Study of the Thermal and Mechanical Properties of Blown Films of High- and Low-Density Polyethylene Blends

Mohsen Mohammadi, Ali Akbar Yousefi, Morteza Ehsani

Department of Plastic Processing, Faculty of Polymer Processing, Iran Polymer and Petrochemical Institute, Tehran, Iran

ABSTRACT: The miscibility of the blown film of low- and high-density polyethylene blends and its implications on melting, crystallization, and mechanical behavior throughout the full composition range and the possible role of blending on the miscibility of the binary pair system have been investigated. Using differential scanning calorimetry it was inferred that the films of blends in solid state are miscible in HDPE-rich compositions, partially miscible at 95% LDPE and completely immiscible at other compositions. The thermal analysis revealed that blending has insignificant effect on lamella thickness of LDPE phase but strong influence on the lamella thickness of HDPE phase. Moreover, analysis of crystallization exotherms was also discussed. XRD measurements also revealed qualitatively similar trend in crystallinity and lamella thickness to DSC results. Measurements on tensile properties in the machine direction of the films showed both positive and negative deviation from linear additivity and improvement of the mechanical properties was found in the film blends containing low amount of LDPE. Especially the strain at break and tensile strength for the film of 5% LDPE blend was higher than that of neat HDPE, which suggests synergistic effects. This supports its larger lamella thickness and better miscibility. Nonetheless, there was negative deviation from the additivity rule in the entire range of composition for the mechanical properties in the transverse direction of the films. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 755–767, 2012

Key words: LDPE; HDPE; blend; DSC; miscibility; tensile properties

INTRODUCTION

Polyethylene (PE) is amongst the most common used commodity commercial plastics.[1] High density polyethylene (HDPE) possesses a linear structure with very slight or no branching and amount of crystallinity of it is high. The degree of crystallinity (X_c) has a pronounced impact on the breakage and yielding of PE. The crystalline phase of polyethylene leads to its mechanical strength, whereas the amorphous phase gives rise to flexibility.[2,3] Increase in the fracture toughness is in general accompanied with declining the degree of crystallinity of linear polyethylenes, but low-density polyethylene (LDPE) with long-chain branches is much less tough.[4] Although HDPE has superior mechanical properties but it is less processable as compared with conventional LDPE. Nevertheless, LDPE has a disordered structure with short and long-chain branches and due to the presence of a large amount of long-chain branches (LCB), its melt strength is typically very privileged compared with that of HDPE with a similar molecular weight. Hence, blending HDPE with LDPE has been attracted a growing interest to attain the most favorable combination of properties.

A large volume of polyethylene blends is used in various applications due to favorable properties.[5–7] The inquiry of miscibility of such blends has not only theoretical, but also considerable practical significance. The miscibility of components of a polymer blend system describes the structure and phase behavior of it. Complete immiscibility gives rise to a heterogeneous structure and inferior properties, whereas miscible polyethylene pairs form homogeneous mixtures.[8] Considering the fact that both constituents of polyethylene blends can crystallize, the blends are complex for the reason that the phase segregation and crystallization process can happen concurrently and/or in contest. Hill and Puig[9] employed thermal analysis to demonstrate that LLDPE/LDPE blends were incompatible. Tashiro et al.[10] confirmed that LLDPE/LDPE blends were immiscible in the crystalline state. Yamaguchi and Abe[11] found miscibility in molten state but the segregation of components during the crystallization process.

A good degree of homogeneity, based on melting and crystallization measurements, was revealed for blends of linear and branched polyethylenes by Neway and Gedde.[12] However phase segregation is frequently reported,[13,14] factors such as molecular

Correspondence to: A. A. Yousefi (a.yousefi@ippi.ac.ir).

TABLE I
Characteristic Properties of the Used Polyethylenes

Polymer	HDPE	LDPE
Density[a]	0.948	0.918
M_n (g/mol)[b]	12016	13012
M_w (g/mol)[b]	108685	108715
PDI (g/mol)[b]	9.04	8.35
Melting point (T_m) (°C)[c]	139	112

[a] Measured by a water-isopropanol density-gradient column at 296 K.
[b] Measured by SEC, mobile phase TCB at 145°C.
[c] Measured by DSC.

weights, degree of branching, and comonomers have important impacts on miscibility.[15,16] By means of small angle neutron scattering (SANS) technique, as a very powerful technique, phase separation was detected and reported for blends of high- and low-density polyethylenes.[15] The deuteration by itself, however, may have changed the molecular characteristics of the constituents. Some other studies were also carried out to characterize blends of LDPE and HDPE[17–19] and films of the blends[20] as well as their wastes.[21] Recently, Munaro and Akcelrud investigated the stress cracking resistance of the blends and according to differential scanning calorimetry (DSC) results they found that incompatibility or heterogeneity affects the resistance.[22] DSC was also used to characterize highly oriented drawn single-phase blend films of HDPE and LDPE.[20] According to results, in as-drawn or melted and recrystallized films at low LDPE contents, no separation of the two polyethylenes was detected. In case of as-drawn films, a low temperature tail appeared as melting peak at 70% LDPE concentration, denoting the onset of phase separation. Nevertheless, in melt-crystallized films two discrete endothermic peaks were observed for 50% LDPE content.

Behavior and structure of blends of low- and high-density polyethylenes with different polydispersity indices (PDI) and weight-average molecular weights (M_w) have been studied,[23–26] but properties of this type of blend with components possessing the same M_w and PDI have seldom been investigated and reported specially in film blowing.

In this study HDPE and LDPE with the same weight-average molecular weight and polydispersity index were selected, in order to remove the effect of differences in PDI and M_w of the constituents on miscibility and investigate a blend which only chain structure of its components is different. The principle aims of this study are to investigate thermal and mechanical behavior of blown films of HDPE/LDPE blends and also to present the effect of blending ratio. Another goal of this study is to infer the miscibility of the film blends through DSC technique.

EXPERIMENTAL

Materials and procedure

The polyethylenes used in this work are commercially available products and provided from Iran Petrochemical in the form of granules. Some characteristics of these materials are listed in Table I.

LDPE has relative branching index (long-chain branches/1000C) of 0.90. The relative branching index is derived from combined size-exclusion chromatography (SEC) and Viscotek differential viscometer results.[27] The data are almost analogous to that reported for one of LDPEs in a study reported by Majeste et al.[28] According to their study based on SEC measurements, their LDPEs had LCB/1000C 0.48 and 0.63. HDPE and LDPE used in this study have almost similar polydispersity index (PDI) and the same weight-average (M_w) and number-average molecular weights (M_n). The only difference of the two polyethylenes remains in their chain structure, i.e., branching structure of LDPE versus linear structure of HDPE, which is reflected in their melting point, density and crystallinity. A large difference in T_m of the polymers once again confirms that the LDPE has a high degree of chaotic branched-chains in comparison with the linear structure of HDPE.

