

Selected Physical Characteristics of Polystyrene/High Density Polyethylene Composites Prepared from Virgin and Recycled Materials

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ABSTRACT: Mixtures of polystyrene and high density polyethylene were injection molded from recycled and virgin polymers to generate cocontinuous structures. The mechanical properties of these blends were evaluated to assess their conformance to rule of mixtures behavior in general and to identify areas of synergy or incompatibility in specific. Flexural and tensile data for recycled blends showed that generally the properties are not additive, except in a cocontinuous region of composition near 35/65 PS/HDPE that has been identified previously for recycled materials. Analysis of crystallinity in the HDPE phase of these blends by differential scanning calorimetry indicates a marked reduction in the level of HDPE crystallinity at the 35/65 PS/HDPE composition. Similar blends of virgin PS/HDPE polymer do not show the differing regions of incom-

patibility and synergy illustrated by the recycled materials, but rather show approximate conformance to the rule of mixtures. Furthermore, the virgin blends show virtually no crystallinity suppression and a more pronounced T_g shift in the polystyrene compared to recycled materials. Detailed characterization of the recycled materials in terms of polymer and particulate impurities should improve understanding of these differences and perhaps provide direction for obtaining enhanced synergistic behavior in virgin polymer blends. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2044–2051, 2006

Key words: blends; crystallization; immiscible; modulus; structure/property relationships

INTRODUCTION

Immiscible polymer blends have been studied extensively as an approach to the synthesis of new engineering materials.¹ Most of these blends rely on the use of compatibilizers to improve the strength of the mechanical linkages between the component polymers. Blends without compatibilizers have not been highly successful, although some studies in our laboratories have shown that promising mechanical properties can be obtained from immiscible blends if the composition and processing parameters are properly selected.^{2,3} The microstructural morphology plays a key role in imparting unique properties to such blends, and such microstructures have been studied extensively for various blends.^{4–6} Studies of cocontinuous materials have attributed the enhanced mechanical properties to mechanical clamping between the phases with concomitant stress transfer,⁷ a feature that also leads to reduced crystallinity.^{8,9} In this article we extend the concept of mechanically interlocking structures and intro-

duce the terminology “mechanical grafting.” This term describes immiscible polymer blends that have nonbonded interfaces and yet have a sufficiently fine interlocking cocontinuous structure that the composites exhibit rule of mixtures mechanical behavior and are stable when annealed near the T_g of the glassy phase.

Mechanical grafting is different from traditional chemical grafting in that there are no chemical bonds between the immiscible phases but, rather, all load transfer is affected by morphology and mechanical clamping. The morphology is generated by composition and processing conditions, and the clamping is generated by volumetric changes in each phase during cooling from the melt processing temperatures. Mechanical grafting is similar to chemical grafting in that the mechanical properties of the blends follow rule of mixtures relationships, as if strong chemical bonds spanned the interface.

The goal of the present work was to produce immiscible polymer composites from blends of polystyrene and HD polyethylene in the laboratory and to assess under controlled conditions the degree of mechanical grafting that occurs as a function of composition and raw material purity as represented by virgin versus recycled raw materials.

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TABLE I
Properties of the Virgin Polymers

Polymer	Melt Flow Data				Tensile yield (MPa)	Flexural modulus (MPa)
	Index (g/10 min.)	Load [kg]	Temp. [°C]	Density (g/cc)		
Extrusion grade high density polyethylene	0.35	2.16	190	0.952	27	1019
Virgin grade polystyrene	7.0	5.0	200	1.04	53.78	3317

EXPERIMENTAL

Materials

Recycled high density polyethylene and recycled polystyrene were obtained from an industrial supplier (Polywood, Inc., Edison, NJ) in the form of flakes and granules, respectively. A general purpose polystyrene (GPPS7 GE Polymerland) and extrusion grade high density polyethylene (HHM 5202 BN Chevron Phillips Chemical Co., LP, Houston, Texas) were used. Properties of the virgin polymers as given by the supplier are shown in Table I. Such properties were unavailable from the suppliers for the recycled materials.

Rheology

Rheology measurements were run on all polymers over a range of shear rates and in the temperature range 200–220°C, the relevant processing temperature. These data are necessary to determine the composition range at which cocontinuous blends are expected. All rheology measurements were performed using a TA AR 2000 rheometer (TA Instruments, New Castle, DE).

