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Influence of phase segregation on the mechanical properties of binary blends of polyethylenes that differ considerably in molecular weight

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Abstract

Phase segregation in melt-extruded blends of polyethylenes that differ considerably in molecular weight was found to exert diverse degrees of influence on various measured mechanical properties. The development of phase segregated morphology was found to depend on blend component viscosity in conjunction with blend composition. The instantaneous tensile deformation properties were insensitive to phase segregation while the high-strain tensile deformation behavior was strongly and adversely influenced by phase segregation. In certain instances, phase segregation was found to favor plane stress fracture resistance. Finally, the bulk crystallization kinetics of such blends also revealed signatures of phase segregation in the form of incomplete co-crystallization of the blend components.

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1. Background

Over ten million metric tons of polyethylene (PE) is consumed in the USA every year. The semi-crystalline nature of polyethylene makes it a suitable choice for a variety of commodity and specialty applications. Crystallinity offers many desirable attributes such as stiffness, strength, barrier to gas (moisture, oxygen) transport, chemical resistance and dimensional stability. The non-crystalline phase imparts such attributes as toughness and resistance to slow crack growth.

Polymer blends, both miscible and immiscible, have been employed commercially for many decades now [1]. Blends of various PEs are also commonplace; in particular, mixtures of linear PE (highly crystallizable PE) with branched PE (branches act as crystallizable defects lowering the maximum attainable crystallinity) are thought to provide a balance in properties. The phase behavior of blends of PEs that differ considerably in their crystallizability has been studied extensively using a variety of experimental techniques such as calorimetry, neutron scattering, X-ray scattering and microscopy [2–16]. In general, these investigations indicate a homogenous melt for such blends as long as the branched PE had less than about 60 short-chain branches per thousand backbone carbon atoms (SCB/1000BC). When such homogenous blends are cooled from their melt state, phase segregation can occur because of differences in the crystallization kinetics of the blend components. Generally speaking, phase segregation will occur in all systems if the cooling is accomplished very slowly. The more similar the crystallization kinetics of the components, the slower is the cooling rate required to cause crystallization-induced solid–liquid phase segregation in the blends. This also implies that co-crystallization of the blend components is favored when the cooling rate is fast enough to prevent crystallization-induced solid–liquid phase segregation.

Bulk of the phase segregation experiments performed on blends of linear and branched PEs have focused on

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components that are not considerably different in molecular weight. Further, some reports suggest that the phase behavior of such blends is not a function of the molecular weight of the components [17,18]. However, these investigations focus on blending the components in dilute solution followed by precipitation in a non-solvent. While this procedure ensures reasonably good overlap of the component molecules in the final specimen, it is far from commercial practice. Finally, the afore-mentioned investigations have paid little attention to the mechanical properties of such blends. In other words, very little is known about the merits of co-crystallization, or lack thereof, from a physical performance perspective. In order to address the above limitations, we have chosen to study binary PE blends whose components differ considerably in molecular weight. In order to closely mimic commercial practice, we employ twin-screw extrusion for blending the components. Because the thermodynamics of such blends have been studied and reported on, we will focus on extrusion melt-mixing wherein phase segregation is anticipated when the viscosity mismatch between the blend components is significant. By studying a series of blends with certain blend compositions exhibiting phase segregated morphologies, we hope to characterize the influence exerted by phase segregation on the mechanical properties of such blends.

2. Experimental

All of the base polyethylenes (blend components) were synthesized using bench-scale polymerization reactors using metallocene-based catalysts. Appropriate amounts of the blend components were physically mixed with suitable amounts of anti-oxidants and tumbled to obtain a reasonably homogenized mixture. Subsequently, the tumbled mixture was extruded (220 °C) using a PRISM 16 mm 25:1 *L/D* co-rotating twin-screw extruder; the extrudate strand was quenched in a water bath and pelletized. All of the bulk crystallization experiments were carried out using a Perkin Elmer Diamond Differential Scanning Calorimeter (DSC), which was calibrated using indium and zinc standards. All of the experiments were performed under a nitrogen blanket. Approximately 5–6 mg samples, in the form of circular disks, were used for all the DSC experiments. Shear rheological measurements, at 190 °C, were made using the ARES-2000 torsional rheometer.

