Miscibility of Fullerene-Containing Polystyrene with Poly(2,6-dimethyl-1,4-phenylene oxide) and with Poly(vinyl methyl ether)

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Received June 24, 1997

Revised Manuscript Received October 1, 1997

Introduction

Fullerene-containing polymers have been the subject of several recent review articles.[1−3] Although the commercial applications of fullerenes have yet to emerge, it is believed that potential applications of fullerenes include their uses as chemical reagents, electrodes, optical filters, and sensors.[4] Therefore, fullerene-containing polymers may offer some unusual and attractive properties.

The development of new polymeric materials through blending of suitable pairs of polymers is a topic of scientific and practical importance. If there are favorable intermolecular interactions between the two component polymers, they will mix intimately to form a miscible polymer blend. The use of fullerene-containing polymers as blend components offers a simple means to impart their properties to some other polymers. However, the incorporation of fullerene is likely to affect the ability of the parent polymer to interact with other polymers and thereby affects the miscibility.

Polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and PS/poly(vinyl methyl ether) (PVME) are two classic examples of miscible polymer blends.[5−10] In this communication, we report the miscibility of fullerene-containing PS (PS-C_{60}) with PPO and with PVME.

Experimental Section

Materials. C_{60} (99.9% purity) was obtained from Peking University, China, and was used as received. Styrene was obtained from Fluka Chemika and was distilled under reduced pressure to remove stabilizer before use. PPO was kindly supplied by General Electrical Co. (Singapore). PVME was purchased from Scientific Polymer Products, Inc.

Three PS-C_{60} samples were synthesized according to Hawker's method.[11] The C_{60} contents of the three samples were determined by isothermal thermogravimetric experiments.[12] Table 1 lists some characteristics of PS-C_{60}, PVME, and PPO. The molecular weight distributions of the PS-C_{60} samples are broad, showing that multiaddition occurred between the azide-functionalized PS and C_{60}.

Preparation of Blends. PS-C_{60}/PPO blends were prepared by solution casting from ethylbenzene at 110 °C to prevent the crystallization of PPO. The blends were further dried in *vacuo* at 110 °C for 48 h. PS-C_{60}/PVME blends were cast from toluene at 90 °C. The blends were further dried in *vacuo* at 90 °C for at least 1 week. To study whether C_{60} could be directly blended with PPO or PVME, C_{60}/PPO (1/9) and C_{60}/PVME (1/9) blends were similarly prepared.

Measurements. The glass transition temperature (T_g's) were measured using a TA Instruments 2920 differential scanning calorimeter with a heating rate of 20 °C/min. The initial onset of slope in the DSC curve was taken as T_g. GPC chromatograms were obtained with a Waters Millipore system using THF as eluent. The lower critical solution temperature (LCST) behavior of various blends was studied using an Olympus BH2-UMA polarizing microscope equipped with a Leitz hot stage.

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Table 1. Characteristics of Polymers

	content of C_{60} (wt %)	$10^{-3}M_n$	$10^{-3}M_w$	T_g (°C)
PS-C_{60}-1.9	1.9	26	114	99
PS-C_{60}-9.9	9.9	30	249	108
PS-C_{60}-13.6	13.6	26	263	120
PVME		47	99	−28
PPO			40.7[a]	219

[a] Viscosity-average molecular weight determined by intrinsic viscosity measurement.

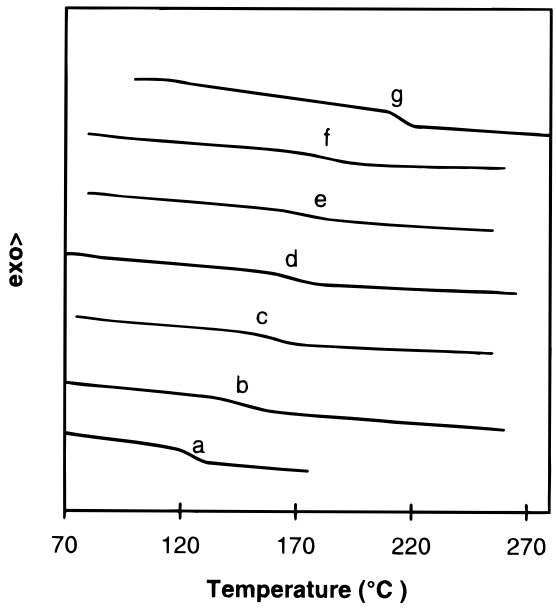

Figure 1. DSC curves of PPO/PS-C_{60}-13.6 blends: (a) 0/100; (b) 1/3; (c) 2/3; (d) 1/1; (e) 3/2; (f) 3/1; (g) 100/0.