Blend formulation

Of all the immiscible blend compositions, the compositions exhibiting cocontinuous morphology typically have the best properties, and various methods exist for approximating the composition of this region. One such method by Jordhamo¹⁰ identifies the region according to the following relationship between the volume fraction (Φ) ratio and the viscosity (η) ratio of the components at the processing temperature:

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

Although such relationships are useful, the entire range was of interest in this study, and estimates of cocontinuous compositions were only made to cluster compositions in the expected ranges, as shown in Table II.

Extrusion and molding

The test materials were injection molded on a Negri Bossi V55–200 molding machine to produce standard test specimens (ASTM D638) for evaluation. All specimens were conditioned at 22°C at ambient humidity for two days prior to performing the mechanical measurements.

Evaluation methods

Flexural measurements were made at room temperature (22°C) on injection molded test specimens using the three point flexural test method described in ASTM D720. An MTS 2000 mechanical testing machine was employed with a crosshead speed of 5 mm/min. Tensile tests were performed at room temperature (22°C) on injection molded samples according to ASTM D638. Crosshead speed was again 5 mm/min. Differential scanning calorimetry (DSC) tests were performed on all compositions using a standard heat-cool-heat procedure between 40° and 180°C at a ramp rate of 10°C/min. The tests were performed on a TA Q-1000 calorimeter (TA Instruments, New Castle, DE).

TABLE II
Compositions of Polystyrene and HD Polyethylene Blends Prepared from Recycled and Virgin Polymers

% polystyrene	% high density polyethylene	Recycled	Virgin
0	100	X	X
10	90	X	
20	80	X	X
25	75		X
30	70	X	X
35	65	X	X
40	60	X	X
45	55		X
50	50	X	X
55	45		X
60	40	X	X
65	35		X
80	20	X	X
100	0	X	X

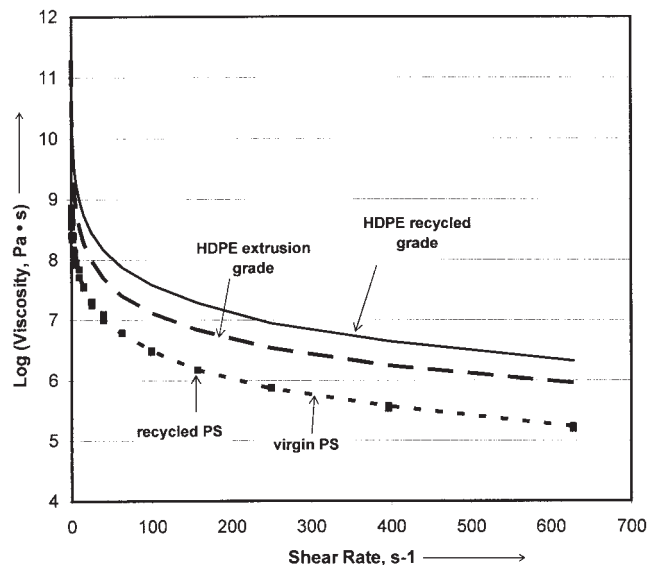


Figure 1 Rheology data for recycled and virgin polystyrene, and high density polyethylene at 200°C.

Electron microscopy

Small rectangular sections from the test specimens were cryo-fractured in liquid nitrogen to obtain a surface with preserved morphology. Most samples were etched with toluene for 15 min to extract polystyrene to improve imaging. After drying overnight, the samples were sputter-coated with gold and analyzed in an Amray 1400T scanning electron microscope under a voltage of 20KV.

RESULTS AND DISCUSSION

Rheology

Viscosity versus shear rate measurements at 200°C for recycled polystyrene, recycled high density polyethylene, virgin polystyrene, and virgin high density polyethylene are shown in Figure 1. The recycled and virgin polystyrene are identical, within experimental error, in their rheological properties, whereas the recycled high density polyethylene is clearly more viscous than the virgin high density polyethylene at all shear rates. According to eq. (1), the recycled blends are expected to be cocontinuous around 25% PS and virgin blends around 32% PS. Shear rates in a single screw extruder are considerably less than the shear rates encountered in injection molding, although precise values are difficult to obtain. Nonetheless, if processing shear rates are higher than the rheology test shear rate range, extrapolation of the nearly parallel curves does not substantially alter the point of cocontinuity. Any change in cocontinuity point as high shear

rates are encountered will be towards lower PS/HDPE ratios.

