

Effect of Additives on the Composition Dependent Glass Transition Variation in PS/PP Blends

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ABSTRACT: The effect of additives on glass transition behavior in melt processed blends of polystyrene (PS) and polypropylene (PP) was studied. Blends of additive-free polystyrene and additive-free polypropylene revealed the known effect of the PS T_g increase in blend compositions where PP surrounds PS. Glass transition behavior in these blends was compared to blends prepared from additive-free PP and commercial grade PS, which contained lubricant additives. The thermal transitions of PS and PP were measured using modulated DSC. Although the behavior of

low PS concentration blends was similar in both systems, the characteristics of the high PS blends differed substantially. These differences and the contrast in the PP T_g behaviors were attributed to the migration of additives from the PS phase across the immiscible interface into the PP phase. Similar T_g variations were observed in blends of commercial grade PS and commercial grade PP. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3987–3992, 2008

Key words: blends; glass transition; additives; polystyrene

INTRODUCTION

Impurities in the form of processing additives are an important part of the polymer processing industry in that they are widely used to facilitate processability and to improve specific resin characteristics. Common additives include antioxidants to prevent thermal degradation, UV stabilizers to prevent photo-degradation, pigments to impart color, flame retardants, antistatic agents, plasticizers to improve processability, oils to improve melt flow, and internal as well as external lubricating agents.¹

The interaction between component phases in a polymer blend significantly influences their mechanical and thermal properties. The T_g values of individual blend components are often used as indicators of miscibility.² A single intermediate T_g is observed in completely miscible blends and inward T_g shifts are observed when there is partial miscibility between blend components. Immiscible blends are just mechanical mixtures of the constituent polymers and such blends generally do not show shifts in their T_g , but rather reflect the properties of the neat components. In some cases, however, physical interactions between the immiscible phases induce shifts in T_g values.^{3,4} Since immiscibility depends considerably on the polymer molecular weight, miscibility may occur to a very small extent in immiscible

systems due to migration of monomers or oligomers, either from the constituent polymers or from additives in commercial polymers, during processing. Greco et al. observed that the PS T_g in PS-PP (polystyrene-polypropylene) blends increased from 100°C for homopolymer PS to a single value of 103°C at other compositions of PS in the blend (80, 70, 50, 30, and 20% PS).⁵ They attributed this behavior to the selective extraction or migration of low molecular weight PS fractions into PP. In blends of PC and ABS, the T_g of PC decreases with decreasing PC concentration, characterized by an initial drop from the 100% PC value with small additions of ABS, followed by lesser decreases and ultimately a leveling off. This effect was attributed to low molecular weight species of ABS migrating to the PC domains.⁶ The migration of additives from one phase to another in polymer blends has been observed earlier. Such instances include the migration of plasticizers and/or internal lubricants from the PVC to a surrounding PS phase across an immiscible domain boundary. These migration effects have been observed to result in a reduction of the PS T_g .⁷

PS and PP are commercially important polymers because of their ready availability, ease of processing, and use in a large variety of commercial and industrial products. The crystallinity of PP, as well as entropic (high molecular weight) and enthalpic (heat of mixing) restrictions, render PP chemically immiscible with PS and hence mechanically incompatible. The addition of compatibilizers, however, such as SEBS (styrene/ethylene-butylene/styrene)^{8–10} permits

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TABLE I
Important Properties of Blend Components

Material	Code	Supplier	Features	Melt index (g/10 min)	Density
Polystyrene (PS)	PS-AF	Aldrich	Additive-free	3.16 (200°C; 5.0 kg)	1.047
Polystyrene (PS)	GPPS	GE Polymerland	Lubricants	7.0 (200°C; 5.0 kg)	1.04
Polypropylene (PP)	PP-AF	Aldrich	Additive-free	4.00 (230°C; 2.16 kg)	0.9
Polypropylene (PP)	PP-1	CP Chem	Antioxidants	0.65 (230°C; 2.16 kg)	0.9

