

# **Effect of additives on the compositional 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 and polypropylene has been studied. Blends of additive-free polystyrene and additive-free polypropylene exhibited the known effect of PS  $T_g$  elevation in blend compositions where PP surrounds PS. When additive-free PP and commercial grade PS are blended, different  $T_g$  behaviors are observed, apparently due to the plasticizing effects of the lubricating additives present in PS. Thermal transitions of PS and PP were measured using modulated DSC.

Although similar behavior was observed for the low PS compositions in both blends, the high PS compositions showed a considerable  $T_g$  shift compared with the invariant  $T_g$  in this composition region for additive-free polymers. These differences and the contrast in the PP  $T_g$  behavior of both the blends were attributed to the migration of additives from the PS phase across the immiscible interface into the PP phase. Similar  $T_g$  variations observed in PS/PP blends where both polymers are of commercial grade.

## 1. 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, anti-static agents, plasticizers to improve processability, oils to improve melt flow, and internal as well as external lubricating agents.<sup>1</sup>

The interaction between component phases in a polymer blend significantly influences their mechanical and thermal properties.  $T_g$  values of individual blend components are often used as indicators of miscibility.<sup>2</sup> 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 really just mechanical mixtures of the constituent polymers and such blends generally do not show shifts in  $T_g$ 's, 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.<sup>3,4</sup> Since immiscibility is an important function of the molecular weight, miscibility may occur to a very small extent due to migration of monomers or oligomers, either from the individual polymers or mainly from the additives in commercial polymers, during processing. Greco et al. observed that PS  $T_g$  in PS-PP 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).<sup>5</sup> 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 reduced with decrease in composition, characterized by an initial drop after addition of a small amount of ABS

to bulk PC, followed by decrease in slope and finally leveling off. This effect was attributed to low molecular weight species of ABS migrating to the PC domains.<sup>6</sup> 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 PS  $T_g$ .<sup>7</sup>

PS and PP are commercially important polymers due to their ready availability, ease of processing, and use in a large variety of commercial and industrial products. The semi-crystallinity of PP, as well as entropic (high molecular weight) and enthalpic (heat of mixing) restrictions, render these polymer pairs chemically immiscible and hence mechanically incompatible. The addition of compatibilizers, however, such as SEBS (styrene/ethylene-butylene/styrene)<sup>8-10</sup> can permit 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 PS  $T_g$  increases from its bulk values when blended with PP.<sup>11</sup> These increases in  $T_g$  are due to changes in blend morphology as composition is varied. The polymers used for the aforementioned studies were laboratory grade and free of additives and processing aids. The present effort was aimed at studying these  $T_g$  effects in blends prepared from commercial grade polymers containing additives and comparing the compositional  $T_g$  variation in these blends with those made from the additive-free, laboratory grade resins.

## 2. Experimental

### *Materials*

Important properties of the blend materials are shown in the Table 1. Two types of polypropylene, one from Aldrich chemicals which had no additives and processing aids, and the other from Chevron Phillips Chemicals (The Woodlands, TX), which 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 PolyOne/GE Polymerland) were used. Different combinations of polystyrene (PS)/polypropylene (PP) were prepared from the available grades to isolate effects of additives. PS-AF/PP-AF is the pure, additive-free PS-PP blend. In order 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 containing by weight were prepared. A summary of the compositions and blends prepared is given in Table 2.

### *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 a Differential Scanning Calorimeter operated in Modulated DSC mode. Sample disks weighing approximately 10 milligrams 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  $T_g$  of both polystyrene as well as polypropylene and a cycle of modulated heat-cool-modulated heat was used. The MDSC parameters were: temperature range  $-40\text{ }^{\circ}\text{C}$  to  $220\text{ }^{\circ}\text{C}$ ; modulation amplitude  $\pm 1.30\text{ }^{\circ}\text{C}$  and period 40 seconds; heating rate  $3\text{ }^{\circ}\text{C}/\text{min}$  and cooling rate  $5\text{ }^{\circ}\text{C}/\text{min}$ . These parameters were chosen after careful optimization. Negative temperatures in the DSC were achieved using a Refrigerated Cooling System and the instrument was calibrated using a standard indium sample.