Tensile measurements were performed on compression-molded dog-bone specimens using ASTM D638. The tensile specimens were 25.4 mm long, 6.4 mm in width and 2 mm in thickness. The crosshead speed was 51 mm/min. Five specimens were tested for each sample. The plane stress impact fracture resistance of the specimens, at room temperature, was measured using the razor-notched Charpy impact test according to ASTM F2231. Specimens for both the tensile and the impact tests were prepared by compression molding (190 °C) followed by slow cooling to room temperature. This ensures a constant thermal history for the test specimens with the assumption that the equilibrium melting temperature for the blends is unchanged.

3. Results and discussion

3.1. Molecular weight and shear rheology

The characteristics of the blend components and blends (of varying composition) investigated are listed in Table 1. First, the high (HMW) and the low (LMW) molecular weight components differ considerably in molecular weight. However, the molecular weight of LMW is considerably higher than the critical entanglement molecular weight of polyethylene. Both components display narrow MWD (molecular weight distribution) with M_w/M_n values well below 3.0. The zero-shear viscosity and the average melt relaxation time of HMW are about four orders of magnitude larger than those of LMW. However, both HMW and LMW are homopolymers (zero short-chain branches). Blends of HMW and LMW will be described as "Blend *XX*/*YY*", where "*XX*" is the weight percent of HMW and "*YY*" is the weight percent of LMW. Both HMW and LMW are believed to be devoid of rheologically significant 'long' branches; this is based on the relationship between zero-shear viscosity and weight average molecular weight [19].

The measured molecular weight and melt rheological attributes of the various blends are consistent with expectation. Fig. 1 shows the dynamic mechanical data (at 190 °C) for the blends. A systematic increase in viscosity is noted with increasing amounts of HMW in the blend, with the magnitude of increase being larger at lower frequencies. This data do not reveal any obvious signs of phase segregation across the entire composition range.

3.2. Mechanical properties

All of the mechanical properties were measured on isotropic specimens prepared by compression molding at 190 °C followed by slow cooling. In Fig. 2, the weight fraction crystallinity (W_C) of the slow-cooled blend specimens is plotted as a function of blend composition. W_C is based on heat of fusion measurements using 293 J/g as the fusion enthalpy for fully crystalline PE [20]. A systematic decrease in crystallinity with increasing HMW composition is evident. This decrease in crystallinity can be attributed to an increased entanglement density that suppresses the overall crystallizability of the blend (for the slow-cooled thermal history imposed).

Table 1
Basic characteristics of the blend components and the blends

Component	M_w (kg/mol)	M_w/M_n	η_0 − 190 °C (Pa s)	τ_η − 190 °C (s)	W_C
HMW	890	2.7	7.5E + 06	5.2	0.58
LMW	37	2.4	1.4E + 02	0.0001	0.84
Blend 20/80	211	15.3	4.9E + 03	0.0002	0.80
Blend 30/70	323	15.2	2.1E + 05	0.34	0.79
Blend 40/60	397	17.3	5.4E + 05	1.36	0.76
Blend 45/55	439	18.7	8.3E + 05	1.95	0.74
Blend 50/50	465	16.3	1.5E + 06	2.85	0.74
Blend 55/45	516	16.1	1.6E + 06	2.76	0.72
Blend 60/40	551	16.6	2.2E + 06	3.26	0.71
Blend 80/20	712	16.4	5.1E + 06	3.91	0.69

