

Mechanical grafting and morphology characterization in immiscible polymer blends

Jayant Joshi, Richard L. Lehman, Thomas J. Nosker

AMIPP Advanced Polymer Center

Rutgers University, Piscataway, New Jersey 08854

Corresponding Author: Jayant Joshi, email: jayjoshi@rci.rutgers.edu

ABSTRACT

Blends of PS/HDPE and PS/PP were investigated for synergism in flexural modulus with varying composition. The evolution of blend morphology was studied and related to the improvement in flexural modulus around the co-continuous composition. DSC studies were conducted to study crystallinity variations in the semi-crystalline component of the blend. We found that co-continuous morphologies help in developing strong mechanical bonds between the components. Crystallization is inhibited in the co-continuous region and is related to the spatial constraints during the solidification process.

INTRODUCTION

Synergism in mechanical properties of immiscible polymer blends can be an efficient way of obtaining superior properties from otherwise mismatched polymers. Immiscible polymers characteristically lack structural integrity and consequently exhibit poor mechanical performance when blended. However, previous research in our laboratory and elsewhere has shown that synergism can exist in certain polymer pairs which leads to enhanced physical properties[1-4]. Hara and Sauer[1] describe the various kinds of synergisms in mechanical properties which can exist between polymer pairs. They treat various cases of compatible polymer pairs (PS/PPO, PP/PB, PVC-copolymer-SAN etc), incompatible polymer pairs (PC/PMMA, PC/SAN, PE/PP, PC/PET etc) and ionomer pairs (SPS Ionomer/PS, PMMA Ionomer/PMMA etc) and analyze the mechanisms by which synergism might be occurring in these blends.

Synergism arising out of purely mechanical bonds is of critical importance as it covers the majority of polymer pairs. This kind of synergism which has been described by us, recently as mechanical grafting[4], and earlier in pioneering work[3] in immiscible blends of recycled PS and HDPE, occurs only in the co-continuous region of the blends. A concurrent dip in crystallinity values is also associated with this phenomenon and has been attributed by the authors to stresses developed during contraction which inhibit growth of crystallites in the semi-crystalline polymer. Co-continuous morphologies also have extensively analyzed for their improved mechanical properties[5, 6]. Willemsen et al [2] reported improved tensile moduli of PS/PP and PS/PE blends. Their study emphasized the importance of co-continuous morphologies[7] to mechanical performance of blends. Recent work in our laboratory has confirmed the existence of synergism in flexural modulus in co-continuous compositions of virgin PS/HDPE blends, and also in PS/PP blends. We have attempted to understand the nature of the synergism which causes the co-continuous morphologies to have superior properties. In this paper, we report some of those results, and also try to analyze the exact nature of the synergism by DSC studies on these blends. Crystallinity measurements have helped to

understand the nature of this synergism and the strong influence of micro-structure in these blends.

EXPERIMENTAL

Table 1. Raw materials and their physical properties.

Material(grade)	Supplier	MFI(conditions)
PS(GPPS7)	GE Polymerland	7.0g/10min(5Kg, 200°C)
PP(isotactic)	Polyone	0.65g/10min(2.16Kg,190°C)
HDPE(HHM5502BN)	Chevron Phillips	0.35g/10min(2.16Kg,190°C)

Table 1 gives the raw materials used, along with some of their properties and suppliers. The polymer pellets were initially mixed thoroughly and extruded in a Brabender extruder at 100 rpm at a temperature of 200°C. In order to retain the micro structural morphology, the extruded rods were directly used for flexural testing rather than injection molding. Five samples of each composition were prepared to eliminate variations that arise from non-uniformity of the rods. Specimens were kept in the test environment for 2 days prior to testing. The testing was done according to ASTM D720 modified for a circular cross section. Cross-head speed was 0.127 cm (0.05 inches) per minute and the span length 5.08 cm (2 inches). The diameter of the specimens was measured around the point of breaking or bending of the specimens.