Results and Discussion

All the PPO/PS-C_{60} blends were clear with a brownish tinge. The color becomes deeper with increasing C_{60} content in PS-C_{60} and PS-C_{60} content in the blend. Each blend showed a composition-dependent T_g, showing that all the blends are miscible. The DSC curves of PPO/PS-C_{60}-13.6 are shown in Figure 1 and the three T_g−composition curves are shown in Figure 2. All the blends did not show sign of phase separation even heated to 300 °C. The C_{60}/PPO (1/9) blend was also brownish in color. However, the blend was not totally homogeneous as the PPO/PS-C_{60} blend, indicating that C_{60} was not well dispersed in PPO.

The formation of a miscible blend requires the presence of favorable intermolecular interaction between the two component polymers. For PPO/PS blends, it has been suggested that miscibility arises from van der Waals interactions between the phenyl groups of PPO and PS.[13] The present study has shown that PS containing 13.6 wt % C_{60} is still miscible with PPO in spite of the presence of the bulky C_{60}. It is possible that the "aromatic" C_{60} may also interact with the phenylene rings of PPO, and thereby miscibility is still retained at this level of C_{60} content.

PVME/PS-C_{60}-1.9 and PVME/PS-C_{60}-9.9 blends were also clear. However, PVME/PS-C_{60}-13.6 blends were hazy. Thus the optical appearance of the blends suggests that immiscibility is induced when PS-C_{60} contains 13.6 wt % C_{60}. The miscibility of PVME/PS-C_{60}-1.9 and

S0024-9297(97)00918-2 CCC: $14.00

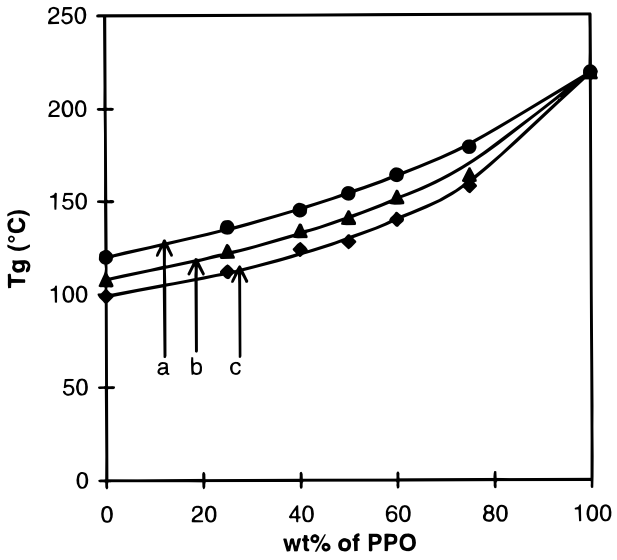

Figure 2. T_g-composition curves: (a) PPO/PS-C_{60}-13.6; (b) PPO/PS-C_{60}-9.9; (c) PPO/PS-C_{60}-1.9.

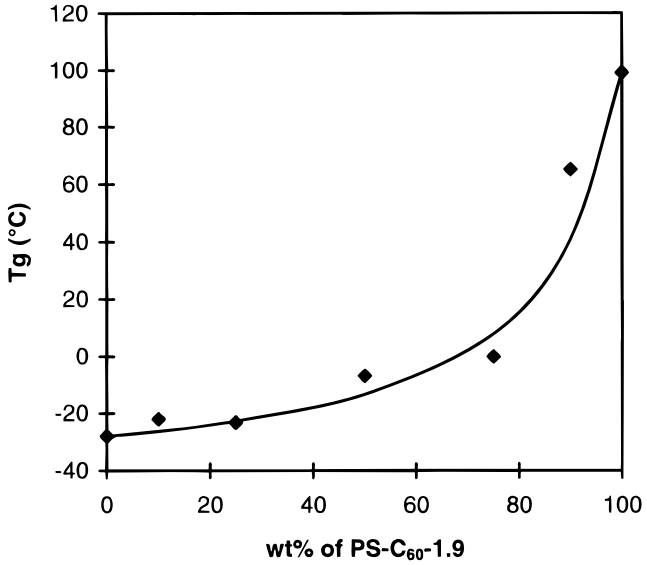

Figure 3. T_g-composition curve of PVME/PS-C_{60}-1.9 blends.

PVME/PS-C_{60}-9.9 blends was confirmed by the existence of a single T_g in each blend. The T_g−composition curve of PVME/PS-C_{60}-1.9 blends is shown in Figure 3. The T_g values of PVME/PS-C_{60}-9.9 blends are close to those of the corresponding PVME/PS-C_{60}-1.9 blends and the T_g−composition curve is not shown. The appearance of two T_g's in PVME/PS-C_{60}-13.6 blends also confirmed the immiscibility of this blend system. Figure 4 shows the DSC curve of PVME/PS-C_{60}-13.6 (1/1) blend. The lower T_g value is higher than that of PVME, indicating the presence of some PS-C_{60}-13.6 in the PVME-rich phase. In contrast, the C_{60}/PVME (1/9) blend was visibly immiscible. The C_{60} separated out as black particles in the transparent PVME matrix. Thus the attachment of C_{60} to a polymer backbone is essential to achieve miscibility.