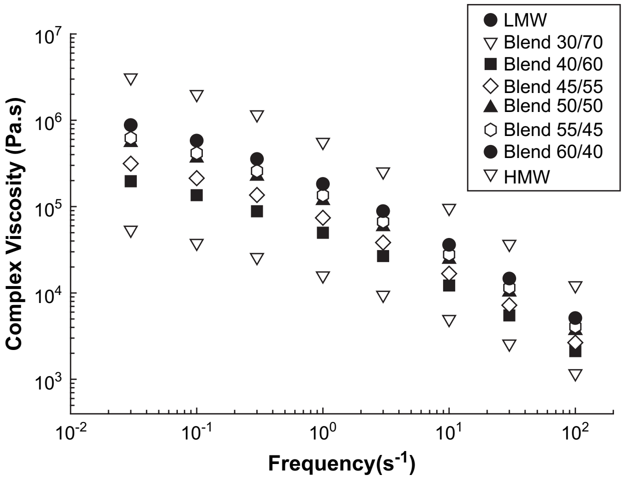

Fig. 1. Dynamic mechanical properties (at 190 °C) for the blends, plotted as complex viscosity versus frequency.

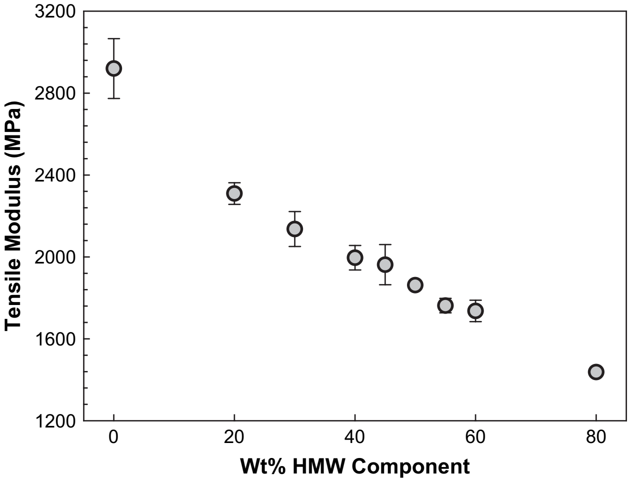

Fig. 3. Tensile modulus plotted as a function of blend composition.

In Fig. 3, the tensile modulus of the blends is plotted as a function of blend composition. The instantaneous tensile properties of unoriented PE are well known to be a unique function of crystallinity or density [20–22]. For the subject blends, the modulus is observed to track crystallinity very well and appears to be insensitive to phase segregation (subsequent results indicate phase segregation in blends wherein LMW is the major component). Similar trends for the tensile yield stress and strain were also evident.

The ultimate tensile properties of unoriented PE are known to be influenced by crystallinity, molecular weight and branching distribution [20,23]. Specifically, the break stress is known to increase with increasing W_C and with increasing molecular weight; preferential placement of branches on the longer molecules also favors higher break stress [23]. For the subject blends, W_C varies from about 68% for Blend 80/20 to about 80% for Blend 20/80; the W_C of LMW is about 84%. While the change in W_C across the blend series is small, the change in molecular weight is considerable (Table 1). Molecular weight is known to exert a stronger influence on break stress relative to crystallinity [23]. Therefore, it is reasonable to expect the break stress to increase with increasing amounts of HMW in the blend. In Fig. 4, the break stress of the blends is plotted as a function of composition. The break stress for blends in which LMW is the major component (≥50 wt%) is considerably lower compared to both the LMW component by itself and the other blends. This is quite surprising considering that the molecular weight of these blends is substantially higher than that of LMW. The break stress of Blend 50/50 is quite similar to that of LMW; Blend 55/45, Blend 60/40 and Blend 80/20 display progressively higher break stress values. Specifically, blends in which HMW is the minor component display break stress values that are considerably lower than that of either blend component. This suggests that some degree of phase segregation exists in blends where LMW is the major component and that the ultimate tensile properties of such blends are sensitive to phase segregation.

