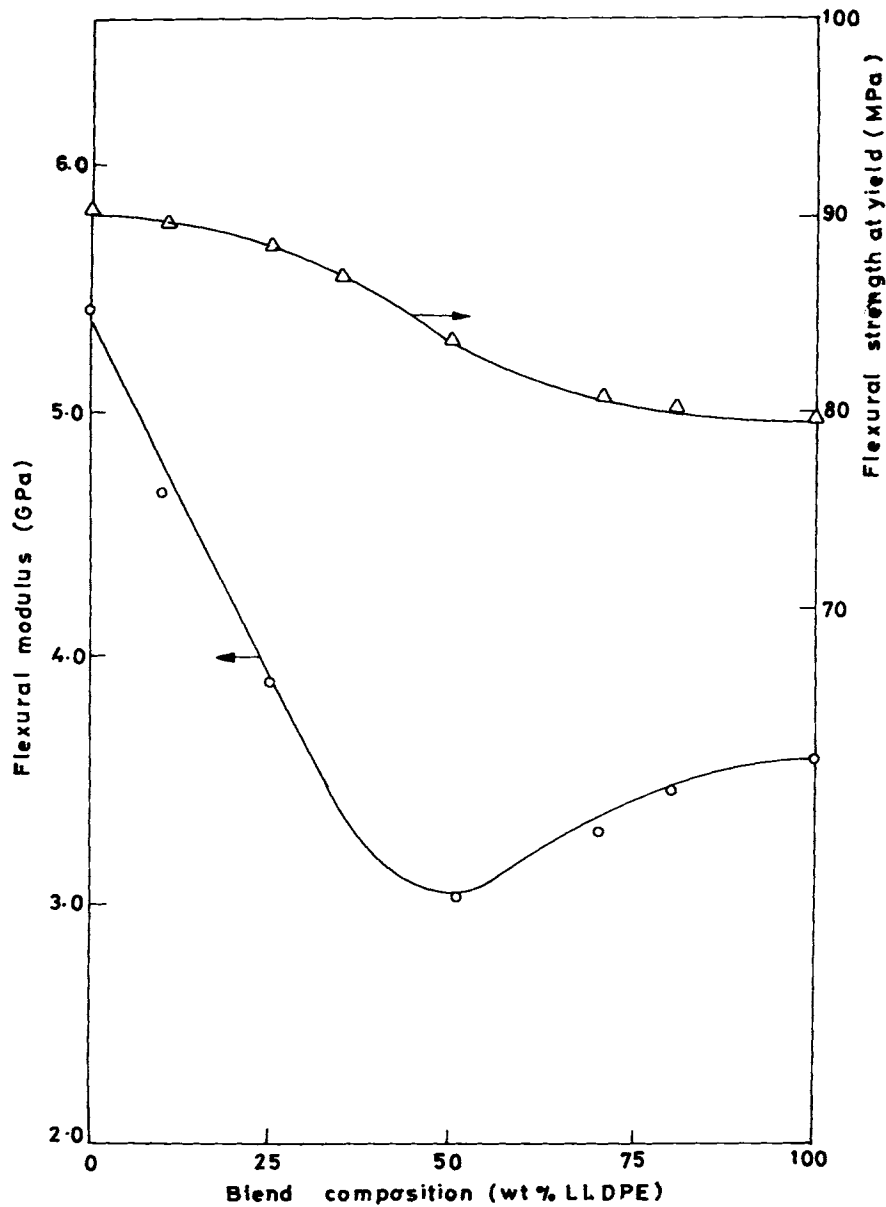

Figure 2 Variation of flexural modulus and flexural strength at yield with blend composition for the HDPE/LLDPE blend.

composition (30–70% LLDPE content). Distinction in the similar three zones of blend composition is also apparent from these results on flexural properties. In the "HDPE-rich" blend, the decrease of flexural modulus with increasing LLDPE content is rapid, while in the "LLDPE-rich" blend, the modulus is almost invariant, or shows a slight decrease, whereas in the "middle region" of blend composition, there is a reversal in the trends. However, this variation of flexural modulus with blend composition differs from the variation of tensile modulus of this blend, reported elsewhere,[5] particularly in the blend composition region of the "LLDPE-rich" blend, where the tensile modulus decreases while the flexural modulus remains almost unchanged with increasing LLDPE content. This difference of tensile and flexural properties of the LLDPE-rich blends may be attributed to the difference of deformation involved in the two cases; the flexural deformation involves both tension and compression at the same time.

