

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 polypropylene revealed the previously known effect of PS T_g increase in blend compositions where PP surrounds PS. Glass transition behavior in these blends were compared to blends prepared from additive-free PP and commercial grade PS, which contained additives in the form of lubricants. The thermal transitions of PS and PP are measured using the modulated DSC technique. Although similar behavior was observed for the low PS compositions in both blends, the characteristics of the high PS composition blends differed substantially. These differences and the contrast in the PP T_g behavior of both the blends was attributed to the migration of additives from the PS phase across the immiscible interface into the PP phase. Similar T_g variations observed in commercial grade PS and PP blends confirmed our observations.

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.¹

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.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 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.^{3,4} 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).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 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.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 PS T_g .⁷

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)⁸⁻¹⁰ 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.¹¹ 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 are 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 fractioned at lower temperatures [70 °C and 50 °C], although there are minor differences in the exotherm peak locations. Fractioned 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.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

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.¹¹ 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.^{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.

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

T_g behavior of PS; commercial and additive-free grades formulated in melt processed blends with additive-free PP was studied. The T_g of additive-free PS in the blends increased with decrease in PS percentage in blend compositions where PP surrounded PS, and remained constant for compositions where PS is the matrix phase. Blends of commercial grade PS and PP showed similar behavior for low PS compositions, but at the higher PS compositions [$>50\%$] unlike additive-free blends, 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 leads us to conclude that the T_g changes 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.

6. References

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Table 1 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

Table 2 Blend compositions by weight percentage.

PS-AF/PP-AF	GPPS/PP-AF	GPPS/PP-1
(wt/wt)	(wt/wt)	(wt/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 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)