In tensile deformation experiments, the low strain deformation is largely driven by the crystalline phase with the interlamellar non-crystalline component helping transfer the load

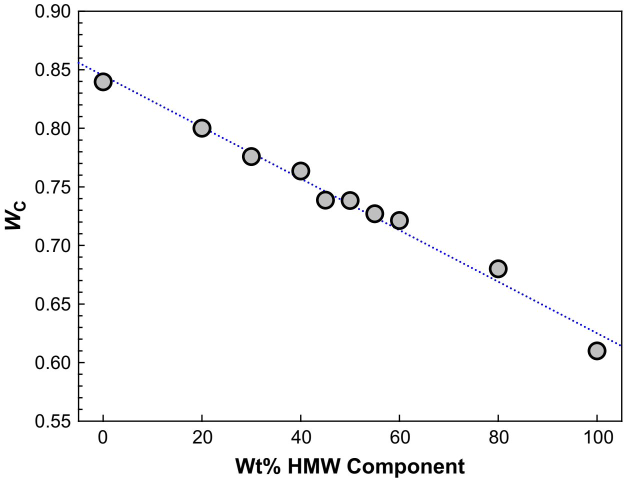

Fig. 2. Weight fraction crystallinity (from heat of fusion), for the slow-cooled molded specimens, plotted as a function of blend composition.

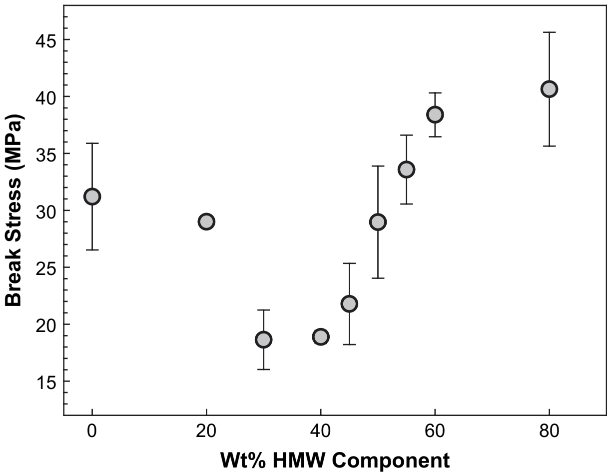

Fig. 4. Tensile break stress plotted as a function of blend composition.

to and inbetween the lamellae. The yield point or the onset of plastic deformation is known to coincide with the onset of crystallographic slip processes with the length of the crystalline stem determining the nucleation rate of the dislocations that trigger the slip phenomena [16,24]. At higher strains, the stresses generated during stretching of the entangled chain segments in the inter-lamellar phase becomes larger than that required for deformations within the crystalline lamellae. Such a sequence of events results in the onset of strain-hardening in a tensile stress–strain experiment. Consequently, the onset of strain-hardening, also referred to as the natural draw ratio or NDR, is thought to be a function of the density of chain entanglements in the inter-lamellar phase [23–29]. For a given thermal or crystallization history, the tensile NDR is thought to be a function of molecular weight and chain architecture. Specifically, the NDR decreases with increasing molecular weight and with increasing concentration of crystallization defects such as short-chain branches [23].

In Fig. 5, the tensile load-deformation traces for Blend 45/55 and Blend 55/45 are shown. The molecular weight and crystallinity of these two blends are very similar. However, their high-strain tensile deformation behavior is very different; Blend 55/45 shows a distinct strain-hardening character that is completely absent in Blend 45/55. Blend 50/50, Blend 40/60, Blend 30/70 and Blend 20/80 also do not display strain-hardening. In other words, tensile strain-hardening was completely absent for blends in which HMW was present at equal to or less than 50 wt% composition. Because the molecular weight (and its distribution), crystallinity and branching distribution for Blend 45/55 and Blend 55/45 are not that different, it is difficult to attribute the tensile observations at high strains to substantial differences in the entanglement density in the inter-lamellar regions. Therefore, we suggest that for blends in which HMW is the minor component, the micro-structure lacks the continuity required for strain-hardening to occur. This lack of continuity in micro-structure may be a consequence of phase segregation in the melt (that develops during melt-mixing) that is preserved in the solid state. In other words, we hypothesize that the strain-hardening signature is evident only in those blends that exhibit complete co-crystallization of the components.

