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IMPACT RESISTANCE OF SELECTED IMMISCIBLE POLYMER BLENDS

Wantinee Viratyaporn, Richard L. Lehman, and Jayant Joshi
AMIPP Advanced Polymer Center
Rutgers University
Piscataway, NJ 08854-8065

Abstract

Immiscible polymer blends were prepared by melt extrusion using a single screw extruder in the systems PS/HDPE and PS/PP to assess the effect of composition and morphology on tensile Young's modulus and impact resistance. Results from the work show that tensile modulus nearly follows rule of mixture behavior for both systems, although better performance is shown by the PS/PP blends. With regard to impact resistance, the PS/HDPE system showed poor, incompatible performance, whereas excellent impact resistance was noted in the PS/PP blends. Indeed, the 20% PS in PP blend possessed an impact strength that was 127% greater than the proportional value for this composition. The PS/PP blends appear to be first-rate engineering materials from the perspective of tensile modulus and impact resistance, especially in the range of 15 – 30% PS.

Introduction

Impact strength and elastic modulus are two critical properties in many engineering design applications. Most structural designs rely heavily on material stiffness to provide the desired properties to the structure. Although ultimate tensile or flexural strength is important, design concepts rarely rely on this region of the stress-strain diagram due to nonreversible deformation effects and fatigue in this region. Impact resistance is critical in most applications since the ability of structures, particularly in the transportation and consumer products sectors, to survive repeated impacts is essential to the robustness of the design. Unfortunately, high stiffness and high toughness are often properties not found in the same material. Polystyrene and polymethylmethacrylate are two examples of high modulus materials that have limited impact resistance, whereas polyethylene and polypropylene are two high strain-to-failure, i.e. tough, materials that have poor stiffness. Exceptions exist, of course, such as polycarbonate which possesses good stiffness and toughness.

Polymer blends and co-polymers are viable approaches to formulating polymeric materials with enhanced stiffness and toughness, such as ABS and compatibilized blends. Melt blending is an attractive way to develop new materials from the perspective of simplicity and economic viability. Most polymer blends are immiscible as evidenced by large solubility parameter differences that lead to poor interfacial adhesion. The generation of non-bonded phase boundaries has both positive and negative ramifications for blend properties. Such interfaces are excellent crack deflection sites that can arrest or deflect fast propagating cracks in brittle polymers such as polystyrene. Deflection generates a more tortuous crack path through the composite, increasing the work of fracture and the toughness. On the other hand, non-bonded interfaces prevent load transfer across the interface, thus weakening the material in some context. In poorly engineering immiscible blends, the interfaces and morphology are gross, thus greatly reducing the strength and toughness of such blends. The preferred remedy for such blends is to use compatibilizers to bond the phases[1-3]. In such compatibilized blends the phase bonding substantially improves the impact toughness but in many cases the modulus and time-dependent properties (e.g. creep) are sacrificed. Yet, in some prominent cases the impact strength of the material is enhanced without loosing tensile and flexural strength[4].

Studies from our group and elsewhere have shown that uncompatibilized immiscible polymer blends provide synergy of mechanical properties when the processing and compositional parameters are near optimum values [5-7]. Such blends are said to be "mechanically grafted" due to the intimate mechanical contact between the phases, nearly replicating the behavior of chemically grafted or bonded structures. Leclair and Favis observed impact strength improvement in uncompatibilized PC/HDPE when PC was functioned as the dispersed phase in a HDPE matrix [7].

In the present work, we studied uncompatibilized immiscible polymer blends in the PS/HDPE and PS/PP compositional systems and evaluated the influence of morphology and mechanical grafting on the combined properties of impact resistance and elastic modulus, particularly at co-continuous compositions.

Experimental Procedure

Three widely used polymers, HDPE, PP and PS were chosen for this study. Supplier and selected physical property data for each polymer is given in the table 1. All polymers were received from the supplier in pellet form. PS/PP and PS/HDPE blends were mixed according to the ratios displayed in table 2 and subsequently melt processed in a single screw extruder, C.W. Brabender Intellitorque Plasti-corder with a screw L/D of 30:1, at 200°C at 60 rpm.

The TA Instruments AR 2000 rheometer with 25 mm diameter parallel plates was used to determine viscosity of polymers at 200°C. The test specimen was prepared by compression molding at 200°C. The collected viscosity data were used to determine the co-continuous region for the blends using the Jordhamo relationship[8]

$$\frac{\eta_A}{\eta_B} \cong \frac{\Phi_A}{\Phi_B} \qquad (1)$$

where η is the viscosity and Φ is the volume fraction of the polymer. From these data the predicted co-continuous morphology of PS/PP and PS/HDPE occurs at 36.4%PS and 37.7%PS, respectively.