Similar to the miscible PVME/PS blends,[10] the miscible PVME/PS-C_{60} blends also undergo phase separation upon heating, showing lower critical solution temperature behavior. The cloud point curves of the two blend systems are shown in Figure 5, and the curve moves to lower temperatures with increasing C_{60} content in PS-C_{60}. The cloud points of the two PS-C_{60}/

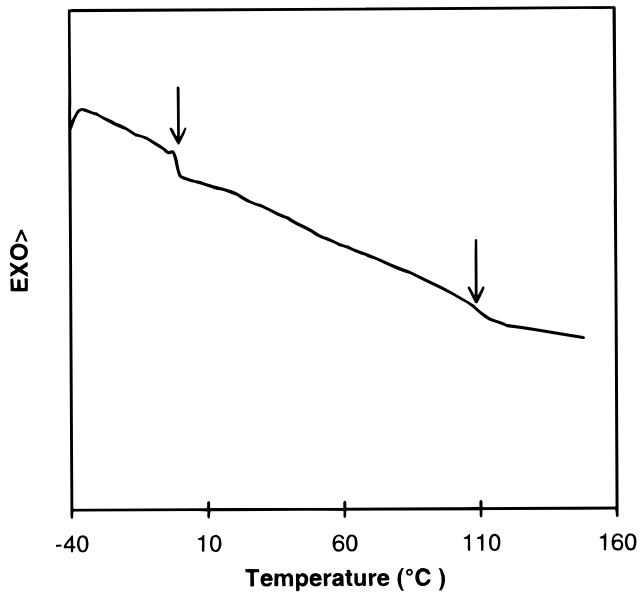

Figure 4. DSC curve of PVME/PS-C_{60}-13.6 (1/1) blend.

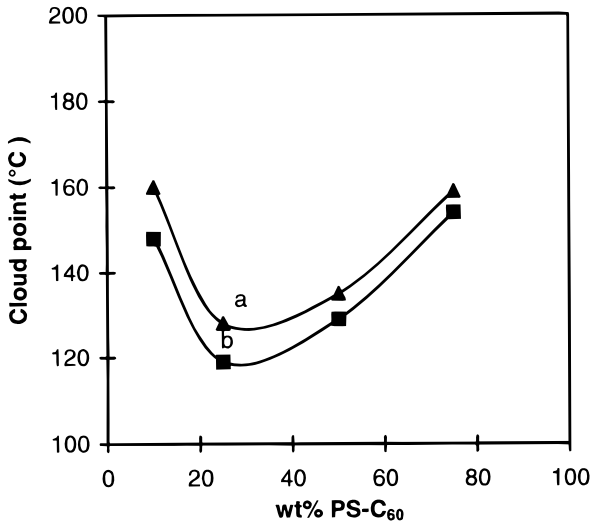

Figure 5. Cloud point curves: (a) PVME/PS-C_{60}-1.9; (b) PVME/PS-C_{60}-9.9.

PVME (9/1) blends were difficult to determine because of the brownish color of the blends.

The miscibility of PVME/PS blends has been extensively studied. The nature of the casting solvent has a profound effect on miscibility. Blends cast from toluene or benzene are miscible, while those cast from chloroform or trichloroethylene are immiscible.[9] The miscibility of PVME/PS blends is considered to arise from weak van der Waals interactions between the phenyl groups of PS and the methoxy groups of PVME.[14−16] Modification of the chemical structure of PS can drastically affect the miscibility. For example, PVME is immiscible with poly(α-methylstyrene)[17] and with poly(*p*-methylstyrene).[18] We have found that PVME is immiscible with poly(styrene-*co*-*p*-methylstyrene) when the copolymer contains 39 wt % or more of *p*-methylstyrene.[18] Nitration of styrene also reduces miscibility.[19,20] PVME is immiscible with poly(styrene-*co*-*m*-nitrostyrene) when the nitrostyrene content in the copolymer is 30 wt % or more.[19] Similarly, copolymerization of styrene with acrylonitrile, acrylic acid, or methyl methacrylate also induces immiscibility with PVME.[21,22] It is, therefore, not too surprising that the incorporation of C_{60} onto PS will eventually lead to immiscibility with PVME.

In conclusion, PPO is miscible with the three PS-C_{60} samples. PVME is miscible with PS-C_{60}-1.9 and PS-C_{60}-9.9 but not with PS-C_{60}-13.6. The miscible PVME/PS-C_{60} blends show LCST behavior.

Acknowledgment. The financial support of this research by the National University of Singapore is gratefully acknowledged.

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MA970918J