

Phase behaviour and borderline miscibility in blends of syndiotactic polystyrene with poly(vinyl methyl ether)

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Abstract

The state of miscibility and possible molecular aggregation in blends of semicrystalline syndiotactic polystyrene (s-PS) with poly(vinyl methyl ether) (PVME) were investigated by using differential scanning calorimetry (DSC), optical microscopy (OM) and scanning electron microscopy (SEM). The results are then directly compared to the classical amorphous PS/PVME blend prepared using exactly the same solvent and procedures. Similar to the classical amorphous a-PS/PVME, the semicrystalline s-PS/PVME exhibit the same scales of various molecular aggregation depending on composition leading to a so-called borderline miscibility, which is thoroughly discussed using the results of T_g -composition relationship and morphology evidence. The behavior of s-PS/PVME agrees mostly with that of a-PS/PVME, indicating that tacticity or crystallinity in s-PS does not affect the phase behaviour of s-PS/PVME in the amorphous domain. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Miscibility; Poly(vinyl methyl ether); Syndiotactic polystyrene (s-PS)

1. Introduction

Amorphous atactic polystyrene (a-PS) is one of the most widely used commodity thermoplastics. Interestingly, although the structure of PS does not possess any functional groups capable of apparent specific interactions, it was found to be miscible with two ether-containing polymers: poly(vinyl methyl ether) (PVME) and poly(1,4-dimethyl-*p*-phenylene oxide) (PPO), respectively. However, among thousands of different homopolymers, they are the only two polymers that were known to be miscible with PS. Traditionally, a-PS/PVME miscibility was demonstrated since an early time [1–3]. Reversible LCST exists in a-PS/PVME blends upon heating to temperatures above the blend's T_g and then slow cooling back to low temperatures. Similarly, a-PS/PPO were widely studied and its miscibility was demonstrated in early time [4–6]. Miscible blends of a-PS with PPO of various compositions have led to a useful commercial product well known as Noryl. Isotactic PS has also been demonstrated to be miscible with PPO [7]. This provides another example of miscibility of blends of polystyrene of different tacticity with ether-containing polymers.

Syndiotactic polystyrene (s-PS) is a relatively new polymer resulting from stereo specific polymerization [8–10] that offers good T_g and T_m or other physical properties. Polymers of different tacticity and effects of tacticity on polymers physical behaviour were interesting subjects of studies. In contrast to the straightforward cases of PS/PPO, the equilibrium phase behaviour of s-PS/PVME, however, is quite complex. The complexity has even been compounded by the fact that direct melt blending for preparing sPS/PVME is prohibited as a result of apparent gross phase separation at relatively low LCST (lower critical solution temperature, at about 120°C–160°C). Solution-blending is the only way for preparation of this blend. However, because of high crystallinity in s-PS, it is mostly insoluble in common solvents. What is a good solvent for s-PS may be a poor one for PVME and vice versa. As a result, solvent-induced changes of phase behaviour of solution-blended s-PS/PVME mixtures must be carefully avoided.

So far, reports in the literature regarding miscibility/compatibility issues of s-PS/PVME system were scant and probably not convincing enough. Silvestre et al. [11] reported that isotactic i-PS is immiscible with PVME (toluene-casting at 60°C). Additionally, they also reported that phase separation was observed in s-PS/PVME blends (casting in *o*-dichlorobenzene at 130°C) [12,13]. Note that

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the cast temperature of 130°C in the Silvestre et al. study is already near or at the LCST reported for the classical a-PS/PVME. The phase separation behaviour of s-PS/PVME (or i-PS/PVME) is in apparent contrast with the miscibility reported for the classical s-PS/PVME. However, curiosity was raised. Why would tacticity influence miscibility or phase behaviour in polymer blends? Can the solvents or temperatures used in blending and casting the mixtures affect the outcome results of phase behaviour of syndiotactic s-PS/PVME? This study was intended to probe these issues.

