Thermal and Rheological Properties of Blends of Polystyrene and Thermotropic Liquid Crystals

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The rheological and thermal properties of composites of polystyrene (PS) and two liquid crystalline low-molecular-weight additives have been studied. Both additives act as plasticizers as evidenced by decreases in the glass transition and the melt viscosity. In addition both are miscible with PS over a broad range of concentrations. Partial phase diagrams of the two systems are presented and discussed.

INTRODUCTION

The effects of reinforcing fibers and fillers on the mechanical properties of polymers are well documented (1,2). In general, fibers and solid fillers tend to increase the modulus of a composite while the effect on strength can be positive or negative depending upon the aspect ratio of the reinforcement. Associated with their effect on stiffness, reinforcing fillers tend to lower the coefficient of thermal expansion of the polymer. In this regard, stiff fibers can be added to a polymer in order to minimize the shrinkage normally encountered upon cooling the material from the melt in common polymer processing operations. For example, the addition of small amounts of chopped glass filaments to a thermoplastic such as polystyrene can result in a significant reduction in film shrinkage during extrusion (3).

Although the addition of fibers to a polymer can improve the mechanical properties, it can also have an adverse effect on the processability of the resultant composite material. For reasons similar to those accounting for the increase in the modulus and the decrease in the coefficient of thermal expansion, the presence of fibers in a polymer melt increases the viscosity (1). The increase in melt viscosity increases the power consumption of the plastics-processing machinery, and in some instances the viscosity may be too high to be practical. Thus, there is an incentive to find alternative methods for effecting modest improvements in the mechanical properties of a polymer without sacrificing a low melt viscosity.

This investigation considers the consequences of adding to a polymer an organic molecule exhibiting a liquid crystalline phase (4). A liquid crystalline material is one that exhibits not only an isotropic liquid phase, but also one or more anisotropic liquid phases, e.g., smectic, nematic, or cholesteric phases (4). Because of their anisotropy, the molecules may be oriented in the shear field characteristic of most processing operations, and as a result lead to preferred orientations of the molecules after cooling the melt. These oriented molecules may impart to the composite many of the same advantages found with fibrous reinforcements, but with the advantage that the additive is a liquid or plasticizer during the processing operation.

In this communication, we will describe the effects of a liquid crystalline additive and an isotropic liquid additive on the rheological behavior of polystyrene. In addition, the effects of these additives on the thermal behavior of the resultant composites is discussed.

EXPERIMENTAL

The polystyrene (PS) used here had a number average molecular weight of 18,000. In all cases the PS was dried at 40°C for 24 hours in a vacuum oven. Two different organic additives were used: terephthal-bis-4-n-butylaniline (TBBA), and N-(p-ethoxy benzylidine)-p-n-butylaniline (EBBA). The TBBA was synthesized by Dr. Edward T. Samulski (University of Connecticut) and the EBBA was purchased from American Liquid Crystal Company. The chemical formulas of these materials are given below; both were used as received.

TBBA
\[ \text{C}_9\text{H}_8 \phi \phi \text{N} = \text{CH} \phi \phi \phi \text{CH} = \text{N} - \phi - \text{C}_8\text{H}_9 \]

EBBA
\[ \text{C}_9\text{H}_9\text{O} \phi \phi \text{CH} = \text{N} - \phi - \text{C}_6\text{H}_9 \]

Blends of either TBBA or EBBA and polystyrene
ranging from 0.2 to 80 percent additive by weight were prepared by mixing on a 2-inch two-roll mill at 150°C for about 8 minutes. The blends were subsequently broken into small pieces and compression molded into 2 millimeter thick, 2.5 centimeter diameter disks at 140°C for 5 minutes.

Melt rheology measurements were made with a Rheometrics Mechanical Spectrometer (RMS) utilizing the eccentric rotating disk technique (ERD) (5). Measurements of $G'$ and $G''$ were made at 137°C, 150°C, and 180°C.

Glass-transition temperatures of the blends were determined using a Perkin-Elmer differential scanning calorimeter (DSC), Model 2, equipped with a mechanical cooling accessory and a Perkin Elmer thermal analysis data station. Samples of about 10 milligrams were crimped inside aluminum pans and the thermal behavior was measured from 280 to 550K with a heating rate of 20K per minute. The temperature of the DSC was calibrated using the melting points of indium and water.

Thermal Optical Analyses (TOA) were made with an optical microscope equipped with a controlled light source, a cross-polarizer, a hot stage, and a photometer detector. Thin films were prepared by compression molding at 150°C. A 16 millimeter square film was mounted between a glass slide and cover plate, and the entire assembly was heated above the glass-transition temperature ($T_g$) of the polystyrene. A uniformly thin sample was then obtained by carefully pressing on the cover glass. The assembly was slowly cooled in order to relieve any stresses induced during the later operation. The sample was heated at a rate of 4°C per minute on the hot stage of microscope, and the intensity of the transmitted light was monitored as a function of temperature.