enhanced mechanical properties over a wide range of blend compositions and increases the utility of this blend system. From a polymer science perspective, the purely immiscible blends provide interesting insight into physio-chemical interactions between the domains and have been the subject of earlier work in our laboratory. In some of these earlier studies, we observed that the PS T_g increases from its bulk values when blended with PP.¹¹ These increases in the T_g occur when immiscible systems are melt processed under high shear to produce a fine micron-scale intertwined domain structure at certain compositions. Such morphologies are correlated with good mechanical properties, i.e., rule of mixtures, and offer the potential for commercial application. Ongoing studies in our laboratory, such as the present one, are directed at understanding and improving the properties of immiscible polymer blends. The glass transition temperatures of the polymers, *in situ*, are an important marker for morphology development in immiscible systems. The polymers used for the above-mentioned study were commercial grade materials readily available from industrial suppliers and which contain small quantities of process enhancing additives. The present effort focused on comparing T_g -shift variations in PS/PP blends prepared from additive-free laboratory grade resins with the same T_g effects observed previously in commercial resins.

EXPERIMENTAL

Materials

Important properties of the blend materials are shown in the Table I. Two types of polypropylene, one from Aldrich Chemicals (St. Louis, MO) that had no additives and processing aids, and the other from Chevron Phillips Chemicals (The Woodlands, TX) that contained antioxidants, were used. These are designated as PP-AF (PP additive-free) and PP-1, respectively.

Two grades of polystyrene, PS-AF (PS additive-free from Aldrich) and GPPS (commercial grade general purpose PS from GE Polymerland, Pittsfield, MA) were used. Different combinations of PS/PP were prepared from the available grades to isolate effects of additives. PS-AF/PP-AF is the pure, additive-free PS-PP blend. To isolate effect of the additives in GPPS, it was blended with PP-AF [GPPS/

PP-AF] and the results compared with the PS-AF/PP-AF blends. GPPS was also blended with a commercial grade PP [GPPS/PP-1] and the T_g results compared to GPPS/PP-AF blends. A full range of blend compositions was prepared. A summary of the compositions and blends prepared is given in Table II.

Processing

The resins were melt compounded in a single screw extruder [Brabender Intellitorque]. Cylindrical blend specimens were extruded with a 25:1 metering single screw having a diameter of 19 mm with mixing elements and a 13 mm die. Temperatures in the three extruder zones were maintained at 220°C and blends were extruded at a screw speed of 50 rpm.

Thermal characterization

The component thermal transitions were examined by differential scanning calorimetry (Q1000 DSC, TA Instruments, New Castle, DE) operated in modulated DSC mode. Sample disks of ~10 mg mass were sliced from the extruded specimens and punched to match the size of DSC aluminum pans. Care was taken to include the section of the extrudate from the center to the edge. The temperature range of thermal analysis included the T_g s of both polystyrene as well as polypropylene and a cycle of modulated heat-cool-modulated heat was used. The MDSC parameters were: temperature range -40°C to 220°C; modulation amplitude $\pm 1.30^\circ\text{C}$, and period 40 s; heating rate 3°C/min and cooling rate 5°C/min. These parameters were chosen after careful optimization. Negative temperatures in the DSC were achieved using a refrigerated cooling system

TABLE II
Blend Compositions

PS-AF/PP-AF (wt %)	GPPS/PP-AF (wt %)	GPPS/PP-1 (wt %)
100/0	100/0	100/0
90/10	90/10	90/10
70/30	70/30	70/30
50/50	50/50	50/50
30/70	30/70	30/70
15/85	15/85	15/85
0/100	0/100	0/100