## **3. Results**

### *Glass transition*

A representative set of  $T_g$  values measured by the DSC for PS-AF/PP-AF is shown in figure 1. Each curve is a derivative of the reversing heat curve, which is a part of the total heat in the modulated DSC signal. The peaks indicate  $T_g$  of PS, and help assign the exact  $T_g$  value, thus eliminating the ambiguity of assigning  $T_g$  using the onset-end-intercept method.

The compositional variation of 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.

PS-AF  $T_g$  in PS-AF/PP-AF blends shows two regions of compositional variation. Bulk  $T_g$  value of PS-AF [approximately 104.8 °C] is persist 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 PS  $T_g$  are observed as the PS concentration decreases to 15% at which point the PS  $T_g$  is 106.8 °C. The behavior of the PS-AF  $T_g$  values is compared with GPPS  $T_g$  in the same GPPS/PP-AF blend matrix. Similar to PS-AF/PP-AF blends, the GPPS  $T_g$  increases with decrease in PS composition, but the nature of the increase is different. The GPPS  $T_g$  increases smoothly with decreasing PS concentration over the entire range of blends, although the rate of  $T_g$  increase monotonically decreases across the composition range. Indeed, the curve has nearly leveled off below 30% PS and any rate of PS  $T_g$  increase is quite small in this region.

Figure 3 shows  $T_g$  of PP-AF when blended with PS-AF and GPPS. 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. Bulk PP  $T_g$  values are represented by the dotted line.

### *Crystallization*

Bulk PP crystallizes at approximately 110 °C [figure 4(a)] 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 compositions below 50% PP. The dynamic/non-isothermal crystallization behavior of the two blends 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 at 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 semi-crystalline 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.<sup>12</sup> 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.<sup>13</sup>

#### 4. 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 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.<sup>11</sup> Isotropic pressure on

the dispersed liquid PS phase due to the crystallizing and faster-shrinking PP phase causes PS  $T_g$  to increase with decrease in composition where PP surrounds PS.

In the GPPS/PP-AF blends a subtle, yet similar behavior is seen at the lower PS compositions, with 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 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.<sup>14,15</sup> 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.

PP  $T_g$  in GPPS/PP-AF measured by DSC is observed to change with composition as shown in figure 3, whereas 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 [*a*PP], during the high temperatures of melt processing and there is an increase in the PS  $T_g$ . This migration also causes a diluent effect in PP portions of the GPPS/PP-AF blends and results in a decrease in 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 percentage of the additives migrating into the PP phase and cause a significant increase in PS  $T_g$ . As more PP is added, the absolute 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  $T_g$  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 GPPS  $T_g$  behavior in both these blends. Compositional dependence of 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 (figure 6). These results indicate that the additives in GPPS do migrate into the amorphous portions of PP, regardless of the PP grade and additives.

## 5. Conclusions

The  $T_g$  of additive-free PS in blends increased with decrease in PS percentage in blend compositions where additive-free PP surrounded PS, and remained constant for compositions where PP is a dispersed phase in the PS matrix. Blends of commercial grade PS and additive-free PP showed similar behavior for low PS compositions, but at the higher PS compositions [ $>50\%$ ] the  $T_g$  increased significantly with composition. PP  $T_g$  in blends with commercial grade PS reduced with decrease in PP composition but remained constant with composition in additive-free blends. These observations lead us to conclude that the  $T_g$  shifts of commercial PS in blends with additive-free PP are solely due to the presence of low molecular weight additive species and their migration into the amorphous region of PP. The additive migration not only increases the  $T_g$  of PS, but also decreases the PP  $T_g$  due to a diluent effect. Similar PS and PP  $T_g$  effects observed in blends of commercial grade PS and PP confirmed our conclusions.

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**Table 1** Important properties of blend components

<b>Material</b>	<b>Code</b>	<b>Supplier</b>	<b>Features</b>	<b>Melt index (g/10 min)</b>	<b>Density</b>
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

**Table 2** Blend compositions by weight percentage.

<b>PS-AF/PP-AF</b> <b>(wt/wt)</b>	<b>GPPS/PP-AF</b> <b>(wt/wt)</b>	<b>GPPS/PP-1</b> <b>(wt/wt)</b>
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 captions

**Figure 1:** Derivative of the DSC reversing heat flow curves showing PS-AF  $T_g$  in PS-AF/PP-AF blends (peaks denote PS-AF  $T_g$ ; dotted line denotes 100% PS-AF  $T_g$ )

