

Mechanical Properties and Morphology of High-Density Polyethylene/Linear Low-Density Polyethylene Blend

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SYNOPSIS

The binary blend of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) in the range of composition from 100% HDPE to 100% LLDPE has been investigated for tensile and flexural properties and the morphology in the deformed state on tensile fracture. Tensile properties (initial modulus, yield stress, and elongation-at-yield, ultimate tensile strength and elongation-at-break, and work of yield and work of rupture) and flexural properties (flexural modulus and flexural yield stress) are studied as a function of blend composition. Behavior, in terms of these properties, is distinguishable in three zones of blend composition, viz. (i) HDPE-rich blend, (ii) LLDPE-rich blend, and (iii) the middle zone. In zones (i) and (ii), the variations of these properties are more or less linear, whereas in the middle region [i.e., zone (iii)], there is a reversal of trends in variation or sometimes a behavior opposite to the expected one. The results are explained on the basis of the effects of cocrystallization and the presence of octene-containing segments in the amorphous phase. Scanning electron micrographs of the tensile fracture surfaces are presented to illustrate the occurrence of transverse bands interconnecting the fibrils.

INTRODUCTION

Linear low-density polyethylene (LLDPE) is a very useful material, both as a single component or as a blend with other polymers. Blends of LLDPE with other grades of polyethylene, viz. high-density polyethylene (HDPE),¹⁻³ medium-density polyethylene (MDPE),^{4,5} low-density polyethylene (LDPE),^{4,5} and ultrahigh molecular weight polyethylene (UHMWPE),⁶ have been studied by various workers. LLDPE cocrystallizes with other grades of polyethylene,^{2,4,5,7} thus providing a possibility of improving the mechanical properties of the various grades of polyethylene by blending with LLDPE.

In a previous study,⁷ we observed a significant effect of the blending ratio on the crystallization behavior of the HDPE/LLDPE blend. The HDPE-rich blends show an increase in crystallinity at about 10% LLDPE content. In the LLDPE-rich blends' region, there is a continuous increase of crystallinity with increasing HDPE content. In this paper, we

investigate the mechanical properties of this blend in the entire range of blend composition, which includes tensile and flexural properties and morphology by scanning electron microscopy in the composition range from 100% HDPE to 100% LLDPE.

EXPERIMENTAL

Materials

HDPE (Hostalene GF 7745F) used was a product of Polyolefin Industries Ltd., Bombay, with a melt flow index of 0.75 g/10 min; density, 0.952 g/cc (believed to be the homopolymer of ethylene⁸); and melting peak temperature, 131°C. The LLDPE was an octene-based copolymer (Dowlex 2740E), a product of Dow Chemicals, U.S.A. The properties of LLDPE measured were melt flow index of 1.00 g/10 min; density, 0.924 g/cc; and melting peak temperature, 126°C.

Blend Preparation

Blends were prepared by melt mixing in a single screw extruder (Betol 1820) of L/D 17, using a

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temperature profile of 160°C at the feed zone, 200°C at the compression zone, and 210°C at the melting zone and the die end. The screw speed was kept at 22 rpm. The extruded strands were cooled in water at 30°C and subsequently granulated after allowing a maturation time of 8 h.

Measurements

(a) Tensile Testing

The granulated samples were injection-molded to test specimens on a Windsor injection machine (Model SP-30), using a temperature profile similar to the one used for the blending extruder. The injection time and cooling period were kept at 3 and 5 s, respectively, and the specimens ejected from the mold were allowed to cool down to room temperature under ambient conditions. Though identical cooling conditions were used to condition all the samples, the residual stresses in the samples may differ depending on cocrystallization kinetics; hence, there might be some initial structural differences that are to be tolerated owing to the impossibility of their correction without full knowledge about them. Hence, identical cooling conditions for all the samples were used.

The tensile properties were measured at room temperature ($23 \pm 2^\circ\text{C}$) after 24 h of maturation

time of the specimens on an Instron Universal tensile tester (Model 4202) in accordance with test procedure ASTM D638. The gauge length was kept at 50 mm with a crosshead speed 50 mm/min. From the stress-strain curves, the following properties (based on averages of five samples) were calculated: Young's modulus (from the initial slope of the stress-strain curve), yield strength, and yield elongation (from the first maxima of the curve), ultimate tensile strength and elongation at break [where the sample fails] and the area under the stress-strain curve.

