Development of Isotropic Compatible HDPE/PP Blends for Structural Applications

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ABSTRACT: In an attempt to provide superior products for the structural applications, this study aimed at preparing isotropic compatible high density polyethylene (HDPE)/ polypropylene (PP) blends without the use of the expensive compatibilization technique. Morphological and structural characterizations of the homopolymers and blends were carried out. In addition, some of the structurally important mechanical and thermal properties were characterized. Such characterizations were performed to investigate whether or not the blends are compatible and therefore acceptable for the structural applications. Scanning electron microscope (SEM) micrographs of the blend samples indicate that the interfacial adhesion between HDPE and PP phases is intimate in the 5/95 HDPE-PP, good in the 85/15 HDPE-PP and 95/5 HDPE-PP, fair in the 30/70 HDPE-PP and very poor in the 50/50 HDPE-PP. Similarly, mechanical and thermal responses of the first three blends are remarkable. The 30/70 HDPE-PP blend displays a fairly good performance. Whereas, the proper-ties of the 50/50 HDPE-PP blend are very poor. This decides that the first three blends are compatible and, therefore, structurally attractive materials. The fourth is partially compatible and, as a consequence, can be rather acceptable for the structural applications. However, the fifth is incompatible and, of course, is not acceptable for such applications. On the other hand, SEM micrographs and differential scanning calorimetry results indicate that the crystalline structures of individual polymers are appreciably affected by blending. Additionally, the study reveals that the end use performance of blends is strongly dependent on the crystalline structure changes occurring in each component due to blending as well as the compatibility between the blend components. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1407–1418, 2010

Key words: HDPE/PP blends; compatibility; morphology; crystallization; mechanical properties; structure-property relations; structural applications

INTRODUCTION

Since the properties of conventional structural materials are presently pushed to their limits, the opportunity to develop superior products for structural applications has sustained the interest in polymer matrix composites (PMCs).[1] Replacement of pure polymer-based composites with polymer blend-based composites is expected to provide composite systems with a better performance/cost ratio. This, in turn, will expand the exploitation of PMCs in structural applications. This is because blending of plastics is an economical and expedient mean for tailoring a plastic compound for specific service requirements that can not be satisfied by a single plastic.[2] Polypropylene (PP) is used as a matrix in numerous PMCs products. The main attractions of PP are its relatively high stiffness, strength, and ther-mal resistance. Its poor impact resistance, however, at low temperatures is overcome by copolymerization with ethylene. High density polyethylene (HDPE) has a high impact resistance even at low temperatures and relatively good stiffness, strength, and thermal resistance.[3] So, it is expected that the HDPE/PP blends will offer an attractive compromise between the characteristic advantages of both plastics and suppress their limitations, i.e. acquire a higher impact resistance than PP at low temperatures and higher stiffness, strength, and thermal resistance than HDPE. They can, therefore, be considered as economical alternatives to the ethylene-propylene copolymers because blend preparation requires only melt mixing of the two plastics in a screw extruder. On contrary, copolymers require controlled, specialized polymerization during manufacture and therefore they are expensive.[3] Hence, HDPE/PP based composites will be superior to those based on their constituents and cheaper than those based on the ethylene-propylene copolymer. However, as the HDPE/PP blends are immiscible such advantages can only be achieved if they are

compatible. Compatible blends are those which achieve the specific applications requirements they tailored for. The majority of their properties nearly reflect the weighted arithmetic average of the properties of the constituent polymers.[2] Accordingly, this research aims at preparing isotropic compatible HDPE/PP blends without the use of the expensive compatibilization technique.

Many attempts were exerted in the literature to prepare isotropic compatible HDPE/PP blends without adding compatibilizers.[4–9] However, morphological, structural studies, and the mechanical properties of blends revealed that few of them only succeeded.[4,8] In such researches, we noted that the physical properties, viscosity and density, of the constituent polymers were so close. On the other hand, Malloy and Thorne[10] found that the mechanical performance of isotropic HDPE/PP blends was enhanced with improved mixing. Also, it was revealed from the works of Jose[9] and Finlay et al.[11] that the higher the cooling, crystallization, rate the better the mechanical properties of isotropic HDPE/PP blends. They reported that at relatively high cooling rates, HDPE and PP crystallize simultaneously deforming the interface between each other and thus increase the interfacial thickness. Therefore, efficient stress transfer is manifested between them. Accordingly, to attain our goal, we combined these three physical means that help in the development of compatible blends upon the preparation of isotropic HDPE/PP blends. All these means haven't been combined upon the preparation of such blends yet to date. Morphologies, mechanical, and thermal properties of the prepared blends were investigated to specify how compatibly the blends are, and consequently, to decide whether or not they are acceptable for the structural applications. Some of the investigated properties, flexural properties, specific mechanical properties and vicat softening temperature haven't been previously studied. Also, the effect of blend composition on crystalline structures of both constituent polymers was studied. This allowed us to interpret mechanical and thermal behaviors of the blends in terms of compatibility between the blend components and crystalline structure changes occurring in each component due to blending. Although, the latter plays a decisive role in determining the mechanical and thermal properties for blends of crystalline polymers, mechanical properties of HDPE/PP blends were only related to the compatibility between the blend components, in previous researches. The one exception is the work of Lovinger and Williams.[12] In that work the mechanical responses of HDPE/PP blends were explained by considering the morphological changes occurring in the PP phase due to blending and the compatibility between the blend components.

EXPERIMENTAL

Materials and blend preparation

Injection molding grades of HDPE (MFI = 26 g/10 min at 190°C, ρ = 953 kg/m³) and isotactic PP (MFI = 35 g/10 min at 230°C, ρ = 905 kg/m³) were supplied by Sidi Kreir Petrochemicals and Oriental Petrochemicals companies, respectively. They were melt-mixed twice in a KS-VX65 single screw extruder to prepare HDPE/PP blends of different compositions. Blend compositions were 5, 30, 50, 85, and 95 wt % HDPE. The screw speed was 80 rpm and the barrel temperatures were set to 175–200–200–220°C in the hopper-to-nozzle direction. The constituent polymers were twice mixed to achieve intimate mixing. The extrudate was cooled in a water bath, cut into beads and then air dried for subsequent compression molding.

Sheet preparation

Isotropic sheets of homopolymers and blends with dimensions of 160 mm × 160 mm × 3 mm were prepared by compression molding at 250°C and 170 kg/cm² for 10 min, using a MP20 DAVENTEST hydraulically controlled hot press. The mold assembly was then water cooled to the ambient temperature. The cooling time was about 5 min.