Films of varying compositions were obtained using a laboratory blown film line (Brabender Plasti-corder, Lab-Station). Blends of HDPE and LDPE were prepared via melt mixing process in a single screw extruder with a screw of length to diameter ratio 25 : 1 at the screw speed of 55 rpm. Extrusion temperature profile from the feed zone to the die was set at 150–210°C. The melt homogeneity of the blends was checked by rheometry and it was found that there was miscibility for the melt state of the materials. In film-blowing line the film die was 25 mm in diameter and fitted with a dual lip air ring. All films were processed under the same conditions. The blow-up ratio and take-off rate were set at 2.5 and 3 m/min, respectively. The prepared film blends were designated as explained in Table II.

TABLE II
Compositions of the Films of the Blends

Film designation	HDPE (wt %)	LDPE (wt %)
FH	100	0
F5LDH	95	5
F15LDH	85	15
F25LDH	75	25
F50LD	50	50
F25HLD	25	75
F15HLD	15	85
F10HLD	10	90
F5HLD	5	95
FLD	0	100

Instrumentation

Thermal characterization of films was carried out on a differential scanning calorimeter (Netzsch DSC 200 F3). The test procedure involved heating a sample of about 5 mg at a heating rate of 10°C/min from 20 to 170°C and isothermally maintaining at this temperature for 5 min followed by cooling to 20°C at a rate of 10°C/min. The percent of crystallinity (X_c) was calculated by

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^\theta} \times 100 \qquad (1)$$

where, ΔH_m is the apparent fusion enthalpy of samples obtained from the integral of melting peaks, and ΔH_m^θ is the theoretical value of fusion enthalpy for a 100% crystalline polyethylene which was taken as 293.6 J/g.[29]

Lamella thickness is an important characteristic of semicrystalline polymers. It was acquired here from thermal analysis given that the melting temperature of polymer crystals is correlated to the lamella thickness (l). The Gibbs-Thomson equation was employed for determination of lamella thickness from T_m (the observed melting temperature of the polymer at the peak of the DSC endotherm)

$$T_m = T_m^o \left(1 - \frac{2\sigma_e}{\Delta h_m l}\right) \qquad (2)$$

where l is lamella thickness and for PE, $\sigma_e = 60.9 \times 10^{-3}$ J/m^2 is the lamellar basal surface free energy, $T_m^o = 415$ K is the extrapolated equilibrium melting temperature as estimated for infinitely thick crystals in polymer of an infinite molecular mass, $\Delta h_m = 2.55 \times 10^8$ J/m^3 is the enthalpy of fusion per unit volume.[30]

Crystallinity of the blend films was measured through X-ray diffraction (XRD) technique on a Philips diffractometer at an accelerating voltage of 40 kV and amperage of 30 Å using CuKα radiation. All materials were scanned at a speed of 0.025 2θ/s in 5 and 50° interval in reflectance mode.

Mechanical test experiments were carried out to investigate the effect of blending with LDPE on the mechanical properties of HDPE over the entire range of composition. Mechanical properties were measured using a tensile tester, Instron 6025 according to the ASTM D882 at room temperature. The blown films were cut into dumbbell specimens in both machine and transverse directions. The specimens having dimensions of 20 mm width and 150 mm length were utilized and the data was recorded at a crosshead speed of 500 mm/min. All specimens were conditioned at 23°C and 50% relative humidity for 24 h prior to be tested. Five specimens were

tested, and the average values were accounted for each composition. Engineering stress and engineering strain were reported during uniaxial stretching of the specimen. Young's modulus, the stress at yield point, and the failure (break point) stress and strain for each specimen were calculated from the collected data. The yield point corresponds to the onset of plastic deformation events in the polymer, as the stress–strain curve deviates from linearity. Because of difficulty in precisely measuring this deviation, the 5% offset yield point as the onset of irreversible deformation is used which is the stress at 0.05 plastic strain. It is practically obtained via the intersection point of the stress–strain curve and an offset line drawn from the 0.05 strain and parallel to the elastic region of the curve.[31]

RESULTS AND DISCUSSION

Thermal analysis

Heating scans

Differential scanning calorimetry is a helpful technique in characterization of melting and crystallization behavior of blend films. When a blend is composed of amorphous polymers, the presence of single or separate glass transitions can be a decisive factor in evaluating miscibility of the polymers, but for blends in which one or both components are able to crystallize, the data's interpretation becomes more complicated.[14,32–34] DSC thermograms of films of blends of a wide range of compositions were obtained at a heating rate of 10°C and are shown in Figure 1. DSC thermograms of neat HDPE and LDPE are also presented for comparison. Although PDI and M_w of the neat polyethylenes are alike, nevertheless their difference in chain structure resulted in obvious dissimilar thermal behavior. The melting temperature of neat HDPE is 133°C, whereas a lower melting peak was observed for LDPE at 112°C. It should be noted that the large difference in melting peak for HDPE and LDPE would be originated from their different ability in crystallization so that linear chains such as high density polyethylene are of a higher tendency to crystallize and larger crystallite size than that of disordered branched-chains such as low density polyethylene.[35] As can be seen in DSC melting endotherms of the films of LDPE-rich blends, there are two discrete melting peaks, at lower temperature the first appearing peak, which is showed by T_m^L (low-temperature melting peak), is assigned to melting of LDPE crystals and at higher temperature the second appearing peak, which is showed by T_m^H (high-temperature melting peak), is assigned to melting of HDPE crystals. Upon incorporating HDPE into LDPE, T_m^L of the films of LDPE-rich blends appears at a temperature
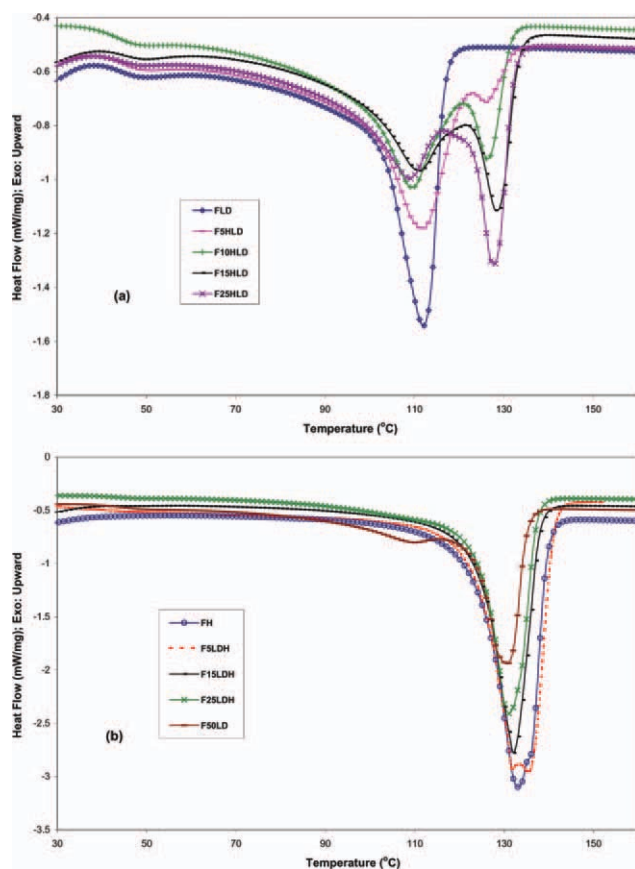
Figure 1 DSC thermograms of films of HDPE/LDPE blends obtained during heating at a rate of 10°C/min (a) predominant fractions of LDPE (b) predominant fractions of HDPE along with 50% HDPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

