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Miscibility of C_{60}-containing poly(2,6-dimethyl-1,4-phenylene oxide) with styrenic polymers

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Abstract

The miscibility of C_{60}-containing poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-C_{60}) with several styrenic polymers was studied. PPO-C_{60} samples containing 6.9 and 19.5 wt% C_{60} are miscible with polystyrene, poly(*p*-methylstyrene), poly(α-methylstyrene) and poly(styrene-*co*-*p*-methylstyrene) based on the optical clarity of the blends and the single glass transition temperature criterion. However, the two PPO-C_{60} samples are miscible with poly(styrene-*co*-acrylonitrile) when the acrylonitrile content of the copolymer is 6.3 wt% or less. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: C_{60}-containing poly(2,6-dimethyl-1,4-phenylene oxide); Styrenic polymers; Miscibility

1. Introduction

[60]Fullerene (C_{60})-containing polymers have received much attention in recent years [1–3]. These polymers are expected to possess the properties of both C_{60} and the parent polymers. Various methods have been developed to attach C_{60} chemically onto polymer chains [4–10]. Recently, we have studied the complexation between C_{60}-derivatives and polymers [11,12].

Blending of suitable pairs of polymers offers a simple means to produce new materials. The properties of a polymer blend depend on the miscibility of the component polymers [13,14]. If the two polymers are able to interact with each other through specific interactions, they are likely to mix intimately to form a miscible blend. Since it can be difficult to link C_{60} chemically onto some polymers, the use of C_{60}-containing polymers as blend components becomes an attractive alternative [15–17]. In this respect, it is important to study how the incorporation of C_{60} could affect the ability of the parent polymer to mix with other polymers.

Polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blend is a classic example of miscible polymer blend [18,19]. A survey on the miscibility and phase behavior of blends related to the PS/PPO system was recently published by Vukovic et al. [20]. In an earlier study, we reported that C_{60}-containing PS with C_{60} content up to 13.6 wt% is still miscible with PPO [15]. Polotskaya et al. [21] recently reported that the addition of C_{60} to PPO improves the transport properties of PPO membranes. We now report the miscibility of two C_{60}-containing PPO samples with the following styrenic polymers: PS; poly(*p*-methylstyrene), P*p*MS; poly(α-methylstyrene), PαMS; poly(styrene-*co*-*p*-methylstyrene), PSMS; and poly(styrene-*co*-acrylonitrile), SAN.

2. Experimental

2.1. Materials

The following commercial polymers were used: PS (BDH Chemicals); P*p*MS (Polysciences, Inc.); PαMS (Aldrich); and PPO (General Electric). Various PSMS and SAN copolymers were prepared by solution polymerization in 2-butanone initiated by azobisisobutyronitrile. The composition of PSMS was determined by ^{1}H NMR based on the intensity ratio of methyl protons to phenyl protons. The composition of SAN was determined from its nitrogen content. The weight-average molecular weights (M_w) and glass transition temperatures (T_gs) of the polymers are given in Table 1. The numbers after PSMS and SAN denote the weight percentages of styrene and acrylonitrile in the copolymer, respectively.

2.2. Synthesis of PPO-C_{60}

Two PPO-C_{60} samples were synthesized using a

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Table 1
Characteristics of polymers

Polymer	M_w (kg/mol)	T_g (°C)
PS	150	100
P*p*MS	240	106
PαMS	113	63
PPO	41	214
PSMS-15	36	107
PSMS-36	33	106
PSMS-54	31	105
PSMS-72	54	104
PSMS-90	38	103
SAN-2.2	21	100
SAN-6.3	32	102
SAN-9.1	20	100
SAN-10.2	74	101

three-step process. PPO was bromobenzylated according to the method of Cabasso et al. [22]. The bromo derivative was then converted to azide. Lastly, the azide group was allowed to react with C_{60} to afford PPO-C_{60} using the Hawker's method [23].

A mixture of PPO (7 g), *N*-bromosuccinimide (0.5 g) and benzoyl peroxide (0.1 g) in 1.2 l of CCl_4 was allowed to reflux for 5 h. The solution was then cooled to room temperature, and the succinimide was filtered and removed. The bromobenzylated PPO (BrPPO) was obtained by precipitation from excess methanol cooled in an ice bath. BrPPO was purified by several dissolution/precipitation cycles using chloroform as solvent and methanol as non-solvent. The BrPPO was found to contain 1.38 wt% Br, corresponding to 2.1 mol.% bromobenzylated PPO unit.

BrPPO (2 g) was allowed to react with NaN_3 (0.1 g) in 120 ml of a mixture of toluene/dimethyl sulfoxide (3/1) at 40–50°C for 2 days. The azido-PPO was obtained by precipitation from excess methanol; it was then purified by several dissolution/precipitation cycles using chloroform as solvent and methanol as non-solvent. The azido-PPO was found to contain 0.74 wt% of nitrogen, corresponding to 2.15 mol.% azido-PPO unit. All the bromine in BrPPO have been quantitatively converted to azide.