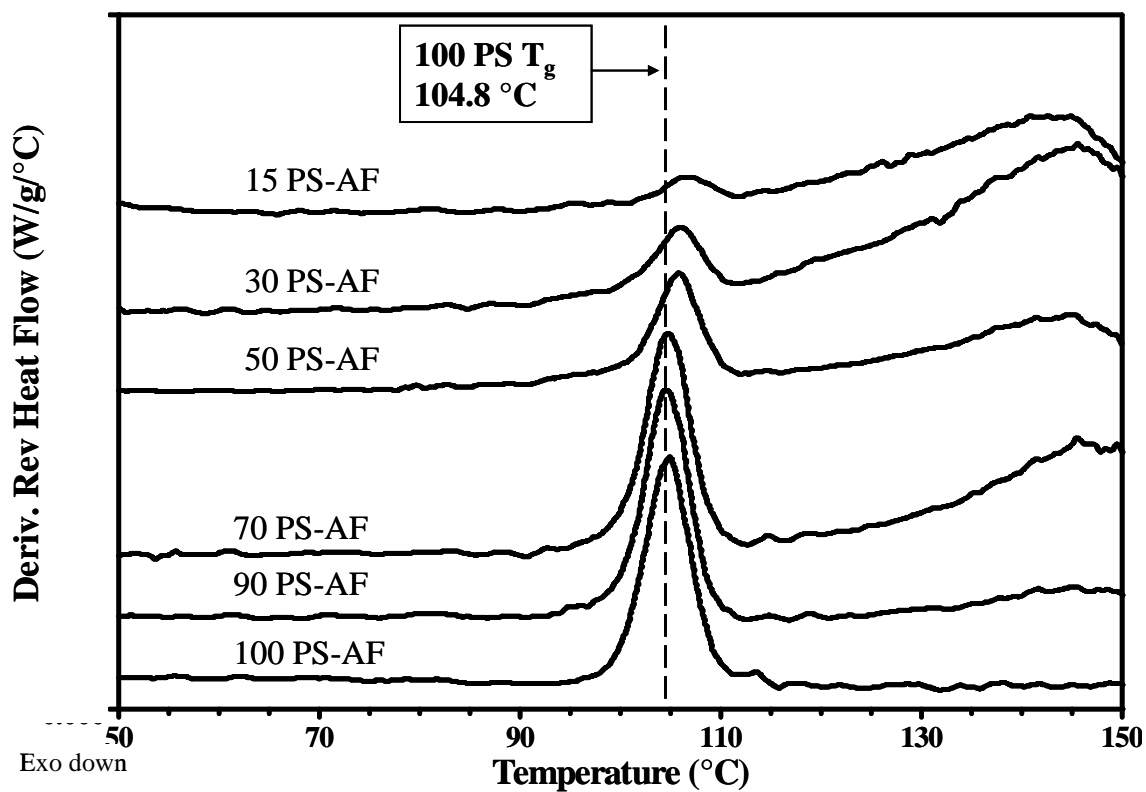


Figure 1 Derivative of the DSC reversing heat flow curves showing PS-AF T_g in PS-AF/PP-AF blends (peaks denote PS-AF T_g; dotted line denotes 100% PS-AF T_g)

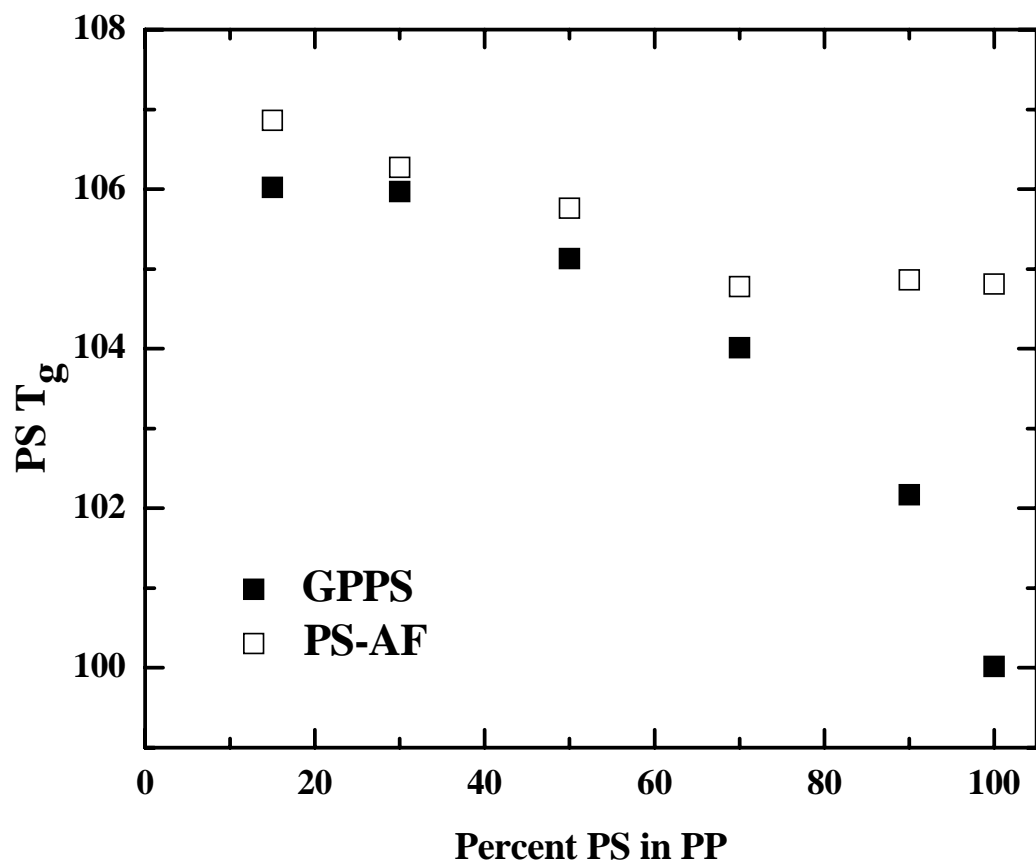


Figure 2 Polystyrene T_g as a function of blend composition in GPPS/PP-AF and PS-AF/PP-AF blends.