(b) Flexural Testing

Injection-molded specimens as per ASTM D 790 geometry were conditioned according to the method described under "Tensile Testing." The specimens were then subjected to three-point bending in a Universal tensile testing machine (Instron 4202) with a crosshead speed of 100 mm/min. The load vs. deflection curve was recorded. The flexural yield stress and flexural modulus were calculated according to the following formulae. The flexural stress (S) is calculated by the relation

$$S = \frac{3PL}{2bd^2}$$

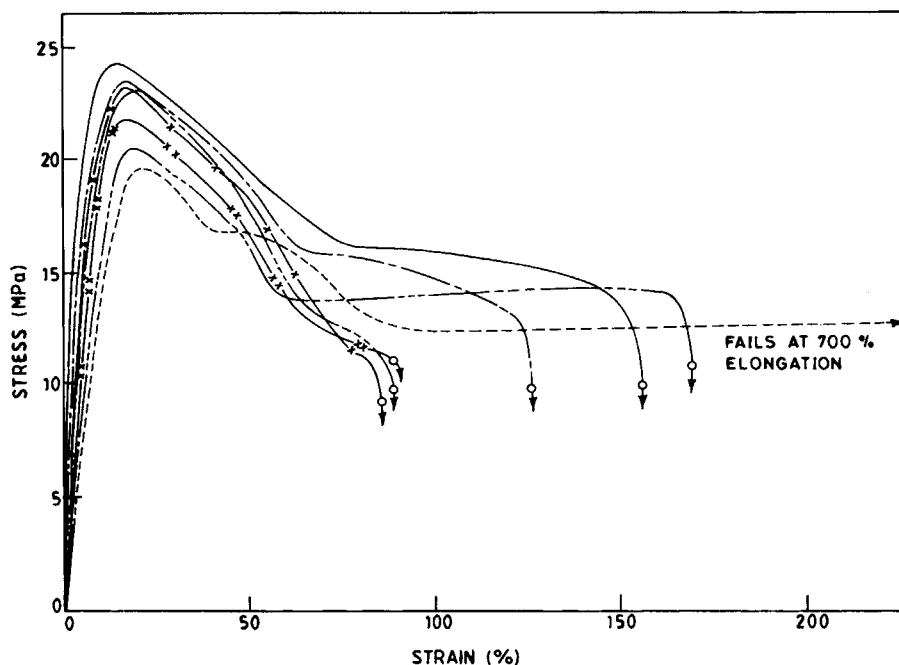


Figure 1 Stress-strain curves of HDPE, LLDPE, and their blends at various compositions (wt % LLDPE): (—) 0; (- · -) 10; (- x -) 25; (- · · -) 35; (- xx -) 50; (- · · · -) 80; (- - - -) 100.

Table I Tensile and Flexural Properties of HDPE and LLDPE and Their Blends

Flexural Properties			Tensile Properties				
Blend (Wt % HDPE: LLDPE)	Flexural Modulus (GPa)	Flexural Yield Stress (MPa)	Modulus (GPa)	Yield Stress (MPa)	Yield Strain (%)	Ultimate Tensile Stress (MPa)	Elongation at Break (%)
100:0	5.40	90.0	1.86	24.5	13.0	11.43	160
90:10	4.66	88.9	1.72	23.8	14.2	10.34	120
75:25	3.90	88.3	1.00	23.0	14.0	9.07	80
65:35	3.50	85.8	0.95	22.7	13.7	9.42	80
50:50	3.00	83.3	1.09	21.6	15.0	10.50	85
30:70	3.80	80.5	1.14	20.8	14.0	11.38	90
20:80	3.43	80.1	1.04	20.4	14.5	11.52	175
0:100	3.70	79.5	0.75	19.3	16.5	10.00	700

and the maximum strain (r) in the outer fibers is given by

$$r = \frac{6Dd}{L^2}$$

where P = load applied on the sample, L = total distance among the three props, b = breadth of the specimen, d = width of the specimen, and D = deflection suffered by the outer fibers of the specimen. The flexural modulus is calculated from the initial slope of the flexural stress-strain curve.

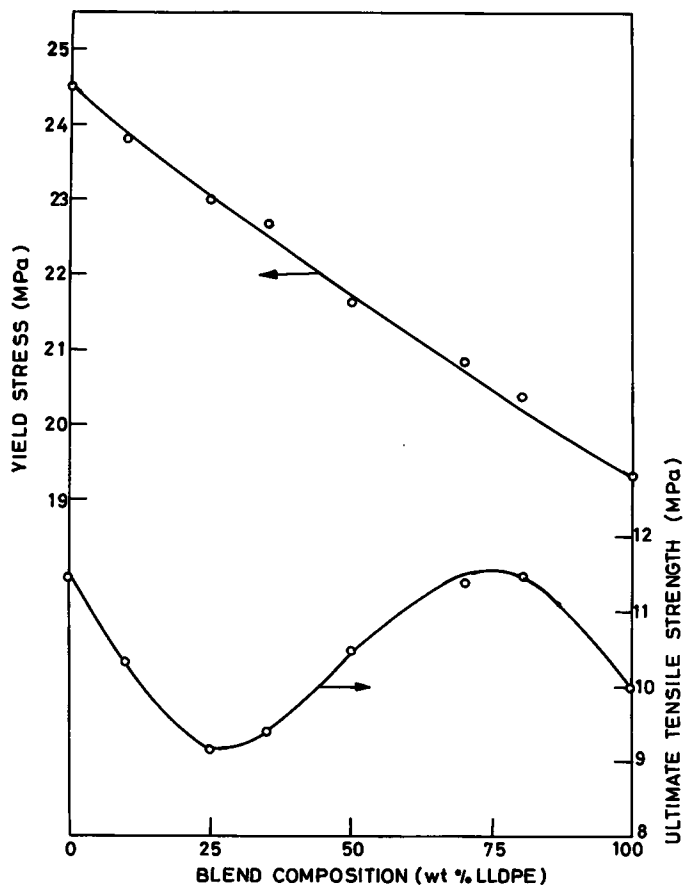


Figure 2 Variation of yield stress and ultimate tensile strength with the blend composition for the HDPE/LLDPE blend.