Impact testing was performed using the Izod impact procedure [ASTM D-256A] and an instrumented pendulum impact machine (Instron POE2000). The impact specimens were injection molded (V55-200 Negri Bossi Molder). The dimension of the Izod specimens was 63 x 12.5 x 3.1 mm. The test was performed at room temperature and all specimens were notched at a 45 degree angle.

Image assessment of the morphology was obtained from fracture surfaces. The specimens were fractured in liquid nitrogen in order to preserve the molecular structure of the polymers, then solvent extraction was performed using a technique described previously[9]. PS was etched from the blend with toluene. Then the fractured specimens were mounted on an aluminum stub and gold coated to reduce charging effects. All prepared specimens were stored in a vacuum desiccator overnight prior to insertion in the Leo-Zeiss Gemeni 982 Field Emission Scanning Electron Microscope at 5 keV. Images were observed and recorded as micrographs.

Results and Discussion

SEM Images

SEM images were taken along a direction normal to the material flow during the mold filling process. The morphologies of PS/HDPE and PS/PP at various combinations are shown in figures 1 and 2, respectively. The morphology of the blends changes over the composition range, beginning as a dispersed phase of the smaller volume fraction species, transitioning to co-continuous morphologies at intermediate compositions, and then producing dispersed morphologies again after the phase inversion point. In both blend systems the co-continuous region is observed at around 40-45% (volume) of PS.

Comparing the PS/PP and PS/HDPE blends, the general relationships of the phases over the blend composition range described above is observed in both blends. However, subtle but important differences are also noted. The 20% and 30% PS blends in both matrices show a distinctly dispersed morphology, although the dispersed phase in the PS/PP blends is distinctly finer, perhaps by a factor of two, than in the PS/HDPE blends. Furthermore, the PS globules in the PP matrix begin to elongate (an initial indicator of continuity development) at the 30% composition whereas this is not seen at the same composition with the HDPE matrix. Both systems show on-going continuity development at 35 and 40% PS, although the PP matrix blends are significantly finer and more elongated. Phase inversion occurs near 40-45% in both systems, consistently above the predicted compositions, and inverted morphologies are observed thereafter.

Young's Modulus

Tensile modulus of PS/HDPE and PS/PP is shown in figures 3 and 4, respectively. The modulus values for immiscible blends will follow either so-called incompatible behavior in which the composite modulus is well below the rule of mixtures or, in the case of mechanically grafted or compatibilized blends, the blends will exhibit either parallel or serial composite behavior (depending on morphology) and will be quite close to the rule of mixtures. Naturally, since the goal of blend formulation is to achieve additive behavior similar to alloy blends, this latter relationship is sought. Behaviors above the rule of mixture are not possible unless orientation or other changes are induced in the polymers that produce increased stiffness in the test direction. Both the PS/HDPE and the PS/PP systems show nearly rule of mixtures behavior, indicating good morphology development and a degree of mechanical grafting. The PS/HDPE system, however, only reaches the rule of mixtures value at the co-continuous composition (~40%) and is below the proportional line to varying degrees at other compositions. This behavior is consistent with other work from our group on virgin and recycled polymers. The PS/PP system, on the other hand, exhibits modulus values somewhat above the proportional line for PS-dispersed compositions slightly below the line for PP-dispersed compositions. The 38.2% increase in PP modulus achieved with the addition of 20% PS is an interesting result of this work and suggests that this composition may be a useful engineering material if good impact strength can also be achieved in this compositional region.

Impact Strength

The PS/HDPE system showed poor impact performance relative to the good impact resistance of HDPE (250 J/m). The impact resistance of the blend compositions was not good and the solid curve in figure 5 illustrates the incompatible impact behavior of these blends. Indeed, the maximum blend value is ~50 at 20% PS, a value only modestly above the ~15 J/m value of neat PS and only 20% of the neat HDPE value. These results are disappointing considering the Young's modulus behavior, which falls much closer to the rule of mixtures. The PS/HDPE system prepared from recycled polymers is used extensively in structural construction members, e.g. bridge beams and railroad ties, due to excellent stiffness and acceptable creep resistance. The impact properties of the commercial recycled composites are unknown. The good modulus behavior in the PS/HDPE system, particularly at the phase inversion point, arises from "mechanical grafting" – the intimate and efficient mechanical contact between phases generated by the fine intertwined morphology as shown in figure 1. However, in spite of the good load transfer evidenced by the modulus data, the morphology appears too coarse to impart the toughening mechanisms of slippage and localized plastic deformation. Rather, the coarse non-bonded interface simply provides a limited degree of crack deflection, a comparatively minor energy absorbing fracture mechanism.