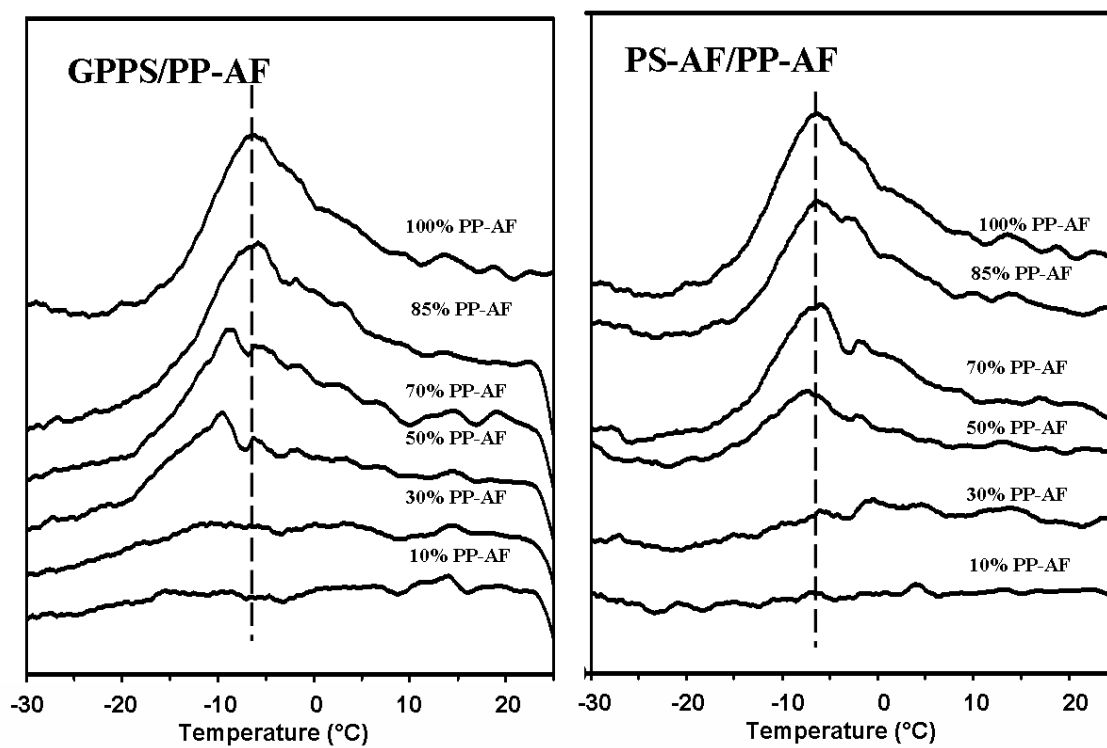


Figure 3 Derivative of the DSC reversing heat flow curves showing PP-AF T_g in PS-AF/PP-AF and GPPS/PP-AF blends (peaks denote PP-AF T_g ; dotted line denotes 100% PP-AF T_g)