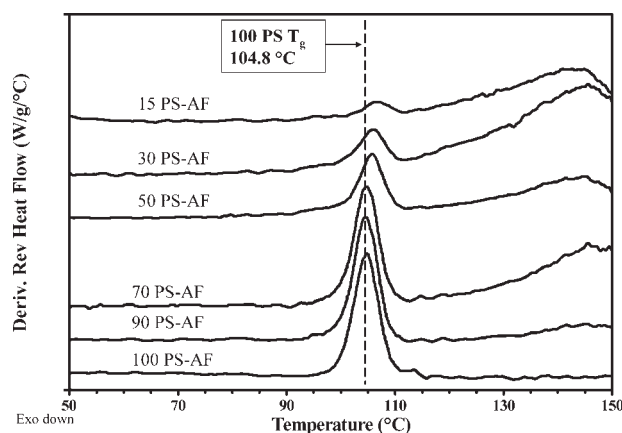


Figure 1 Derivative of the DSC reversing heat flow curves for various weight percent blends of PS-AF/PP-AF. Peaks denote the PS-AF T_g in blends; the dotted line is the 100% T_g .

and the instrument was calibrated using a standard indium sample.

RESULTS

Glass transition

DSC curves of derivative reversible heat flow for PS-AF/PP-AF are shown in Figure 1. Glass transition values for PS were determined by the peak positions, thus reducing the ambiguity associated with the onset-end-intercept method.

The compositional variation of the PS T_g in PS-AF/PP-AF and GPPS/PP-AF is shown in Figure 2. The PS-AF T_g values are an average of six T_g measurements made during the heating cycles of three DSC heat-cool-reheat runs, whereas the GPPS T_g values are an average of two measurements. Data were pooled in a statistical design to generate error bars representative of the variability of the measurements.

The PS-AF T_g in PS-AF/PP-AF blends shows two regions of compositional variation. The T_g of bulk PS-AF [$\sim 104.8^\circ\text{C}$] persists as PP is added to neat PS until the blend reaches approximately the 50/50 composition, at which point the PS T_g increases to 105.8°C . Further increases in PP concentration generate additional increases in the PS T_g until the PP concentration is 85% at which point the PS T_g is 106.8°C . When GPPS replaces PS-AF in the blends (solid data points in Fig. 2), a different dependence of PS T_g on composition is observed. The neat GPPS glass transition is lower (100°C) but the T_g in the blends rises sharply with increasing additions of PP-AF. Close to the 50% composition the two curves nearly merge and the low PS concentration behavior is similar for both PS-AF and GPPS blended with PP-AF.

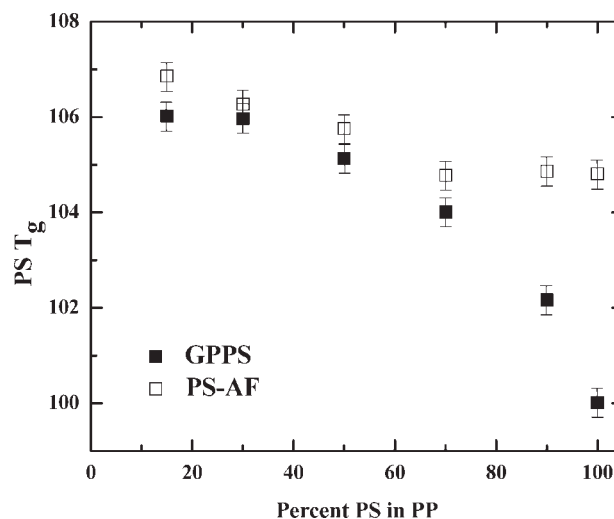


Figure 2 Polystyrene T_g as a function of blend composition (weight percent) in GPPS/PP-AF and PS-AF/PP-AF blends. Error bars are mean $\pm \sigma$.

The derivative heat flow data in Figure 3 reveal the T_g s of PP-AF when blended with PS-AF and GPPS. The PP T_g , indicated by the peaks, does not change with composition when blended with PS-AF. In contrast, the PP-AF T_g in GPPS/PP-AF blends changes with composition, with the values decreasing with decrease in PP composition. The bulk PP T_g values are represented by the dotted line.

