

Miscibility and Crystallization Behavior of the Solution-Blended Sulfonated Poly(phenylene oxide)/Poly(styrene-co-4-vinyl pyridine) Blend

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ABSTRACT: The miscibility and crystallization behavior of the solution-blended lightly sulfonated poly(phenylene oxide) (SPPO)/poly(styrene-co-4-vinylpyridine) (PSVP) blend were investigated by conventional and modulated differential scanning calorimetry (MDSC). It was found that the original blend film is actually composed of a crystalline SPPO phase and a noncrystalline compatible SPPO-PSVP phase. The original phase-segregated structure will evolve to a noncrystalline homogenous structure by subsequent high temperature annealing. The resulting good miscibility was attributed to two aspects: one is that the SPPO crystalline structure could be destroyed as annealing temperature is high enough; the other is that the acid-base interaction between the sulfonic group of SPPO and the pyridine ring of PSVP could promote mixing of different components effectively. And such acid-base interaction was demonstrated by ^{13}C NMR spectra. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2843–2848, 2001

Key words: miscibility; sulfonated poly(phenylene oxide); poly(styrene-co-4-vinylpyridine); acid-base interaction

INTRODUCTION

It is well-known that the poly(phenylene oxide) (PPO)/polystyrene (PS) blend is miscible over the entire composition range, although there does not exist specific interaction between PPO and PS.^{1–4} However, our recent research showed^{5,6} that the original solution-cast film of PPO/PS blend is actually phase separated, which is composed of a crystalline PPO phase and a noncrystalline compatible PPO-PS phase. This was attributed to the fact that PPO could crystallize fairly readily in

the presence of solvent or solvent vapor.^{7–10} And it was found that the existence of PS chains in a PPO/PS mixture solution almost has no effects on the crystalline behavior of PPO chains. However, the original PPO/PS blend film could evolve to a homogenous miscible system by subsequent thermal treatment, since PPO could not thermally crystallize. On the other hand, the original solution-cast film of lightly sulfonated poly(phenylene oxide) (SPPO)/PS blend also holds crystalline SPPO structure. But the SPPO/PS blend film could not evolve to a homogenous system after high temperature annealing because of the aggregation of ionic groups into physical crosslinking sites, which impedes the thorough mixing of different components.

Since no specific interaction exists between PPO and PS, it is an interesting problem to see that after some specific ion interaction has been introduced

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into the PPO/PS system, whether the original solution-cast film of this functionalized PPO/PS blend could still hold the PPO crystalline structure and how the phase structure of the functionalized blend varies after annealing. Therefore, in this paper, utilizing the interacting species of sulfonic acid and pyridine, we shall investigate the solution-cast film of the lightly sulfonated PPO (SPPO)/poly(styrene-co-4-vinylpyridine) (PSVP) blend. The objective is to observe its crystallization behavior and miscibility, and to compare it with that of the PPO/PS and SPPO/PS blends.

EXPERIMENTAL

Sample Preparation

The start PPO and 4-vinylpyridine (4VP) were purchased from Aldrich Chemical Co. The molecular weight of PPO was measured by gel permeation chromatography (GPC) ($M_n = 29,200$, $M_w = 67,500$). The SPPO and PSVP were prepared as refs. 11 and 12 described, respectively. For x-SPPO, the x represents the mol % of the sulfonation degree, and for PSVP-y, the y is the mol % of 4-vinylpyridine in the copolymer. The molecular weight of PSVP is approximately $(1.8 \sim 2.2) \times 10^5$ g/mol.

Blends of SPPO and PSVP were prepared by solution mixing. The used solvent is chloroform/methanol (96/4/v/v) mixed solvent. Film specimens were cast from solution at room temperature. Before measuring, the films were dried under vacuum for 3 days at 60°C to constant weight. The films were inspected by pyrolysis mass spectrometric analysis. Almost no residual solvent could be detected.

Measurement

Miscibility and crystallization studies were performed by TA 2910 modulated differential scanning calorimetry (MDSC) under a nitrogen atmosphere. Conventional differential scanning calorimetry (DSC) was measured at a heating rate of 10°C/min, while modulated DSC was measured at a heating rate of 5°C/min, with a temperature modulation amplitude of 1.0°C and an oscillation period of 60 s. Dynamic mechanical thermal analysis (DMAT) employed Metravib MAK-04 at a frequency of 7.8 Hz and heating rate 5 K/min under a nitrogen atmosphere.