(c) Scanning Electron Microscopy

Micrographs were recorded on a Cambridge scanning electron microscope (Stereoscan 360) of the tensile fracture surfaces of the samples. The tip of the fracture surfaces were cut and mounted on the sample holder, keeping the surface normal to the electron beam, and the samples were silver-coated by vacuum deposition.

RESULTS AND DISCUSSION

Tensile Properties

Stress-strain curves of the HDPE/LLDPE blend at its various compositions and the pure components, presented in Figure 1, show a systematic variation with the blending ratio. All the samples show yielding at around 20% strain. The yield stress is highest for the HDPE and lowest for the LLDPE and varies quite systematically with the blend composition as shown in Table I. Necking in HDPE and

the HDPE/LLDPE blend samples occurs at around 60–75% elongation and, thereafter, the samples undergo easy drawing without much increase in stress. The LLDPE shows two-step yielding with a necking zone at 40 and 90% elongation and a large elongation-at-break (about 700%). The two-step yielding process in LLDPE, in contrast to HDPE and the HDPE/LLDPE blend, is apparently indicative of the association (dipolar or other interactive) of the comonomer units used in LLDPE, which become dissociated in the second step of yielding, i.e., around 90% elongation.

(a) Strength and Modulus

The yield stress and ultimate tensile strength vary with blend composition as shown in Figure 2. The yield stress decreases almost linearly from 24.5 to 19.3 MPa in the entire range of blend composition from 100% HDPE to 100% LLDPE. The ultimate tensile strength, on the other hand, shows a nonlinear variation (Fig. 2) such that on initial addition

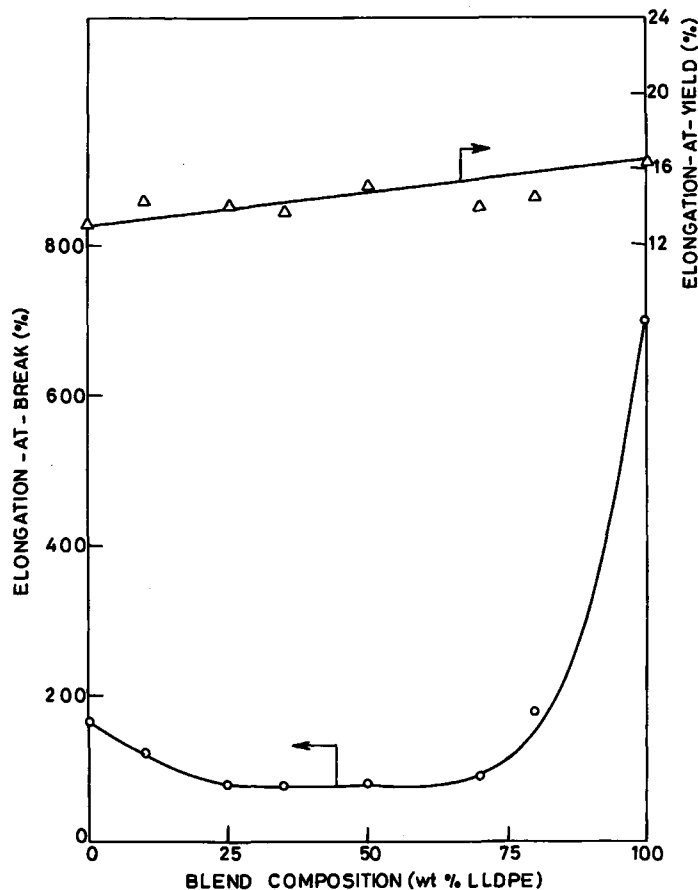


Figure 3 Variation of elongation at yield and elongation at break with the blend composition for the HDPE/LLDPE blend.

of up to 25% LLDPE it decreases and then increases on further addition of LLDPE up to 80% LLDPE content of the blend and, thereafter, decreases again. The decrease of tensile strength in the region of the HDPE-rich blend (i.e., from 0 to 25% LLDPE content) seems attributable to an increase in the distribution of crystallite size. Such a change in the distribution of crystallite size was found from X-ray diffraction and DSC crystallization exotherm analysis reported in a previous paper.⁷ In the middle zone, i.e., 25–75% LLDPE content, the crystallite size distribution is reported quite narrow, whereas the crystallinity decreases, which might be responsible for the observed increase of tensile strength in this range. Linearity in yield stress variation seems to be attributable to the behavior at small deformation, which is apparently not affected by the co-crystallization parameters.