At this point, it is worth mentioning that the matching of homopolymers properties, the intimate mixing between the constituent polymers and the rapid cooling of the molded sheets were applied to prepare compatible blends of these polyolefins.

Blend characterization

Morphological studies

The morphological changes accompanying blending were monitored by scanning electron microscopy using a Jeol-JSM-5300 scanning electron microscope (SEM). Samples were prepared for morphological studies through two steps. Firstly, the compression-molded specimens were etched according to the permanganic etching technique reported in the work of Olley et al.[13] However, the etching was carried out at room temperature. Etching time was about 50 min. Secondly, the etched samples were sputter coated with gold under vacuum using a fine coating JFC-1100 Eion sputtering Jeol device. The SEM was operated at 15 kV and the images were captured at a magnification of ×3500.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to estimate the mass fraction crystallinities of the

homopolymers and their corresponding phases in blends. In addition, melting and crystallization temperatures were also estimated. In other words, the technique was employed to characterize the parameters describing the internal structure of a crystalline polymer. So, sufficient information can be obtained about the crystalline structure changes occurring in each polymer phase due to blending.

The DSC melting and crystallization thermograms for homopolymers and blends were recorded using a Perkin–Elmer DSC-7. Samples around 5 mg were cut from the homopolymers and all the blends, accurately weighed, sealed in aluminum pans and placed in the DSC cell. The samples were then heated at 10°C/min from ambient to 200°C then cooled to 25°C, under a nitrogen environment. Heats of fusion, melting and crystallization temperatures were calculated by the supplied software.

The mass fraction crystallinities of the homopolymers were calculated using the following relationship:

$$W_c = \frac{\Delta H_f}{\Delta H_c} \tag{1}$$

where

ΔH_f is the measured heat of fusion for HDPE or PP sample, J/g.

ΔH_c is heat of fusion of perfectly crystalline HDPE (293 J/g) or PP (209 J/g).[4]

On the other hand, the mass fraction crystallinities of HDPE (W_{cHDPE}) and PP (W_{cPP}) phases in the blends were separately calculated using the following equations:

$$W_{cHDPE} = \frac{\Delta H_{fHDPE}}{\chi_{HDPE}\Delta H_{cHDPE}} \tag{2}$$

$$W_{cPP} = \frac{\Delta H_{fPP}}{(1 - \chi_{HDPE})\Delta H_{cPP}} \tag{3}$$

where

ΔH_{fHDPE} and ΔH_{fPP} are the measured heats of fusion of HDPE and PP phases, respectively.

ΔH_{cHDPE} and ΔH_{cPP} are the heats of fusion of perfectly crystalline HDPE and PP, respectively.

χ_{HDPE} is the blend composition, weight fraction of the HDPE phase.

Mechanical testing

Tensile and flexural tests were performed on a computerized LLOYD Universal testing Machine, (model LR5K Plus). The tests were performed according to the ASTM D638 and ASTM D790 test methods at cross-head speeds of 5 mm/min and 2 mm/min, respectively. Mechanical properties were calculated by the supplied software.

The notched Izod impact test was carried out using a Ceast Izod Impact tester (model 6546/000, 2 J Hammer), according to the ASTM D256 test method. Hardness was measured using a Ceast Shore D Hardness apparatus (model 6756), according to the ASTM D2240 test method. All the mechanical tests were performed at room temperature. In each test, three samples were tested for each material.

Density measurements

Densities of homopolymers and blends were measured using pycnometery.[14] Such data are necessary for the calculation of the specific mechanical properties (property-to-density ratio), which are very important for the structural applications.

Thermal testing

Vicat softening temperatures of homopolymers and blends were measured using a Ceast Vicat apparatus (model 65,051/000), according to the ASTM D1525 test method. The heating rate was 2°C/min. Three samples were tested for each material.

RESULTS AND DISCUSSION

Morphology

The SEM micrographs of the homopolymers and blends are presented in Figure 1. The homopolymers (PP and HDPE) in Figure 1(a,g) exhibit the typical spherulitic morphology with average spherulite sizes (S_{av}) of about 6.5 and 5 μm, respectively. Concerning the blends, as the interfacial adhesion is the key feature that determines whether the blend is compatible or incompatible, in what follow, analysis of the interfacial characteristics for each blend will receive the primary attention. A quick perspective at the SEM micrographs of the blends revealed that the 5/95 HDPE-PP blend [Fig. 1(b)] shows the finest morphology. For this blend, HDPE is dispersed in the PP matrix as very small spherical domains with an average domain diameter of about 0.7 μm. Besides the circular domains we can see thin rods of HDPE dispersed in the PP matrix, located in the right-hand side of the image. Such unique morphology was only obtained by Finlay et al.,[11] for the 10/90 HDPE-PP blend. It offers an intimate adhesion between the blend components because dispersion of HDPE as thin rods within the PP matrix allows a large interfacial area between the two phases. Apparently, that all the HDPE domains are surrounded by bright edges. In addition, lamellae grow out from few of them penetrating the PP phase. Such observations are evidences for the intimate adhesion between the
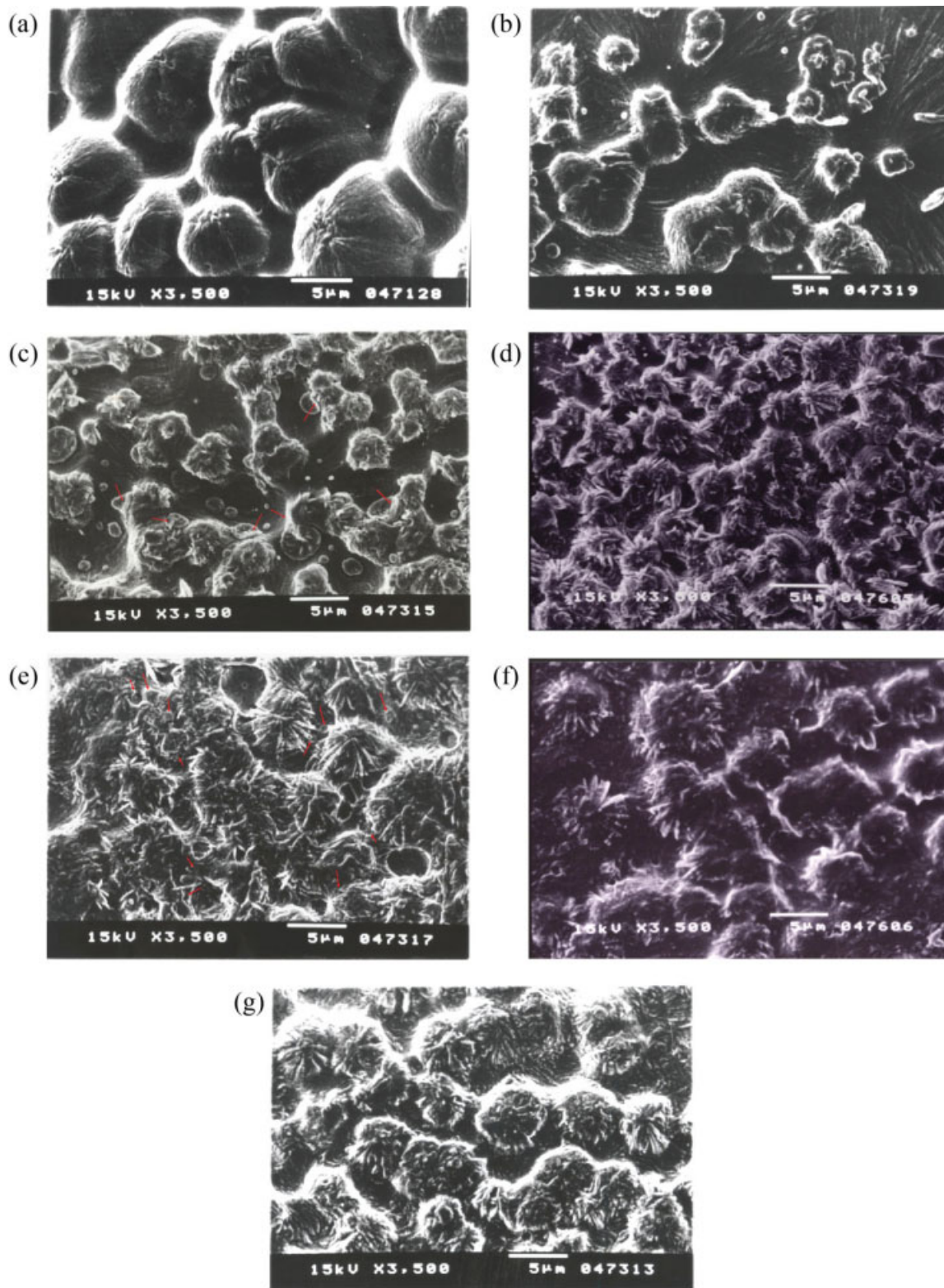
Figure 1 SEM micrographs of HDPE/PP blends: (a) 0/100, (b) 5/95, (c) 30/70, (d) 50/50, (e) 85/15, (f) 95/5, (g) 100/0. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