Morphology—SEM microscopy

The high shear rate of the injection molding process generated fine structured morphologies (Fig. 2,3) where domain sizes were of micron dimensions and varied with PS/HDPE ratio. The sample surfaces shown in the micrographs are fracture surfaces (77 K) and are perpendicular to the polymer flow direction during mold filling. The areas where polystyrene was removed by etching can be seen as the darker areas in the micrographs, up to 60% PS for virgin and up to 35% PS for recycled. Above this percentage the polystyrene is the major phase, and the images of the etched samples are less distinct. Etching was not attempted for the 80/20 virgin blend.

The virgin PS/HDPE blends (Fig. 2) show a distinctly dispersed morphology from 20 to 35% polystyrene compositions. The blends become more continuous and finer at 45% PS, and attain a cocontinuous structure between 50 and 60% PS. Beyond 60% PS composition, the virgin blend structure shows signs of collapse from the etching process, indicating that PS was the major phase at these compositions while the polyethylene phase was partially continuous or dispersed. Finally, at 80% PS, a finely dispersed structure of polyethylene in a polystyrene matrix is observed. Overall, these blends are finer in texture than the recycled blends discussed below.

The recycled blends show a region of polystyrene continuity (Fig. 3) at much lower PS percentages (30%) as compared to virgin blends. At 35% PS, the structure shows widely protruding domains of polyethylene, suggesting a high degree of continuity in both the polystyrene and polyethylene phases. Cocontinuous structures are expected around this composition, as predicted by the Jordhamo relation. The structure at this composition clearly shows that the cocontinuous morphology is not as fine as that observed with virgin blends. Beyond the 35% PS composition, the structure collapsed due to polystyrene removal during etching and no distinct structure was observed.

Mechanical properties

Flexural test data for recycled and virgin PS/HDPE blends are shown in Figure 4. For recycled blends, the data indicate an initial period of poor properties below the rule of mixtures (incompatibility) followed by an improvement in flexural properties in the 20 to 50% PS composition region, the region of cocontinuity. Virgin blends, on the other hand,