Crystallization

Bulk PP crystallizes at $\sim 117^\circ\text{C}$ [Fig. 4(b)] and for all the blends containing up to 50% PP, crystallization is observed at this temperature. However, there are differences in the crystallization behavior of PP at

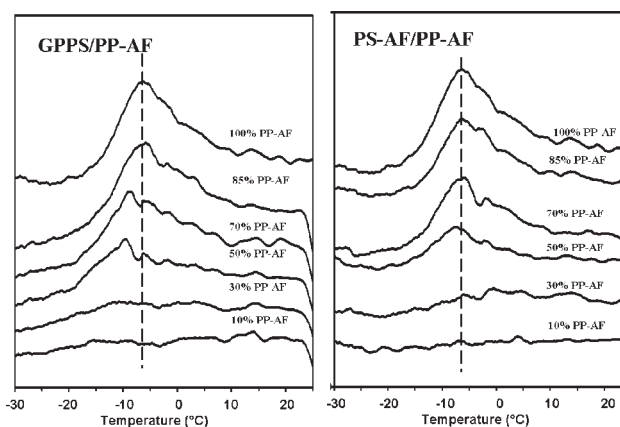


Figure 3 Derivative of the DSC reversing heat flow curves (vertical axis, relative units) for various weight percent blends of PS-AF/PP-AF and GPPS/PP-AF. Peaks denote the PP-AF T_g in blends; the dotted line is the 100% T_g . The vertical axes are derivative reversing heat flow ($\text{W/g}/^\circ\text{C}$).

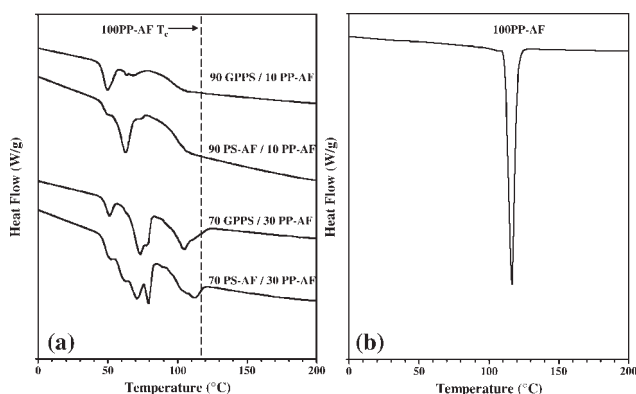


Figure 4 DSC cooling thermograms showing crystallization exotherms of (a) 30% and 10% PP-AF in blends with PS-AF and GPPS and (b) 100% PP-AF.

blend compositions below 50% PP. The dynamic/nonisothermal crystallization behavior of the two blend systems for the 30% PP and 10% PP compositions are compared in Figure 4. In blends with PS-AF and GPPS, fractional crystallization at lower temperatures is observed for 30% PP and 10% PP compositions. Crystallization behavior of the 30% PP composition is fairly similar in both blends, where part of the PP crystallizes near 110°C, and most of the crystallization exotherms are fractionated at lower temperatures [70°C and 50°C], although there are minor differences in the exotherm peak locations. Fractionated crystallization in semicrystalline polymers is well known to be a domain size and continuity dependant phenomenon based on the concentration of heterogeneities in the polymer. The crystallization mechanism changes gradually from heterogeneous-dominant to homogeneous-dominant, requiring a greater degree of undercooling as the dispersed domain size diminishes.¹² In blends containing 10%PP-AF blends, crystallization temperature [T_c] in the PS-AF blend is 60°C, with a shoulder at 50°C. PP T_c in GPPS blends occurs mainly at 50°C, with a shoulder at 60°C. The difference in exotherm peaks, which is a measure of PP particle size, indicates that the PP in GPPS/PP-AF blends is more finely dispersed than in the PP in the PS-AF/PP-AF blends. Since the fractional crystallization of PP-AF occurs at similar temperatures regardless of the type of PS environment, this is clear evidence that homogeneous nucleation dominates. This crystallization regime is characterized by small PP domains in which the area of the domain interface is sufficiently small to preclude the occurrence of significant heterogeneous nuclei.¹³