blend components. The bright edges imply that many lamellae from each phase span the interface region, connecting the two phases together with strong bonds. On the other hand, penetration of the PP phase by HDPE lamellae implies that there is a good degree of interaction between the two phases. Further addition of HDPE results in larger domains as seen in the 30/70 HDPE-PP blend [Fig. 1(c)]. This

is due to the coalescence phenomenon.[9] For this blend, HDPE is dispersed in the PP matrix as spherical domains with an average domain diameter of about 1.2 μm. Such morphology allows a lower interfacial area and, as a result, a less adhesion between the blend components than the above one. It can be observed that, some of the dispersed HDPE domains are partially engulfed under the PP spherulites. This reveals that a portion of the HDPE phase was firstly crystallized on cooling. Then some of the PP crystals were nucleated on the surfaces of the HDPE crystals. It can be also observed that there are few PP lamellae, indicated by arrows, crystallized on the surfaces of some of the HDPE domains and grew into the nearest PP spherulites, connecting the two phases with strong bonds. However, the most distinct feature is that, most of the HDPE domains appear to be surrounded by a dark collar. This is an etching artifact, implying that the amorphous material is collected at the phase boundary, connecting the two phases with mechanically weak bonds, which were easily penetrated by the etchant. This informs that the interfacial adhesion between the two phases is relatively fair. Figure 1(d) shows that the 50/50 HDPE-PP blend incorporates both of the co-continuous and the droplet-matrix morphologies. Formation of continuous regions of HDPE within the blend reveals that the coalescence of HDPE particles reaches maximum at 50 wt % HDPE. It can be observed from the image, that the continuous HDPE regions either are partially engulfed under the PP spherulites or have more than one PP spherulites located on them, indicating the copious nucleation of the PP crystals on the surfaces of the HDPE crystals. Again, all the HDPE domains appear to be surrounded by a dark collar, implying that the interfacial adhesion between the HDPE and PP phases is very weak. Phase inversion is observed for the 85/15 HDPE-PP blend [Fig. 1(e)] (now HDPE is the major phase). For this blend, PP is dispersed in the HDPE matrix as small and moderate domains with different geometrical shapes. As the small domains cannot be easily detected from the image, we refer to them with arrows. The figure shows that most of the dispersed domains are attached to the HDPE spherulites and surrounded by rough and bright edges. However, a thin dark band encapsulates few of them. This observation can be considered as an evidence for good interfacial adhesion between the HDPE and PP phases. Figure 1(f) shows that the morphology of the 95/5 HDPE-PP blend is similar to that of the 85/15 HDPE-PP blend. However, the PP domains are much finer than those in the 85/15 HDPE-PP blend. This is expected because as the concentration of the dispersed phase decreases the coalescence of the dispersed particles decreases and the particles appear finer.[9] The finer

phase domain is an indication of better interfacial adhesion between the blend components. It is worth mentioning that all the geometrical shapes assumed by the PP dispersed domains in both blends give a larger interfacial area and, therefore, a better adhesion between the two phases than those given by the spherical shape, obtained in the literature.[9,11] This means that our HDPE-rich blends are more compatible than their correspondings in the literature.

Comparing Figure 1(b) with Figure 1(f), one can observe that the 5/95 HDPE-PP blend shows a finer morphology than the 95/5 HDPE-PP blend. This agrees with the observations of Jose,[9] Finlay et al.,[11] and Na et al.[15] It emphasizes that the PP-rich blends are more compatible than the HDPE-rich blends.

The preceding analysis recommends that the blends for which the content of the two polymers is very different (5/95 HDPE-PP, 85/15 HDPE-PP, 95/5 HDPE-PP) are compatible and the 5/95 HDPE-PP blend shows the maximum compatibility. However, the central blend (50/50 HDPE-PP) is incompatible and the 30/70 HDPE-PP blend appears marginal; there is a partial compatibility between the two phases within this blend.