Fig. 6 shows the impact energy (plane stress fracture resistance) of the blends plotted as a function of composition. A systematic increase in impact energy with increasing amounts of HMW is evident. The rate of increase in impact energy with blend composition is much greater for blends in which HMW is the minor component. It might be argued that pockets of HMW dispersed within the specimen does a better job absorbing energy under impact loading relative to a fully-mixed composition of HMW and LMW. Such an impact-toughening approach is similar to that employed in commercial products such as high-impact polystyrene (HIPS) and impact-modified polypropylene. In other words, we suggest that phase segregated pockets of HMW serve as impact-toughening agents for such blends.

3.3. Melt-mixing and morphology

Mechanical property measurements indicate, indirectly, some degree of phase segregation for blends in which LMW is the major component. Let us consider this hypothesis from the perspective of previous reports on the melt-mixing of polymers that differ in viscosity. It is well known that the mixing of two fluids that differ considerably in viscosity depends on the composition of the mixture [30–32]. For polymer blends prepared by melt extrusion, it is desirable for the higher-viscosity component to also be the major component. This enables the transfer of stress from the high-viscosity fluid to the low-viscosity fluid such that a better dispersion of the minor component is easily accomplished. In our blends where the components differ considerably in melt viscosity, we propose that the mixing was inadequate when HMW was the minor component such that co-crystallization of the components was at least partially inhibited during cooling. However, when HMW was the major component, efficient stress transfer that occurred consequently during the twin-screw extrusion

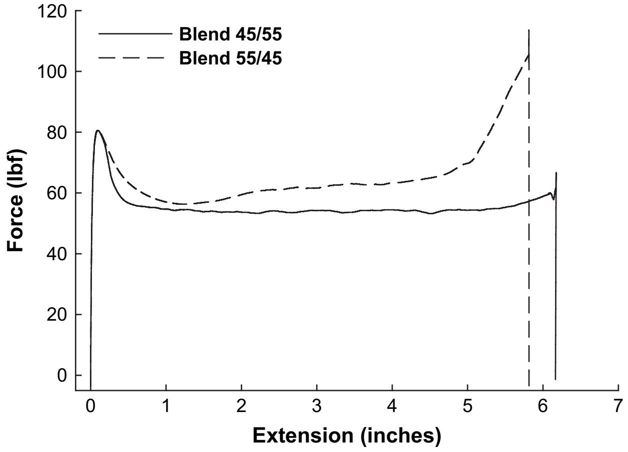

Fig. 5. Representative tensile stress–strain curves for Blend 45/55 and Blend 55/45.

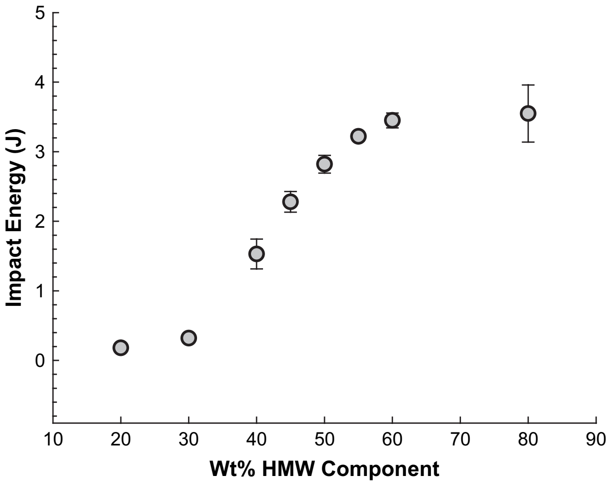

Fig. 6. Razor-notched Charpy impact energy plotted as a function of blend composition.

blending of the components probably ensured a well-mixed system that enabled co-crystallization to occur.