lower than the melting temperature of neat LDPE and also, the lower the content of LDPE in the films of blends, the less the intensity of the low-temperature first melting peak is. Moreover, scrutiny on T_m^H and second melting peak indicated that even for the film of blend with a very low amount of HDPE such as 5%, the high-temperature second melting peak clearly appears and upon increasing HDPE content in the films, the intensity of the high-temperature second melting peak becomes larger and the peak shifts towards higher temperatures [Fig. 1(a)]. It can be noted that the LDPE, as the minor and less crystalline phase, in the blend crystallizes surrounding the congealed HDPE to a lesser extent than the neat homopolymer and the HDPE phase having thick crystals may act as a nucleating agent for low-density phase having thin lamellae. Besides, one should note that due to the severe chaotic structure and highly branching of LDPE chains, there is no strong driving force for its chains to accord with crystallization process of readily crystallizing HDPE linear chains. Therefore, at temperatures where HDPE has begun to crystallize, the ability of LDPE chains to

enter crystal front of HDPE and form new discrete crystal species with separate middle melting peak different from that of neat LDPE and HDPE would be feeble [see Fig. 1(a)]. This suggests immiscibility for the LDPE-rich blend films in crystalline phase. The film of 95% LDPE blend showed lower sharpness in the melting peak corresponding to T_m^L and the peak was broader than that of neat LDPE film (full width at half maximum of the peak was 16 and 10 for the film of 95% LDPE blend and neat LDPE film, respectively). Likewise, its T_m^H shifts to a temperature 7°C below melting temperature of neat HDPE film. These would be due to partial miscibility in solid state in the film of blend containing very low amount of HDPE.

The DSC heating curves of the films of HDPE-rich blends [Fig. 1(b)] show a completely different behavior, through which a single-peak character at compositions with 5–25% LDPE in the blends can be deduced. With an increase of more than 5% in LDPE content the peak melting temperature decreases and the peak height diminishes, which suggests thinner crystallites as well as lower crystallinity. However, incorporation of more than 25% of LDPE in blend composition changes the thermal behavior of the films of blends to a double-peak melting character, in such a manner that low-temperature melting peak assigned to LDPE phase evidently emerged but it is much smaller and weaker than that of neat LDPE film. Since both components of polyethylene blends crystallize; emergence of only one melting peak in DSC endotherms of blends would be an indication of cocrystallization.[36–38]

Analysis of DSC thermograms in terms of peak half-width, Δw, provides a good insight on thermal behavior of polyolefin-based blends.[34,39,40] The peak half-width (Δw) is related to the distribution of crystallite size; the narrower the width, the more uniform will be the crystallite size. The width of the endotherms corresponding to HDPE melting peak (i.e., high-temperature peak) for films of HDPE-rich blends is wider compared to that of the films of LDPE-rich blends. Thus it can be enunciated crystallite size distribution corresponding to HDPE phase in the HDPE-rich films is broader than that of the films of LDPE-rich blends. In the range of HDPE composition of 100–85%, as the HDPE content decreases the melting peak width reduces, which indicates crystallite size distribution of HDPE phase gradually becomes narrower. An exception was observed for film of 5% LDPE blend in which the width of endotherm was close to and to some extent wider than that of neat HDPE film.

A plot of percentage crystallinity (X_c) of the films of blends as a function of composition is illustrated in Figure 2. The solid line represents the estimated X_c obtained by assumption of linear additivity. The
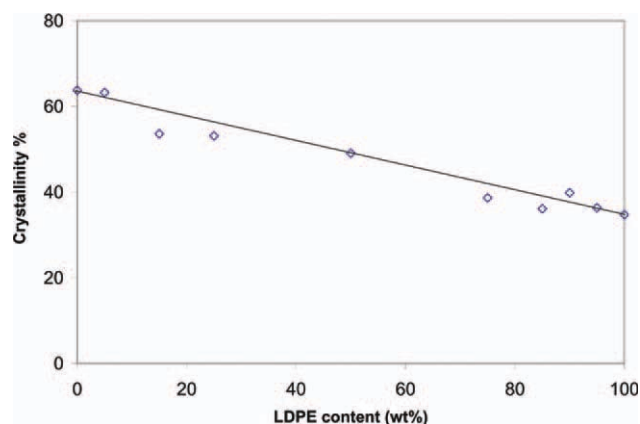
Figure 2 Percentage crystallinity of the films of blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plot shows a downward trend in the X_c that is not perfectly additive with respect to the blend composition. The small deviation from the additivity suggests that the presence of some species of crystal in the film blends influences the capability of other species to crystallize from the melt. The percentage of crystallinity of the LDPE is considerably lower than that of the HDPE which is another characteristic property of polyethylenes with disordered molecular structure.

As illustrated in Figure 3, lamella thickness of LDPE phase in the films obviously remains almost unchanged at different compositions, which suggests that blending has insignificant effect on crystallite size of LDPE component. However, lamella thickness of HDPE phase showed higher values and had evidently different trend compared to that of LDPE with changes in compositions. The lamella thickness of HDPE phase was influenced by the presence of the LDPE, so that the thickness diminishes as the LDPE content increases, and the highest value was
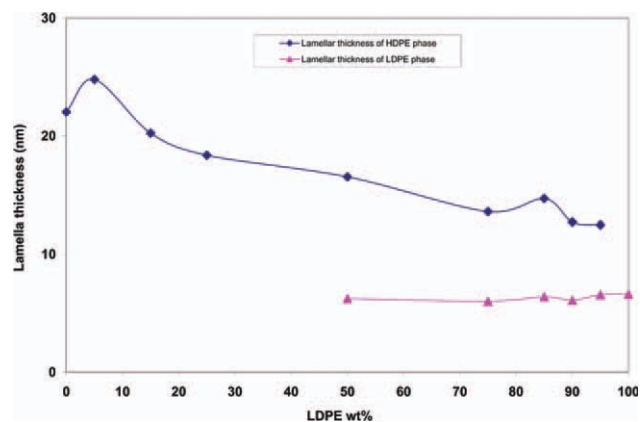
observed for 5% LDPE, which the value was even higher than that of neat HDPE film.

Crystallization behavior

Figure 4 shows the traces of DSC exotherms of the films of HDPE/LDPE blends. One should note that after a heating up to 170°C, samples were maintained for 5 min at this temperature in order to eliminate their preceding thermal history established during film preparation (under biaxial orienting conditions), then all samples were cooled from melt under same conditions without any stretching, in this way effect of blending ratio on crystallization of samples can be investigated.