Concerning the crystalline morphologies of both phases, the photomicrographs of homopolymers and blends show that the presence of material in one phase had a definite and pronounced effect on the crystalline morphology of material in the other phase. It can be observed that the regular spherulite patterns of the homopolymers tend to become irregular with blending and their average size (S_{av}) decreases as the content of the other polymer in the blend increases. Thus no spherulites can be detected for either of them when the other polymer forms the matrix phase. These observations are in agreement with those made by Lovinger and Williams,[12] Bartczak et al.,[16] and Schurmann et al.,[17] upon studying the effect of blending on the crystalline morphology of PP. Obviously, that for PP-rich blends, the decrease in the S_{av} of the PP is much larger than that of the HDPE, for HDPE-rich blends.

The irregularity in the matrix spherulitic patterns can be attributed to the simultaneous crystallization of the blend components upon water-cooling. As reported in the literature,[9,11] this causes the two components to deform the interface between each other, which is in most cases the edge of the matrix spherulites or even a part of them, as shown in the SEM micrographs of blends.

DSC results

The recorded DSC melting and crystallization thermograms of homopolymers and blends agree with those presented in the literature.[9,11,18,19] Melting thermograms of blends display two melting peaks

TABLE I
Melting Parameters of HDPE/PP Blends Calculated From DSC Thermograms

Sample	T_m (°C)		ΔH_f (J/g)		Mass fraction crystallinity	
	HDPE	PP	HDPE	PP	W_{cHDPE}	W_{cPP}
PP	–	165.5	–	90.4	–	0.43
HDPE/PP (5/95)	129	164	1.1	81.8	0.075	0.41
HDPE/PP (30/70)	129.5	162.5	46.9	48.6	0.53	0.33
HDPE/PP (50/50)	130	160	86.1	33.2	0.59	0.32
HDPE/PP (85/15)	130.5	160	151.6	7.2	0.61	0.23
HDPE/PP (95/5)	130	159	173.5	0.86	0.62	0.08
HDPE	131	–	190.6	–	0.65	–

corresponding to the HDPE and PP phases while crystallization thermograms display a single apparent crystallization peak. The melting endotherms were used to characterize melting temperatures (T_m) and mass fraction crystallinities of the homopolymers and their corresponding phases in blends (W_c, W_{cHDPE}, W_{cPP}). Also, the crystallization exotherms were used to characterize crystallization temperatures (T_c) of the homopolymers and blends.

The melting parameters are listed in Table I. Obviously, that the T_m of HDPE and PP phases decreases as the content of the other component in blend increases. Albano and Sanchez[5] reported that the decrease in the melting temperature of each component could be due to the interplasticizing action caused by a molecule of one of the components, which acts as a diluent inside the crystalline structure of the other component. They added that the reduction of the spherulitic order could also cause this behavior. We agree with the explanation of Albano and Sanchez[5] because the SEM micrographs of blends show that the two phases are either attached to or located on each other. Furthermore, in some blends, there are few lamellae growing out from one phase into the other phase. These observations enhance the probability of the presence of few molecules of one component into the crystalline structure of the other component. On the other hand, clearly that the spherulitic order of each polymer is reduced by blending. It is seemed that the plasticization of the PP phase is higher than that of the HDPE phase; the decrease in the T_m of the PP phase is more significant than that of the HDPE phase. Also, the larger reduction in the PP average spherulite size upon blending contributes to that behavior.

As well as T_m, the mass fraction crystallinity of one crystalline polymer decreases as the content of the second polymer in the blend increases. Again, the decreasing behaviors for the two phases are not similar. The results show that the W_{cPP} decreases steadily as the content of HDPE in blend increases. However, the W_{cHDPE} does not change much with

the PP content in the HDPE-rich blends but decreases significantly with the PP content in the PP-rich blends. It can be also noted that, for the 5/95 HDPE-PP blend there is an abrupt decrease in the W_{cHDPE}.

The apparent T_c is plotted against the blend composition in Figure 2. It increases synergistically as the HDPE content in the blend increases. Such synergistic behavior indicates that the two phases within blends crystallize at higher temperatures than the corresponding pure polymers, as reported by Finlay et al.[11] They attributed the rise in T_c of HDPE and PP to the increase of the nucleation density of each polymer within blend samples. They deduced from the work of Bartczak et al.[16] that the increase of HDPE nucleation density was caused by the migration of heterogeneous nuclei from PP melt to HDPE melt during the mixing process. On the other hand, the increase of PP nucleation density was coming from the nucleation of PP crystals on the surfaces of HDPE crystals situated on the interfaces between HDPE and PP phases.

In fact, the increase of the nucleation densities of HDPE and PP phases within blend samples is not only responsible for the increase of T_c but also for the decrease of average spherulite size and mass
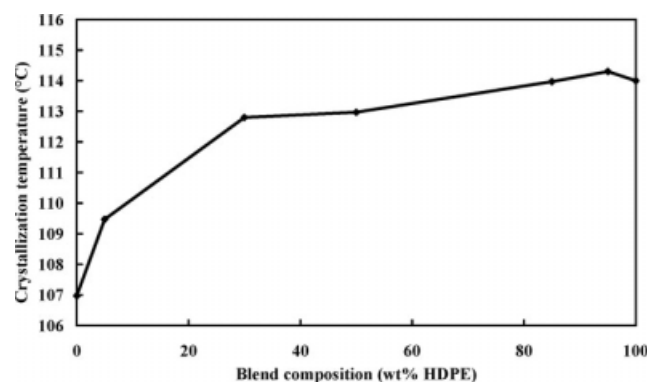