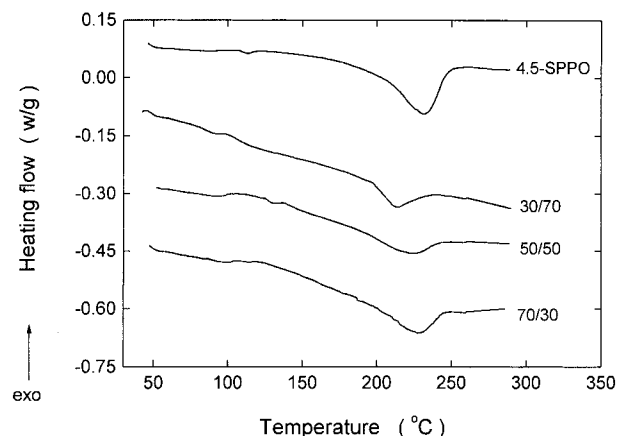


Figure 1 DSC heating curves of the original solution-cast films of 4.5-SPPO/PSVP-4.6 blends with different composition.

The ^{13}C NMR spectra were measured on a Bruker 400 MHz NMR spectrometer with DMSO as solvent.

RESULTS AND DISCUSSION

Crystalline Behavior of the SPPO/PSVP Blend

Crystalline behavior of the original solution-cast films of 4.5-SPPO/PSVP-4.6 blends with different composition was investigated by DSC. The results are shown in Figure 1. The heating DSC curve of the original solution-cast film of single 4.5-SPPO shows only a wide endothermic melting peaks, whose melting point and melting enthalpy are almost identical with those of single PPO film.⁵ It means that introducing a very small amount of sulfonic group into PPO scarcely affects its crystalline capacity. Like the single SPPO, the heating DSC curves of the blends with different composition all show a wide endothermic peak. It indicated that each of these original blend films still holds SPPO crystalline structures. But the melting point decreases gradually with the increase of the fraction of PSVP. It indicates that the crystalline structure of SPPO becomes more imperfect as the content of PSVP in mixture increases.

At the same time, it seems that there is an ambiguous glass transition at 100 ~ 150°C in the heating DSC curves. As we know, sometimes the detection of T_g becomes difficult since glass transition usually overlaps with relaxation behavior. Fortunately, the new thermal analysis technique,