(b) Elongation

Elongation-at-yield increases linearly with increasing LLDPE content (Fig. 3) with a slight scatter of data points, in spite of which the increasing trend

is discernible. Elongation-at-break (Fig. 3), on the other hand, decreases with respect to its value for HDPE with increasing LLDPE content of the blend up to 35% LLDPE content and then remains almost unchanged on further addition of LLDPE up to 70% LLDPE content, and, thereafter, its increase is very sharp up to the value for pure LLDPE. The LLDPE, which has greater extensibility than does HDPE, contributes very little to the increasing of the elongation-at-break of the blend. Entrapment of molecular segments in cocrystallites leaves quite small lengths of LLDPE segments in the amorphous region, which might account for the low elongation-at-break of the blend samples. This indicates that breaking occurs before the LLDPE component contributes to the elongation of the sample beyond the limit of maximum elongation of HDPE. The lower values of elongation-at-break for the blend than for the pure LLDPE suggest that the major portion of the LLDPE gets involved into cocrystallized regions and at the boundary region of crystalline and amorphous phase and, hence, does not produce any significant variation of the elongation-at-break as a function of LLDPE content. The decrease of elon-

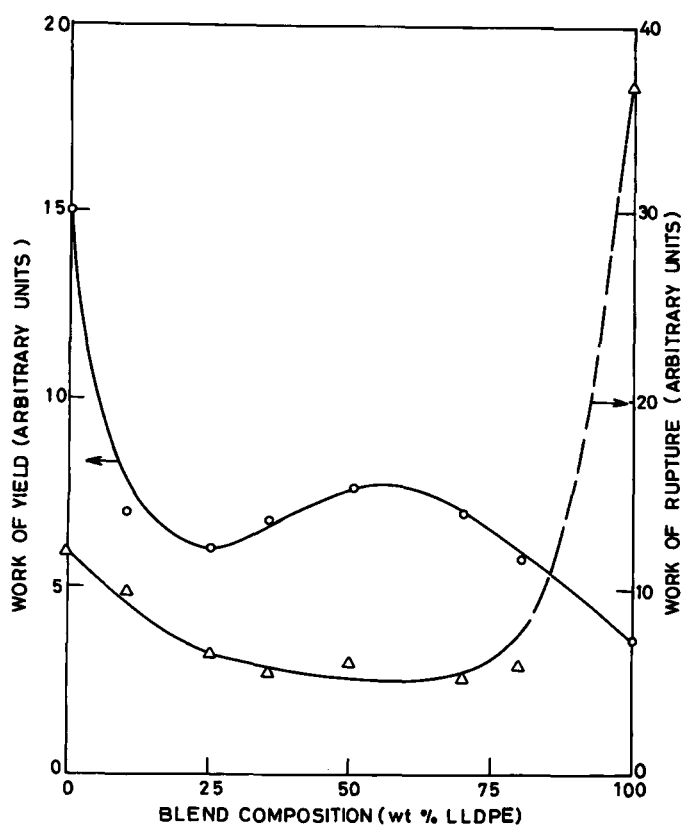


Figure 4 Variation of work of yield and work of rupture with the blend composition for the HDPE/LLDPE blend.

gation-at-break at the initial addition of 10% LLDPE is due either to the shortening of amorphous regions owing to increased crystallinity⁷ in the presence of LLDPE or to the role of the boundary phase that contains a greater abundance of comonomer (octene)-containing segments of LLDPE. The comonomers will cause greater separation of the molecular chains and thus weaken their intermolecular forces, hence, facilitating the failure.

The behavior at small deformation (i.e., at yield) would have a different role of LLDPE than does the behavior at ultimate failure. The increase of elongation-at-yield with increasing LLDPE content, at the high LLDPE contents, may be because the comonomer units present in LLDPE act to increase the free volume, and, thus, the flexibility or extensibility is increased. The decrease in stress required for yielding also supports this. On the other hand, at very high elongations (i.e., at break), such an advantage of increased segmental mobility is not possible due to many segments already being in a highly extended (strained) state.

(c) Work of Yield and Work of Rupture

The area under the stress-strain curve, which is directly proportional to the energy involved in the de-

formation process, can be interpreted in two parts. The first one, i.e., the area under the yield peak from the origin up to the onset of necking, is proportional to the "work of yield." The second one is the total area under the stress-strain curve from the origin up to the breaking point, which is proportional to the "work of rupture." The respective areas are presented in Figure 4 as the "work of yield" and "work of rupture" in arbitrary units without going into the values of the constant of proportionality. As shown in Figure 4, the "work of yield" varies with increasing LLDPE content of the blend, such that at up to an initial 25% LLDPE content, it shows a sharp decrease followed by a slight increase and then a decrease after 50% LLDPE content. The initial decrease of work of yield implies that LLDPE facilitates the yielding, as is also apparent from the lowering of yield stress in this region (see Fig. 2). This trend of variation of work of yield is different from that of the elongation-at-yield, which is apparently due to the difference of stress levels of the two processes. The yielding occurs at a higher stress than the stress corresponding to the elongation-at-yield.