Exotherm of neat LDPE film was so broad in temperature range of 100–30°C, whereas exotherm of neat HDPE film was narrow which witnesses a wider crystallite size distribution in neat LDPE. Besides, two exothermic peaks for LDPE are observed, one is strong and sharp emerging at 96°C and another is a small and broad shoulder emerging at about 60°C. This is an indication of existence of crystallites with various thicknesses. Furthermore,
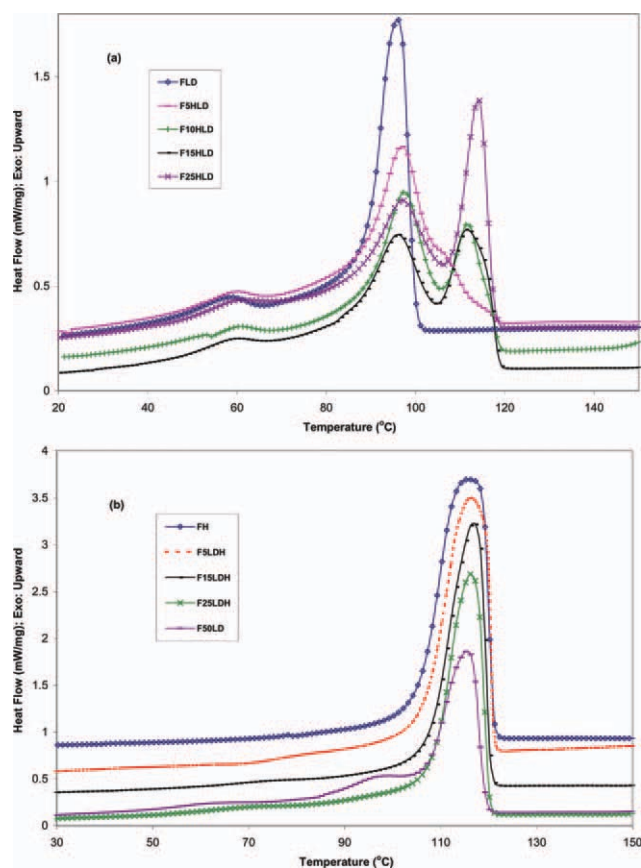

Figure 3 Crystalline lamella thickness for the films of blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 DSC traces of cooling of films of HDPE/LDPE blends (a) predominant fractions of LDPE (b) predominant fractions of HDPE along with 50% HDPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
DSC Results of the Films

Film code	T_m^H (°C)	T_m^L (°C)	ΔH_m (J/g)	T_c^H (°C)	T_c^L (°C)	ΔH_c (J/g)	T_c^{onset} (°C)	Δw
FLD	–	112	−102	–	96.1	119.1	100	–
F5HLD	126.1	111.8	−106.7	shoulder	97	129	118	7.8
F10HLD	126.4	110.1	−117	111.2	97.6	128	118.5	6.9
F15HLD	128	111	−106	111.6	96.8	135.4	118.8	5.6
F25HLD	128	110	−113.5	114.3	97	141.3	118.8	7.5
F50LD	130.7	110.2	−144.1	115.7	98.6	165	119.2	8
F25LDH	131.2	–	−156	116.4	–	171.8	120.1	8.8
F15LDH	132.2	–	−157.4	116.8	–	183.6	120.3	9.5
F5LDH	134	–	−185.7	116.38	–	213.7	121	11.1
FH	133	–	−187.2	115.7	–	222.1	121	10.2

smaller crystallites content (the shoulder peak) is less than that of larger ones. These double crystallization peaks are also an indication of a high degree of branching found in LDPE. More-branched chains form more defected and less stable crystals that form at lower temperature.

As illustrated in Figure 4 all films of blends showed a high-temperature crystallization peak (T_c^H) which increases as LDPE content decreases. However, a second low-temperature crystallization peak (T_c^L) in addition to the peak corresponded to T_c^H was emerged only for films of 50–95% LDPE blends. Crystallization temperature of LDPE phase in film of 50–95% LDPE blends revealed that T_c^L is discernibly shifted. The observed shifts may be ascribed to nucleation effects originated by the existence of HDPE crystals during the crystallization of the LDPE phase. Such nucleation effects have already been reported in polypropylene/metallocene-based ethylene-α-olefin copolymers blends as well as blends containing ultra-low-density polyethylene and HDPE.[41,42] On the other hand, broadening of the exotherms by the existence of diverse crystal sizes with various degrees of perfection may cause the shifts.[43]

In Figure 4(a), the DSC crystallization curves of the films of LDPE-rich blends are shown. The films showed two crystallization peaks during cooling, which is an indication of incompatibility. The origin of the double crystallization peaks could be attributed to the formation separated phases of two populations of crystallites of different thicknesses. One phase had crystallites of large size because it was formed at high temperatures, which is certainly attributed to the polymer with linear chains, i.e., HDPE. But another phase had low crystallite size because it was formed at lower temperatures; this is characteristics of the polymers containing high degree of branching, i.e., LDPE; due to much structural chaos LDPE cannot crystallize at high temperatures. Moreover, in polymer blends, there would be very small local inhomogeneity in the melt; this might be an additional force for occurrence of immiscibility of the blends in the solid state and

therefore, an origin of formation of two distinct crystal populations of LDPE and HDPE in the blend.

Nonetheless, the film of 95% LDPE blend showed a completely different crystallization behavior, so that there are three crystallization peaks (in 90–120°C temperature range) as one major peak pertaining to LDPE phase is accompanied with two shoulder peaks. The weak shoulder at higher temperature (but lower than T_c of neat HDPE film) represents HDPE component but the intermediate shoulder is possibly attributed to cocrystallization.[10] Furthermore, approaching T_c^L and T_c^H of the film supports partial compatibility of the film of 95% LDPE blend in solid-state.

Figure 4(b) demonstrates DSC traces of cooling for the films of HDPE-rich blends. As illustrated the films with composition of 0–25% LDPE showed only a single exothermic (crystallization) peak like that of neat HDPE film and the DSC exotherms are gradually varying in area on temperature scale with varying HDPE weight percent but there is a slight increase (about 1°C) in crystallization peak temperature (T_c^H) (Table III). Adding 50% LDPE to the films of blend caused appearing a second exothermic peak at lower temperature (T_c^L) which is much smaller than the first high-temperature exothermic peak. An interesting observation is that the exothermic peak at highest point for the films of blends is sharper than that of neat HDPE film. Likewise, width of exothermic peak at half height for the films of blend is smaller as compared with neat HDPE film that supports wider crystallite size distribution in neat HDPE film. Altogether, this crystallization behavior of the films of 5–25% LDPE blends would be a manifestation of miscibility of the blends.

Table III has listed onset crystallization temperature (T_c^{onset}) of the samples. The temperatures for neat LDPE film and neat HDPE film are 100 and 121°C, respectively. For the films of blends as HDPE content declines there is a slight and continuing fall in T_c^{onset} from 121 to 118°C. It has been reported that the exotherm peak temperature and onset crystallization temperature in polyolefin blends are related
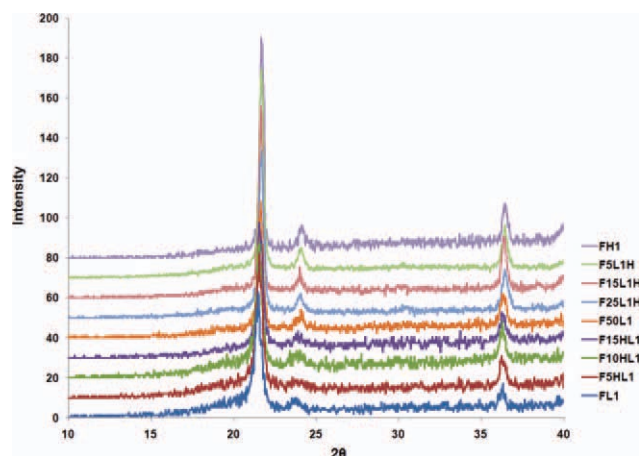
Figure 5 XRD patterns of the films of blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to crystallization rate.[34,39] In view of the fact that exothermic peak temperature (i.e., T_c^H) and T_c^{onset} of the films of blend slowly grow by a decrease in LDPE content, the crystallization rate increases as LDPE content decreases.