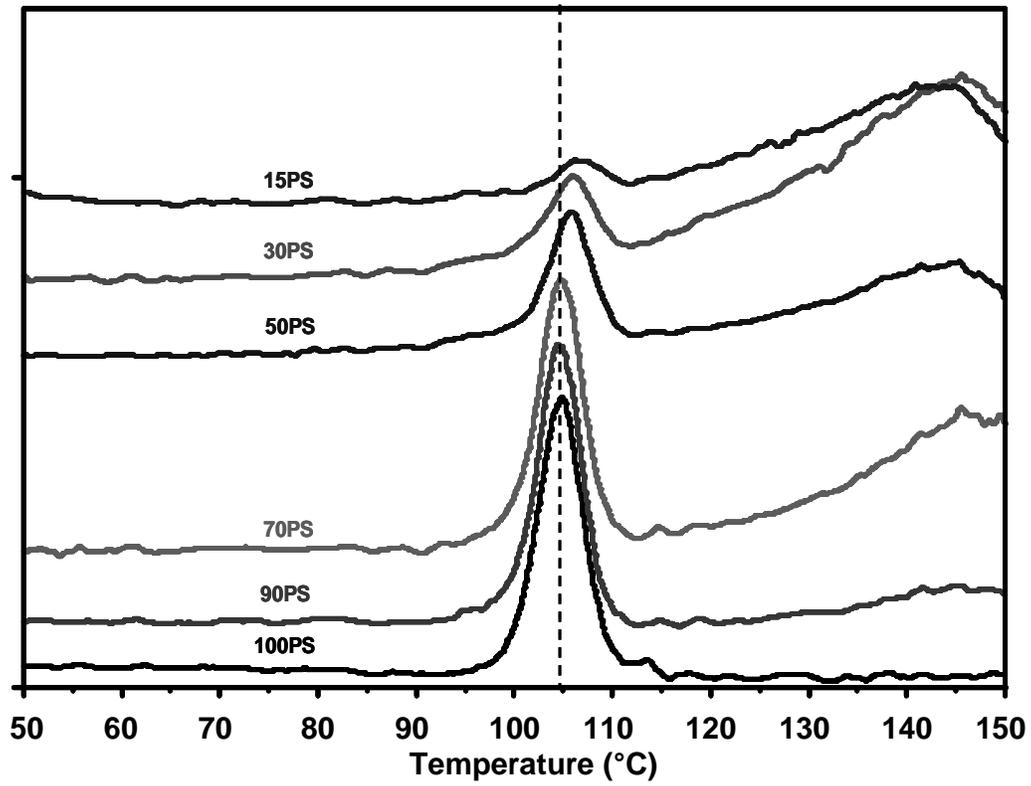
**Figure 2** Polystyrene  $T_g$  as a function of blend composition in GPPS/PP-AF and PS-AF/PP-AF blends.

**Figure 3** Derivative of the DSC reversing heat flow curves showing PP-AF  $T_g$  in PS-AF/PP-AF and GPPS/PP-AF blends (peaks denote PP-AF  $T_g$ ; dotted line denotes 100% PP-AF  $T_g$ )