Figure 2 Variation of the crystallization temperature as a function of blend composition.
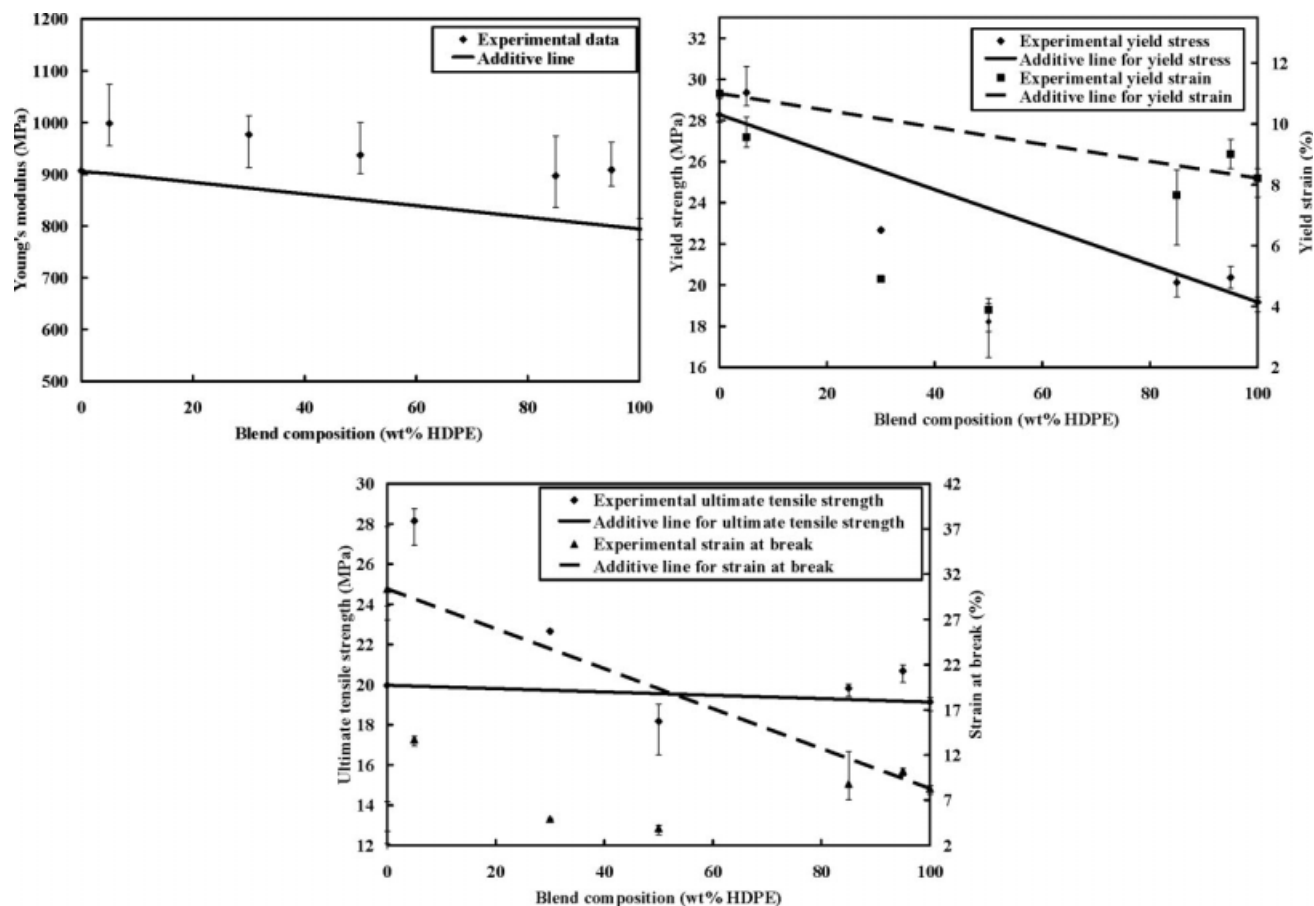
Figure 3 Variation of the tensile properties as a function of blend composition.

fraction crystallinity of each polymer upon blending. This is because the increase of the primary nuclei concentration in a crystalline polymer increases the T_c and consequently the supercooling degree of the polymer. Accordingly, its solidification is accelerated, so that polymer molecules having significantly different molecular weight from the average molecular weight have not enough time to assume their lowest energy conformation and then pack together in crystalline zones. Therefore these molecules are rejected into the amorphous phase. The number, the size and the perfection of the crystallites within the polymer decrease, leading to the decrease of average spherulite size and mass fraction crystallinity of such polymer.

Mechanical properties

Tensile properties

Tensile behavior of the blends is summarized in Figure 3. It is evident from the figure that the Young's modulus and the ultimate tensile strength of all blends show a positive synergism with a maximum at 5 wt % HDPE. However, the trends of the remaining properties with blend composition are affected by the extent of compatibility between the two phases within blend samples. Such trends, emphasize that the 5/95 HDPE-PP, 85/15 HDPE-PP and 95/5 HDPE-PP blends are compatible. But, the 30/70 HDPE-PP blend is partially compatible and the 50/50 HDPE-PP blend is incompatible. This is because, for the first three blends, yield stress is synergistic, for the 5/95 HDPE-PP blend and additive, for the 85/15 HDPE-PP and 95/5 HDPE-PP blends. Strain at yield shows a fairly narrow negative deviation from the rule of mixtures and such deviation becomes much more significant for the strain at break. Conversely, the other two blends have deteriorated properties, i.e. their properties are worse than those of the weaker constituent polymer (HDPE). The one exception is the yield stress of the 30/70 HDPE-PP blend. It shows a significant negative deviation from the rule of mixtures.

Comparisons between the ultimate tensile strength measurements are unlikely to be meaningful. This is because the synergism in ultimate strength of the blends is not due to the increase of the ultimate strength of the polymeric constituents upon blending but is due to earlier fracture of the blends than PP. In other words, earlier fracture of the blends causes the fracture force to be much higher than in the case

of PP. As a result, the ultimate strength, computed from the original cross-sectional area of our specimens, is vastly higher in all blends. In contrast to the ultimate tensile strength, Young's modulus of the blends reflects a true positive synergism. Such synergism results mainly from the copious nucleation of PP crystals on the surfaces of HDPE crystals. This is because such phenomenon results in superimposition of most PP domains on HDPE domains, as shown in the SEM micrographs, and as a result formation of a very large interfacial area between the blend components. This, in turn, leads to the profusion of the interlinking molecules between them. Primarily, because at relatively high crystallization rates, the blend components deform the interface between each other, i.e. form interlinking molecules between each other. Therefore, efficient stress transfer is manifested between the blend components, and consequently, large improvement in Young's modulus of the blends is achieved. On the other hand, the reduction of the average spherulite sizes accompanying the decrease of the percentage crystallinities of polymeric constituents upon blending reduces the depression in the Young's moduli of the polymeric constituents, arisen from lower percentage crystallinity. The reduction of the average spherulite size of a crystalline polymer usually leads to a modest increase in the impact resistance, stiffness, strength and ductility of that polymer because this serves to increase the concentration of the tie molecules connecting lamellae from different spherulites.[12,20] The net result of these competing effects (profusion of interlinking molecules between the blend components, reduction of average spherulite sizes and percentage crystallinities of the constituent polymers) is a synergistic improvement in the Young's modulus of all blends. Primarily, because the interlinking molecules can efficiently withstand and transfer the applied stresses between the blend components at low strain levels involved in Young's modulus determination.