Fig. 7a and b shows scanning electron micrographs of the surfaces of specimens from Blend 40/60 and Blend 60/40. The micrograph for Blend 60/40 (7b) reveals the usual features of lamellar morphology. However, Blend 40/60 (7a) shows several distinct droplets that are dispersed within the specimen. Some of these droplets are highlighted (dotted circles) for emphasis. We propose that droplets of HMW are dispersed within the blend because of poor mixing during twin-screw extrusion. These droplets are then preserved during the solidification step. In other words, when LMW is the major component, the inefficient stress transfer between the low-viscosity major component and the much higher-viscosity minor component resulted in incomplete mixing that caused droplets of HMW to be dispersed within the continuous LMW phase. Because HMW and LMW are homopolymers, it is important to note that there are no thermodynamic drivers for their blend to phase segregate; phase segregation is driven by the inability of LMW to completely assimilate HMW during the twin-screw compounding step. Consequently, co-crystallization between HMW and LMW is incomplete in blends in which LMW is the major component.

3.4. Bulk crystallization kinetics

In order to probe the existence, or lack thereof, of co-crystallization in the subject blends, we performed select bulk crystallization kinetics experiments. Specifically, non-isothermal melt-crystallization experiments were performed using a DSC. The blends were cooled from the isotropic melt state (170 °C) at 10 °C/min and the resulting exotherm was analyzed to yield the temperature (T_{mc}) at which half the total crystallization was complete. The crystallization exotherm for Blend 40/60 and Blend 60/40 are shown in Fig. 8. Blend 40/60, which is known to exhibit some degree of phase segregation, displays a broad exotherm relative to that of Blend 60/40. This is perhaps indicative of a lack of complete co-crystallization in Blend 40/60. In fact, the crystallization exotherm for all phase segregated blends was found to be broader compared to that of the well-mixed blends. Therefore, we suggest that a narrow crystallization exotherm is indicative of co-crystallization, while a broad exotherm represents the lack of complete co-crystallization.

T_{mc} for all the blends is plotted as a function of blend composition in Fig. 9. The non-isothermal crystallization kinetics for HMW is slower (compared to LMW) because of its higher molecular weight. For the blends, a distinct discontinuity in T_{mc} is evident at the 50/50 composition. Blends with HMW as the major component ($\geq$55 wt%) display a distinctly lower T_{mc} that also appears to be somewhat independent of composition. On the otherhand, T_{mc} decreases systematically with decreasing amounts of LMW for blends in which HMW is the minor component ($\leq$50 wt%). These observations suggests that co-crystallization occurs readily in blends in which HMW is the major component. However, the crystallization characteristics for blends in which HMW is the minor component suggests a phase segregated micro-structure with incomplete co-crystallization of HMW and LMW. In other words, we propose that the broader crystallization exotherm for the phase segregated blends includes contributions from the crystallization of pure-HMW and a mixture of HMW and LMW.

3.5. *Effect of ''HMW'' molecular weight*

The mechanical property and bulk crystallization observations indicate that blends in which HMW is the minor component exhibit a phase segregated melt that is preserved upon solidification. Specifically, only blends in which HMW was at least 55 wt% of the composition exhibited complete co-crystallization. In the example we have discussed thus far, the M_w of HMW and LMW were 890 and 37 kg/mol, respectively. In this section, we will discuss phase segregation in blends wherein the M_w difference between the components is not as great as it is for the current system. Specifically, we prepared and examined blends with the same LMW component and various HMW components. The M_w of the various HMW components we have studied are as follows: 790, 475, 350 and 290 kg/mol. The blend compositions studied are identical to the blend system that has already been discussed in