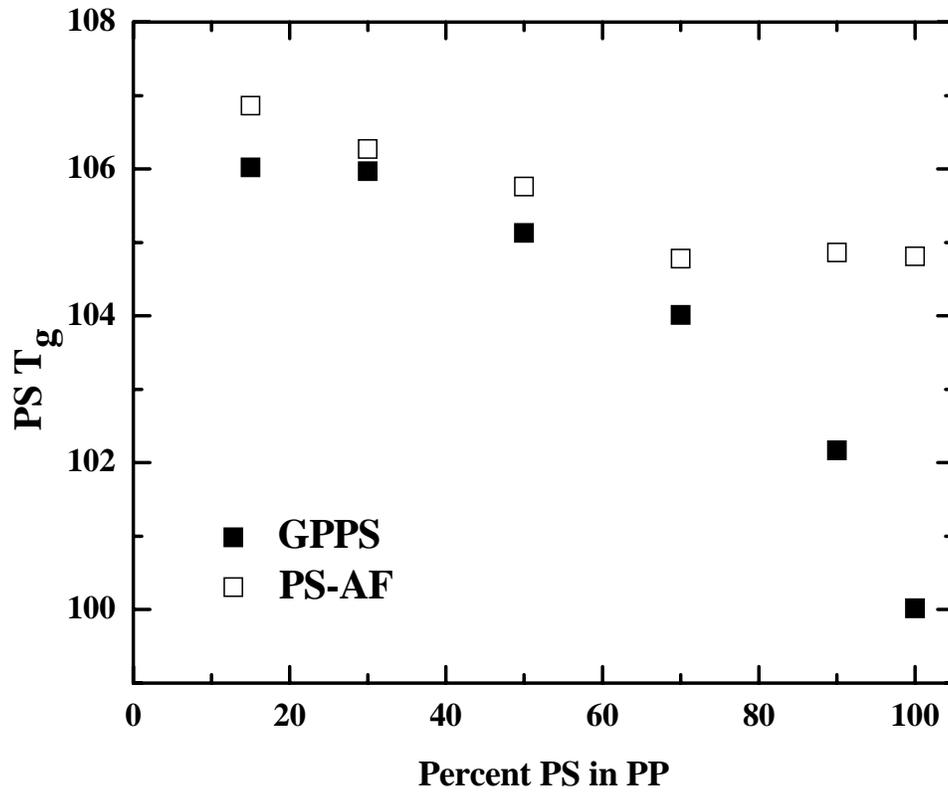
**Figure 4** DSC cooling thermograms showing crystallization exotherms of  
(a) 30% and 10% PP-AF compositions in blends with PS-AF and GPPS and  
(b) 100% PP-AF

**Figure 5** Polystyrene  $T_g$  as a function of blend composition in GPPS/PP-AF and GPPS/PP-1 blends.

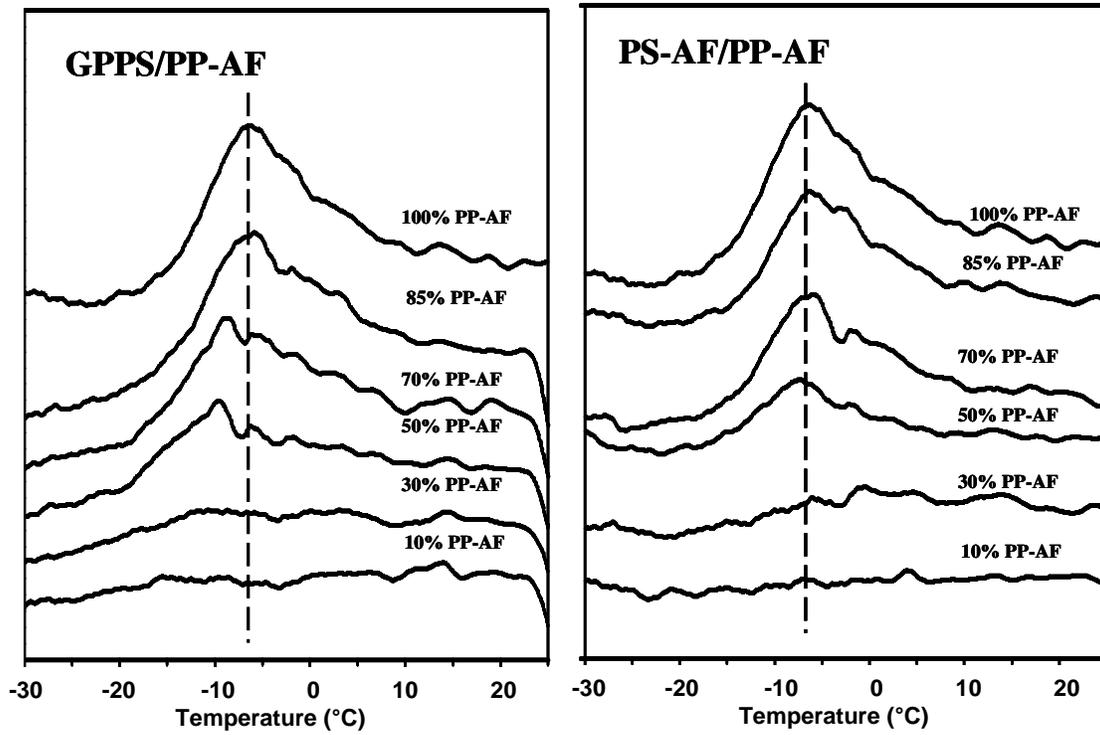
**Figure 6** Derivative of the DSC reversing heat flow curves showing PP-1  $T_g$  in GPPS/PP-1 blends (peaks denote PP-1  $T_g$ ; dotted line denotes 100% PP-1  $T_g$ )