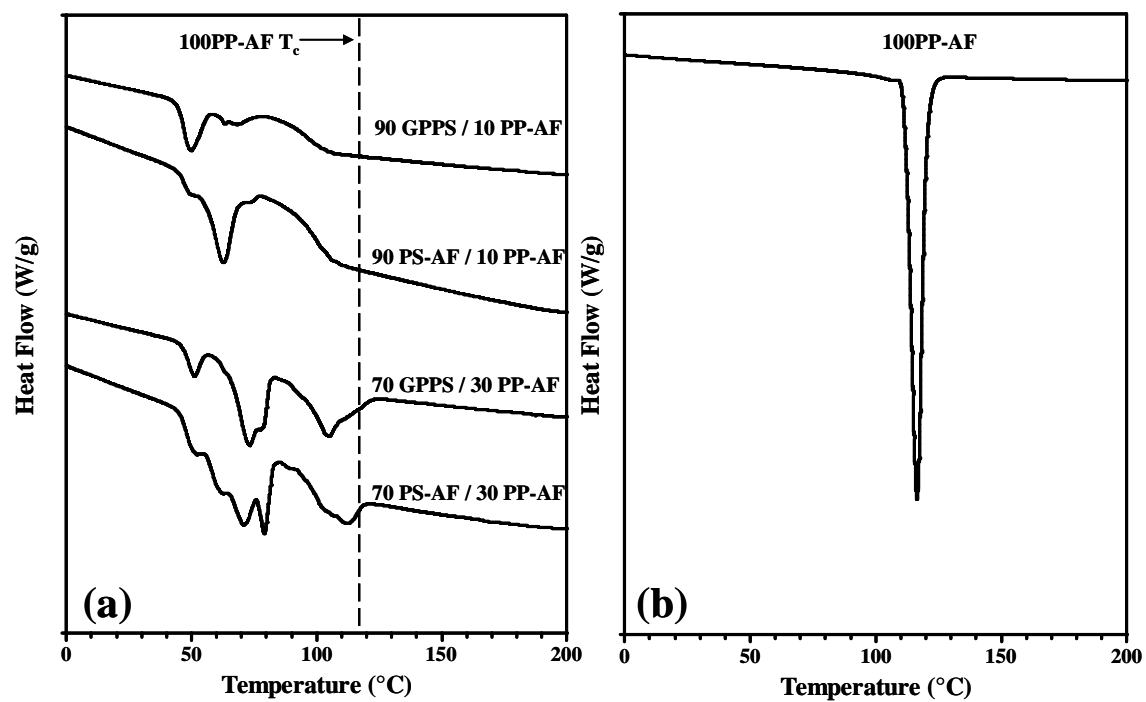


Figure 4 DSC cooling thermograms showing crystallization exotherms of
(a) 30% and 10% PP-AF compositions in blends with PS-AF and GPPS and
(b) 100% PP-AF