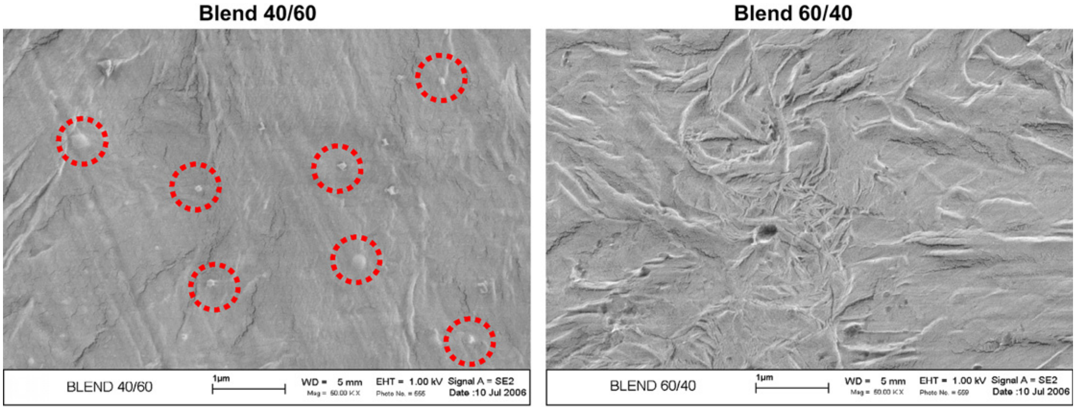

Fig. 7. Surface scanning electron micrographs for (a) Blend 40/60 and (b) Blend 60/40. Some of the dispersed HMW droplets are circled for emphasis in the phase segregated Blend 40/60.

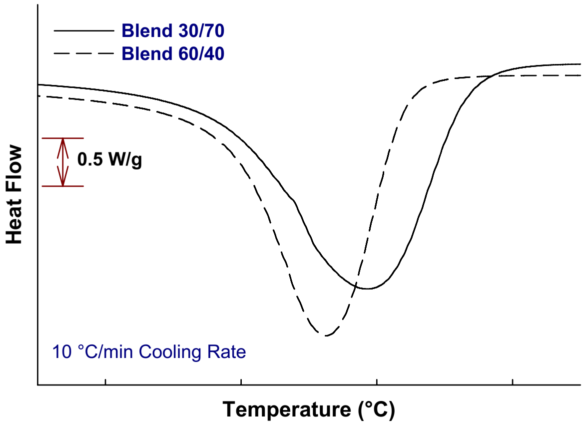

Fig. 8. Representative DSC non-isothermal crystallization exotherms for Blend 30/70 and Blend 60/40. These exotherms were generated by cooling the blend specimens from the isotropic melt state at 170 °C at 10 °C/min.

detail. We use the tensile strain-hardening behavior as an indicator of a well-mixed blend with complete co-crystallization of the components. In other words, any blend that displays a distinct strain-hardening character is thought to be a well-mixed one with complete co-crystallization; blends that do not display strain-hardening are considered to be phase segregated. With this criteria, we observe that the critical HMW concentration necessary for a well-mixed blend depends quite strongly on its M_w. In Fig. 10, this critical (or minimum) HMW composition required to eliminate melt-phase segregation during twin-screw extrusion is plotted for the various blend sets. Essentially, smaller the difference in M_w between the blend components, lower is the concentration of the HMW component required for producing a well-mixed blend. Further, for blends wherein the molecular weights of the components are not very different, complete co-crystallization of the components is possible even when HMW is the minor component (~40–45 wt% of the composition).

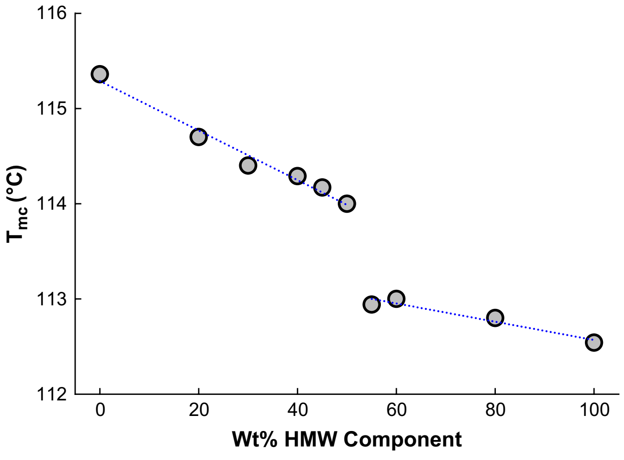

Fig. 9. The peak crystallization temperature (temperature at which 50% of the crystallization is complete) from the non-isothermal crystallization exotherm plotted as a function of blend composition.