The slope of initial portion of the exotherms (at higher temperature side) is essentially influenced by the initial process of crystallization, namely the nucleation, in such a manner that an increase in the slope is accompanied by an increase in rate of nucleation.[34,39,40] As can be seen in Figure 4, for the peak corresponding to T_c^H of films containing lower than 25% LDPE, the slope does not vary but for other films of blends it dwindles as HDPE content reduces. It signifies that the rate of nucleation of HDPE phase for films of HDPE-rich blends is not influenced by presence of LDPE chains, whereas for films of 50–95% LDPE blends it is obvious that the rate of nucleation of HDPE phase is affected by presence of LDPE chains, so that it declines as LDPE content increases.

Observation on the slope of initial portion of the T_c^L exothermic peak (at higher temperature side) for films of 50–95% LDPE blends indicates that addition HDPE into LDPE causes clear change in the slope, so that the slope gradually reduces by growing the HDPE content. Consequently, it can be expressed that the rate of nucleation of LDPE phase in the film blends is lower than that of neat LDPE film. This is due to the presence of HDPE crystals in the melt of LDPE phase, thus the LDPE chains starts to crystallize on the existing nuclei (i.e., HDPE crystals). As a result, this leads to less nucleation of LDPE in the blends in comparison with that of neat material. This again supports that the crystals of HDPE phase has nucleation effects during the crystallization of LDPE phase in the immiscible films of blends (as already mentioned).

Heats of crystallization exotherms, ΔH_c calculated from the area under the exothermic per unit weight of the crystallizable components of a film, are also tabulated in Table III. As observed for the films of blends, the higher LDPE content in the films resulted in more continuously decrease in ΔH_c. This is for the reason that fraction of highly crystallizable chains, i.e., HDPE is replacing with low crystallizable chains.

In brief, two distinct melting peaks and also two distinct crystallization peaks were obvious for the films of blends containing more than 25% LDPE, signifying that separate crystals are formed. Therefore, these films of blends are completely immiscible in crystalline phase, and the exception was the film of blend containing 95% LDPE, in which partial miscibility was observed. In previous reports thermal analysis via DSC showed two melting peak in the blends of low- and high-density polyethylenes describing immiscible systems.[44,45] Nonetheless for the films of present blends containing lower than 25% LDPE, DSC study showed only a single peak in melting and crystallization that can be asserted there was only one crystalline phase as well as no separate crystals, so they can be reported to be miscible in solid-state in the limited composition range.

X-ray diffraction

The intensity-2θ plots of the film blends are shown in Figure 5. Three peaks around 2θ = 21.6, 24, and 36.4 corresponding to the (110), (200), and (020) reflections are observed in the figure. The diffraction patterns of the films have similar features, however peak of (200) reflection was very smaller for films of LDPE-rich blends compared with that of the others. The Bragg's equation was used to calculate the d-spacing. Measured d-spacing values for the (110) and (020) reflections of the film blends are demonstrated in Figure 6(a). The d-spacing values for the (020) reflection showed a very slight composition dependence. Nevertheless, the d-spacing values measured from the (110) reflection are largest for LDPE and smallest for HDPE, whereas the values gradually decreases as LDPE content of the film blend reduces. The total change in d_{110} is less than 0.1 Å, which is not ignorable as it is systematic and regular over the whole range. Some researchers have reported such small variation in d-spacing for blends of different kinds of polyethylene.[46,47]

Crystallite size (or lamella thickness) and crystallinity information of the films is also presented in Figure 6(b). Crystallinity decreased with increasing LDPE content. The crystallite size was calculated by the Scherrer's equation from the half-width of 110 diffraction peak.[48] A reduction is observed in the crystallite size with increasing LDPE content. Moreover, the crystallite size of film blend with 5% LDPE
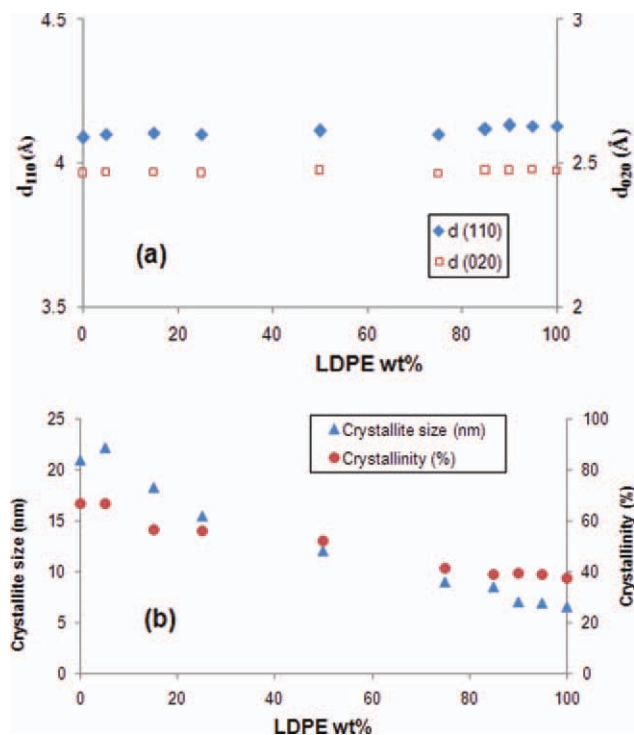
Figure 6 (a) The *d*-spacings as a function of LDPE content for the (110) and (020) reflections of the samples, (b) crystallinity percent and crystallite size measured by XRD technique for the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was higher than that of HDPE film. The reduction of crystallite size may be ascribed to the hindrance of mobility of HDPE chains by the LDPE chains, which might restricts thickening of crystallites. At low LDPE content (namely, 5%), the LDPE seems to facilitate the mobility of HDPE chains owing to increased free volume due to the presence of side-chain branches, which helps formation of thicker crystallites. Based on these observations, the XRD results supports conclusions based on DSC.