To observe the morphology of the extrudates, the cylindrical specimens were cryogenically fractured in liquid nitrogen along a plane perpendicular to the extrusion direction. The PS from the surface of these fractured specimens was leached out by stirring in a bath of toluene for 15 minutes. They were then sputter coated with Au-Pd for 2 minutes. All micro structural observations were made using a Leo-Zeiss Gemini 982 field emission scanning electron microscope at voltage of 5 keV.

Crystallinity measurements were obtained by slicing about 10 g of sample from the surface of the specimens. A TA Instruments Q1000 DSC instrument was used for the measurements. The heating cycle chosen was heat-cool-mdsc heat cycle. For the first heat cycle, the ramp rate was 10°C per minute and for the cooling cycle the rate was 5°C per minute. All crystallinity measurements were made in the cooling cycle of the runs to include only the effects of morphology on the crystallization behavior of the blends.

RESULTS AND DISCUSSION

Synergism in PS/HDPE blends

Studies by our group have previously shown synergism in recycled PS/HDPE blends³[4], in which a significant improvement in the mechanical properties was observed around the co-continuous composition. The properties were seen to approach or exceed the rule of mixtures level around 35 % PS. In this study we have found similar results with virgin PS/HDPE blends using extrusion and measurement of the flexural properties of the as extruded cylindrical rods.

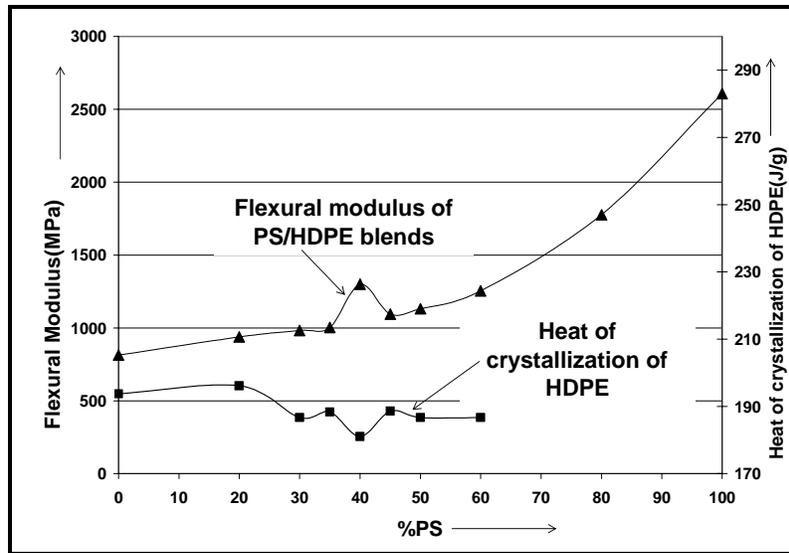


Figure 1. ▲ : Flexural modulus properties of PS/HDPE blends
 ■ : Heat of crystallization of HDPE in PS/HDPE blends

Flexural measurements in figure 1 show that for most of the compositions, the flexural modulus of these blends falls much below the rule of mixtures level. However, at around 40 % PS composition, there is a marked increase in flexural modulus which tends to approach the rule of mixtures level. This improvement in flexural modulus has a strong correlation to the presence of co-continuity which is predicted to be around 40 % PS composition using Jordhamo's equation[8] for these blends. Figure 2 a) shows the morphology development in these blends. Around 40 % PS, the blends are co-continuous as above this composition the PE domains appear to reduce in size as compared to the PS domains. The increase in flexural modulus may be related to the presence of strong mechanical bonds which develop during the solidification process after extrusion. Co-continuous morphologies are ideally suited for this kind of "mechanical grafting" because the interpenetrating nature of the domains helps to develop an efficient stress transfer mechanism.

The exact nature of the stresses is not fully understood, but we expect that the inherent contraction of the semi-crystalline phase during crystallization combined with the volumetric constraints of the co-continuous morphology result in the reduced crystallinity. A study of the heat of crystallinity of the HDPE phase reveals a drop in crystallinity around 40 % PS composition. This is related to the presence of co-continuity and the strong improvement in flexural modulus at this composition. Co-continuous morphologies are believed to behave differently because of the enhanced stress transfer mechanism which can take place in this kind of morphology. It is the fine structure produced which leads to the improvement in flexural modulus. The domain sizes in this morphology are small, such that the stresses are readily transferred across even weakly bonded interfaces by virtue of the entangled structure and the fine size. This morphology and behavior are the essence of mechanical grafting.