Scanning Electron Microscopy

The scanning electron micrographs (Fig. 3) of the tensile fractured samples show intense interfibrillar connectivity at high LLDPE content, apparent as interfibrillar penetration. The interfibrillar connectivity may be due to their cocrystallization and may also be regarded as a reason for explaining the flexural behavior of this blend in the three regions of composition. The sharp decrease of flexural modulus in the blend composition region 0–50% LLDPE content could be attributed to (i) the addition of low modulus component, viz., the LLDPE, and (ii) the lack of interconnectivity at such low LLDPE content. As the LLDPE content increases, the interfibrillar connectivity comes into play and reverses the trend of variation of flexural modulus until it becomes almost invariable in the "LLDPE-rich" blend composition region.

The variation of flexural strength at yield with blend composition seems to suggest two different
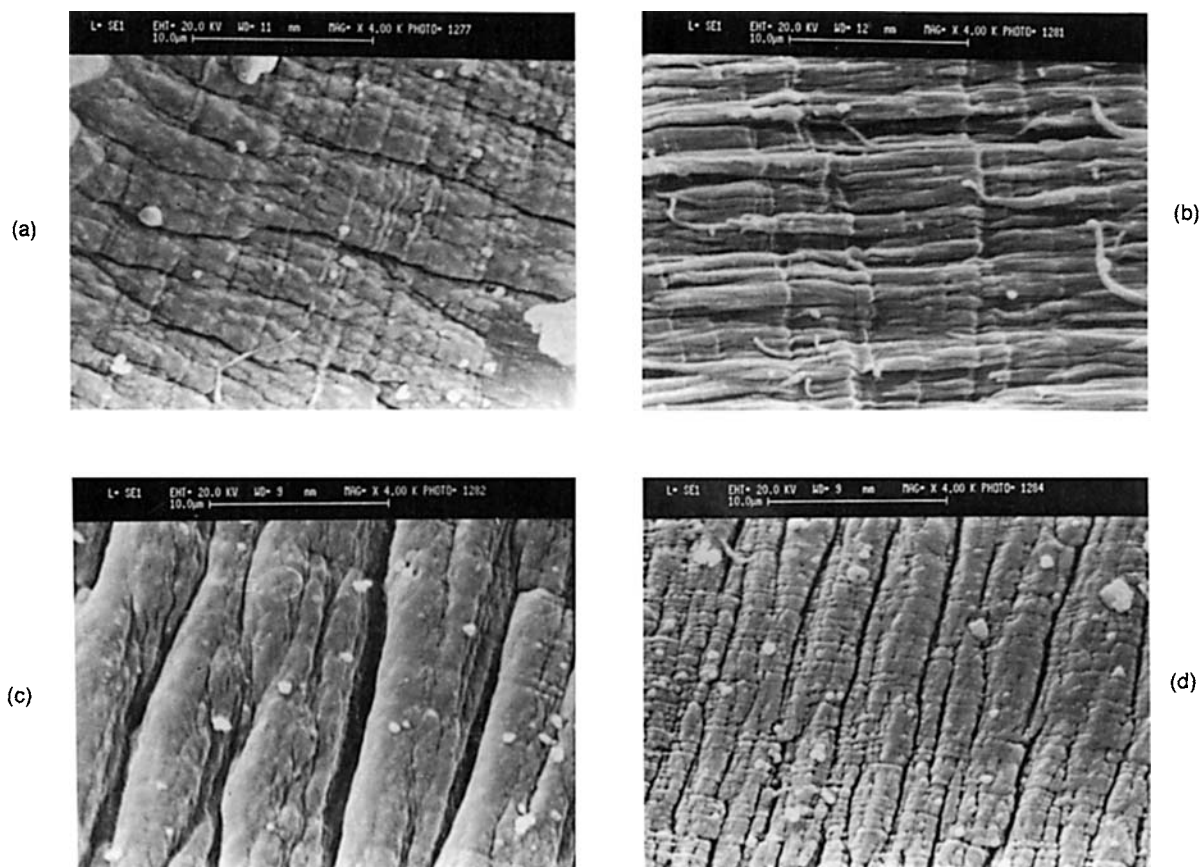
Figure 3   Scanning electron micrographs of tensile facture surfaces of the HDPE/LLDPE blend at various LLDPE contents (wt %): (a) 0, (b) 35, (c) 50, (d) 80.