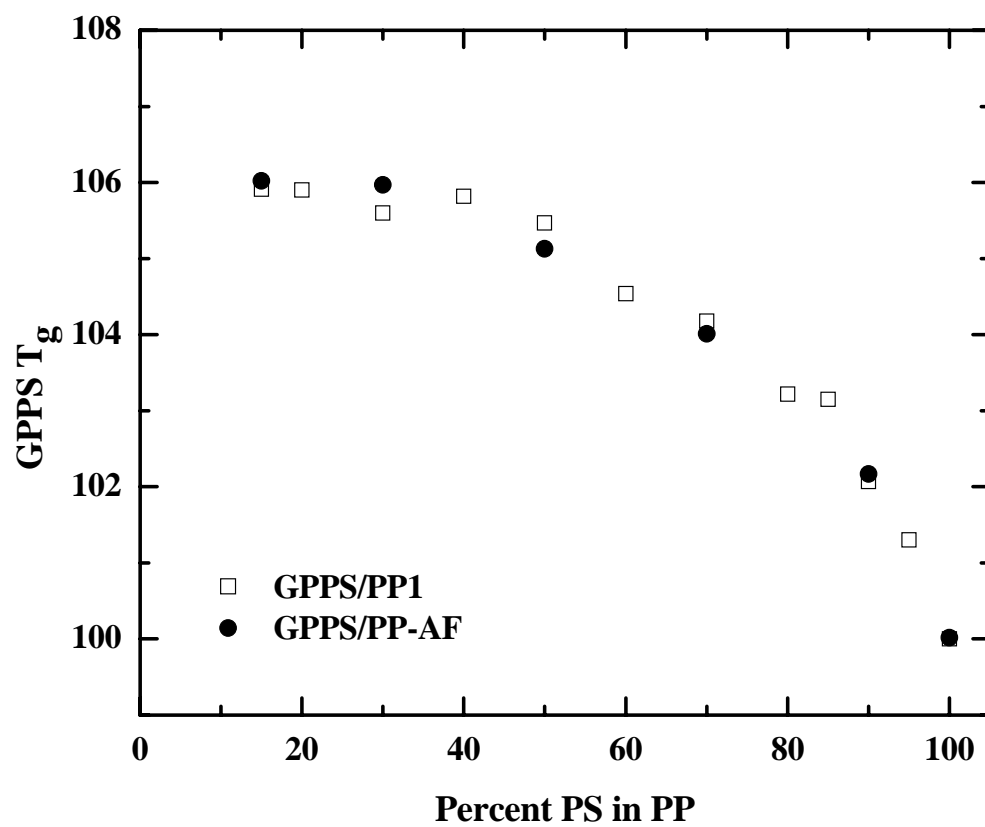


Figure 5 Polystyrene T_g as a function of blend composition in GPPS/PP-AF and GPPS/PP-1 blends.

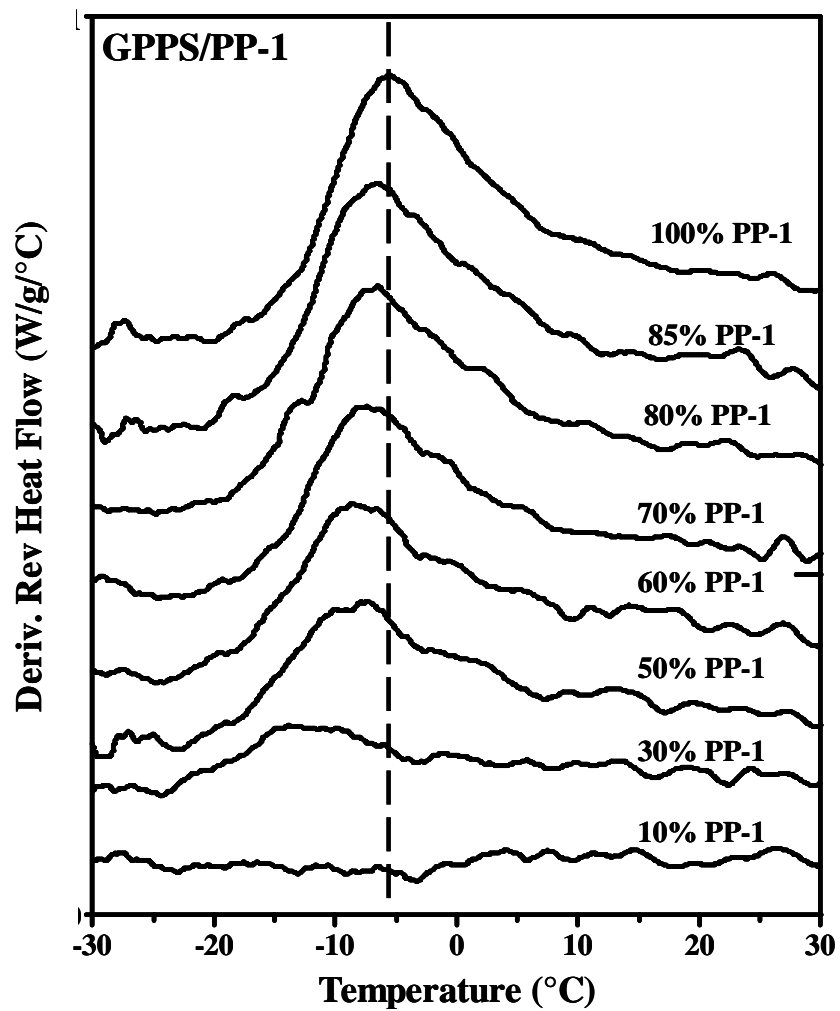


Figure 6 Derivative of the DSC reversing heat flow curves showing PP-1 T_g in GPPS/PP-1 blends (peaks denote PP-1 T_g ; dotted line denotes 100% PP-1 T_g)