2. Experimental

2.1. Materials and preparation

Semicrystalline syndiotactic polystyrene (s-PS) was obtained as a courtesy research material from Idemitsu Petrochemical Co., Ltd. (Japan) with $M_w = 241,000 \text{ g mol}^{-1}$ and PI (M_w/M_n) = 2.41. Atactic polystyrenes (a-PS, $M_w = 1.92 \times 10^5$) were purchased from Poly-science, Inc. Syndiotactic polystyrene (s-PS) and amorphous polystyrene (a-PS) were used without purification. Poly (vinyl methyl ether) (PVME) (Scientific Polymer Products) was obtained as 50% solution in water. It was purified three times by dissolution in water and isolation by warming the solution. It was then dried under vacuum at 80°C for 72 h. The average molecular weight of PVME, $M_w = 9 \times 10^4$ (GPC). The solvents, 1-chloronaphthalene ca. 90%/2-chloronaphthalene, 10% (Aldrich) and *n*-heptane (Fisher Scientific), were used as received.

2.1.1. Preparation of blends

Blends were prepared using solvent-mixing followed with film casting or precipitation. Direct melt blending would require that the polymers be heated above T_m (ca. 280°C) of s-PS, but this could not be used because of a relatively low temperature of gross phase separation (LCST), which is located at below the melting temperature of s-PS. The blends s-PS and PVME were prepared by two different methods based on solution blending. In the first method, the blends were prepared by casting into films from 1%–2% (w/v) solution of the two components in 1-chloronaphthalene ca. 90%/2-chloronaphthalene at about 120°C. Solvent after blending was allowed to evaporate at the same temperature. The resulting films were dried further in vacuum at 120°C for 72 h. In another method, blend samples were prepared by dissolving the two polymers in the same solvent at 120°C, followed by precipitation into *n*-heptane. The precipitated blends were then dried at 120°C for 72 h in a vacuum oven. For direct comparison of possible solvent effects, blends of atactic polystyrene with PVME were also prepared using exactly the same procedures as those for s-PS/PVME. The a-PS/PVME blends were also prepared by casting from the same solvent and same temperature as in the case of s-PS/PVME solvent cast

blend. Note that heating at 120°C may be close to the LCST, but only for compositions near 50/50. For most other compositions, 120°C is quite safely away from LCST. The reason why we had to use 120°C but not lower temperatures was a compromise. Lowering the temperature would lead to gelation of s-PS.

2.2. Apparatus and procedures

2.2.1. Optical microscopy

A polarized-light microscope (Nikon Optiphot-2, POL) equipped with UFX-DX automatic exposure was used for following microscopic phase structure and for monitoring LCST of blend upon heating. Blend samples were cast as thin films (solvent casting at controlled temperatures and vacuum drying) and placed on a microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer) for OM examination.

2.2.2. Scanning electron microscopy

The morphological homogeneity of the fracture surfaces of the solvent-cast blends were examined using a scanning electron microscope (SEM) (JEOL, Model JXA-840). Thicker blend films (ca. 0.3–0.5 mm in thickness) were prepared. They were then fractured across the thickness (after dipping into liquid nitrogen), subsequently, the fractured surfaces were sputter-coated with gold for SEM examination.

2.2.3. Differential scanning calorimetry

The thermal transitions of PS/PVME blends were characterized with a differential scanning calorimeter (DSC-7, Perkin-Elmer) equipped with an intracooler for quenching and cooling. Wherever extremely fast quenching was needed, blend samples after melting treatment were dipped in liquid nitrogen rather than quenching in DSC cells. Prior to DSC runs, the temperature and heat of transition of the instrument were calibrated with indium and zinc standards. For determining the transition temperatures, a heating rate of 20°C min⁻¹ was used. A continuous nitrogen flow in the DSC sample cell was maintained to ensure minimal sample degradation.