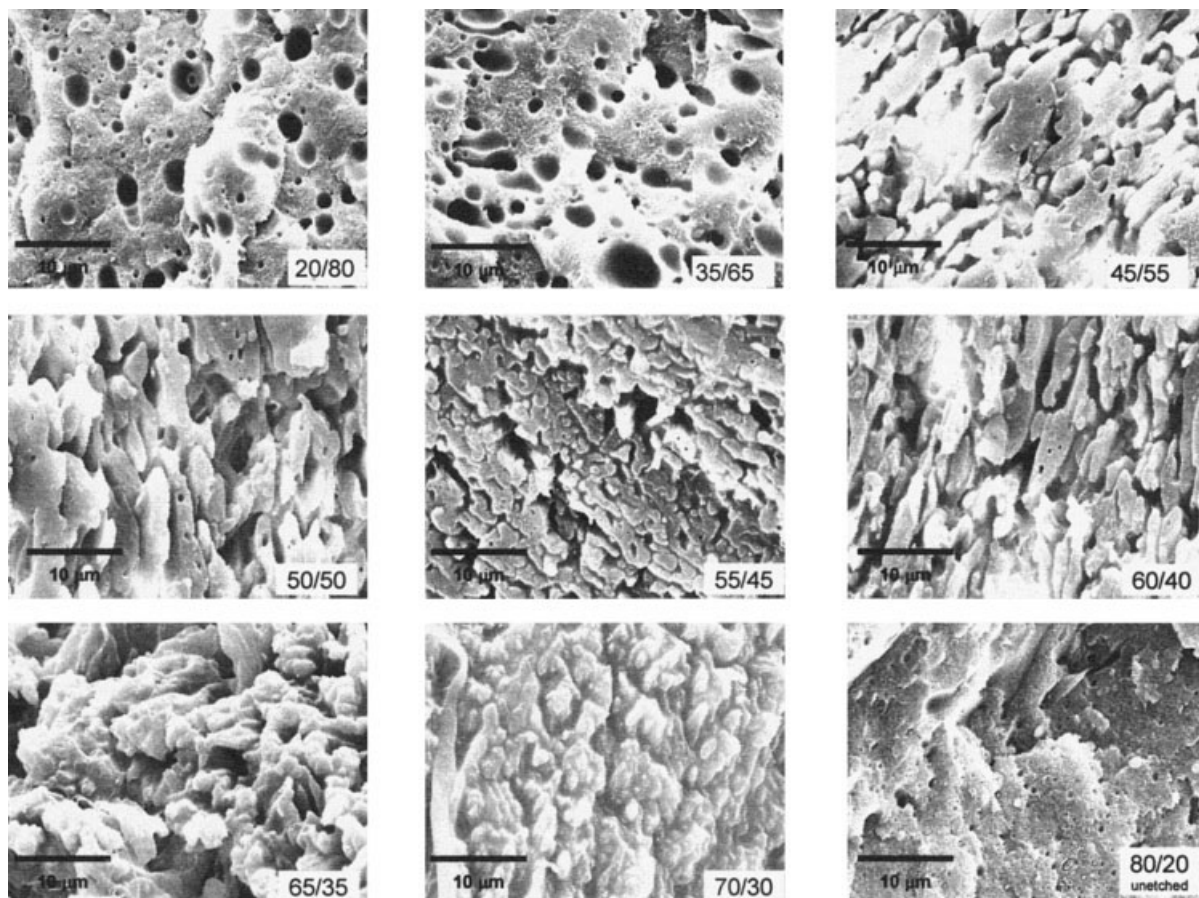


Figure 2 Morphology of virgin PS/HDPE blends as shown by electron microscopy.

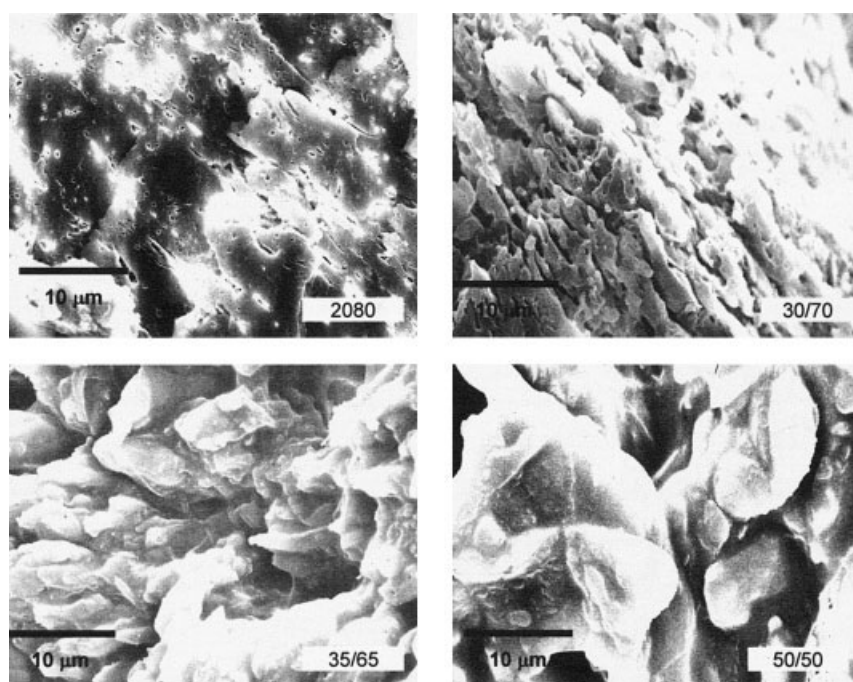


Figure 3 Morphology of recycled PS/HDPE blends as shown by electron microscopy.