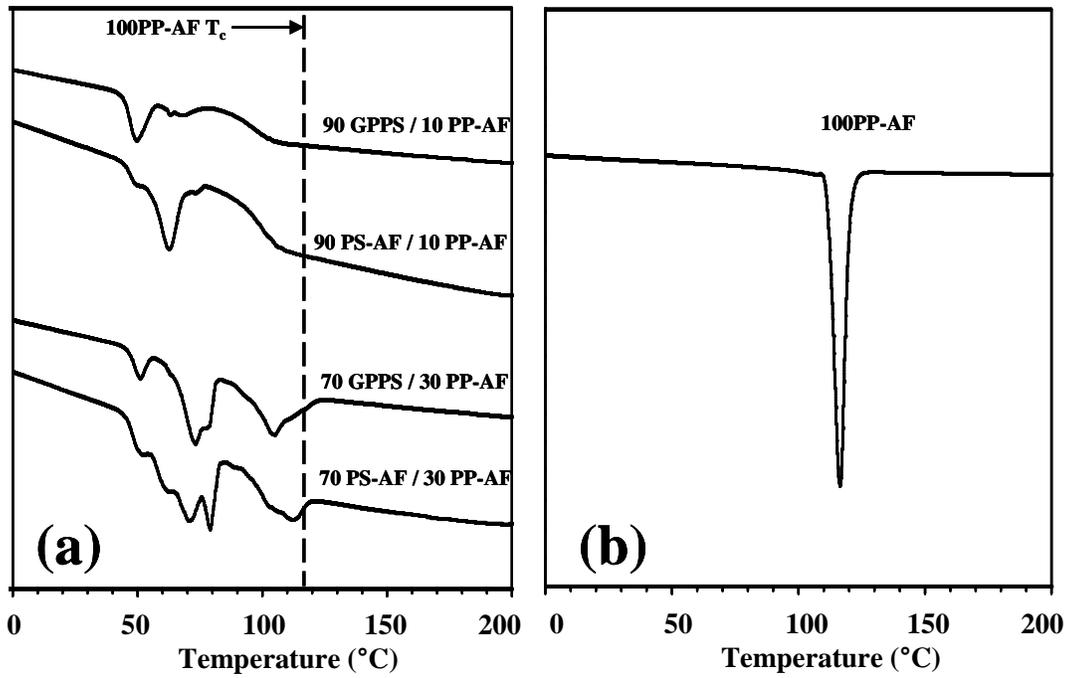
**Figure 1** Derivative of the DSC reversing heat flow curves showing PS-AF  $T_g$  in PS-AF/PP-AF blends (peaks denote PS-AF  $T_g$ ; dotted line denotes 100% PS-AF  $T_g$ )



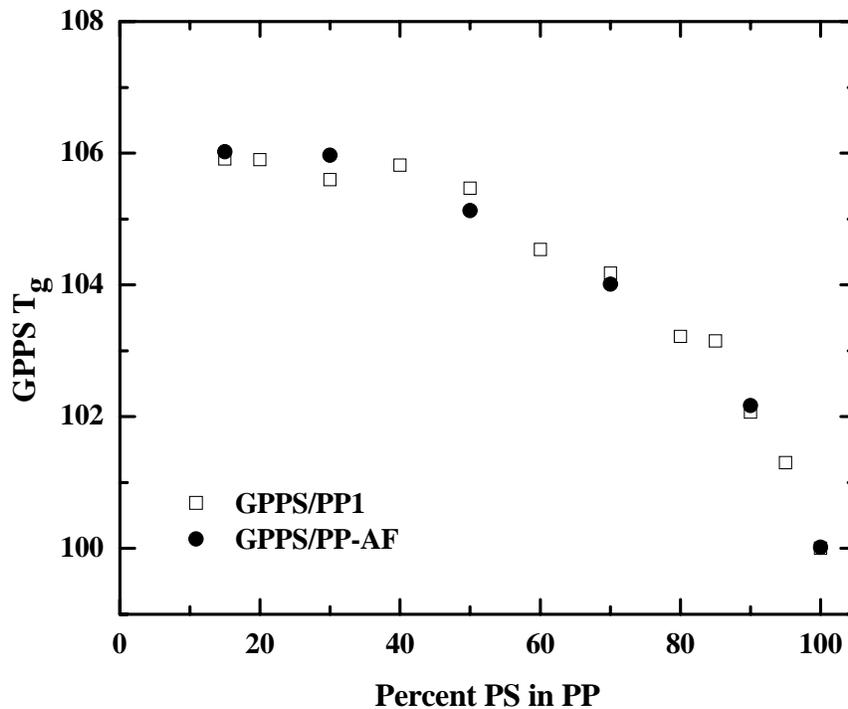
**Figure 2** Polystyrene T<sub>g</sub> as a function of blend composition in GPPS/PP-AF and PS-AF/PP-AF blends.