3. Results and discussion

3.1. Blend morphology

The blends of all compositions were preliminarily examined using an optical microscope. The blend films were first examined at ambient temperature, then the temperature was raised gradually up to where a cloud-point transition occurred. The optical results (not shown) indicated that the blends of as-cast films of all compositions were homogeneous, but displayed some textures associated with presence of crystallinity. At above LCST, distinct phase

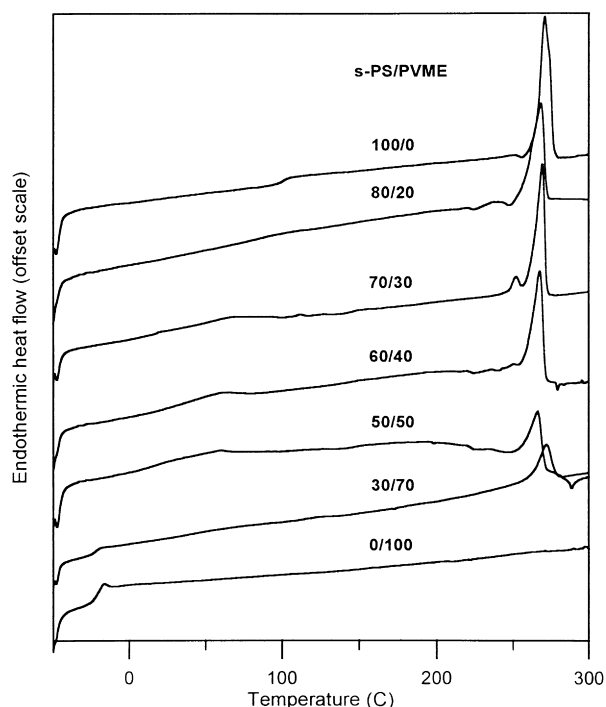


Fig. 1. DSC thermograms for solution-cast s-PS/PVME blends of various compositions as indicated.

separation could be easily observed in an optical microscope. Exact determination of initiation of LCST in the s-PS/PVME blend was difficult as a result of presence of s-PS crystallinity. In addition, the morphology of the as-cast blend films (fractured across thickness) were examined using s.e.m. to provide further evidence of phase homogeneity

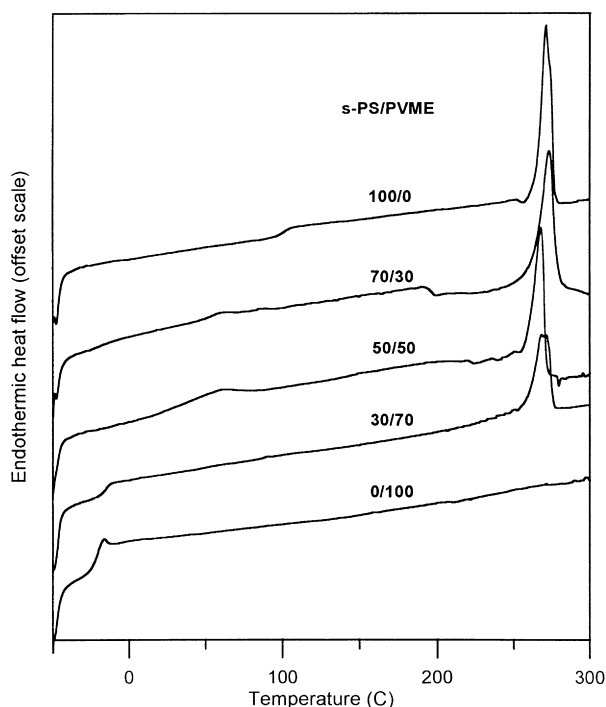


Fig. 2. DSC thermograms for precipitated s-PS/PVME blends of five compositions (a–e).

within the resolution limits of 4000–5000 \times . For brevity, the micrographs are not shown. A brief discussion is provided here. The morphology of s-PS/PVME (70/30, 50/50) was found to be as homogeneous as a-PS/PVME of the same compositions (70/30, 50/50) prepared with exactly the same solvent-cast procedures. The microscopic results showed that no grossly separated phase domains could be identified in the as-cast s-PS/PVME blend in the s.e.m. resolution of about 0.1 μm or better.