types of molecular rearrangement involved in yielding in HDPE-rich and LLDPE-rich regions of the blend, both leading to an almost insignificant variation of yield stress with blend composition. The difference between the two plateau values of flexural strength at yield, at the two extreme regions of blend composition, suggests that the flexural yielding of this blend is governed by the yielding of the major component, such that the HDPE-rich blend has a higher flexural strength at yield than the LLDPE-rich blend. In the middle region, the flexural strength at yield decreases from the higher plateau value.

The effect of strain rate on the flexural properties is illustrated by the flexural stress–strain curves at different crosshead speeds, shown in Figure 4, for HDPE, LLDPE, and their 50/50 blend. In general, the flexural strength at yield and modulus are higher

at higher crosshead speed. The variation of flexural strength at yield with log (strain rate) is shown in Figure 5 for the various compositions of the blend. Analysis of these results, in terms of the Ree–Eyring equation,[7,8] leads to the following findings.

According to Ree-Eyring equation:

$$\frac{d\sigma_y}{d \ln \dot{\varepsilon}} = \frac{2\,kT}{v}$$

where, σ_y is the flexural strength at yield, $\dot{\varepsilon}$ is the strain rate, k is Boltzman constant, T is absolute temperature, and v is the activation volume. A variation of $2\,kT/v$, determined as the slope of σ_y vs. ln $\dot{\varepsilon}$ plots, as a function of blend composition, is shown in Figure 6. Also shown in Figure 6 is the variation of x-ray crystallinity values from our pre-
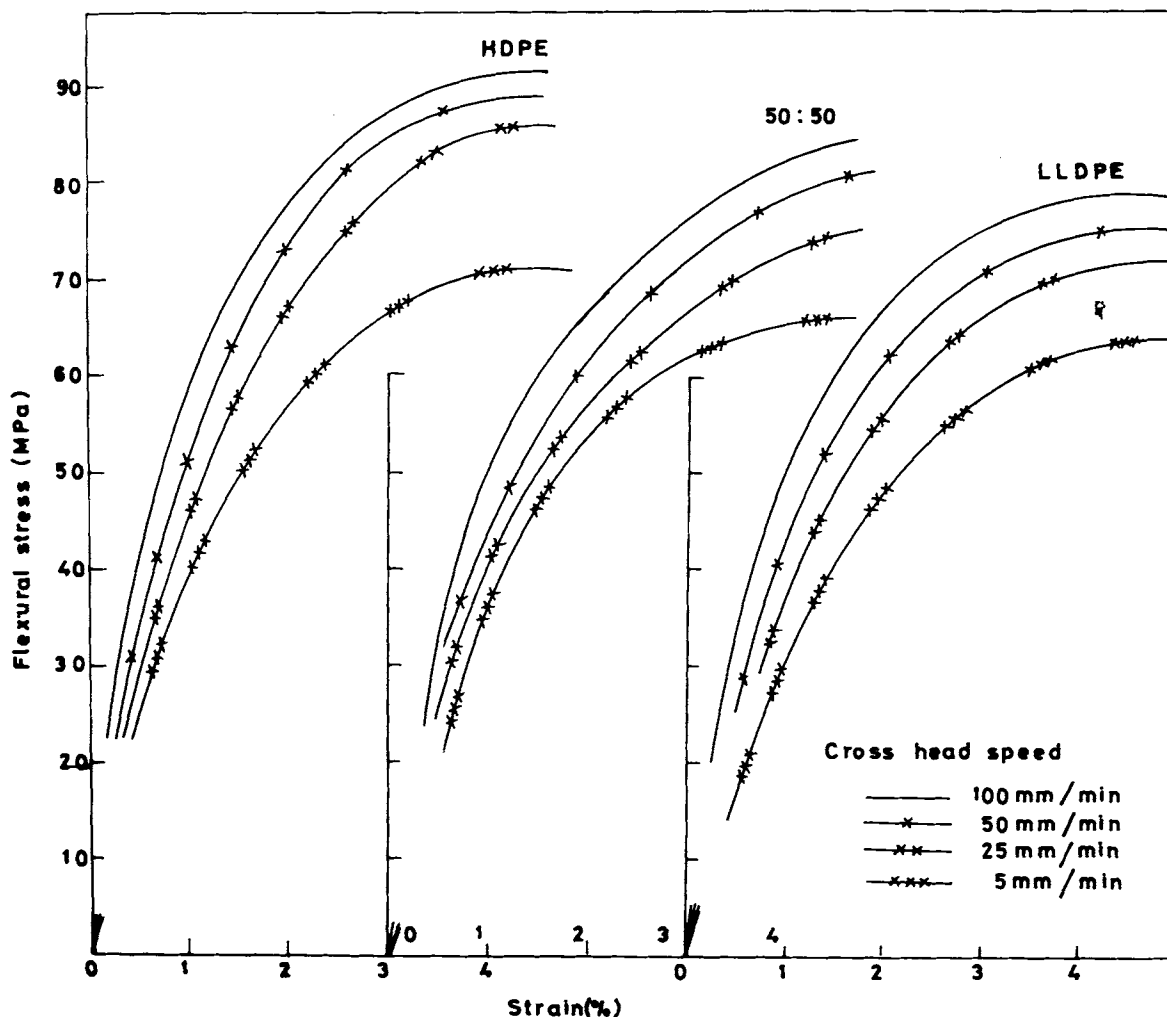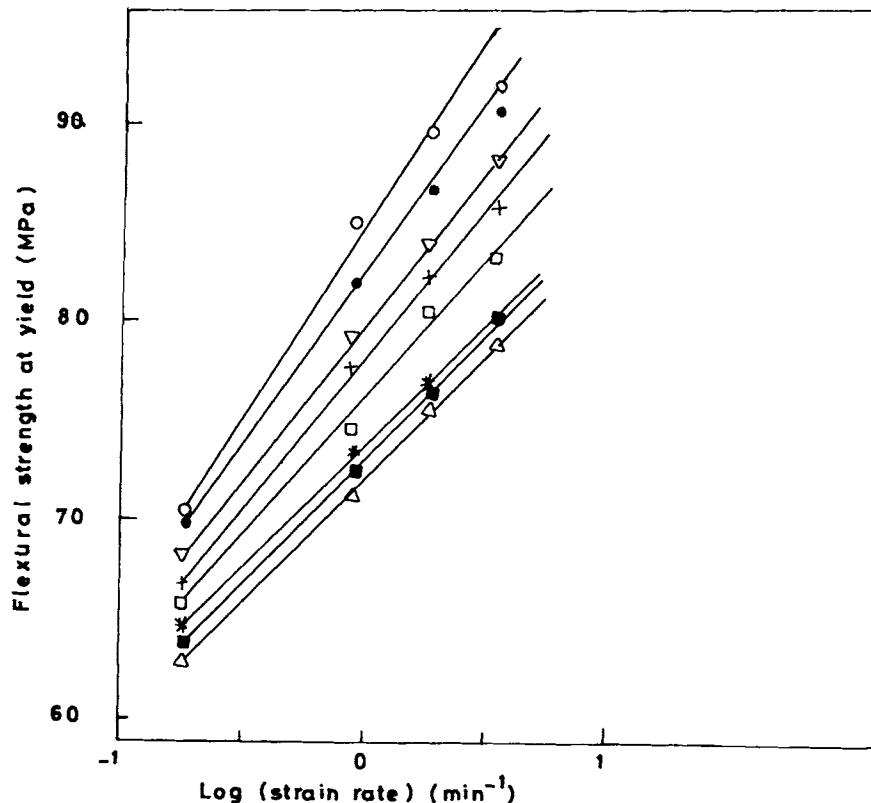

