Morphological effects on Glass Transitions in Immiscible Polymer Blends

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ABSTRACT

This paper describes the effects of structures on the glass transition of glassy polymers blended with a semi-crystalline polymer. Immiscible blends of PS/PP and PS/HDPE were prepared from commercially available polymers using melt processing and extrusion without additives. The weight fractions of the components were varied from 0 to 1. SEM analysis of the blends showed a range of morphologies over the composition range from small inclusions at low volume concentrations through intertwined co-continuous structures at specific intermediate compositions, and a reversal of this configuration at high volume fractions. The glass transition of the glassy polymer was measured with differential scanning calorimetry using the sensitive and high resolution modulated DSC method. A systematic change in glass transition of glassy polymers is observed as a function of composition in various immiscible polymer blends. Results show that the glass transition of polystyrene increases with a reduction in volume fraction, by approximately 5.4°C in polypropylene and 6.5°C in polyethylene. Probable models which might explain this effect are mentioned.

INTRODUCTION

Immiscible Polymer Blends (IMPB's) are of significant interest due to their potential to provide properties near the constituent rule of mixtures without requiring alloying or compatibilization of the blend. The combination of a glassy polymer and a semi-crystalline one combines the complementary properties of strength and toughness of the respective polymers. These types of blends have been investigated by various researchers due to their attractive end-use applications. [1-3] The morphologies of these blends, ranging from dispersed to co-continuous structures are capable of influencing certain physical properties of the components such as crystallization temperature and crystal growth rates and the crystallinity.[4] Whereas glass transition variations with compositions are widely observed in miscible polymer blend systems due to their chemical interactions, this effect is not expected with immiscible polymer systems.[5] T_g of polystyrene films were observed to change with their thickness and size.[6, 7] This effect was seen in polymer having dimensions on the order of nanometers. T_g shifts in the soft phase, such as polybutadiene have also been observed in the presence of a hard matrix, such as polystyrene in ABS systems, due to differences in thermal expansion coefficients of the constituent phases.[8, 9] Mucha concurred that there are physical interactions between phases which cause the T_g of aPS and iPP to change in an aPS/iPP blend.[10] Greco et al. did not see a linear variation in the T_g with composition in PS/PP systems, but saw the T_g increase to a single higher value from the homopolymer value at a certain composition.[11] The authors attributed this to the migration of low molecular weight species into the PP phase. Other work reported that the T_g of PET in a PET/PC blend was higher than that of the pure polymer and this was attributed to the 'wall effect' due to the presence of a rigid polycarbonate phase.[12] We have

investigated the effects of phase relationships and morphologies on the glass transition of the glassy polymer in blends of polystyrene/polypropylene and polystyrene/polyethylene

EXPERIMENTAL

Materials and Processing

The polymers were obtained from commercial sources. The polystyrene used was GPPS7 (Polyone; melt flow = 7.0 g/10 min), and the polypropylene (melt flow = 0.7g/10min) and polyethylene (melt flow = 0.3 g/10min) were obtained from CP Chem.

Blend compositions of polystyrene/polypropylene and polystyrene/polyethylene were prepared via melt processing. Compositions ranging from 10% to 90%, by weight of the components were prepared in a ¾" single screw Brabender lab extruder with a 25:1 mixing screw. The extruder screw had some mixing elements to obtain more uniform and homogeneous mixing. All the blends were extruded into rods at screw speeds of 100 rpm. The temperatures in all the four zones of the extruder were maintained at 220°C.

Characterization

The blends were fractured in liquid nitrogen and their morphology was characterized with a Field Emission Scanning Electron Microscope. Samples were coated with sputtered gold-palladium to overcome charging effects. Thermal analysis was carried out in the sensitive and accurate Modulated DSC technique [MDSC]. The MDSC technique was particularly useful because of its ability to separate out the glass transition from other events such as the enthalpic relaxation.[13] This enabled us to get accurate measurements of the glass transition. Samples were heated at an underlying heating rate of 3°C/min, modulated at +/-1.3°C/min every 40 seconds from 30°C to 230°C. Samples were taken through a modulated heat-cool-modulated reheat cycle. The first heat cycle was to erase any thermal history of the sample. The T_g was measured for both the first and the second heat cycles.