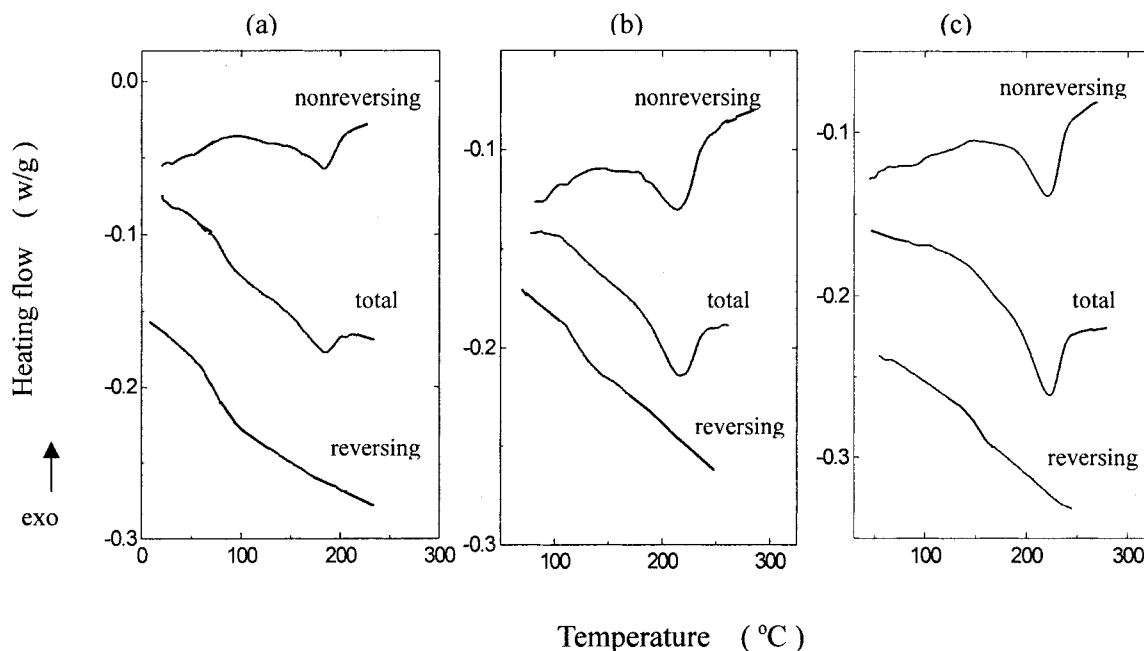


Figure 2 MDSC heating curves of the original solution-cast films of 4.5-SPPO/PSVP-4.6 blends. (a) 4.5-SPPO/PSVP-4.6 (30/70), (b) 4.5-SPPO/PSVP-4.6 (50/50), and (c) 4.5-SPPO/PSVP-4.6 (70/30).

MDSC,¹³⁻¹⁵ has become available. It subjects a material to a linear heating method that has a superimposed sinusoidal temperature oscillation (modulation), resulting in a cyclic heating profile. Deconvolution of the resultant heat flow profile cannot only provides the total heat flow obtained from conventional DSC but also separates that total heat flow into its heat-capacity-related (reversing) and kinetics (nonreversing) components. Thus, MDSC offers a better method for separating the glass transition and the associated relaxation because the glass transition is a reversing phenomenon in MDSC. Then, the identical specimens were measured synchronously by MDSC; the results are shown in Figure 2. It is obvious that there indeed exists a glass transition corresponding to the reversing component and a melting peak corresponding to the nonreversing component. And the T_g and melting enthalpy all enhance with the increase of the fraction of SPPO in mixture. This suggests that each of these original solution-cast films consist of two kinds of structural regions: the noncrystalline compatible SPPO-PSVP mixture and SPPO crystalline structures. These experimental facts indicated that partial SPPO chains in mixture solution still tend to aggregate and form crystalline structure in the process of macromolecular condensation

via evaporating solvent, although there exists acid-base interaction between the SPPO and PSVP. But the existence of PSVP makes the resultant crystalline structure of SPPO more imperfect.

Figure 3 shows the DSC heating curves of the 4.5-SPPO/PSVP-4.5 blend films with different composition after annealing at 200°C for 2 min. Compared with those original films as shown in

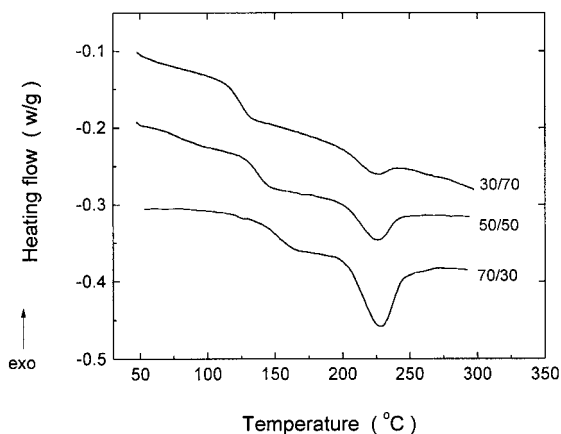


Figure 3 DSC heating curves of the 4.5-SPPO/PSVP-4.5 blend films with different compositions after annealing at 200°C for 2 min.

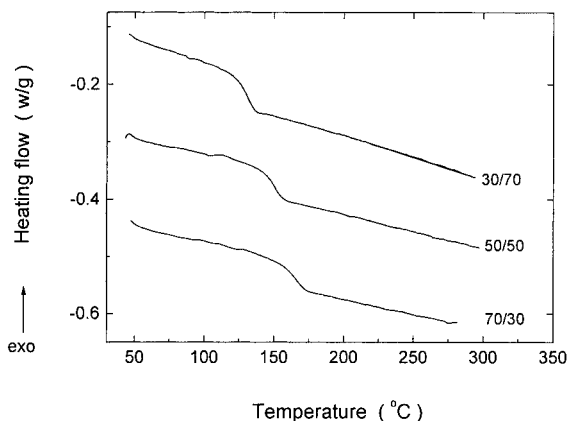


Figure 4 DSC heating traces of the 4.5-SPPO/PSVP-4.5 blend films with different composition after annealing at 250°C for 2 min.