Work of rupture, on the other hand, shows quite a similar trend in variation (Fig. 4) as the elongation-at-break (Fig. 3). With increasing LLDPE

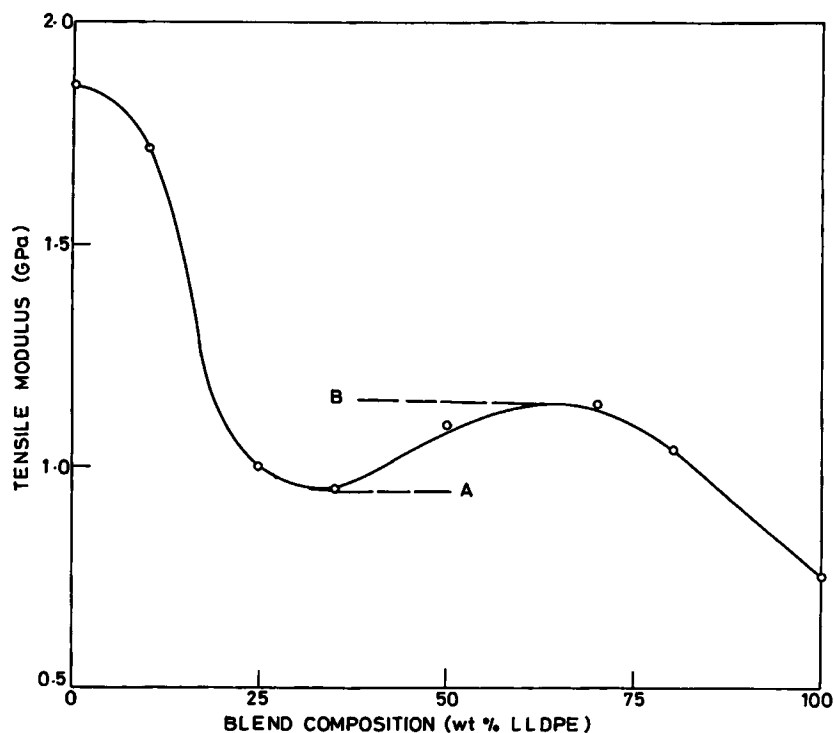


Figure 5 Variation of tensile modulus with the blend composition for the HDPE/LLDPE blend. The plateaux A and B are described in the text.

content, work of rupture decreases quite rapidly up to 35% LLDPE content, followed by an inappreciable change in the middle zone of the blend composition, further followed by a rapid rise up to the value for pure LLDPE. This suggests that the factors responsible for ease of elongation would also account for a reduction in the energy of deformation.

(d) Modulus

The modulus varies with the blending ratio, as shown in Figure 5. The modulus varies in a nonlinear manner with some discontinuity at the middle region of composition, i.e., 50/50 blending ratio. The trends in variation are well discernible in the two regions: (i) 0-30% LLDPE content, called the "HDPE-rich blend," and (ii) 70-100% LLDPE content, called the "LLDPE-rich blend."

In the HDPE-rich blend, as shown in Figure 5, the modulus shows a sigmoidal transition from its value for pure HDPE to a value corresponding to

plateau A. On the other hand, in the LLDPE-rich blend, the modulus increases from its value for pure LLDPE on addition of HDPE up to a value corresponding to plateau B. There is discontinuity between plateaux A and B that is consistent with an apparent increase in the modulus with an increasing proportion of low modulus material, viz. the LLDPE, in contrast to the common belief. This might be due to the involvement of LLDPE in cocrystallization with the other component of the blend, viz. the HDPE.

Flexural Properties

The flexural modulus and flexural strength at yield of these samples have values as shown in Table I. The flexural modulus of LLDPE is lower than that of HDPE. In case of the HDPE/LLDPE blend, both flexural strength at yield and flexural modulus are lower than those of HDPE. The decrease of flexural