RESULTS

Morphology

Figure 1 shows the representative morphologies of the PS-PE blends at various compositions. The polystyrene in 15% PS and 30% PS blends has each been selectively etched with toluene for 15 minutes to get a better contrast between phases. Figure 1a shows the 15% PS-85% PP blend with the polystyrene phase dispersed homogeneously throughout the polypropylene phase. The sizes of dispersed polystyrene particles increase as its composition increases to 30%, as shown in Figure1b. The 50% PS composition in Figure 1c shows both phases interlocked with each other indicating a co-continuous structure, though this cannot be completely verified by a two-dimensional SEM image. There are portions in this structure where one phase surrounds the other and vice versa. The composition at which this kind of structure is obtained is approximately indicated by the Jordhamo equation which takes into account the viscosity ratio of the two phases.[14] As the composition of the PS is increased, the co-continuous structure breaks down to a structure of polyethylene dispersed in polystyrene.
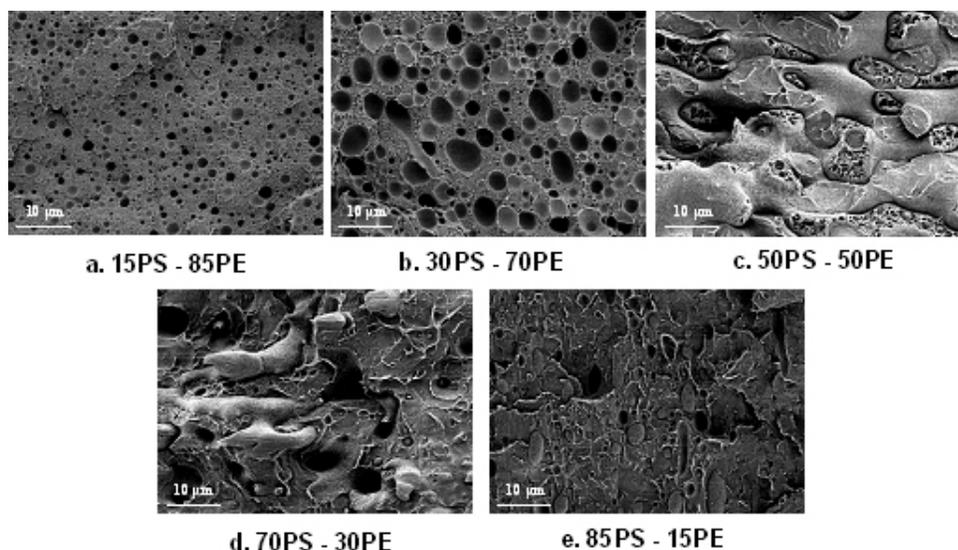
Figure 1 Morphology of the PS-PE blends.

Thermal Analysis

The graph in Figure 2 shows the behavior of polystyrene T_g as a function of composition in blends with polypropylene. Figure 3 plots the same characteristics for blends of polystyrene with polyethylene. All the glass transition values have been taken from the reheat cycle of the MDSC procedure. The reversing heat curve obtained by modulating the heating rate in the DSC is used for the T_g observation. The derivatives of these curves were used to get the exact T_g values, as this eliminates the ambiguity created by measuring the T_g using the onset-end intercept method.

From the figures it can be clearly seen that the T_g value of the polystyrene increases with the decrease in its composition. This behavior is not linear, and shows a sudden increase from the homopolymer value, at the higher PS (i.e. after the addition of very little polypropylene or polyethylene) compositions, with increments in the T_g values decreasing after each of the preceding value. The curve seems to reach a plateau at the low polystyrene compositions, maintaining the high value of the T_g. It is interesting to note that both the polystyrene/polypropylene as well as the polystyrene/polyethylene blends show similar kinds of behavior.
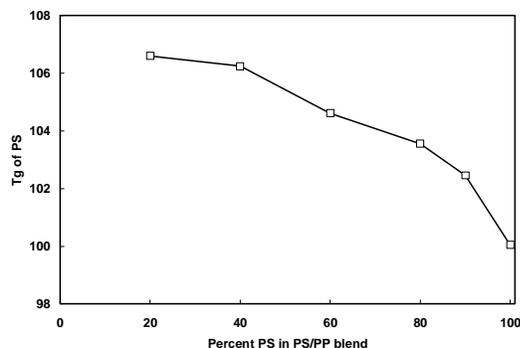
Figure 2 T_g of polystyrene as a function of composition in polystyrene/polypropylene blend
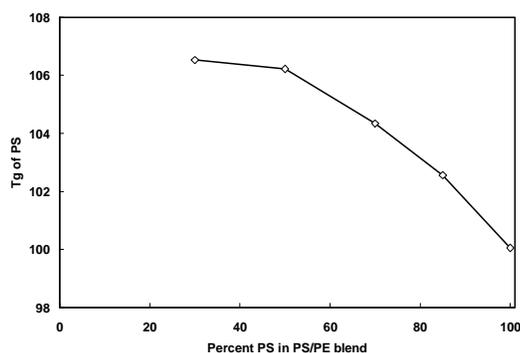

Figure 3 T_g of polystyrene as a function of composition in polystyrene/polyethylene blend

PS/PE and PS/PP systems have been extensively studied and are widely recognized as immiscible.[1, 15, 16] Nonetheless, when Tg shifts are observed, a common approach is to look for or infer limited miscibility. However, in this work we note that if the two components of the blends were alloying, then the T_g of the PS is expected to move towards the much lower T_g of polyethylene or polypropylene. The opposite effect is observed, i.e. the polystyrene T_g moves to higher temperatures. This observation indicates less likelihood of miscibility between the polystyrene and the glassy phase of the semi-crystalline component.