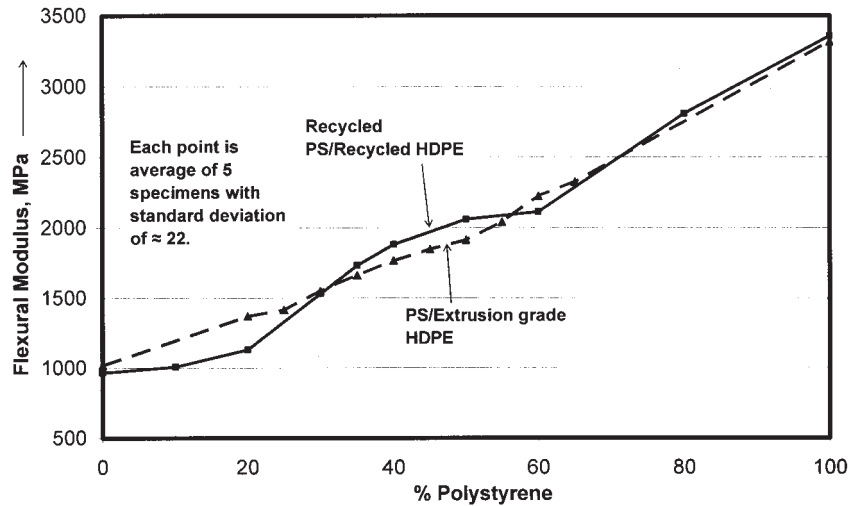


Figure 4 Three point flexural modulus versus polystyrene composition for recycled and virgin PS/HDPE blends.

show much more linear behavior, with no distinct region of incompatibility or synergy.

To further investigate this unusual behavior, tensile tests were performed, and the results (Fig. 5) for recycled and virgin blends show similar behavior to the flexural studies. The only significant difference is a slightly higher tensile modulus value for the 100% recycled high density polyethylene material in tension as compared to flexural. This effect may be due to impurity polymers (PET, PVC, PP) forming reinforcing fibers in the center of the molded specimen, thus increasing tensile values but having less effect in flexure. Overall, the virgin polymer tensile data match up well with the flexural data, showing nearly linear properties.

There are two important conclusions arising from the mechanical data. First, a synergy is observed in the range of 30–50% PS only for recycled PS/HDPE, in which both the tensile modulus and flexural modulus show an increase relative to neighboring compositions. The maximum modulus in this synergistic region reaches approximately the rule of mixtures value, but never exceeds it. Thus, this synergistic region is an area where the morphology is cocontinuous and mechanical bonding between the phases constitutes “mechanical grafting.” So-called incompatible regions bound the synergy region on both sides, with associated poor properties. Secondly, the virgin polymers show no such region of relative synergy, but rather track a path just slightly

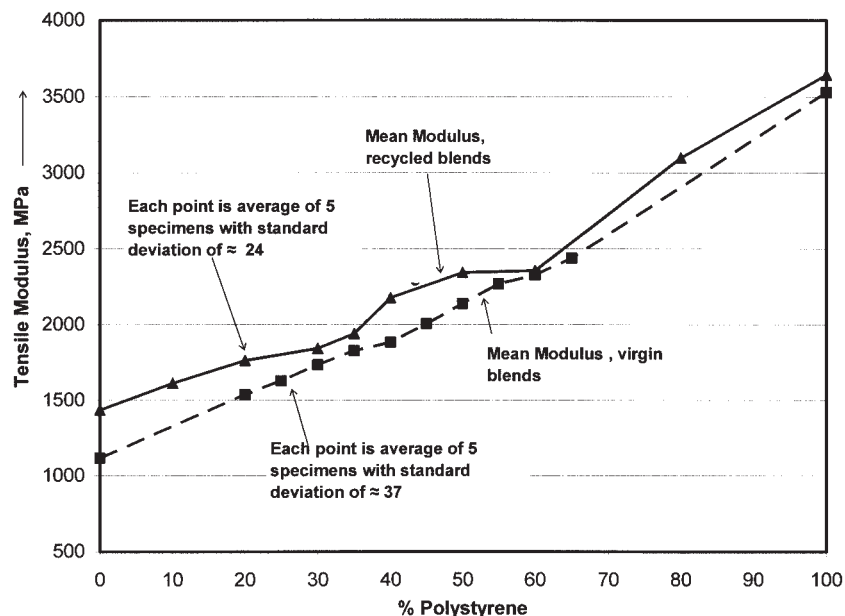


Figure 5 Tensile modulus of recycled and virgin PS/HDPE blends.