The trend of variation of crystallinity and crystallite size values measured by XRD and DSC techniques is qualitatively almost similar. Some difference in the values obtained by DSC and XRD might be due to the different principles of measurement in the two instruments. Beside, XRD-based crystallite sizes are a measure of the average crystallite size of a polymer system, but the DSC results are based on the peak melting temperature, which is related to the mainly plentiful crystallite size present in a system.[2]

Mechanical properties of films of neat polyethylenes and PE blends

Figure 7 illustrates measurement of engineering stress versus engineering strain curves of a selection of the film blends which are stretched in machine

direction at a constant rate of 500 mm/min. As Figure 7 shows a three-stage behavior was observed for the films: The sample extends elastically and shows a linear behavior in the first region. There is recoverable deformation in the first region followed by the second region where the slope of stress–strain curve decreased while approaching zero, in which point the polymer yields and plastic deformation appeared. In this region the polymer experiences a cold drawing behavior over which the films develop a neck. Finally, in the third region strain hardening happens over which the slope of the curve increased gradually in consequence of growing value of the elastic modulus with molecular orientation until the film breaks.

As seen in Figure 7 the yield point for LDPE films (and also films of LDPE-rich blends) is a region of curvature approaching lower slope in the stress-strain curve, as no obvious maxima peak was observed. But for neat HDPE film as well as HDPE-rich blend films a distinct maximum is appeared. The obviously observed yield point for neat HDPE film vanishes gradually as LDPE content in the film blends increases. Similar was recently reported for the yield point of blends of PE and polypropylene by Mourad.[49] He expressed that this observation might reveal that the two polymers are partially miscible. The strain at which yielding happens is almost at a similar strain, around 10% for all films of HDPE/LDPE blends or neat components. This is in accord with other reports that strain at yield is independent of factors such as crystallinity,[50] molecular weight and temperature.[51,52] Whereas, yield stress changes with increasing HDPE content in the films of the blends, which can be attributed to total crystallinity of the films.

As seen in Figure 7, cold drawing after the yield point is observed for all films of blends, which means that there must be a strain-hardening process;
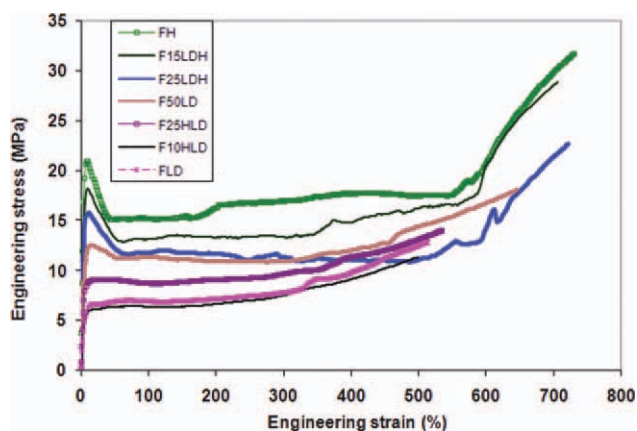

Figure 7 Engineering stress–strain curves for the films of blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

otherwise, the material would break without cold drawing at the reduced cross section where necking took place. In appearance of the films which are tested, cold drawing was appeared as a necking of the films through elongating. Cold drawing influences molecular arrangement of polyethylene chains so that the crystalline phases orient in such a way that the direction of the polyethylene chains are parallel. In addition, it causes chains in amorphous phases become aligned in the direction of stretching. Peterlin[53,54] reported that during cold drawing plastic deformation of crystals, which destroys crystalline structure, as well as chain slippage takes place. Since the slippage and displacement of polymer molecules with respect to each other are in general not recoverable, a permanent deformation comes about in the second region.

In third region, molecular orientation during stretching is in general a cause of strain-hardening which finally causes growing up the modulus and tensile strength. For the case of present films of PE blends, the strain-hardening might come somewhat from strain-induced crystallization, which is more pronounced in neat HDPE film due to its linear structure. For all films the maximum engineering stress, i.e., ultimate tensile strength is the same stress at which the film fracture happens, i.e., fracture stress.

The stress–strain curves showed that all films are flexible, tough and ductile and neat HDPE films is of higher modulus, yield stress, and ultimate tensile strength than those of neat LDPE films. Doubtlessly, this general behavior of low density and high density polyethylene films is powerfully influenced by crystalline/amorphous structure and content of crystallinity.[1] There exists an important factor that makes HDPE tougher. Easily disentanglement of interlamellar links may be the reason of sooner fracture. There is an important type of interlamellar connection, called "tie molecules" which are the intercrystalline or amorphous polymer chains that begin and end in adjacent lamellae, thus play the role of connectors.[3,4] Tie molecules owing to covalent bonds are strength. Strength originates principally from the tie molecules, because during stretching the tie molecules hold crystalline layers together. The lower fracture toughness of the LDPE evinced that fewer tie molecules are formed in comparison with the HDPE case. Since the LDPE have a number of long-chain branches, the distance between the ends to the molecules will be reduced compared with the end-to-end distance of a linear PE with the same M_w. Consequently, the possibility of forming a tie molecule is decreased.[3]

There is still another factor that affects toughness of HDPE. As it is known entanglements in amorphous regions strongly affect strength of polymers.

Thus, due to branching in LDPE chain structure, there is less chain entanglement for LDPE chain than HDPE chains (for a given molecular weight). Therefore, this can be another reason for lower tensile strength and strain at break of neat LDPE film. This is in agreement with results of investigations done by Wayman et al.[55] and Toggenburger et al.[56], where tensile properties of linear and branched polystyrene were studied. They also corroborated that branched polystyrene showed lower tensile strength and strain at break due to low level of entanglements between its chains in comparison with linear polystyrene. Thus, so that polystyrene is not crystalline they were able to interpret the effect of chain branching, in absence of complex effect of crystallinity.

For films of blends, while HDPE content in the films of blends declines the shape of stress–strain curve approaches that of neat LDPE films and strain-hardening behavior gradually fades. This is due to the diminishing percent and ability of crystallization which accompanied with a decrease in HDPE content of the films of blends. Furthermore, the tensile properties (strength and strain at break) of LDPE-rich film blends are lower as compared with those of HDPE-rich film blends because:

1. Higher LDPE content in the blends results in a reduction in the number of the tie molecules and fraction of large crystallites;
2. There is a lower number of physical entanglements in amorphous regions of the blends;
3. There are large number of weak interfaces and imperfection. So that boundaries between different crystal species may act as defects and stress concentrators for the premature fracture (failure), due to the phase segregation and separated crystals (based on thermal analysis data).

The values of the tensile properties of the films of blends in the machine direction (MD) are analyzed as follows.