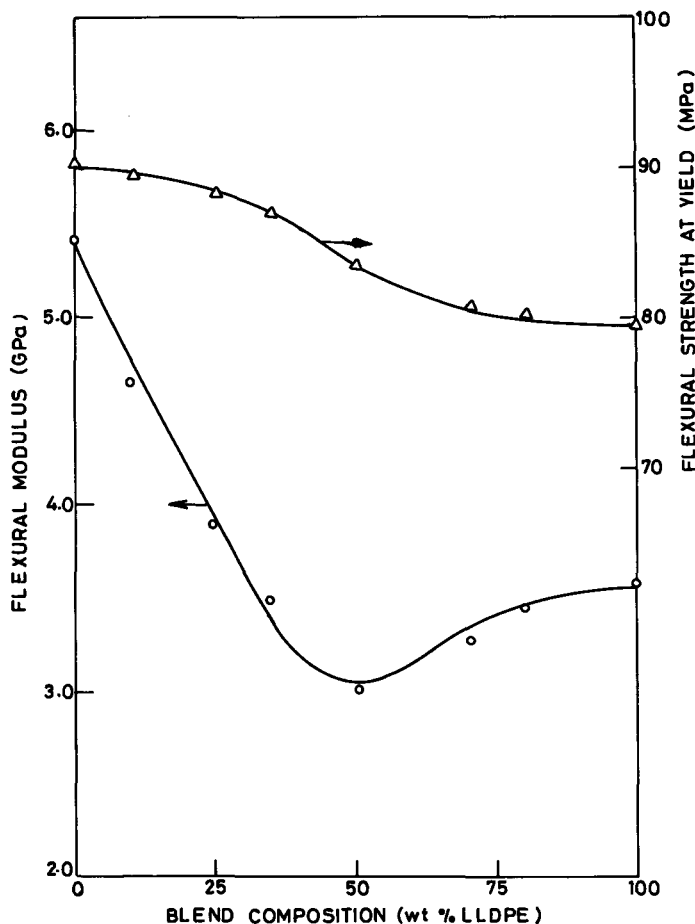


Figure 6 Variation of flexural modulus and flexural strength at yield with the blend composition for the HDPE/LLDPE blend.

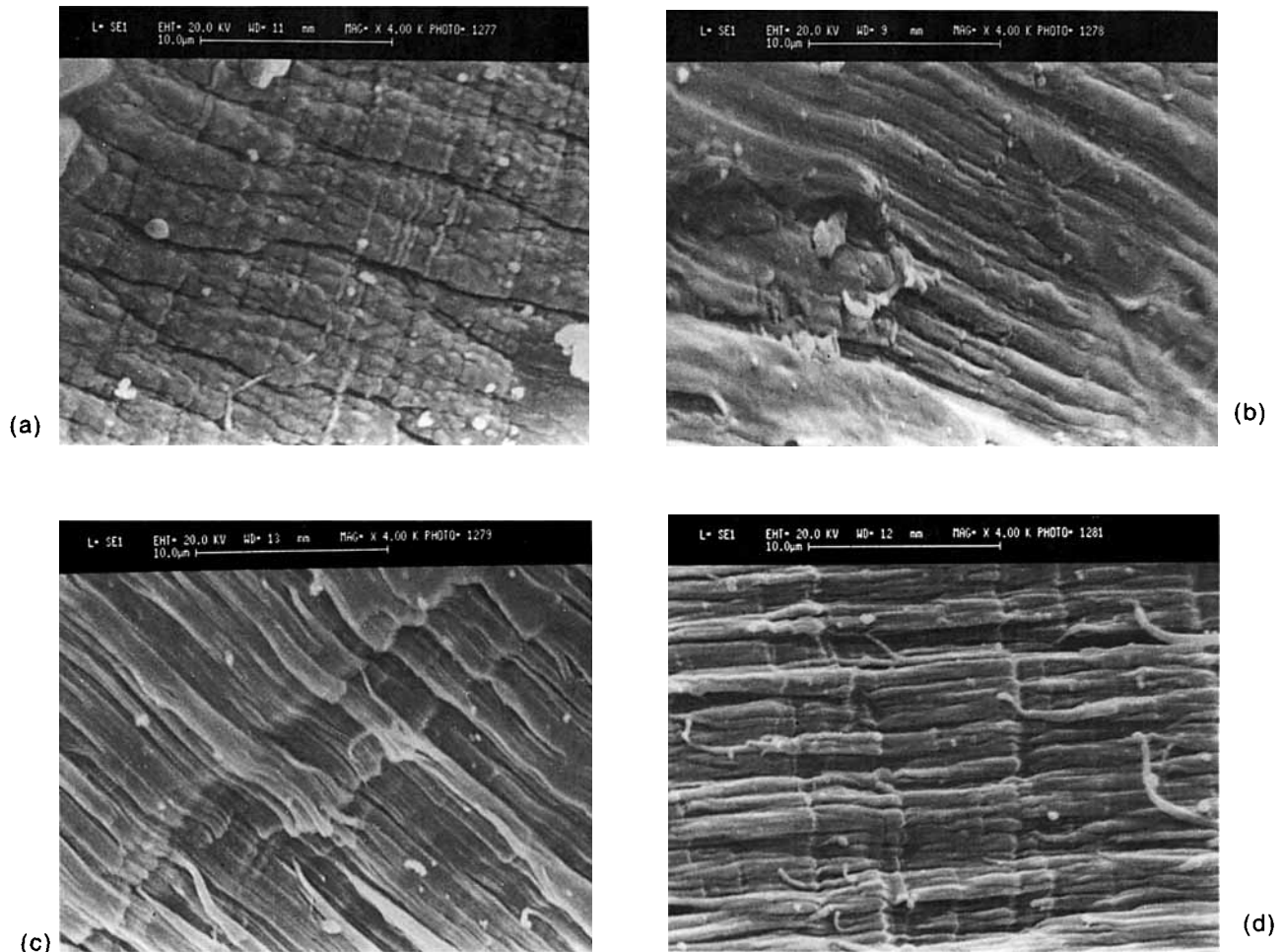


Figure 7 Scanning electron micrographs of tensile fracture surfaces of HDPE and LLDPE, and their blends at various compositions (wt % LLDPE): (a) 0; (b) 10; (c) 25; (d) 35; (e) 50; (f) 70; (g) 80; (h) 100.