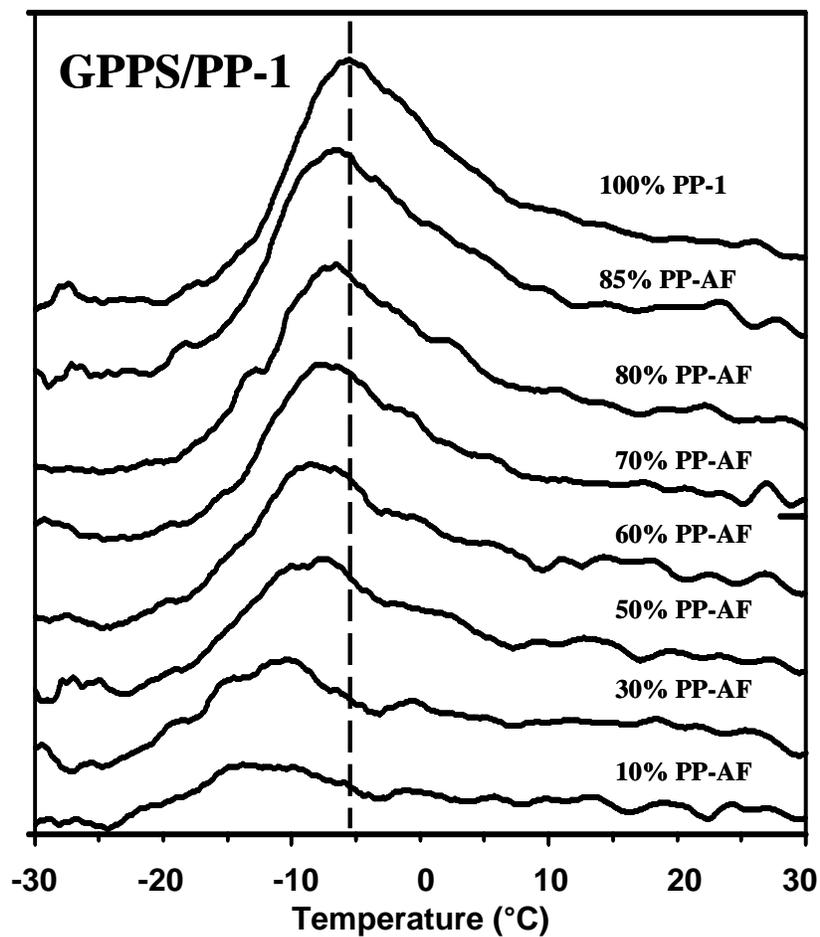
**Figure 3** Derivative of the DSC reversing heat flow curves showing PP-AF  $T_g$  in PS-AF/PP-AF and GPPS/PP-AF blends (peaks denote PP-AF  $T_g$ ; dotted line denotes 100% PP-AF  $T_g$ )



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



**Figure 5** Polystyrene T<sub>g</sub> as a function of blend composition in GPPS/PP-AF and GPPS/PP-1 blends.



**Figure 6** Derivative of the DSC reversing heat flow curves showing PP-1  $T_g$  in GPPS/PP-1 blends (peaks denote PP-1  $T_g$ ; dotted line denotes 100% PP-1  $T_g$ )