Figure 1, It becomes very clear that each curve exhibits a obvious glass transition and a melting peak. And the melting point is higher. This indicates that after annealing at a temperature near the melting point, partial imperfect crystals will melt and recrystallize with more stable crystal nuclei. Then the crystalline structure become more ordered.

Figure 4 shows the DSC heating curves of the 4.5-SPPO/PSVP-4.5 blend films after annealing at 250°C for 2 min. Only a single increasing glass transition temperature is observed in each curve and no melting peak appears. This means that the SPPO crystalline structure in the original film has been destroyed drastically as the annealing temperature is up to 250°C, then all SPPO and PSVP form a homogenous mixture.

Miscibility of the SPPO/PSVP Blend

The past research has indicated that attaching a small number of ionic groups to a component polymer can exert profound effects on the blend miscibility. Hsieh and Peiffer also reported¹¹ that even when the level of sulfonation of SPPO is as low as 3%, the SPPO/PS is immiscible because of the aggregation of the ionic groups due to ion-pair interaction. However, in the present work, the 4.5-SPPO/PSVP-4.6 blend is miscible after annealing at 250°C. Additional, a series of blends composed by lightly sulfonated PPO with PSVP were prepared by solution blended. Miscibility of these blends was investigated by DSC. The results are shown in Figure 5. After annealing at 250°C for 2 min, these blends all show a single glass transition tem-

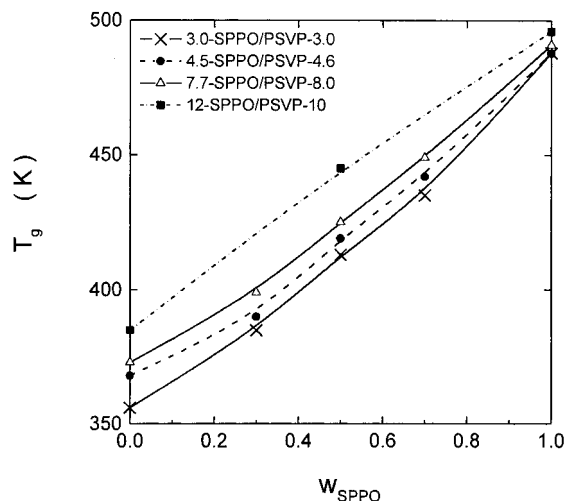


Figure 5 Variation of glass transition temperature with composition for PPO/PSVP blend films.

perature (T_g), even the sulfonation degree of SPPO is up to 12%. These experimental T_g almost agree with or deviate positively from the Fox equation¹⁶:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where W_1 and W_2 represent the weight fractions of the blend components, and T_{g1} and T_{g2} are their respective glass transition temperatures. It can be considered as an indication of miscibility and specific attractive interaction.

Since it is often difficult for DSC to detect minor phase, the same samples were measured

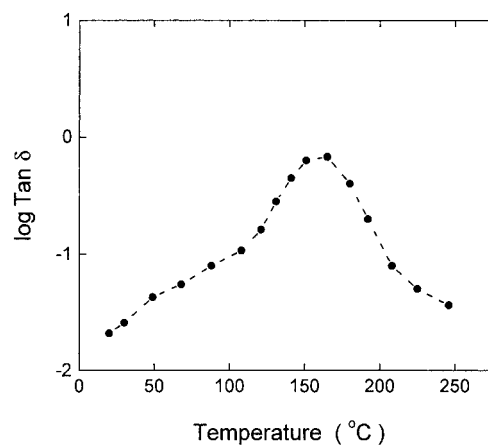


Figure 6 Variation of $\tan \delta$ with temperature for 7.7-SPPO/PSVP-8.0 (50/50) blend film after annealing at 250°C for 2 min.