strength at yield with increasing LLDPE content is sigmoidal, while the decrease in flexural modulus is quite rapid up to 50% LLDPE content followed by a slight increase with increasing LLDPE content, as shown in Figure 6. The flexural strength at yield shows very little variation in the two extreme regions and a quite significant decrease with increasing LLDPE content in the middle region of the blending ratio. The middle zone of blend composition (i.e., 30–70% LLDPE content) is quite intriguing in terms of the various tensile properties discussed above. It may be recalled that in this range of blending ratio some unique features are observed in the tensile properties, viz. ultimate tensile strength shows a reversal of trend of variation (Fig. 2), consistent with the behaviors of elongation at break (Fig. 3), work of rupture (Fig. 4), and tensile modulus (Fig. 5). Some features observed in the morphological study, presented in the subsequent section of this blend,

are also consistent with the uniqueness of the behavior in this middle range of the blend composition.

Scanning Electron Microscopy

The micrographs of the tensile fracture surface of pure polymers and blends are shown in Figure 7 (a–h). Fibrillar structure is visible in these tensile fracture surfaces at all the compositions of the blend. The thickness of the fibrils are of the order of 3–8 microns. The distinctness of the fibrils vary from sample to sample. The LLDPE [Fig. 7(a)] shows some transverse connections. The blend corresponding to 80% LLDPE content has transverse striations and forms transverse connections, which are not so prominent as in the case of LLDPE. The HDPE has quite thick fibrils, and distinct interfibrillar separation is seen in the micrograph of Figure 7(h). At all the blend compositions, the fibrils are