With higher strains, large differences in yield and fracture properties between the compatible, the partially compatible and incompatible blends are expected. Primarily, because the interfacial characteristics of the compatible blends are distinctively different from those of the partially compatible and incompatible blends. This is evident in the SEM micrographs of the blends which show a bright interface between the HDPE and the PP phases in the compatible blends but a thin dark band encapsulated the dispersed HDPE domains in the partially compatible and incompatible blends. As mentioned earlier, these observations can be considered as evidences for good and poor interfacial adhesions between the HDPE and PP phases in the compatible and the incompatible blends, respectively. This is

why the interlinking molecules between the blend components in the compatible blends can withstand the applied stress and transfer it from the matrix to the dispersed phase at low and high strain levels. Whereas those involved in the partially compatible and incompatible blends can withstand the applied stress and transfer it from the matrix to the dispersed phase only at very low strain levels. Thus with relatively higher strain levels, property-deterioration takes place because the poor coupling between the blend components hastens cracks origination and growth at the interface and consequently fracture at interphase boundaries, as reported by Jose et al.[9] However, the few PP lamellae spanning the interface between HDPE and PP phases in the 30/70 HDPE-PP blend, as depicted in the SEM micrograph of that blend, offer a better interfacial adhesion between the blend components. This is why the yield stress of the 30/70 HDPE-PP blend does not deteriorate but exhibits only a significant negative deviation from the rule of mixtures.

For the compatible blends, comparing the trends of tensile properties with blend composition shows that, the degree of improvement in tensile properties accompanying addition of PP to HDPE decreases as the strain level increases. This is reflected much more strongly in the ultimate elongation of the blends, which shows a significant negative deviation from the rule of mixtures. As the strain level increases, the concentration of cracks across the interface increases. So, the interlinking molecules get weaker, and as a result, their stress transmittance efficiency decreases. Therefore the extent of the improvement in the tensile properties due to the profusion of the interlinking molecules within blend samples decreases and reaches a minimum at fracture. Thus, the influence of the numerous interlinking molecules connecting the blend components along with the lower average spherulite size of each component can't compensates for the depression of the ductility of blends, arisen from lower percentage crystallinity. This is why the yield strain shows a fairly narrow negative deviation from the rule of mixtures and such deviation becomes much more significant for the strain at break.

Flexural properties

Upon the flexural test, the homopolymers, 5/95 HDPE-PP, 85/15 HDPE-PP and 95/5 HDPE-PP blends did not break. The 30/70 HDPE-PP blend yielded and drew to some extent before breaking. However, the 50/50 HDPE-PP blend broke immediately after yielding. This, again, confirms that the first three blends are compatible, but the fourth is partially compatible whereas the fifth is incompatible.

Flexural properties of the blends are presented in Figure 4. For materials that did not break, the stress corresponds to a 5% strain is reported as the flexural strength.[21] Evidently that the addition of PP to HDPE is accompanied by an increase in the flexural modulus, yield and flexural strengths. The flexural modulus synergistically increases, Figure 4(a). Whereas, the yield and the flexural strengths monotonically increase, Figure 4(b). This reveals that the net result of the improvement of properties resulting from the profusion of interlinking molecules along with the lower average spherulite size of each component and the deterioration of properties resulting from the lower percentage crystallinity of each component diminishes as the strain level increases. As mentioned earlier, this can be attributed to the reduction of the stress transmittance efficiency of interlinking molecules with the increase of strain level.

Fracture of the partially compatible and incompatible blends is arisen from earlier origination of cracks at the weak interface formed between the
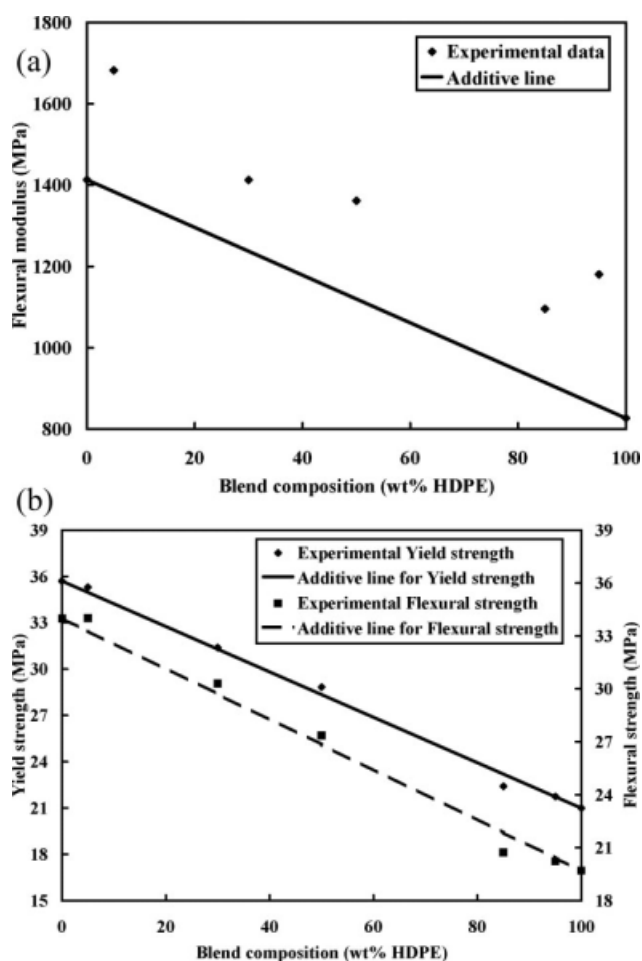

Figure 4 Variation of the flexural properties (a) flexural-modulus, (b) yield and flexural strengths, as a function of blend composition.
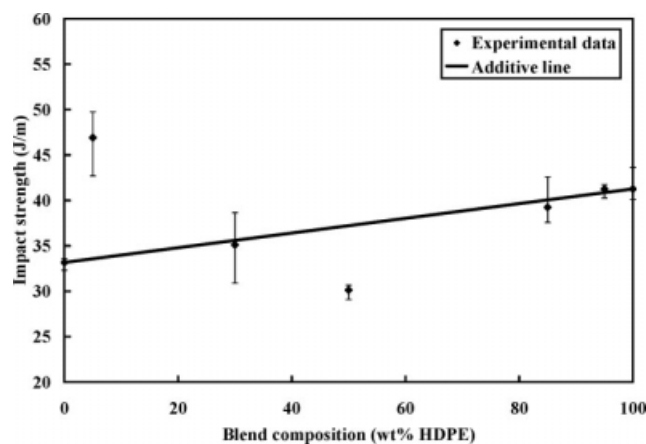

Figure 5 Variation of the impact strength as a function of blend composition.

blend components. Being so weak, cracks propagate rapidly through the interface formed in the 50/50 HDPE-PP blend leading to fracture at interphase boundaries immediately after yielding and hence brittle failure of its samples. However, the better interfacial adhesion involved in the 30/70 HDPE-PP blend delays the interfacial fracture and, as a consequence, the failure of its samples to some extent after yielding. This is why the 50/50 HDPE-PP blend broke earlier than the 30/70 HDPE-PP blend. Ultimate strains for the two blends are about 4.5% and 7.5%, respectively.