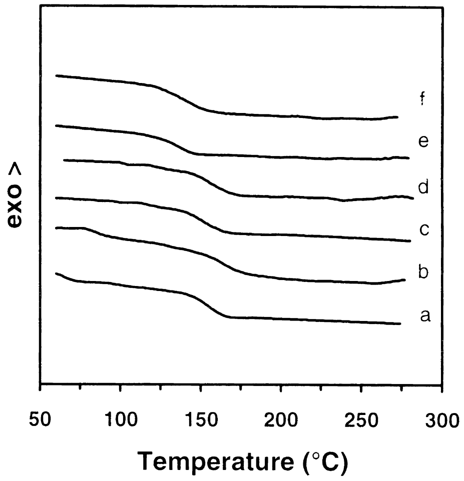

Fig. 1. DSC curves of blends: (a) PPO-C_{60}-6.9/PS; (b) PPO-C_{60}-19.5/PS; (c) PPO-C_{60}-6.9/P*p*MS; (d) PPO-C_{60}-19.5/P*p*MS; (e) PPO-C_{60}-6.9/PαMS; (f) PPO-C_{60}-19.5/PαMS.

Azido-PPO (2.0 g) was stirred with C_{60} (0.33 g, 1.3 times the molar amount of azide groups) in 120 ml of chlorobenzene. After the complete dissolution of C_{60}, the mixture was refluxed under nitrogen until the strong IR band of the azide group at 2095 cm^{-1} had completely disappeared. Chlorobenzene was removed by rotary evaporation. The residue was dissolved in chloroform and the excess C_{60} was removed by centrifugation. To completely remove the unreacted C_{60}, the chloroform solution was washed repeatedly with *n*-hexane until the *n*-hexane layer was colorless. The PPO-C_{60} sample was found to contain 6.9 wt% C_{60} by isothermal thermogravimetry. The C_{60} content of the sample is less than the expected value of 11.4 wt% assuming mono-addition between azide and C_{60}, showing that some of the C_{60} have reacted with two or more azide groups. Similar procedures were used to prepare another PP0-C_{60} sample containing 19.5 wt% C_{60}. The two PPO-C_{60} samples dissolve readily in common organic solvents such as chloroform, dichloromethane, benzene, toluene, ethylbenzene and chlorobenzene. The UV–vis spectra of the two PPO-C_{60} samples show the characteristic absorption of C_{60} at 330 nm.

2.3. Preparation and characterization of blends

Various binary blends in a weight ratio of 1:1 were prepared by solution casting from toluene. After the evaporation of the solvent on a hot-plate at 90°C, the blends were then dried in vacuo at 90°C for two weeks. The optical appearance of the blends was examined using an Olympus BH2-UMA polarizing microscope.

The C_{60} contents of the two PPO-C_{60} samples were estimated by isothermal thermogravimetry using a TA Instruments SDT2960 DTA–TGA under a nitrogen atmosphere. Sample was kept at 580°C until a constant weight was reached. The difference in the amounts of residue of PPO and PPO-C_{60} was taken to be the C_{60} content. The C_{60} contents of the two samples were found to be 6.9 and 19.5 wt% and were designated as PPO-C_{60}-6.9 and PPO-C_{60}-19.5, respectively.

The glass transition temperatures of various samples were measured using a TA Instruments 2920 differential scanning calorimeter under a nitrogen atmosphere with a heating rate of 20°C/min. The initial onset of the change of slope in the DSC curve was taken as T_g. The T_gs of PPO-C_{60}-6.9 and PPO-C_{60}-19.5 are 218 and 228°C, respectively. The incorporation of C_{60} increases the T_g value of PPO.

3. Results and discussion

PPO is miscible not only with PS but also with P*p*MS [24–26] and PαMS [24,27]. In addition, PPO is miscible

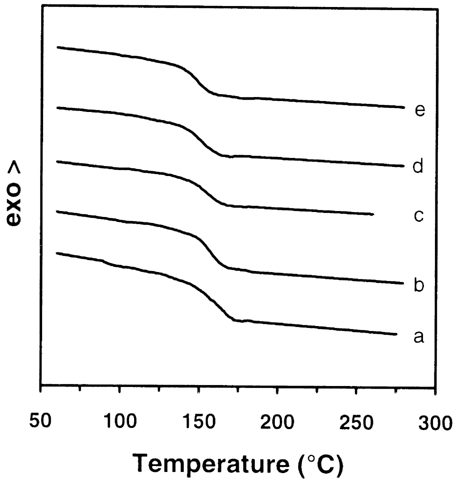

Fig. 2. DSC curves of PPO-C_{60}-6.9/PSMS blends: (a) PSMS-15; (b) PSMS-36; (c) PSMS-54; (d) PSMS-72; (e) PSMS-90.

with PSMS over the whole copolymer composition range [28].

Fig. 1 shows the DSC curves of various blends of PPO-C_{60} with PS, P*p*MS and PαMS. Each blend showed the existence of a well-defined glass transition with a T_g value intermediate to those of PPO-C_{60} and the styrenic polymer. In addition, all these blends were optically clear. It is therefore concluded that PPO-C_{60} with a C_{60} content of 19.5 wt% is still miscible with the three styrenic polymers.