3.2. Thermal transition behaviour

Fig. 1a–g shows the calorimetric evidence of single T_g in each of the DSC thermograms for the solution-cast s-PS/PVME blends of various compositions, as indicated in the plotted curves. The as-cast blend samples might contain some solvent-induced crystallinity as the s-PS component in the blends is semicrystalline. The blends could be brought to amorphous by quenching from above the melt state. However, because of phase separation phenomenon at lower critical solution temperature, quenching into an amorphous state could not be used in this system without inducing phase separation in the blends. Note that the DSC thermograms for certain s-PS/PVME compositions (e.g. 50/50, 70/30) show significant broadening of the T_g transition.

To further confirm the T_g behaviour of this blend system and to examine possible influence of slow phase change during solvent evaporation, blend samples were prepared by an alternate method. The same solvent was used in mixing these two components, but, instead of casting into films by evaporation, the mixtures were fast precipitated out from solution by adding methanol. The blend samples after precipitation and filtering were properly dried and their T_g was characterized. Fig. 2a–e shows again single T_g in each of the DSC thermograms for the precipitated s-PS/PVME blends of five compositions. Again, the precipitated blend samples might contain some crystallinity as solvents are known to induce crystallization in s-PS. The T_g behaviour of the blend sample in this figure is generally similar to that of the solution-cast blend samples, suggesting that the phase stability was not influenced by the different methods of blend preparation (i.e. slow evaporation/casting versus fast precipitation). In this figure, two s-PS/PVME compositions (50/50, 70/30) show significant broadening of T_g transition, which is similar to the T_g broadening phenomenon observed in the previous figure shown earlier. The T_g broadening phenomenon may raise concerns of uncertainty of miscibility in the s-PS/PVME. However, experiments were performed in this study to demonstrate, to be shown in following sections, that the broadening scales in the s-PS/PVME blends are roughly the same as those observed in classical a-PS/PVME miscible blend systems prepared using the same solvent and same solution casting method.

For direct comparison between the phase behaviour of s-PS/PVME with classical a-PS/PVME, blends of a-PS/PVME were prepared using exactly the same solvent and

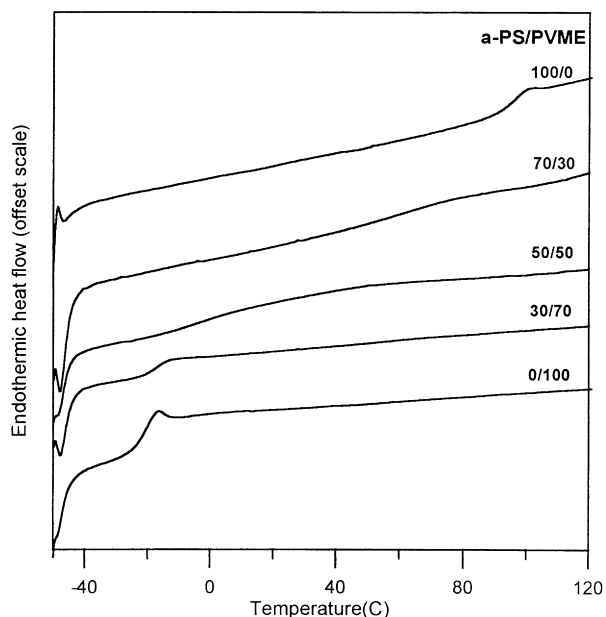


Fig. 3. Glass transition for a-PS/PVME blends of three compositions (30/70, 50/50 and 70/30) in comparison with neat a-PS and PVME.