Table 1 Melting point values of polyethylene in PS/PE blends

Percent PS in PE	First heat Melting point	Second heat Melting point
15	129.7	129.8
30	130.3	130.1
50	129.7	129.8
70	128.4	128.6
85	127.1	128.3

In addition to T_g shifts in these blends, unusual supercooling effects were observed in the semi-crystalline phase at certain compositions. In particular, the melting point of the semi-crystalline polymer shifts to lower temperature, as shown by the values in table 1.The melting point of the polypropylene and polyethylene decreases as the composition of the semi-crystalline

polymer decreases. Two causative mechanisms are possible. An interaction may occur between the glassy polymer and the crystalline part of the semicrystalline polymer, thus inhibiting crystallization.[10] On the other hand, the melting point is also affected by the volume of available material. At low levels of PP or PE in a PS matrix, the volume of the dispersed phase is quite small, a factor which increases the activation energy for nucleation and growth and results in additional supercooling.

The peaks of the reversible heating curve derivatives which signify the T_g are shown in Figure 4. The intensities of the peaks decrease because of the reduction in the PS content. The T_g value of the lowest PS content shows the highest value, as mentioned earlier in Figure 3. The width of the peaks, indicated by the full width half maximum (FWHM) does not show any broadening or sharpening with the change in composition. This indicates that there is no distribution of T_g values within the peaks.
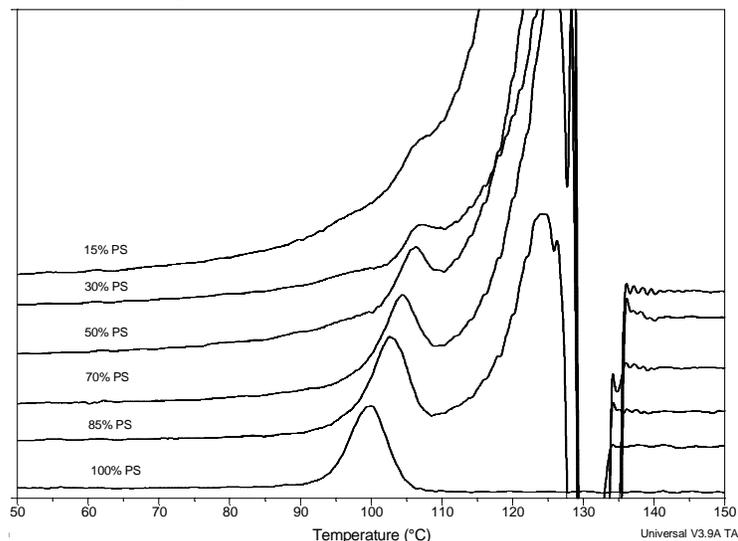

Figure 4 Derivative of the reversible DSC heat curves for PS/PE blends

The elevated T_g values of PS at low PS concentrations are likely due to the differential shrinkage of the semi-crystalline and the glassy component. As the PP or PE crystallize while the dispersed PS phase is still liquid, the PS is put in compression. This compressive stress increases the T_g.[17] This model continues to apply for all compositions where the glassy phase or parts of it are surrounded by the semi-crystalline phase, i.e. up to and into the co-continuous region. However, this model fails at higher PS concentrations where considerable amounts of PS are not surrounded by the semicrystalline polymer. Indeed, the elevated PS T_g begins to decline towards the bulk value as the semicrystalline polymer falls below 50%. If viewed from the other end of the composition range, i.e. the perspective of the neat PS endpoint with the addition of small amounts of semicrystalline polymer, a sharp increase is seen in PS T_g even for small additions of the semicrystalline phase. Although the model for this behavior is less clear, it seems that the presence of even a small volume percentage of finely dispersed PP or PE particles is sufficient to pin the motion of PS chains as they reorganize to form a glass, thus raising the T_g. Overall it appears that different mechanisms govern different areas of the T_g curve; the pressure effect dominating at lower PS compositions and the PS chain pinning effect dominating at the higher PS compositions. More details on the suggested models are provided in ref 18. [18] Further experiments are underway to establish either or both these models.

CONCLUSIONS

Blends of polystyrene/polypropylene and polystyrene/polypropylene, though known to be immiscible, show variations in glass transition values. These variations appear to result from the combined effects of the morphology and the interactions between phases present. The T_g of polystyrene in PS/PP blends increases from a bulk value of 100°C to 105.4°C and to 106.5°C in PS/PE blends. A combination of two models is proposed to be the cause for this T_g increase.

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