Figure 4 Flexural stress–strain curves of HDPE, LLDPE, and their blend at 50/50 composition at various crosshead speeds.

Figure 5 Variation of flexural strength at yield against the strain rate at various LLDPE contents (wt %): (— O —) 0, (— ● —) 10, (— △ —) 25, (— X —) 35, (— □ —) 50, (— ＊ —) 70, (— ■ —) 80, (— ▽ —) 100.

vious article.[4] The activation volume represents the number of mobile segments involved in the yielding process. It is apparent from Figure 6, where the curve has a slightly concave profile, that the initial addition of LLDPE in HDPE causes a rapid decrease of $2\ kT/v$ (i.e., the activation volume increases sharply) in the HDPE-rich blend. In the middle range of blend composition, the decrease is moderate (i.e., the activation volume remains approximately constant). In the LLDPE-rich blend, the curve shows little variation with blend composition (i.e., the activation volume remains almost unchanged). As activation volume represents the mobile portion of molecular chains, it should correspond to the amorphous phase content of the blend. The disagreement of the variation of activation volume, and the amorphous phase content in the region 0 to 10% LLDPE content, is clearly seen from the Figure 6. That is, the amorphous phase content decreases (or crystallinity increases), whereas the activation volume increases. However, both this amorphous phase content and activation volume maintain consistent trends with increased blend composition above a 10% LLDPE content.

This lack of correspondence of activation volume and the amorphous phase content leads us to assume that the amorphous phase may be comprised of two parts:

1. Amorphous phase, containing freely mobile chain segments, which respond quickly to the stress or strain applied, and comprises the activation volume.
2. Amorphous phase, containing entangled[9] chain segments, which move as a whole to adjust to stress or strain applied, and may not contribute to the activation volume.