In Figure 8(a), the Young's modulus in the MD of the neat LDPE film is 164 MPa, whereas that of neat HDPE film is 717 MPa and there is a synergistic behavior in the films of polyethylene blends with low LDPE content, which is due to solid-state miscibility of the blends in the studied composition range. However, the Young's modulus in other compositions negatively deviate from the theoretical direct line drawn between the modulus of the films of neat components (namely the theoretical line that represents the situation where the observed modulus is additive) especially in predominant fractions of LDPE, which might be due to immiscibility occurred in the films of the blends. It was also suggested by thermal analysis.
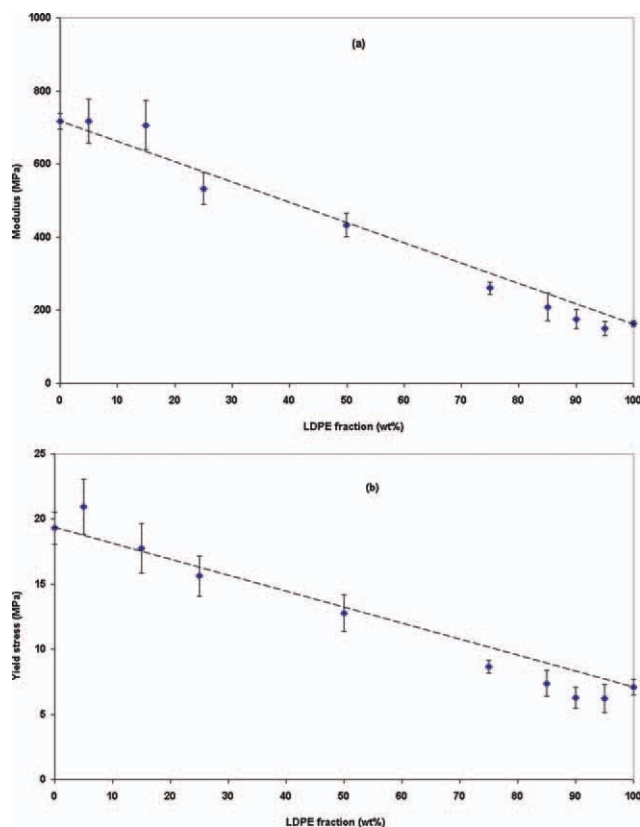
Figure 8 Young's modulus and yield stress vs. LDPE fraction for the film blends in the MD of film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The stress at yield in the MD of the films of blends is plotted against composition in Figure 8(b). As also seen, the values of stress at yield, with the exception of the films of 5–15% LDPE blends, are close and lower than the simple rule of mixtures. Moreover, the plot of the stress at yield is almost similar as that corresponds to Young's modulus. This is usual in polymer blends, in which the behavior with respect to linearity of both low strain properties is generally very analogous.[57–59] As can be seen, both modulus and yield stress do not show a linear behavior with composition. Deviation from the rule of mixtures has been observed in miscible or immiscible polymer blends. Deviation from linear behavior in blends might be a major consequence of phase separation in immiscible blends and/or due to change in crystallinity of the components of the blends upon blending.[60–63]

The tensile strength (TS) values in the MD of the films of PE blends as a function of the composition are shown in Figure 9(a). The maximum values for the tensile strength belongs to the film of blend with 5% LDPE (37.5 MPa). The minimum values for tensile strength was 9.8 MPa corresponds to the film of blend with 5% HDPE. The tensile strength for the films of LDPE-rich blends was even smaller than

that of the film of neat LDPE, i.e., presence of low amount of HDPE in the films of blends has an unfavorable effect causing a diminished TS. As explained in thermal analysis section, incompatibility and phase separation in the film blends might be the reasons for lower TS of the films. This is consistent with findings reported for blends of HDPE with conventional LDPE, which formed separate crystal structures with generally poorer properties.[60,63–65]

As it is observed in Figure 9(a) the tensile strength of the film blends did not change regularly over composition range of LDPE. The TS of the films of blends containing high amount of HDPE was above that of predicted by the direct rule of mixtures (broken line), and a strong synergism was observed in the TS of the film of the LDPE/HDPE blend 5/95, and the TS value was very close to the reference linear line for the films of 15% LDPE blend, but was lower than that predicted by the simple additive rule in the films of LDPE-rich blends. Interestingly, the TS values of the films of 25–75% LDPE blends change linearly with composition, although they were located below the prediction of linear additivity. In some reports, practical properties of blends of high- and low-density polyethylenes were observed to be proportional to blend ratio.[66,67]
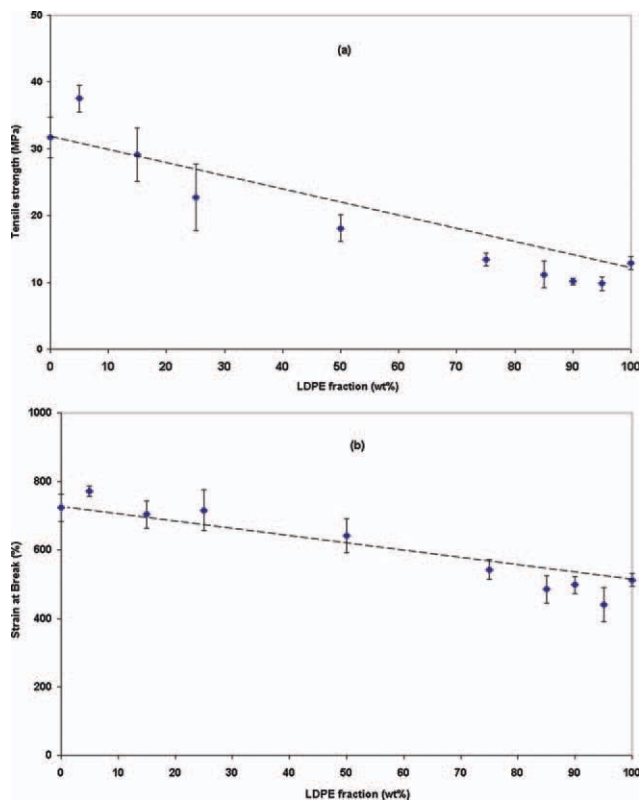

Figure 9 Tensile strength and strain at break vs. LDPE fraction in the MD of the films of blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
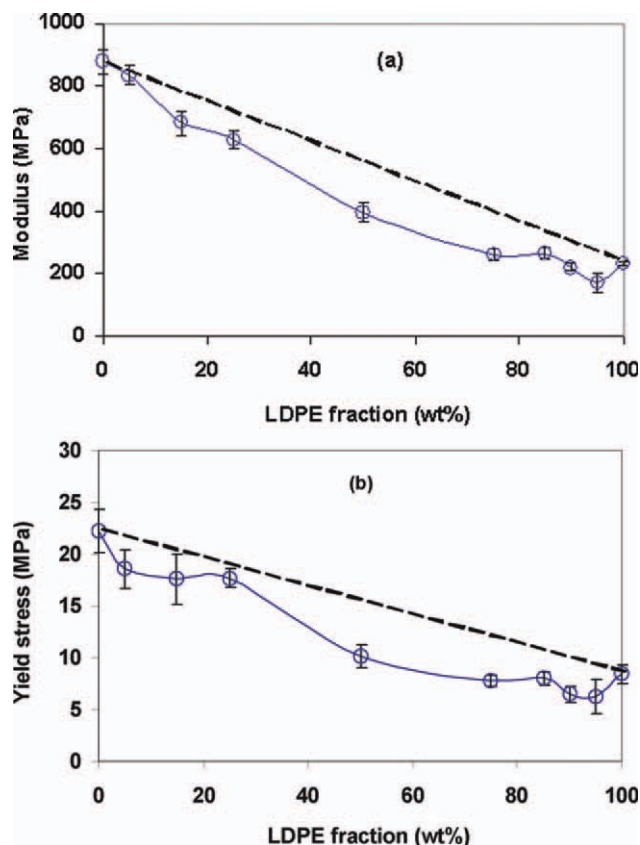
Figure 10 Young's modulus and yield stress vs. LDPE fraction for the film blends in the TD of film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The strain at break of the films of blends and pure polyethylenes, as measured in machine direction (MD) is illustrated in Figure 9(b). From the figure, the break strain of neat HDPE film was higher than that of neat LDPE film. And the break strain of the films of HDPE-rich blends was higher as compared to that of LDPE-rich blends. There is a significant improvement in the strain at break at 5% LDPE; this suggests synergistic effects at low LDPE compositions. In some previous studies was also reported synergistic improvement of properties such as film draw-down and stiffness in blends of HDPE and low-density polyethylene.[64,66] However, for LDPE concentrations higher than 15% the strain at break of the film blends reduces. Therefore, as can be observed, the strain at break of the films of blends does not follow the rule of mixtures. For many polyethylene blends it is reported that tensile properties were found to violate linear rule and show positive and/or negative deviations.[64,68–71] Improvement of toughness of film of 5 % LDPE blends is a result of its higher crystallite thickness and good miscibility.