DISCUSSION

The T_g behavior of PS-AF in PS-AF/PP-AF blends is readily explained based on blend morphology. Since

the melt viscosities of both the components in this blend are almost equal, the phase inversion region is approximately the 50/50 composition. There is a clear distinction between the T_g behavior of compositions below and above the phase inversion. The PS-AF T_g remains essentially constant for compositions where the PS surrounds PP, before phase inversion occurs at 50% PS. On the other hand, for compositions where PP surrounds PS, the T_g increases with decreasing PS compositions. This phenomenon has been explained by our earlier work and can be attributed to differential shrinkage between the blend components.¹¹ Isotropic pressure on the dispersed liquid PS phase due to the crystallizing and faster shrinking PP phase causes the PS T_g to increase with decreasing concentration in the region where PP surrounds PS. A one degree elevation of the PS T_g corresponds to a compressive pressure of about 3.2 MPa.

In the GPPS/PP-AF blends a subtle, yet similar behavior is seen at the lower PS compositions, with the GPPS T_g increasing from 105.1°C at 50%PS to 106.0°C at 15% PS. However, the pressure theory fails to explain the T_g behavior at the higher PS compositions, where the PS T_g increases significantly with small additions of PP to the PS matrix. One possible explanation is the glass transition of matrix PS takes place in the presence of a rigid PP phase and might cause the PS T_g to increase by pinning at the interface, as has been observed by researchers in PC/PET blends and PS blends with glass beads.^{14,15} However a similar behavior is not observed in PS-AF/PP-AF blends. Alternatively, the only difference between the two blends, PS-AF/PP-AF and GPPS/PP-AF is the presence of low molecular weight species in the form of lubricants and antioxidants in GPPS, which cause the inherent bulk PS T_g to decrease.

The PP T_g in GPPS/PP-AF measured by DSC changes with composition as shown in Figure 3, whereas the PP T_g in PS-AF/P-AF blends remains constant with composition. From these above-mentioned reasons, it is proposed that the lower molecular weight additives migrate from the PS phase into the amorphous PP phase [aPP], during the high temperatures of melt processing with a concomitant increase in the PS T_g . Such migration also causes a diluent effect in PP portions of the GPPS/PP-AF blends and results in a decrease in the PP T_g value. The T_g value of GPPS appears to be following a solubility limit curve, where with a small addition of PP-AF, a large fraction of the additives migrate into the PP phase and cause a significant increase in the PS T_g and a significant decrease in the PP glass transition. As more PP is added, the cumulative quantity of additive migration increases, but the percent increase over the previous composition is less. At

the 50/50 composition, the migration reaches a solubility limit and further increase in the T_g is due to the pressure effect of shrinking PP phase.

GPPS was also blended with a commercial grade of PP [PP-1], which unlike PP-AF is not additive-free, to compare the GPPS T_g behavior in these blends. Compositional dependence of the GPPS T_g in these blends, as shown in Figure 5, is strikingly similar to GPPS/PP-AF blends. The T_g of amorphous portions of PP, aPP also decreased with decrease in PP composition indicating diluent interactions with the additives migrating from GPPS (Fig. 6). These results suggest that the additives in GPPS migrate into the amorphous portions of PP regardless of the PP grade and its additives.

CONCLUSIONS

The T_g behavior of two types of polystyrene, commercial grade and additive-free grade, were studied in melt processed blends with additive-free PP. The T_g of additive-free PS in blends increases with decreasing PS concentration where PP surrounded PS, and remains constant for compositions where PS is the matrix phase. Blends of commercial grade PS and additive-free PP showed similar behavior for low PS compositions, but at higher PS compositions [$>50\%$] the T_g showed a much stronger dependence on composition. The PP T_g in blends with commercial grade PS decreased with decreasing PP concentrations, but this effect was not observed in blends with additive-free polystyrene. Similar results were obtained when commercial grade polypropylene was substituted for the additive-free PP.