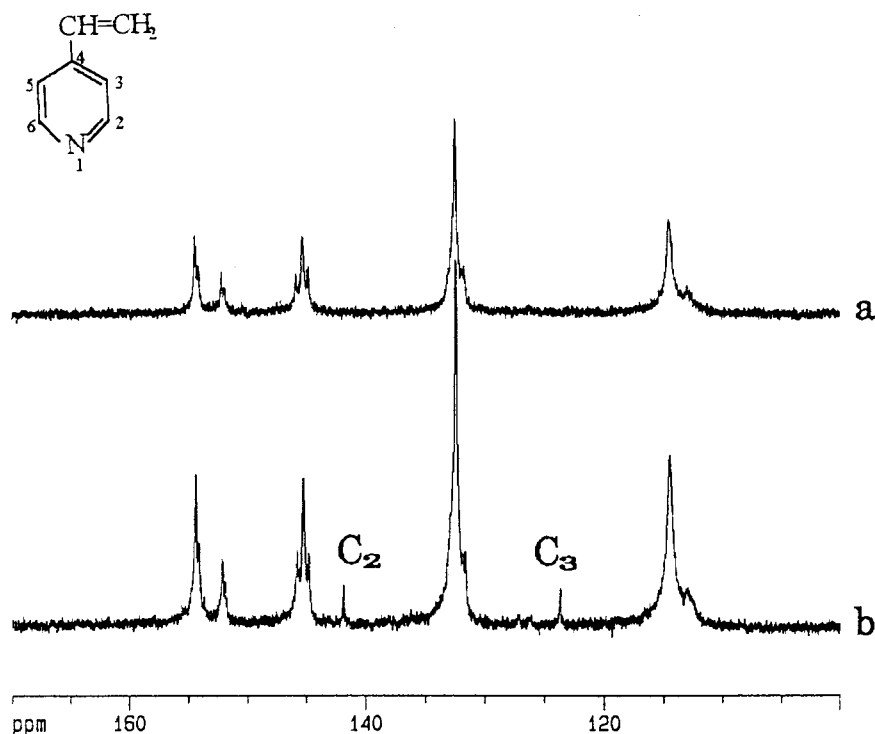


Figure 7 The ^{13}C NMR spectra of 45-SPPO (a) and 45-SPPO/4VP blend (b). Used solvent is DMSO.

by dynamical mechanical thermal analysis (DMTA). It was found that the DMTA results support the judgment due to DSC. For example, Figure 6 is the variation of $\text{Tan } \delta$ with temperature for 7.7-SPPO/PSVP-8 (50/50 wt) blend after annealing at 250°C for 2 min. It shows a single peak at ca. 160°C , which coincides with the single T_g obtained by DSC. It further demonstrates the good miscibility. Compared with the SPPO/PS blend, which shows two glass transition temperatures,¹¹ it is reasonable for us to suggest that it is the acid–base interaction between the sulfonic groups of SPPO and the pyridine groups of PSVP that improves miscibility effectively. Such acid–base interaction may be very strong when the content of functional groups is high enough. Since it was observed that as sulfonation degree of SPPO is up to 12%, insoluble complex occurred between 12-SPPO and PSVP-10 in solution. Moreover, the resulting complex is insoluble in any solvent and cannot be melted, but showing only single T_g . Obviously, the strong acid–base interaction makes the complex exhibit similar properties to that of crosslinking polymer.

Acid–Base Interaction in the SPPO/PSVP Blend

To demonstrate the acid–base interaction resulted from the proton transfer between sulfonic group and pyridine group, ^{13}C NMR spectra were employed to probe the formation of protonated pyridine group (VPH^+). As the sulfonation degree of SPPO is very low, the information on the specific interaction between SPPO and PSVP is too weak to be detected. While the sulfonation degree of SPPO is up to 12%, insoluble complex occurs. Therefore, the sample chosen for investigation was 45-SPPO/4VP.

The ^{13}C NMR spectra for 45-SPPO and 45-SPPO/4VP blend in DMSO solution are shown in Figure 7. The main difference of the two spectra can be noticed in the pyridine ring region. In the latter, two new signals appeared at 142.2 ppm and 123.8 ppm, which correspond to C_3 (*meta* to the nitrogen) and C_2 (*ortho* to the nitrogen) of pyridine ring, respectively. As we know the chemical shift of C_3 (*meta* to the nitrogen) and C_2 (*ortho* to the nitrogen) of pure 4-vinylpyridine is 150.2 and 120.7 ppm, respectively. Obviously, the carbon signals of pyridine ring in the 45-SPPO/4VP

blend were shifted downfield, indicating the change from pyridine (VP) to pyridinium units (VPH⁺). It confirms the existence of proton transfer between the sulfonic acid of SPPO and the 4VP.

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