In comparison, the PS/PP system exhibits much better impact performance as shown in figure 6. Compared with the impact resistance of the end-member polymers, PS (15 J/m) and PP (49 J/m), all of the blend compositions exceeded the rule of mixtures and a region of greatest synergy was observed, approximately, in the 15 – 30% PS concentration range where a maximum impact resistance of 95 J/m was measured for the 20% PS blend. This represents a 127% increase in impact resistance over the 20/80 rule of mixtures value and a 94% increase over the impact resistance of neat PP. Referring to the micrographs of figure 2, the 20 and 30% morphologies are not co-continuous but rather are composites of PS dispersed in PP. Interestingly, the Young's modulus data correlate with the impact resistance data quite well, showing a maximum value relative to the rule of mixtures at these same compositions. Thus, we are required to conclude that, in this blend system, the dispersed PS blends produce improved load transfer and toughening mechanisms that the co-continuous blends do not. The reason for this is unclear, since both HDPE and PP are fully immiscible with PS as evidenced from solubility parameter data [HDPE = 7.9, PP = 8.0, and PS = 9.1 $(\text{cal/cm}^3)^{0.5}$] and by the morphology shown in the micrographs. Although the solubility parameter difference between the pairs differs by about 9%, this is not thought to be a significant difference. However, the tacticity of PP probably is important since the ~5% of atactic PP contained in the otherwise isotactic polymer may have a compatibilizing effect on the interface between PS and PP, thus increasing the load transfer for the modulus data and increasing energy absorption mechanisms and the impact resistance.

Summary

The Young's modulus and impact behavior of two immiscible polymer blends, PS/HDPE and PS/PP, were studied under tensile and impact loading. In both systems, the tensile modulus was shown to follow approximately rule of mixtures behavior although the PS/HDPE blend curve reached the proportional level only at the co-continuous composition, whereas the tensile modulus of the PS/PP blends were at or above the proportional relationship at all compositions on the PS rich side of the phase inversion.

Remarkably contrasting impact properties were observed in this study. The PS/HDPE system exhibited poor impact performance with values barely exceeding the value of neat PS. On the other hand, the PS/PP blends showed outstanding impact resistance throughout the blend range, but particularly in the 15 – 30% range where impact resistance was 127% higher than the rule of mixtures value.

PS/PP blends appear to be excellent engineering materials from the perspective of tensile modulus and impact resistance. Both properties show a common region of greatest synergy in the range of 15 – 30% PS. Thus, a 20% PS/PP blend possesses tensile modulus that is 38.2% greater than neat PP and with an impact resistance that is 94% greater.

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Key Words

Immiscible polymer blends, Izod impact, Co-continuous polymer blends

Table 1: Raw material information

Polymer	Supplier	Density (g/cc)	MFI (g/10min.)
HDPE	CP Chem	0.952	0.350
PP	CP Chem	0.900	0.650
PS	Polyone	1.040	7.000

Table 2: The blends compositions

PS/HDPE	PS/PP
0/100	0/100
20/80	20/80
30/70	30/70
35/65	35/65
40/60	40/60
45/55	45/55
50/50	50/50
60/40	60/40
80/20	80/20
100/0	100/0

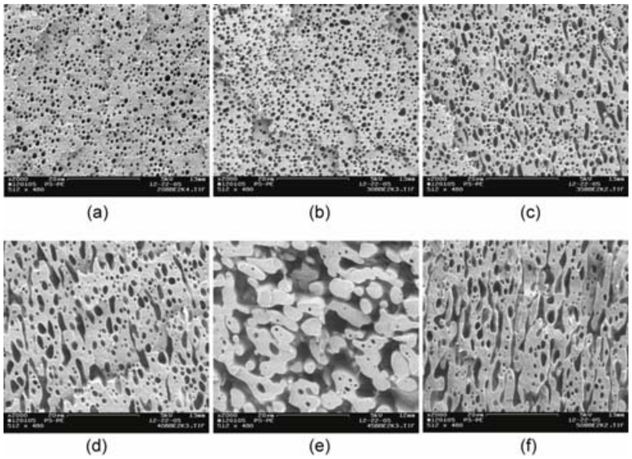

Figure 1: Morphology of PS/HDPE blends taken at 2000x: (a) 20%, (b) 30%, (c) 35%, (d) 40%, (e) 45%, and (f) 50%PS