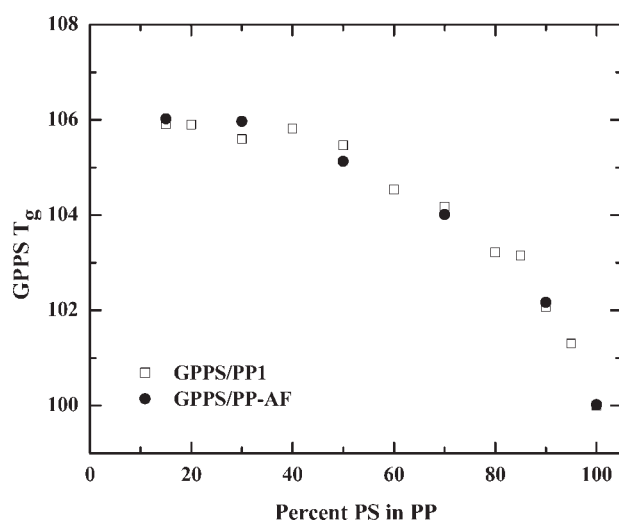


Figure 5 The polystyrene T_g as a function of blend composition (weight percent) in GPPS/PP-AF and GPPS/PP-1 blends. Error bars, not shown for clarity, are mean $\pm \sigma$, $\sigma = 0.27^\circ\text{C}$

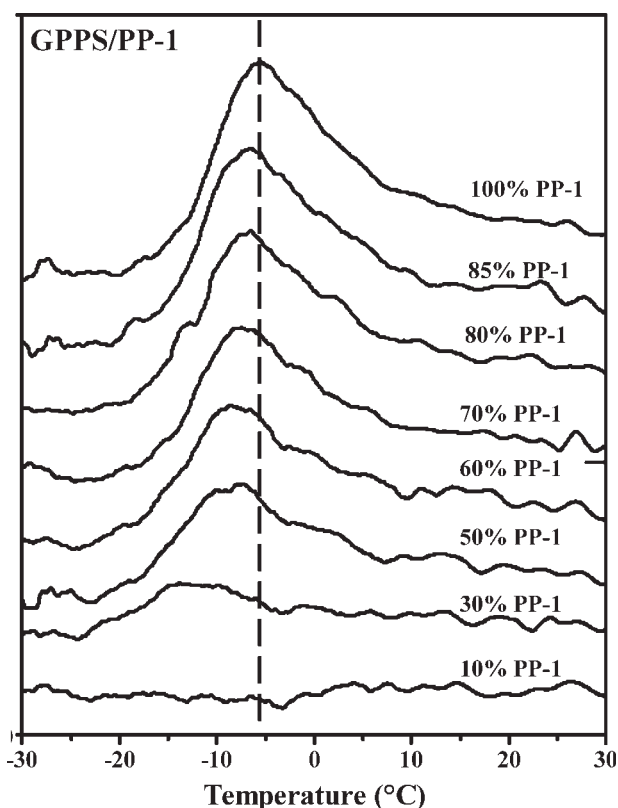


Figure 6 Derivative of the DSC reversing heat flow curves for the indicated weight percent blends of GPPS/PP-1. Peaks denote the PP-1 T_g in blends; the dotted line is the 100% T_g . Vertical axis is derivative reversing heat flow ($\text{W/g}/^\circ\text{C}$).

These observations lead us to conclude that the T_g shifts observed for polystyrene in PS/PP blends are generated by two different mechanisms depending on the composition of the blend. At low PS concentrations where PP surrounds PS, isotropic pressure from the solidifying PP raises the PS T_g . At high PS concentrations where PS is the matrix phase, additives in the PS migrate from the PS into the dispersed PP phase, thus increasing the T_g of the PS and lowering the T_g of the PP. When additive-free PS is used, no change is observed in this region.

The difference in T_g shift effects and the observed difference in the size of dispersed PP domains are indications that composite structures prepared from immiscible polymer blends are very sensitive to impurities and additives, an effect that has major implications for composites prepared from low-grade or recycled raw materials.

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