Impact strength

The impact strength of the blend samples is shown as a function of composition in Figure 5. Clearly, that the impact strength of the 5/95 HDPE-PP blend rises well above the additive line. But those of the 30/70 HDPE-PP, 85/15 HDPE-PP and 95/5 HDPE-PP blends fit it, whereas the impact strength of the 50/50 HDPE-PP blend shows a drastic deterioration.
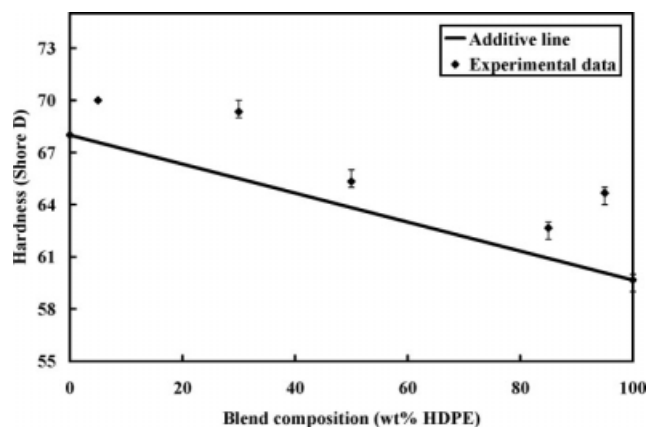

Figure 6 Variation of hardness as a function of blend composition.

In contrast to tensile and flexural properties, the decrease in the percentage crystallinities of the polymeric constituents upon blending results in an improvement of their impact strength. Thus, the synergistic improvement in the impact strength of the 5/95 HDPE-PP blend can be attributed to the intimate adhesion between the blend components along with the significant lower crystallinity and average spherulite size of each component. However, In the case of the 95/5 HDPE-PP and 85/15 HDPE-PP blends, as revealed from SEM micrographs, the decrease in the S_{av} of HDPE is small. In addition, the interfacial adhesion between the blend components is less than that involved in the 5/95 HDPE-PP blend. So, they show additive impact strengths. On the other hand, although the interfacial adhesion in the 30/70 HDPE-PP blend is significantly less than those in the 95/5 HDPE-PP and 85/15 HDPE-PP blends, its impact strength fits the additive line too. Primarily, because the morphology and crystallinity changes that occur during blending are much more pronounced for the 30/70 HDPE-PP blend. But, in the case of 50/50 HDPE-PP blend the interfacial adhesion between the blend components is very poor. Thus, the improvement of impact strength resulting from the significant lower crystallinity and average spherulite size of each component can not compensate the deterioration of impact strength resulting from the poor interfacial adhesion and, as a consequence, property-deterioration takes place.

Hardness

The variation of hardness with blend composition is presented in Figure 6. Likewise the tensile and flexural moduli, hardness of all blends shows a pronounced positive deviation from the additive line. It doesn't depend on the compatibility of the blends, as reported in the literature.[9] The synergy of hardness implies that the improvement of hardness resulting from the profusion of interlinking molecules between the blend components along with the lower average spherulite size of each component overcomes the deterioration of hardness resulting from the lower percentage crystallinity of each component. This is because, being a surface property, a relatively small load is applied to measure the hardness of the polymeric material. Therefore, the interlinking molecules in all blends can efficiently withstand and transfer the applied stress from the matrix to the dispersed phase. Accordingly, a large improvement in the hardness of blends is achieved.

Specific mechanical properties

The variation of density with blend composition is presented in Figure 7. The figure shows that the
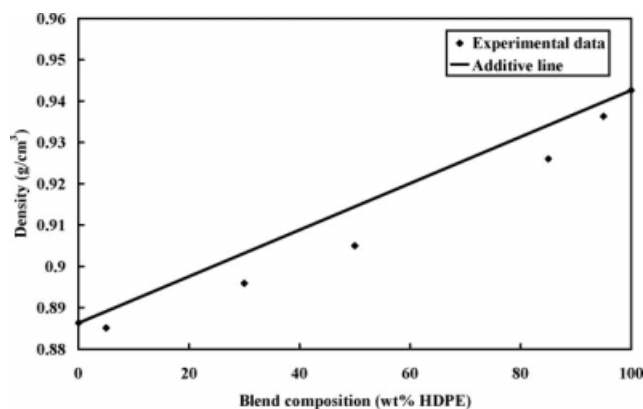

Figure 7 Variation of density as a function of blend composition.

densities of all blends negatively deviate from the simple linear dependence. Such behavior is a direct consequence of the reduction of the component crystallinity upon blending.

Since the structural applications need primarily high stiffness-strength to weight ratio, specific stiffnesses (Tensile/flexural modulus-to-density ratio), specific yield strengths (Tensile/flexural yield stress-to-density ratio) and specific impact strength (Impact strength-to-density ratio) of the homopolymers and blends are calculated. The results are plotted versus blend composition in Figure 8. Obviously, that the specific properties exhibit the same trends presented by the corresponding mechanical properties with blend composition. However, more improvement is observed for the specific mechanical properties because the densities of all blends negatively deviate from the simple linear dependence. Remarkable specific properties of the compatible blends suggest that the composite systems based on them will be acceptable for the structural applications.

Thermal properties

Vicat softening temperature

The vicat softening temperature of the blend samples is plotted in terms of blend composition in Figure 9. The 5/95 HDPE-PP blend displays the highest softening temperature amongst all the samples. Softening temperature changes about linearly with the blend composition for the 30/70 HDPE-PP, 85/15 HDPE-PP, and 95/5 HDPE-PP blends, whereas softening temperature of the 50/50 HDPE-PP blend shows a pronounced negative deviation from the additive line.