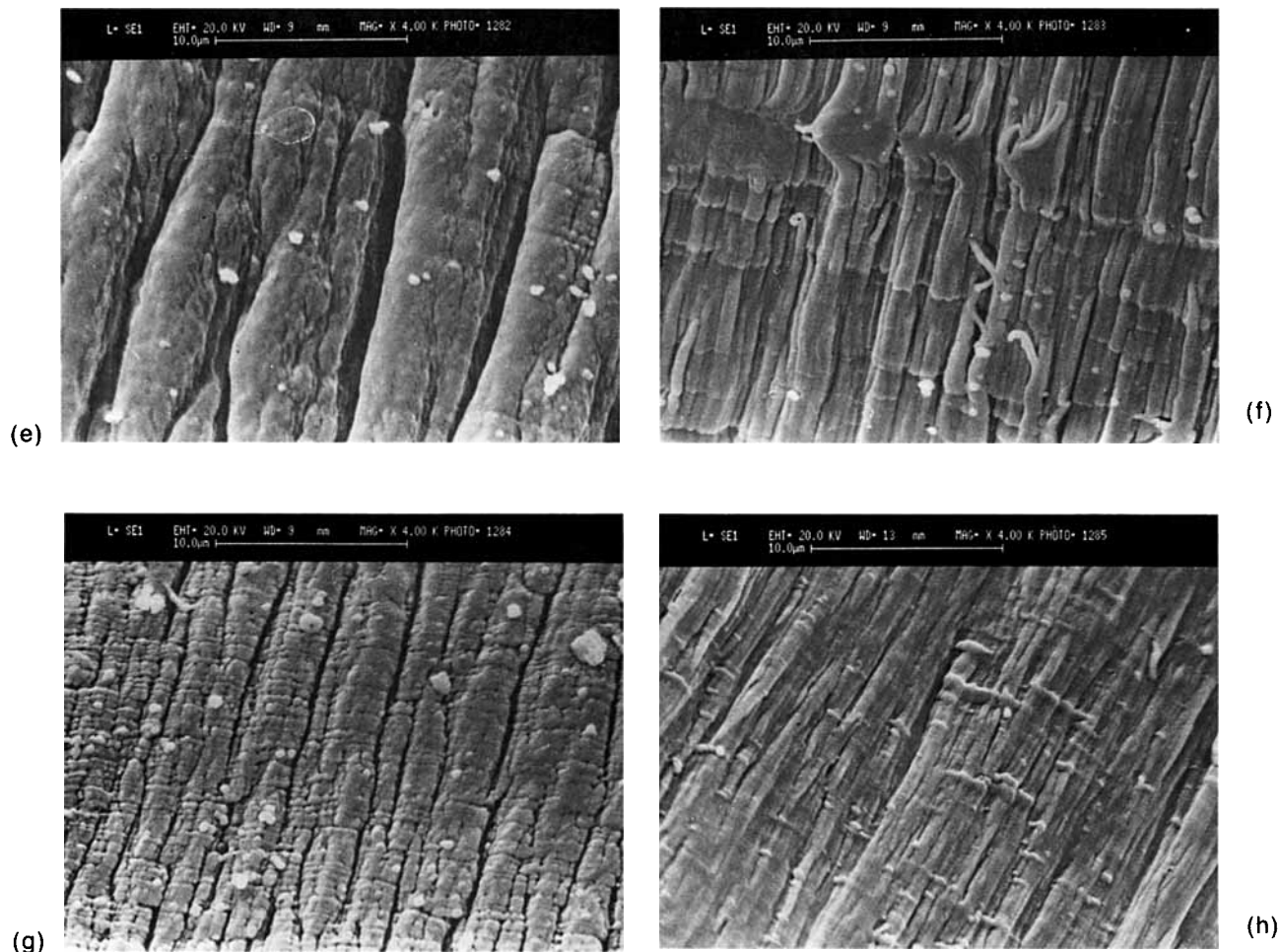


Figure 7 (Continued from the previous page)

sufficiently fine with interfibrillar linkages except in the case of the 50/50 blending ratio. Considering the interconnectivity of LLDPE and the tendency of the HDPE to form distinct interfibrillar separation, one could expect the role of LLDPE in controlling the fibrillation mechanism of HDPE, which is apparent from the micrograph [Fig. 7(a-h)]. However, the blend containing 80% LLDPE shows some rather strange characteristics, viz. fine fibrils with good separation and prominent transverse striations in the fibrils. The reason for this is not clear and more detailed investigation would be necessary. Thus, LLDPE, which has a distinct role to play in the retarding fibrillation mechanism of HDPE, may be useful in reducing the fibrillation tendency of the HDPE tape.⁹

Cocrystallization of LLDPE and HDPE

Some findings about the cocrystallization of the LLDPE/HDPE blend reported in our recent paper⁷

are summarized here, as they are useful in understanding these results. The single-peak character of the DSC crystallization exotherms, the absence of peak broadening, and the slight increase of d -spacing corresponding to both (110) and (200) reflections in the X-ray diffraction patterns of this blend at all the compositions are evidence in favor of cocrystallization. The cocrystallization varies with blend composition such that (i) in the HDPE-rich blend addition of LLDPE slows down nucleation and enhances growth; and (ii) in the LLDPE-rich blend, addition of HDPE increases the overall growth rate while the nucleation rate first decreases and then increases above 20% HDPE. These variations of nucleation and growth of crystallization produce differences in crystalline morphology in the respective regions of the blend composition, thus explaining the observed differences in the mechanical properties in these regions.

The slow rate of nucleation coupled with an enhanced growth rate produces a morphology with a

wide distribution of spherulite size (i.e., simultaneous occurrence of very small and very large spherulites), which explains the decrease of mechanical properties like tensile strength and elongation in the HDPE-rich blend with increasing LLDPE content. On the other hand, in the LLDPE-rich blend, the increased overall growth rate predominates such that it increases the crystallinity and thus the tensile strength with increasing HDPE content. The elongation, however, decreases, which is apparently the effect of smaller lengths of the chain in the intercrystalline region.

Cocrystallization of the two components of the blend may also be responsible for the production of transverse interconnections or bands apparent, at certain compositions of the blend, in the scanning electron micrographs. This tendency of the LLDPE phase is clearly seen in the micrograph of the pure LLDPE sample [Fig. 7 (h)] where the transverse bands are in abundance. This suggests that the intercrystalline LLDPE phase may have its segments in several crystallites, thus providing the interconnectivity of the crystallites or fibrils and reducing the fibrillation.

CONCLUSION

Tensile and flexural properties of the HDPE/LLDPE blend vary with the blending ratio and the variations are sharper and nonlinear at large deformations (i.e., at break) and less sharp and sufficiently linear at small deformation (i.e., at yield), implying a significant role of fibrillation and its dependence on the blending ratio.

From the nonlinear variations of the properties, distinct behaviors are identified in the three zones of blend composition, viz. (i) 0–30% LLDPE content (i.e., HDPE-rich blend), (ii) 70–100% LLDPE content (i.e., LLDPE-rich blend), and (iii) the middle zone. Variations of the properties in zones (i) and (ii) are more or less expected, whereas the variation in the middle region of the blend composition [i.e., zone (iii)] is unique, as it shows an increase of ultimate tensile strength and tensile mod-

ulus with an increasing proportion of the low strength and low modulus material, viz. the LLDPE. This behavior is attributed to the involvement of the second component (LLDPE) into the cocrystallization with HDPE. The cocrystallization leaves smaller lengths of LLDPE segments free for elongation, which is the cause of the difference in the trends of the variation of properties at low deformation than at breaking point. Furthermore, the variation of morphology of the cocrystallized phase, discussed in detail in a previous paper of the authors,⁷ accounts for these unique variations in tensile and flexural properties.

Fibrillation occurs at all the compositions of the blend, as seen from the scanning electron micrographs of its tensile fracture surfaces. Some quite prominent transverse connections between the fibrils are seen that are apparently due to the intercrystalline LLDPE phase, thus suggesting that LLDPE has a role in reducing the weakness in the transverse direction through fibrillation.

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