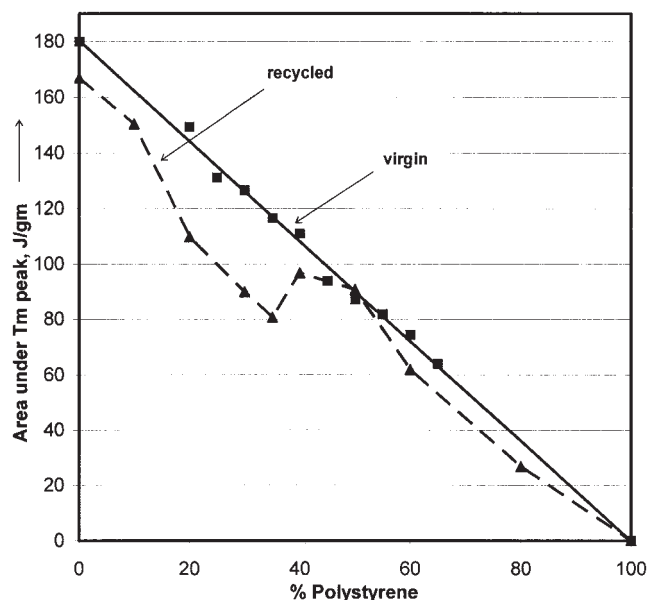


Figure 6 Crystallinity as a function of polystyrene composition for recycled and virgin PS/HDPE blends.

below the rule of mixtures over nearly the entire compositional range. The greatest deviation from the rule of mixtures for the virgin blends occurs in the middle of the composition range. The properties of these blends are too close to the rule of mixtures to call them incompatible, but yet they do not conform closely enough to term them "mechanically grafted." Additional work is needed to further optimize the processing of these mixtures to produce mechanically grafted blends.

Differential scanning calorimetry

To shed light on the relative synergy peak in the recycled polymer blends, thermal analysis was con-

ducted and crystallinity and glass transition effects were evaluated. Crystallinity reductions have been observed for recycled blends,¹¹ but no data are available in the literature regarding T_g shifts in such materials. The crystallinity of high density polyethylene was substantially reduced (Fig. 6) in the composition region from 10 to 40%, the same cocontinuous region where the modulus peak was observed. The virgin blends show no crystallinity reduction. Generally, it seems that the intricate, constrained environment of cocontinuity may inhibit crystallization, although an explanation for why this does not occur in virgin blends is lacking. Some possible explanations include the presence of polymer and pigment impurities in the recycled high density polyethylene and the greater sensitivity of high molecular weight high density polyethylene to crystallinity perturbations. Fine structured blends should be more prone to inhibited crystallization than coarse blends, but in this study the recycled blends were slightly coarser than the virgin blends.

The glass transition temperature of the polystyrene component varied with temperature at all compositions, increasing with decreasing polystyrene content (Fig. 7). The slope of the T_g versus composition curve is greatest for the virgin blends ($\sim 2^\circ\text{C}/10\%$ composition change), consistent with the slightly finer structure of these blends, but counter to the crystallinity reduction data. Similarly, the recycled blends showed a lesser effect ($\sim 0.6^\circ\text{C}/10\%$ composition change).

Modeling the observed behaviors

Clearly the physical state of the polymer composite is constraining the formation of polyethylene crystals

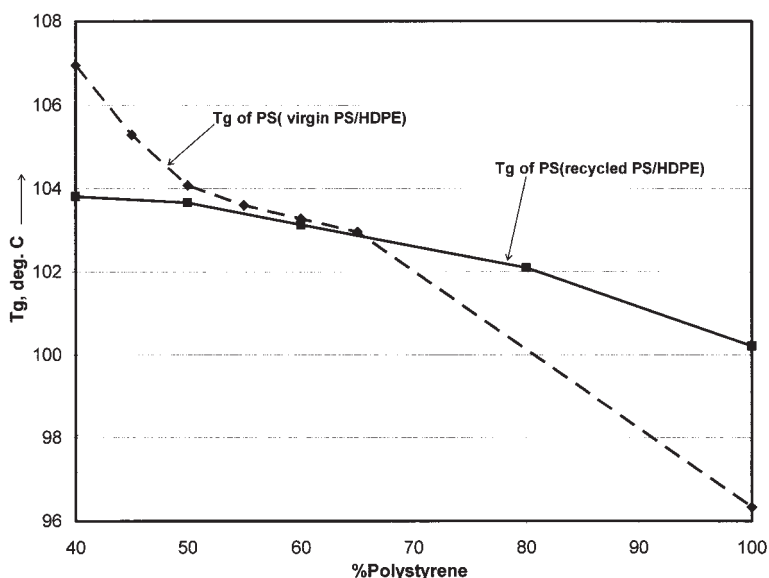


Figure 7 T_g variations with composition for polystyrene phase in virgin and recycled PS/HDPE blends.