Generally speaking, the crystalline material is known to have a higher thermal resistance, and therefore, a higher softening temperature than amorphous material. Accordingly, the crystalline lamellae occupying the interfacial region in the compatible
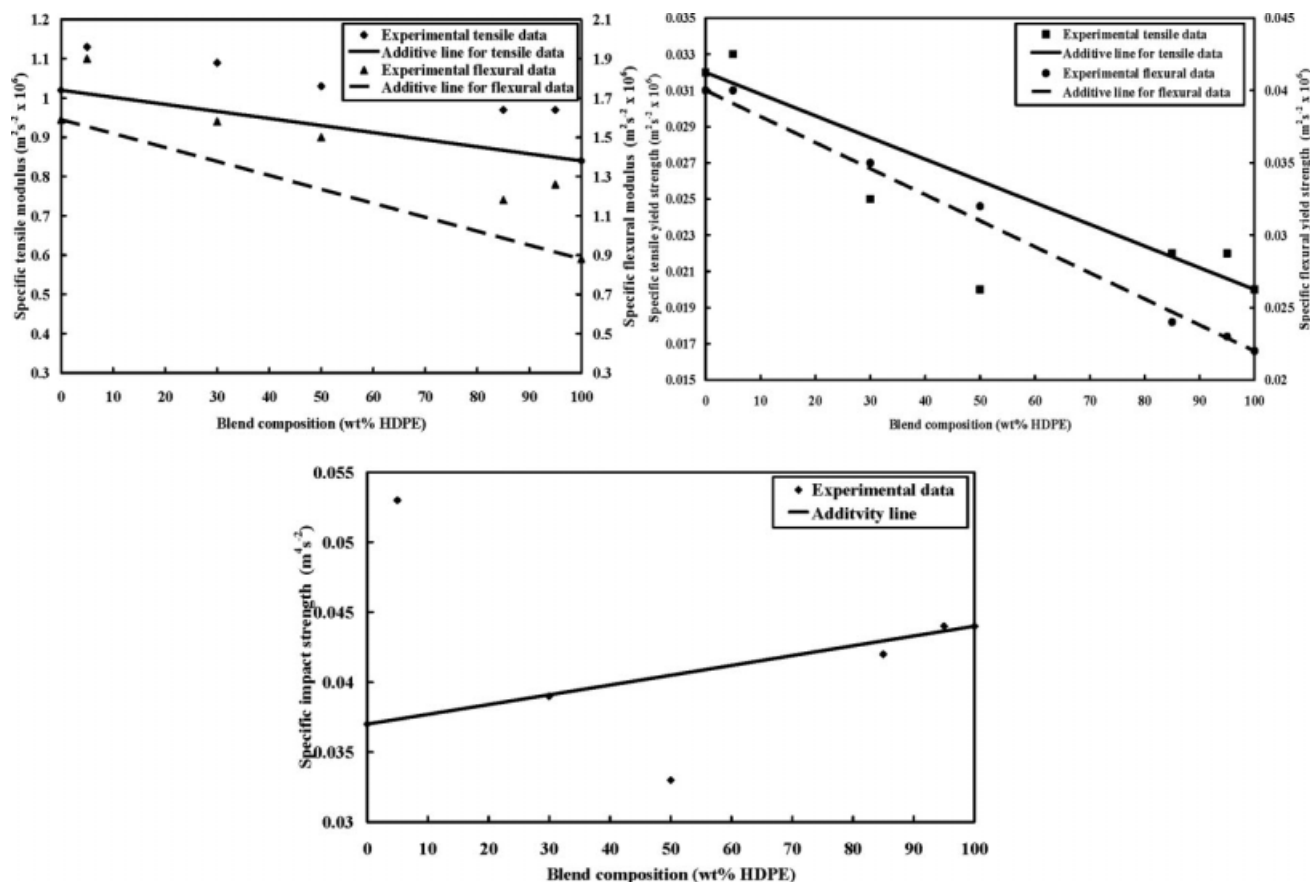
Figure 8 Variation of the specific mechanical properties as a function of blend composition.

blends enhance the interface, and therefore, the blend thermal resistance. However, the enhancement is much more remarkable for the 5/95 HDPE-PP blend because PP lamellae, the more thermally resistant material, dominate the interfacial region in that blend. On the other hand, HDPE lamellae, the less thermally resistant material, dominate the interfacial region in the 95/5 HDPE-PP and 85/15 HDPE-PP blends. In addition, the interfacial adhesion between the blend components, i.e. the concentration of crystalline lamellae occupying the interfacial region is maximum for the 5/95 HDPE-PP blend. This is why the improvement of the thermal resistance due to strong interface overcomes the deterioration of the thermal resistance due to the lower crystallinity of each component, in the 5/95 HDPE-PP blend while only compensates it, in the other compatible blends. On the other hand, although the amorphous material is accumulated at the interphase boundaries in the partially compatible and incompatible blends, the softening temperature of the partially compatible 30/70 HDPE-PP blend fits the additive line. Primarily, because the PP amorphous phase dominating the interfacial region and the few PP lamellae spanning it relatively improve the thermal resistance of the interfacial region. But, absence of these two effects in the case of the 50/50 HDPE-PP blend along with the lower crystallinity of each component are plausible explanations for the negative deviation exhibited by the softening temperature of this blend.
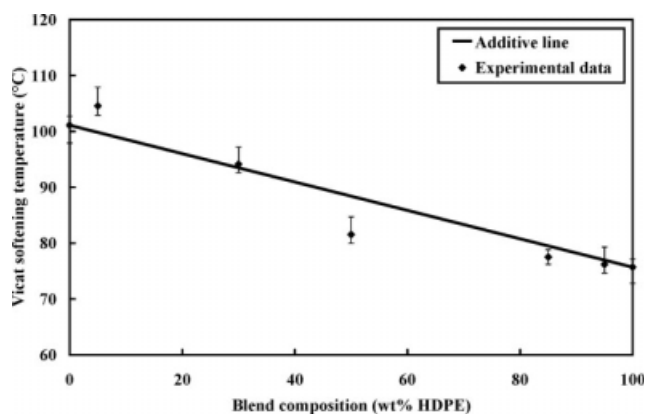

Figure 9 Variation of the vicat softening temperature as a function of blend composition.

CONCLUSIONS

Morphological features, mechanical and thermal responses of the 5/95 HDPE-PP, 85/15 HDPE-PP

and 95/5 HDPE-PP blends reveal that such blends are compatible and, therefore, structurally attractive materials. On contrary, the coarse morphology, poor mechanical and thermal responses of the 50/50 HDPE-PP blend inform that it is incompatible and, of course, is not acceptable for the structural applications. The 30/70 HDPE-PP blend appears marginal; its fairly good morphology and performance decide that it is partially compatible and, as a consequence, can be rather acceptable for the structural applications. On the other hand, SEM micrographs and DSC results indicate that the crystalline structures of individual polymers are appreciably affected by blending. This implies that there is a certain degree of interaction between HDPE and PP phases in all the blends. Additionally, preceding analyzes reveal that the low stress mechanical properties are sensitive to the extent of interlinking molecules between the blend components and crystalline structure changes occurring in each component due to blending. But, the high stress mechanical properties and vicat softening temperature are strongly dependent on the extent of compatibility between the blend components, which is determined by the characteristics of the interlinking molecules formed between them. Also, they are sensitive to the crystalline structure changes occurring in each component due to blending. This decides that all of these factors have to be considered, when designing isotropic blends of crystalline polymers for particular applications.

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