blending methods. Although the phase behaviour of classical a-PS/PVME was extensively reported, none of the results were obtained using the solvent that we used here for s-PS/PVME. Thus, it was worthwhile for side-by-side comparison to perform the same experiments on this classical a-PS/PVME pair prepared using the same solvent (1-chloronaphthalene). As it was for comparison purposes, only three compositions of a-PS/PVME were prepared and characterized. Fig. 3a–c shows single T_g for the a-PS/PVME blends (solution-cast) of three compositions (30/70, 50/50 and 70/30). The T_g behaviour of the a-PS/PVME blend sample in this figure is generally similar to that of the s-PS/PVME blend samples of corresponding compositions. Again, two a-PS/PVME compositions (50/50, 70/30) show significant broadening of T_g transition. This phenomenon is similar to the T_g broadening phenomenon

observed in the s-PS/PVME shown in previous figures. Bank et al. [2] suggested that apparent single T_g (but broadened) in classical a-PS/PVME (toluene cast) blend systems does not necessarily imply uniform molecular-scale miscibility and that a possibility can not be precluded that molecular aggregation is small and beyond the detection limit of the thermal transition technique. This may be the same case in the present s-PS/PVME blend.

Table 1 lists the numerical values of glass transition temperature and the transition breadth for s-PS/PVME blend in comparison with those for the a-PS/PVME blend. Apparently the results for these two systems are reasonably comparable, indicating the phase behaviour of these two blend systems are similar. Thus, the tacticity does not seem to be a factor influencing the miscibility state of the blend systems.

3.3. Effects of solvents

For the classical blends of a-PS with PVME, it was reported that the phase behaviour of this blend is strongly influenced by solvent. Bank et al. [2] found that clear films of PS-PVME are obtained upon casting from toluene or benzene, but, the blends appeared visually incompatible (phase separation) upon casting from methylene chloride, trichloroethylene or chloroform. Note that toluene or benzene could not be used in preparing s-PS/PVME mixture as the semicrystalline s-PS was not soluble. The results in this study also indicated that the different blending solvent (or temperature) influenced the phase behaviour. A high-boiling solvent of 1-chloronaphthalene (120°C) was used in this study. Using this solvent, the results indicated that the behaviour of s-PS/PVME was similar to that in a-PS/PVME. Thus, this study proceeded by performing experiments on samples prepared using this method. For close comparison, blend samples of s-PS/PVME were prepared and another set of a-PS/PVME samples were also prepared using exactly the same procedures. Both sets of

Table 1
Glass transition temperature and the transition breadth of s-PS/PVME blends

% s-PS	T_g (°C)	Transition breadth (°C)
s-PS/PVME blend		
0/100	– 29	8.0
30/70	– 22.6	7.9
50/50	– 9	35
60/40	10.5	37
70/30	30	32
80/20	56	25
100/0	97	7.0
a-PS/PVME blends		
0/100	– 29	8
30/70	– 22	8.1
50/50	– 15	32
70/30	35	36
100/0	90	9.1

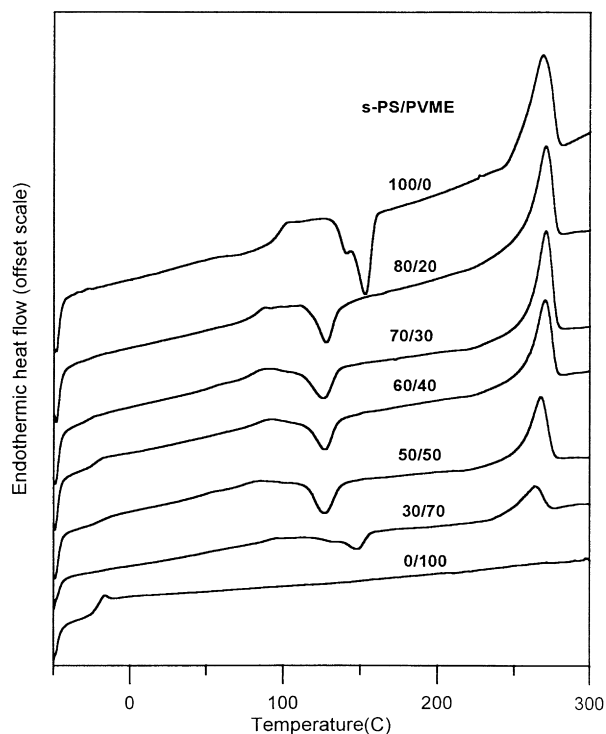


Fig. 4. DSC thermograms of s-PS/PVME blends (five compositions) showing two distinct phases after being quenched from 300°C to -50°C.

samples were characterized and analysed and compared directly to avoid possible sensitive effects of solvents, temperatures or other preparation procedures.