and constraining the relaxation of the super cooled liquid to a glass of lower T_g . We have conceived of two possible qualitative structural models to explain these effects. The immiscible polymer blends contain feature sizes in the general range of 0.5–20 microns, a dimension sufficiently small to alter the dynamics of crystal and glass formation for the large molecules associated with high density polyethylene and polystyrene. Furthermore, the cocontinuous region of these blends is characterized by mutually intertwined polymer networks whereby mechanical forces arising from thermal contraction and crystallization can be efficiently transferred from one phase to the other. The two proposed models address these issues and are discussed in greater detail below.

Polyethylene and polystyrene, like most polymers, have very long backbone chain molecules, often exceeding 40,000 carbon atoms. The process of crystal formation in the semicrystalline polymers (e.g., high density polyethylene) requires bending and folding of these chains to form the lamellar crystalline structures. These lamellae can be quite large, on the order of microns. The microstructural morphology of the composite evaluated in this work is quite small, often less than one micron, as discussed above and shown in Figures 2 and 3.

Hence, the immiscible polymer domains in these composite are quite small and confine the polymer molecules to a considerable extent, thus raising the activation energy for their reorganization into crystal lamellae. Reduced crystallinity is expected when the semicrystalline polymer appears in small-dimensioned structures, as has been observed in the recycled blends in the cocontinuous region. Similar arguments can be made for the relaxation processes associated with glass formation and the observed shift in T_g over the composition range.

Another qualitative model is equally plausible and involves stresses generated in the two phase system and their effect on the crystallinity and glass transition temperature of the polymers. Consider a two component immiscible polymer blend where one polymer is semicrystalline, the other is amorphous, and the T_g of the amorphous polymer is less than T_m of the semicrystalline polymer. In geometries where the semicrystalline polymer surrounds the amorphous polymer, a tensile stress occurs in the semicrystalline polymer and a compressive stress in the amorphous polymer as the composite is cooled through T_m . These stresses result principally from the volume reduction occurring during crystallization. Indeed, as these stresses increase, they can reach a critical level where further crystallization is inhibited. The amorphous polystyrene phase, still above T_g , is in hydrostatic compression. As the temperature further cools to T_g , the liquid polymer transforms to a glass. The resulting T_g is higher than the bulk polymer T_g owing to the com-

pressive stresses and the pressure dependence of T_g . On the other hand, in areas where the glassy phase surrounds the semicrystalline phase, crystallinity and T_g should be unaffected since the semicrystalline phase contracts away from the glassy phase during cooling.

Additional studies of morphology and crystallinity variations are required to determine whether one or both of these models are appropriate to explain these phenomena.

CONCLUSIONS

Immiscible PS/HDPE composites have been prepared by melt processing of virgin and recycled polymers, and the morphology, elastic modulus, crystallinity, and T_g behaviors have been characterized. The composites are fine structured with regions of cocontinuity and with average domain dimensions in the micron range. The virgin blend morphologies are nominally finer than those of the recycled blends. The composites show nearly additive properties over the composition range, although the behaviors of virgin and recycled materials were quite different. Recycled blends show significant regions of incompatibility, but also a pronounced region of synergy in the cocontinuous range centered at 40% PS, whereas the virgin blends are more consistently linear in their behavior. Crystallinity is reduced and PS glass transition temperatures are increased relative to bulk polymer values. The shifting of these parameters appears to arise from spatial and mechanical constraints inherent in the composite system. The crystallinity reduction is observed in the cocontinuous region of the recycled polymer blends, but not in the virgin blends. The T_g shift occurs most prominently in the virgin blends.

Two models, one based on the geometric constraints of the composite morphology and a second based on micromechanical effects, are proposed to explain these behaviors. Further studies on morphology and crystallinity variation will be carried out to quantify these models and to support or refute the premises underlying each.

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