In the plot of the strain at break, Figure 9(b), the positive deviation for film blends with low LDPE content can be attributed to solid-state miscibility,

but the negative deviation observed at low HDPE contents can be a result of heterogeneity in crystalline phase as beforehand suggested through DSC thermograms.

The Young's modulus and the yield stress of the film blends as a function of the LDPE content is given in Figure 10 in the transverse direction (TD) of the film. The Young's modulus, as shown in Figure 10(a), decreases from 878 MPa to a minimum of 171 MPa at 95% LDPE. These data are below the prediction of additivity rule (broken line).

The trend in the values of the yield stress [Fig. 10(b)], the tensile strength and the strain at break in the TD of the film (Fig. 11) was revealed similar, i.e., the data versus composition show intensive decreasing trend with LDPE content initially, but they increase at 15 and 25% LDPE and after that, again decrease up to and including 95% LDPE. Besides, the yield stress and the tensile strength in the TD of the film are very low and far from the reference line of the direct rule of mixtures, however the strain at break was rather close and below the line.

Comparing the mechanical properties in the machine and transverse directions, it can be
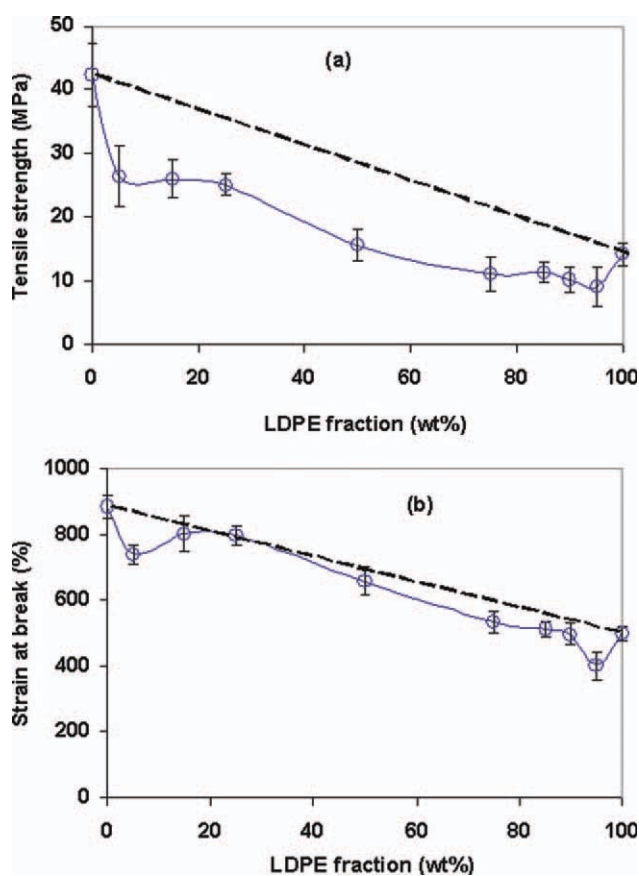

Figure 11 Tensile strength and strain at break vs. LDPE fraction in the TD of the films of blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

comprehended that unlike the tensile properties in the MD of the film, which showed improvement for the film blends containing low amount of LDPE, it was not observed any improvement in the tensile properties in the TD of the film. It suggests no synergistic effects in the TD of the film, even at low amount of LDPE. Since the films were made using a lab-scale film blowing equipment which induces biaxial orientation in the films, anisotropic behavior is recognized through different values of mechanical properties in the MD and TD for the film blends at the same compositions.

CONCLUSION

LDPE and HDPE with almost same molecular weight and similar PDI were selected to produce film of HDPE/LDPE blend system via film blowing extrusion. Thermal and mechanical behavior of the blends with systematically variable composition was investigated. The technical importance of this research and its findings remains in prediction of polyethylene blends mechanical properties and morphology based on the chosen starting materials.

According to DSC thermal analysis, the overall picture of the solid-state miscibility/immiscibility in two ranges of blend composition can be described. Double melting peaks and also two distinct crystallization peaks for the films of blends having more than 25% LDPE were observed, which both manifest organization of separated crystal phases. This supports immiscibility in solid-state for these film blends. A film of 95% LDPE blend was an exception in which partial miscibility was deduced. Nevertheless, for the films of HDPE-rich blends, single melting and crystallization peaks affirmed the presence of one population of crystallites as well as no segregation in crystalline phase. Subsequently, they are judged to be miscible in solid-state in a limited range of composition.

The decrease of crystallinity was resulted as LDPE content reduced and it did not perfectly follow the additivity rule of mixtures. The lamella thickness corresponding to HDPE phase extends as the LDPE content reduces, and the thickest crystallite size was detected for film of 5% LDPE blend. However, blending showed no impact on the lamella thickness of LDPE phase in the film blends.

Exothermic crystallization curves revealed that in the films of HDPE-rich blends the addition LDPE did not change the nucleation rate (i.e., the slope of initial position of the exotherms) and a small upward shift in crystallization peak temperature compared to that of the neat HDPE. Furthermore, the crystallite size distribution of HDPE phase in the film blends was wider than that in the film blends with predominant fractions of LDPE.

XRD measurements supported conclusions made based on DSC results. Moreover, XRD-crystallite size was also reconfirmed that the film blend with 5% LDPE had the thickest crystallites and an increase of more than 5% in LDPE content results a decrease in crystallite size.

The tensile properties (strength and strain at break) of the films of LDPE-rich blends were found to be lower as compared with those of film of HDPE-rich blends. This is mainly due to lower amount of tie molecules, number of physical entanglements, and crystallinity percent as well as smaller crystallites and also the presence of a large number of weak interfaces and defects which are formed at boundaries of segregated phases. Likewise, as HDPE content in the films of blends diminishes the shape of stress–strain curve approaches to that of neat LDPE films and strain-hardening behavior gradually fades.

There are some improvements in mechanical properties in the MD of the film blends with low LDPE contents, and a synergistic effect was observed for the film of 5% LDPE blend. But all mechanical properties in the TD of the films were lower than the predictions of linear additivity rule and no synergistic effect was observed in properties of the film the TD.

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