RESULTS AND DISCUSSION

The phase transitions of TBBA and EBBA are shown in the DSC thermograms given in Figures 1 and 2, respectively. The TBBA exhibits a crystalline melting transition at 385K, three different smectic phases (The SMc→SmA transition is not apparent at the attenuation shown in Figure 1), and one nematic liquid crystalline phase before it becomes an isotropic liquid at 509K. The EBBA melts to a nematic state at 309K, well below the $T_g$ of PS (365K), and becomes an isotropic liquid at 353K. Therefore, the TBBA is expected to be a liquid crystal at polymer processing temperatures, above the $T_g$ of PS, while the EBBA will be an isotropic liquid. Both materials are normally crystalline solids at room temperature.

The effect of the addition of small amounts of TBBA and EBBA on the glass-transition temperature $T_g$ of polystyrene is shown in Fig. 3. Both additives depress $T_g$, though EBBA appears to be a much more effective plasticizer. This is not surprising given the lower melting point of the latter. The fact that these materials have a significant effect on $T_g$, however, suggests that they are compatible with PS. Further evidence of this is found in the clarity of the composites, which suggests that both additives dissolve in the polystyrene matrix below concentrations of 10 percent.
The frequency behavior of $G'$ and $G''$ for various compositions of TBBA/PS and EBBA/PS in the melt are given in Figs. 4-7. All the compositions exhibited pseudo-plastic behavior, increasing $G''$ with increasing frequency, and the dynamic modulus, $G'$, increases with increasing frequency. As the concentration of either TBBA or EBBA is increased, both $G'$ and $G''$ decrease. This result is consistent with the $T_g$ data and indicates that these materials are plasticizing the PS. The results for the TBBA/PS composites in Figs. 4 and 5 are master curves constructed from data taken at three different temperatures. The fact the superposition is applicable to these curves indicates a single relaxation mechanism over the time-temperature regime studied. This is interesting in light of the fact that the temperature spans three different liquid phases of TBBA ($Sm_B$, $Sm_C$, and $Sm_A$), and this result is again consistent with what might be expected if the composites were homogeneous.

The thermal optical analysis (TOA) thermograms of TBBA and EBBA are shown in Figs. 8 and 9, respectively. The transitions as represented by changes in the intensity of transmitted light are consistent with the
DSC results described earlier (Figs. 1 and 2). Both the heating and cooling curves are shown. The TOA thermograms of mixtures of TBBA and PS with concentrations up to 80 percent TBBA are shown in Fig. 10. There is no variation of the transmitted light with temperature for concentrations up to 11 percent TBBA. Above 15 percent TBBA, changes in light intensity are observed and the temperatures of the transitions are consistent with the phase transitions of the liquid crystal. As the concentration of liquid crystal increases, increasingly more detail of the TBBA phase transitions are observed in the TOA thermograms. These results indicate that above 15 percent TBBA, phase separation of the TBBA occurs. In all cases, the initial transition appears near 115°C, which is consistent with the crystalline melting point of a pure TBBA phase.

The TOA thermograms of PS/EBBA mixtures are shown in Fig. 11. There is no variation of light intensity up to 20 percent. Above 40 percent EBBA the phase transitions of an EBBA phase become apparent. This indicates that PS and EBBA are miscible up to at least 20 percent EBBA. Both this result and the previous conclusion of miscibility of TBBA and PS up to 11 percent TBBA are consistent with visual observation of the mixtures. Below these concentrations films of these mixtures are optically clear, while above 11 percent TBBA or 20 percent EBBA the films become opaque.

From the DCS and TOA data, one may construct partial phase diagrams of the two composite materials; these are shown in Figs. 12 and 13. In Fig. 12 three regions are apparent: a single-phase region, isotropic liquid-liquid crystal two-phase region, and a glass-crystalline solid two-phase region. The boundaries are constructed by the glass-transition temperatures and the clearing point of the mixtures. \( T_g \) decreases with the addition of small amounts of TBBA, a result consistent with a plasticization phenomenon. Above 15 percent TBBA, however, \( T_g \) becomes independent of TBBA concentration. This result is expected if the TBBA separates into a separate phase at a concentration of 15 percent TBBA in the composite. The clearing points of the mixtures, i.e., the highest temperature transition observed by TOA, increase with increasing TBBA concentration.

The phase diagram for PS/EBBA is shown in Fig. 13. A dramatic decrease of some 60°C is observed in \( T_g \) for EBBA concentrations approaching 40 percent, and these compositions are quite flexible. As with the TBBA mixtures, \( T_g \) becomes independent of EBBA concentration above the concentration where phase separation occurs.
CONCLUSION

Liquid crystal additives such as TBBA and EBBA can effectively plasticize polystyrene. This is evidenced by decreases in $T_g$ and the melt viscosities of composites of these materials and PS. TBBA and EBBA are found to be miscible with PS at all temperatures below liquid crystal concentration of 11 and 40 percent, respectively. Above these concentrations the liquid crystals form separate phases at low temperatures, but an isotropic phase is formed at elevated temperatures. Despite the fact that the composites were two-phase systems at some of the conditions studied, melts of these mixtures appear to be thermorheologically simple. Time-temperature superposition was applicable to the TBBA/PS materials over the set of temperatures and frequencies studied.

Additional studies are needed to confirm that time temperature superposition is applicable under all conditions. Mechanical studies are warranted to determine the effect of the liquid crystal additives on the modulus and strength of these composites.

REFERENCES