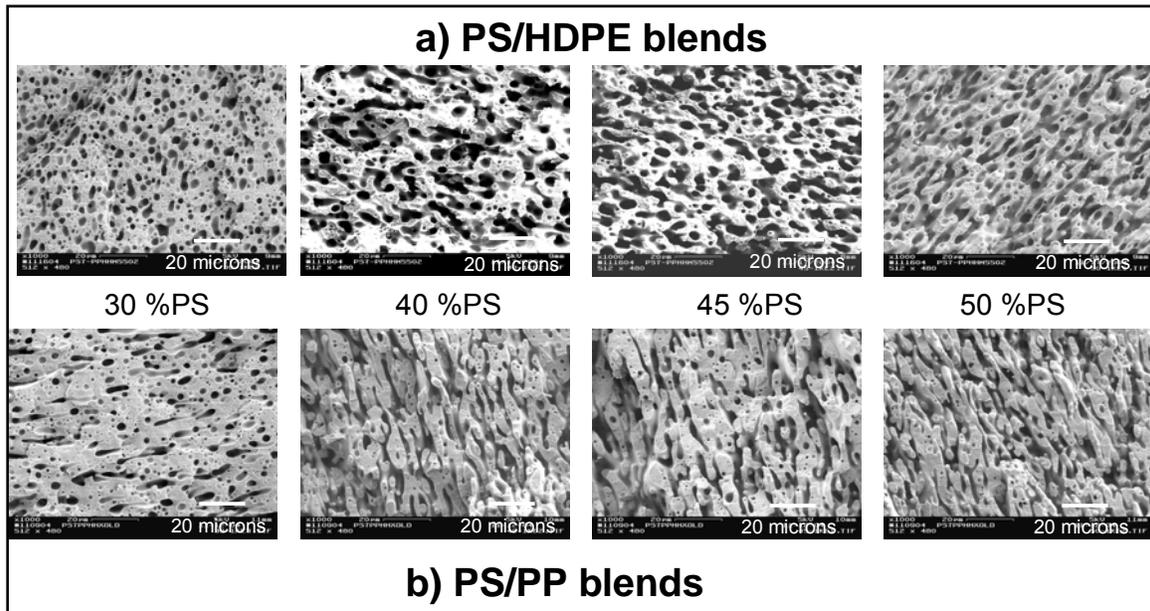


Figure 2. Morphological variations of a) PS/HDPE and b) PS/PP blends

Synergism in PS/PP blends

Figure 1b) shows the morphology development of PS/PP blends as composition is varied. At around 40% PS, the blends achieve maximum co-continuity, a feature that is reflected in their flexural modulus properties. Flexural modulus values measured for these blends are shown in figure 4. As with PS/HDPE blends, here too we see a poor flexural performance for all compositions except the co-continuous composition. The flexural modulus falls well below the additive rule of mixtures line except at 40% PS where it tends to approach it.

The structural significance of the co-continuous morphology is evident in the enhanced flexural performance for this composition. Similar to PS/HDPE blends, the improved modulus is explained in terms of stress transfer mechanisms which are much more effective for a co-continuous morphology.

DSC analyses of the crystallization exotherms of these blends reveals a sharp reduction in crystallization ability of PP around its co-continuous composition as shown in figure 4. The absolute value of the slope of the crystallinity curve between 20 – 40% PS is less than the value between 40 to 50 %PS. This results from the sudden change of morphology of the blend between 40 and 45% PS composition. The domain size of PP is affected rather slowly as more and more PS is added to the blend because of the lower viscosity of the PS phase as compared to the PP phase. On the other hand, domain size change is more drastic when a small percentage of PP is added to PS as you approach the co-continuous composition for the same reason mentioned above.