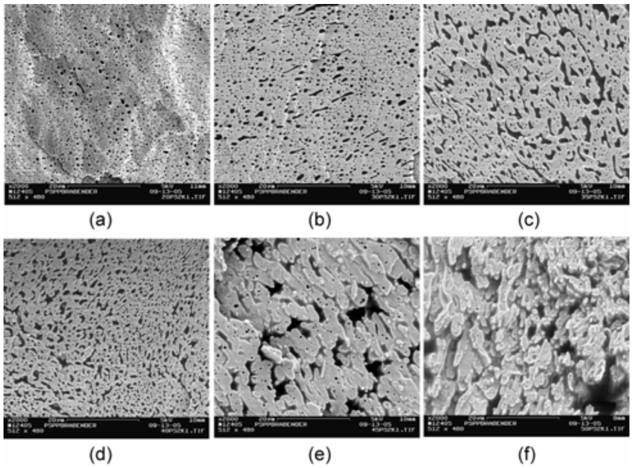

Figure 2: Morphology of PS/PP blends taken at 2000x: (a) 20%, (b) 30%, (c) 35%, (d) 40%, (e) 45%, and (f) 50%PS

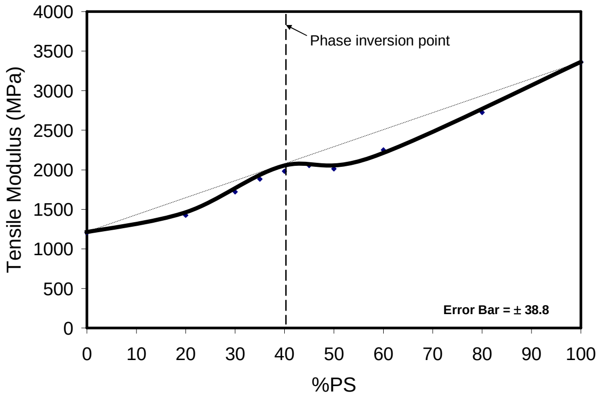

Figure 3: Tensile modulus for PS/HDPE blends at various compositions

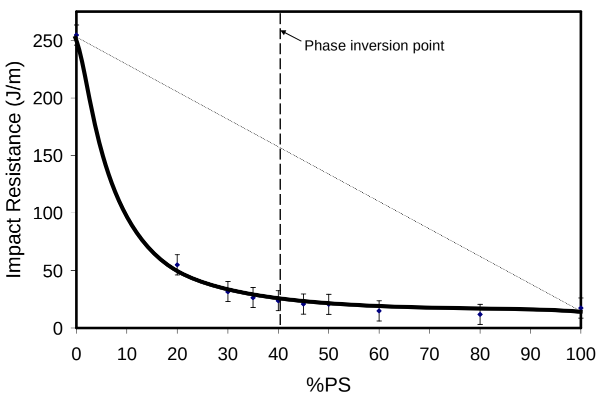

Figure 5: Impact resistance for PS/HDPE blends at various compositions

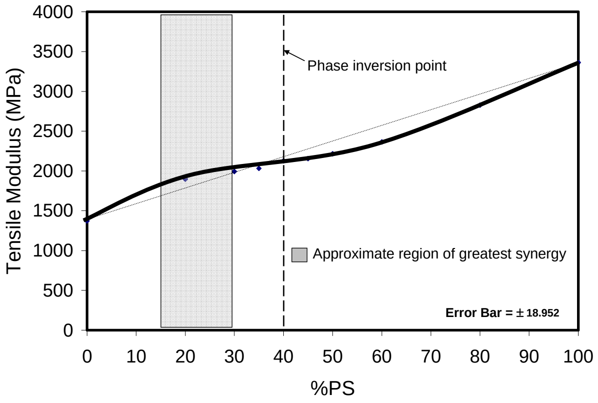

Figure 4: Tensile modulus for PS/PP blends at various compositions

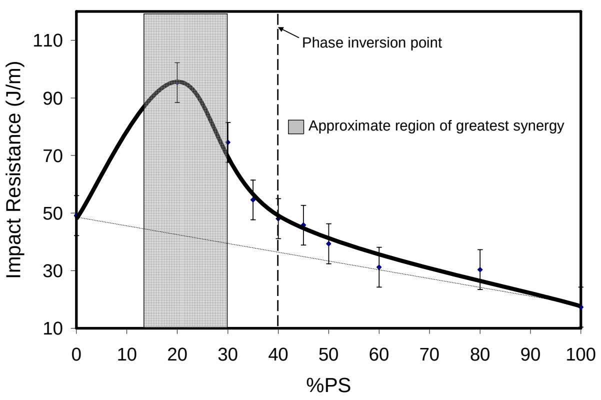

Figure 6: Impact resistance for PS/PP blends at various compositions