The freely mobile phase displays a behavior that is close to the properties of the ideal amorphous phase. The entangled part of the amorphous phase deviates appreciably from the ideal. This entangled phase is believed to behave as inflexible bodies at low extension. This entangled amorphous phase differs from the crystalline boundary phase, where the entanglements and the chain folds may be present together. The prime difference, we believe, between those two phases is that the folded chain region may not take
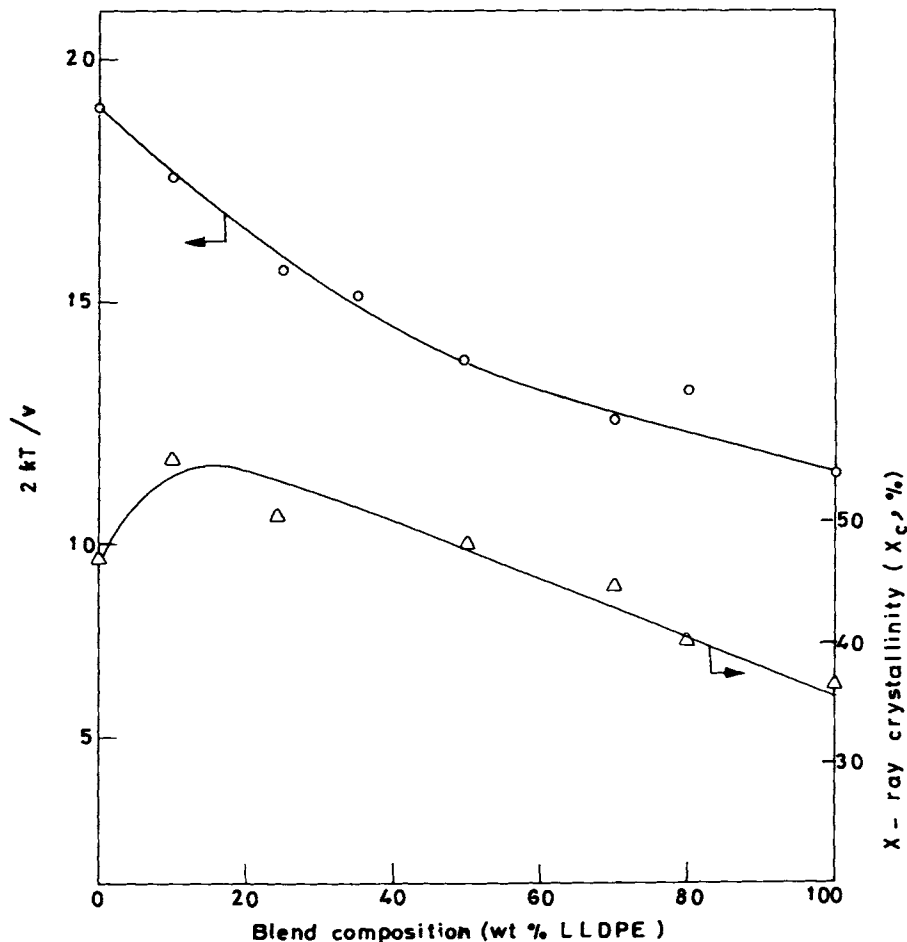
Figure 6 Variation of x-ray crystallinity and activation volume with blend composition for the HDPE/LLDPE blend.

part in extension on application of load, unless the crystallites, to which they are attached, break. However, the entangled phase may become disentangled, depending upon the magnitude of load and nature of entanglement. The amorphous content, as determined by x-ray diffraction, is also comprised of this folded chain region, in addition to the freely mobile phase and the entangled phase. The role of LLDPE in this amorphous phase is not fully understood. However, considering the crystallization[4] of HDPE and LLDPE, one may expect role of LLDPE in both of these types of amorphous phases to be due to the additional restriction in segmental mobility, from the bulky group of the comonomer used. The observed[4] decrease of crystallinity and increase of mean crystallite size, with increasing LLDPE content of the HDPE/LLDPE blend, is apparently due to the effect of such restrictions on the segmental mobility, slowing down the crystallization process and resulting in less crystallinity.

It also reduces the rate of nucleation, which causes some crystallites to grow large, while others, nucleated at a later time, remain small in size, thereby resulting in large average size crystallites.