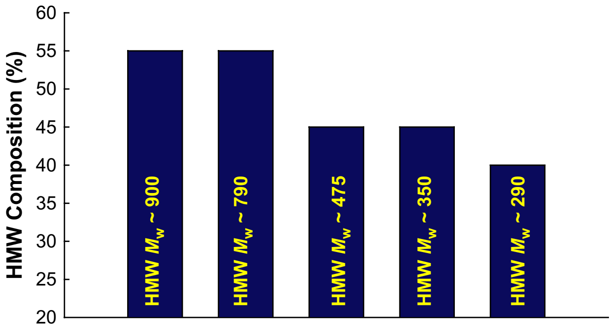

Fig. 10. The minimal HMW composition (in 5 wt% increments) at which distinct strain-hardening was observed for blends in which the molecular weight of HMW was varied.

4. Conclusions

While phase segregation (both liquid–liquid and liquid–solid) for blends of linear and branched PEs have been extensively studied in the past, those studies were limited to blend components of fairly similar molecular weights. Further, almost all of those efforts focused on solution-blended mixtures. Lastly, none of the previous efforts considered the consequences of phase segregation (or lack of complete co-crystallization) on the mechanical properties of the blends. In this investigation, we report on the influence of phase segregation on the mechanical properties of binary PE melt-blends (twin-screw extrusion) in which the components differ considerably in molecular weight. In our investigation, phase segregation is triggered by inadequate mixing during the melt-extrusion blending step; mixing is inhibited at certain blend compositions because of the large viscosity mismatch between the components.

The crystallizability of the blend components used in our investigation was very similar; consequently, probing phase segregation using bulk crystallization kinetics experiments becomes a challenging task. Nevertheless, crystallization kinetics experiments suggested a phase segregated melt for blends in which HMW (high molecular weight component) was the minor component. It was also apparent that phase segregation hindered the complete co-crystallization of the blend components upon cooling from the melt state. However, complete co-crystallization was evident for blends in which HMW was the major component. The influence exerted by blend composition on phase segregation, for melt-mixed systems, is consistent with previous reports on the subject matter [30–32]. However, our investigations on the influence of phase segregation on the mechanical properties of the blends have shed some light on the morphological length-scale critical for each measured property.

The dynamic mechanical measurements (at 190 °C) and the instantaneous tensile properties were observed to be insensitive to phase segregation. The instantaneous tensile properties were found to depend exclusively on crystallinity. However, the plane stress fracture resistance was observed to benefit from phase segregation. Specifically, the rate of increase in impact energy with molecular weight was noticeably steeper when HMW was the minor component in the phase segregated blend. This suggests that some degree of phase segregation, at least in the form of dispersed pockets of HMW within the blend specimen, is beneficial for impact toughness in a manner similar to rubber-toughened thermoplastics. Further, the tensile stress at break and the tensile strain-hardening characteristics displayed a strong dependence on phase segregation. The break stress for blends in which phase segregation was evident was considerably lower than that of either blend component. Further, the phase segregated blends did not display strain-hardening during their tensile deformation at high strains. This contrasts the high tensile break stress and distinct strain-hardening characteristics for well-mixed blends whose molecular weight and crystallinity were only slightly different from those of the phase segregated blends.

In summary, we have demonstrated that phase segregation can occur in melt-extruded blends of PEs that do not differ considerably in their crystallizability. This phase segregation, driven by differences in molecular weight and consequent melt viscosity, can impart substantial influence on the high-strain tensile deformation properties, which in turn may be used to gauge the existence and degree of phase segregation in such polyethylene blends.

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