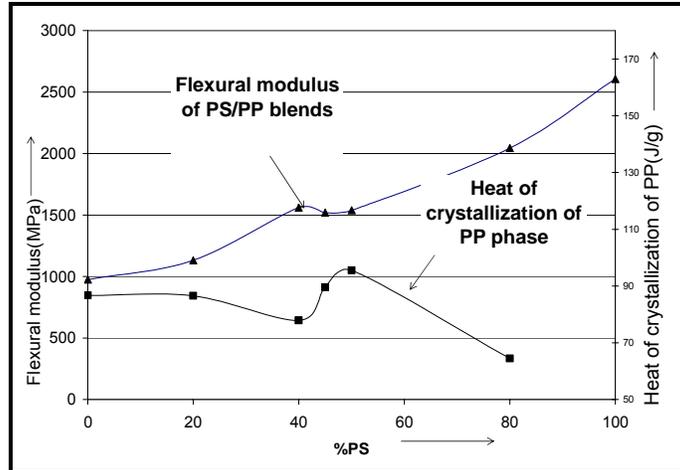


Figure 4. ▲ : Flexural modulus properties of PS/PP blends
 ■ : Heat of crystallinity of PP in PS/PP blends

This effect can be explained on the basis of the asymmetric coalescence behavior of dispersed blends on either side of the co-continuous region, depending on the viscosity of the respective component. This effect is beyond the scope of the present paper and will be discussed in detail in upcoming papers.

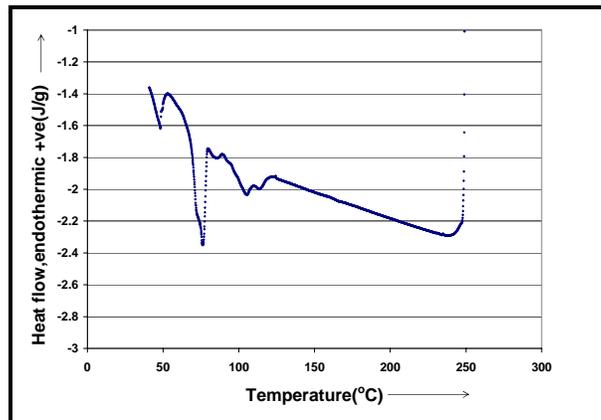


Figure 5. Heat of crystallization of PP in PS/PP 80/20 blends

The second drop in crystallinity which occurs at high PS compositions ($> 60\%$) is likely related to the different nucleation mechanisms which begin to occur at such high compositions during crystallization. At high PS compositions, the PP crystallization exotherm peak breaks up into two or more distinct peaks which occur over a range of temperatures as shown in figure 5. Chun et al[9] report that the highest crystallization temperature is consistent with heterogeneous nucleation of crystallites while the lower temperature is consistent with homogenous nucleation. In our work, a second super-cooled PP crystallization peak is observed near 50°C . This peak is observed only at the lowest level of PP in PS where very small particles of PP are highly dispersed in PS. We propose that this extreme supercooling results from the small volume of polymer which inhibits the ability of chain assembly and folding to produce the necessary

nucleus for subsequent crystallization. Thus, the cooling data in figure 5 represent areas of heterogeneous nucleation, homogenous nucleation, and spatially constrained homogeneous nucleation respectively as the melt is cooled.

SUMMARY AND CONCLUSION

We have observed that both PS/HDPE and PS/PP blends show a synergism in their flexural modulus around their co-continuous compositions. This synergism is related to the co-continuous morphology which occurs at a composition determined by the viscosity ratios of the component polymers. A highly effective stress transfer mechanism that occurs from the fine intertwined morphologies associated with co-continuous blends results in the improved modulus values. This condition, which requires proper formulation and processing, is termed mechanical grafting. Reduced crystallinity has been observed at these compositions which gives further clues to the mechanical grafting process. We suggest that either the compressive stresses generated during solidification or the fine structure of the morphology causes the reduction in crystallinity. The difference in slopes of the crystallinity reductions around 40% PS in PS/PP blends is related to the difference in fluid dynamics and dispersed phase coalescence of the blends on each side of the phase inversion composition.

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