Figs. 2 and 3 show the DSC curves of PPO-C_{60}-6.9/PSMS (1:1) and PPO-C_{60}-19.5/PSMS (1:1) blends, respectively. Similarly, each blend exhibited one glass transition and the T_g value is intermediate between the component polymers. The existence of a single glass transition together with their optical clarity shows that the two PPO-C_{60} samples are miscible with PSMS over the whole copolymer composition range.

Kressler and Kammer [29] reported the miscibility of PPO with SAN. PPO is miscible with SAN when the AN content of the copolymer is 10.5 wt% or less; it is immiscible with SAN when the AN content is 12.4 wt% or more. In other words, the miscibility–immiscibility boundary is around 11–12 wt% AN. Blends of PPO-C_{60}-6.9 or PPO-C_{60}-19.5 with SAN having 2.2 and 6.3 wt% AN were clear, whereas blends of the two PPO-C_{60} samples with SAN having 9.1 and 12.5 wt% AN were hazy. Thus the optical clarity of the blends suggests that the miscibility–immiscibility boundary is between 6.3 and 9.1 wt% AN. The DSC curves of the two PPO-C_{60}/SAN blend systems are shown in Figs. 4 and 5. Indeed, a single T_g is observed when the AN content of SAN is 2.2 or 6.3 wt% while two T_gs are observed when the AN content is 9.1 wt% or more. The upper T_g of the PPO-C_{60}-19.5/SAN-12.5 blend is difficult to detect. Nevertheless, the hazy appearance and the existence of a glass transition close to that of SAN-12.5 are sufficient to show the immiscibility of this blend.

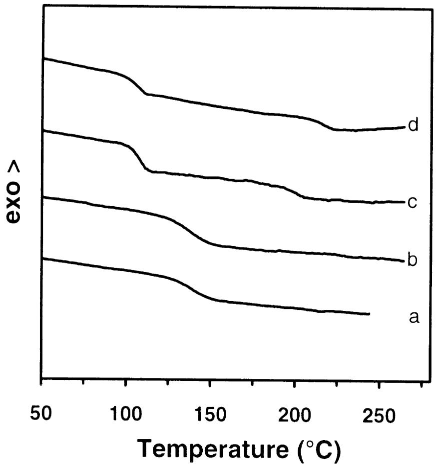

Fig. 4. DSC curves of PPO-C_{60}-6.9/SAN blends: (a) SAN-2.2; (b) SAN-6.3; (c) SAN-9.1; (d) SAN-12.5.

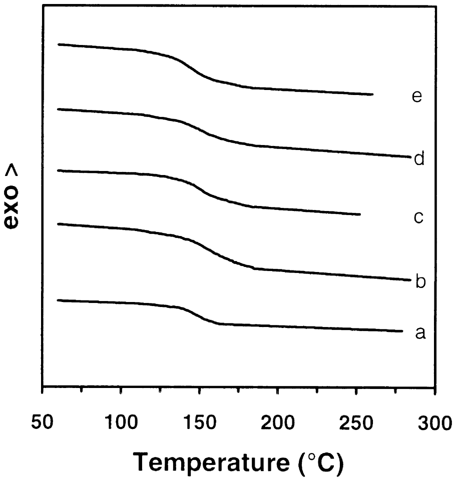

Fig. 3. DSC curves of PPO-C_{60}-19.5/PSMS blends: (a) PSMS-15; (b) PSMS-36; (c) PSMS-54; (d) PSMS-72; (e) PSMS-90.

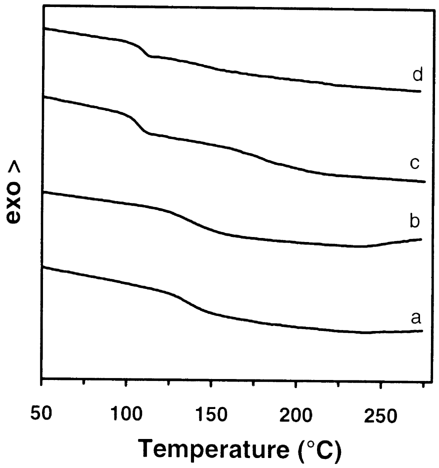

Fig. 5. DSC curves of PPO-C_{60}-19.5/SAN blends: (a) SAN-2.2; (b) SAN-6.3; (c) SAN-9.1; (d) SAN-12.5.

Therefore, immiscibility sets in when the AN content in SAN is about 7–8 wt%. As compared to the PPO/SAN system, the incorporation of C_{60} onto PPO reduces the ability of PPO to mix with SAN.

In summary, PPO-C_{60} containing up to 19.5 wt% C_{60} is still miscible with PS, P*p*MS, PαMS and PSMS. The two PPO-C_{60} samples are miscible with SAN if the AN content of the copolymer is less than about 7 wt%.

Acknowledgements

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