Impact Strength

The variation in the Izod impact strength with blend composition is presented in Figure 7. Upon the addition of LLDPE to HDPE, the impact strength initially decreases up to 10% LLDPE content and then increases at higher LLDPE content. The magnitudes of impact strengths appear to be small, but showing systematic variations, suggesting that LLDPE may not produce much impact modification of HDPE, since both of them have reasonably high impact strength. The systematic variation of impact strength with blend composition, and its similarity with the variation of crystallization behavior[4] of these blends, confirms the previous findings of co-crystallization of HDPE and LLDPE. With respect
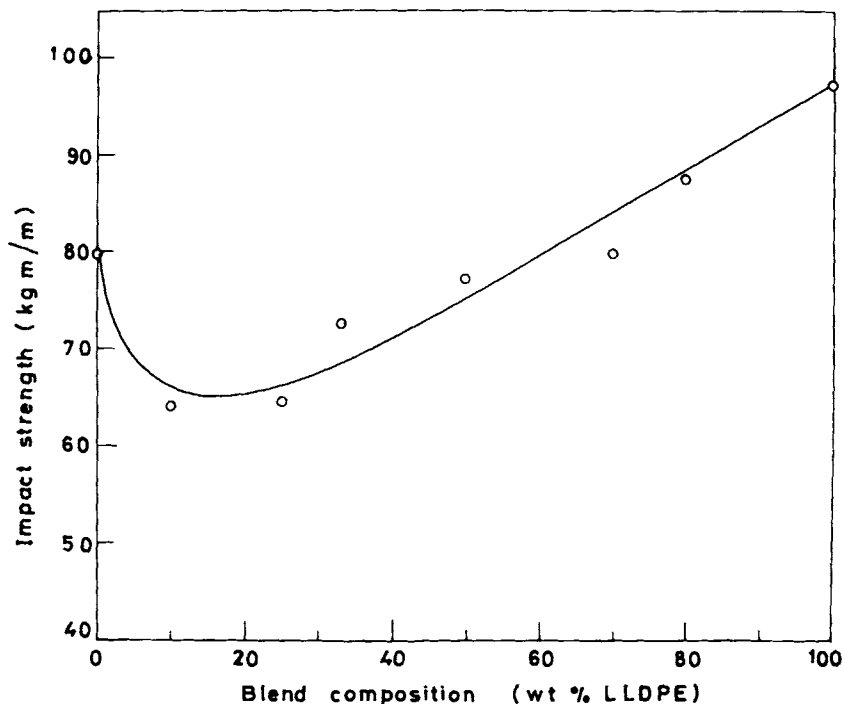
Figure 7   Variation of impact strength with blend composition of the HDPE/LLDPE blend.

to the cocrystallization of HDPE and LLDPE, the x-ray crystallinity goes through a peak value of 56% at 10% LLDPE content of the blend, whereas it is 46 and 36% for HDPE and LLDPE, respectively, while the crystallite size and the d-spacing show insignificant variations over the entire blend composition range. The higher crystallinity, as compared to HDPE, and the comparable crystallite size in the blend containing 10% LLDPE, would contribute to a greater abundance of crystallite–crystallite interfaces, which would ultimately facilitate failure. The cohesion between the crystallite amorphous interfaces is poor and the large number of such interfaces would provide low energy notch propagation paths for the blend containing 10% LLDPE. The approximate linear decrease in impact strength from HDPE to the blend containing 10% LLDPE and, thereafter, the linear increase up to pure LLDPE, could be attributed to corresponding changes in the amorphous content of the blend.

CONCLUSIONS

Flexural behavior of the binary blend of HDPE and LLDPE is distinguished by three regions of blend composition [viz., HDPE-rich blend (0–30% LLDPE content), LLDPE-rich blend (70–100% LLDPE content), and the middle region]. The flexural strength at yield varies insignificantly when either of component is a minority, while the strength changes rapidly in the middle region of blend composition. Flexural modulus, on the other hand, shows a rapid decrease in the HDPE-rich blend, while it shows a slight increase in the LLDPE-rich blend, and a reversal of trend in the middle region of blend composition. Like the previously reported case of tensile properties,[5] these flexural results are explained on the basis of structural changes produced by cocrystallization[4] of the HDPE and LLDPE.

The interpenetration of the fibrils is observed in the tensile fractured samples at sufficiently high LLDPE content of the blend, that is, in the region of composition where flexural modulus shows a reversal of trend or increases. This is apparently an advantage of blending these two polymers, as it might reduce fibrillation in stretched films.

The impact strength of the blend, although not greatly improved in comparison to the impact strength of HDPE, shows a systematic variation with blend composition, which is similar to the variation of the total amorphous content of the blend.

Two types of chain segments are identified in the

amorphous phase, viz., mobile and immobile (or entangled), on the basis of their response to the applied load. The mobile part readily adjusts to load because of its flexible nature, while the immobile part moves as a whole, depending upon the magnitude of the load and the intensity of entanglements.

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