3.4. Temperature dependence of phase behaviour

The LCST phenomena were extensively reported for classical blends of a-PS/PVME [14,15]. Nishi et al. [15] suggested that there may exist an unstable region where phase separation can take place by a spinodal mechanism rather than by nucleation and growth. For the classical a-PS/PVME system, a lower critical solution temperature (LCST) of approximately 120°C–160°C (depending on composition) was reported for most compositions except for two extreme compositions. The cloud point (lower critical solution temperature) transition for the s-PS/PVME blend samples could not be conveniently observed because of presence of crystallinity. Nevertheless, dependence of phase stability on temperature of these blends of various compositions was tentatively examined using an optical microscope. The blend samples were microscopically inspected on a microscope heating stage at slowly elevating temperatures up to 300°C to monitor whether or not a cloud-point transition could be observed. For this s-PS/PVME, the presence of crystallinity would somewhat obscure observation of precise temperature location of LCST. However, solution-cast films of s-PS/PVME would appear semi-transparent if the films were made thin enough. At temperatures of about 120°C and above, the originally transparent/translucent thin film (with some crystallinity) of s-PS/PVME blend

was found to transform into a more cloudy appearance, indicating gross phase separation.

To investigate the transition and phase behaviour of s-PS/PVME after being heated to above LCST, samples were thermally treated at 300°C prior to DSC scanning. Note that there might be some degradation of PVME at 300°C, but the thermal exposure at 300°C was kept short (rapidly heated the samples to 300°C, then quenched immediately). The slight extent of degradation of PVME would not be regarded to interfere with our interpretation. Fig. 4a–e shows the DSC thermograms of s-PS/PVME blends (5 compositions) after being quenched from 300°C, which is above the melting temperature of s-PS. Note that this temperature of 300°C is also well above the LCST temperatures of the s-PS/PVME blend of all compositions. Apparently in this figure, two T_g s (at -25°C to -30°C and 80°C, respectively) are seen in each of these five compositions (s-PS/PVME = 30/70, 50/50, 60/40, 70/30 and 80/20). Expectedly, if phase separation took place at above LCST and the chain mobility was frozen, the phase-separated structure can be preserved as a result of fast quenching to temperatures below LCST (also below the blends T_g). Thus, two T_g s representing these two phases should be observed. The fact that the T_g s of these two separated phases are slightly different from those of two neat components (-30°C for PVME and 95°C for s-PS) indicates that each of the separated phases (PVME-rich and s-PS rich, respectively) retains part of the other component. At above LCST, phase separation took place and led to two partially miscible phases, with one phase being PVME-rich and the other being s-PS rich. In this discussion, the crystalline phase of s-PS is excluded as the miscibility issue is generally confined to amorphous domains.

Again, for direct comparison of this s-PS/PVME blend with the classical a-PS/PVME system, quenched samples of a-PS/PVME of three compositions were prepared and characterized. Fig. 5a–c shows the DSC thermograms of a-PS/PVME blends after being quenched from 300°C. Two T_g s (at -25°C to -30°C and 75°C to 80°C, respectively) are seen in each of the thermograms (a-PS/PVME = 30/70, 50/50, 70/30). This phenomenon of 'frozen' phase separation in quenched samples for the classical a-PS/PVME blend is strikingly similar to that observed in the s-PS/PVME blend discussed in the previous figure. Again this comparison demonstrates that the phase behaviour of the s-PS/PVME and a-PS/PVME system is similar.

Table 2 lists the numerical values of glass transition temperature of two separated phases in quenched s-PS/PVME blend samples in comparison with those for the a-PS/PVME blend of same compositions. Since the transition breadth for the separated phases is significantly reduced and becomes approximately the same for most glass transition, thus, the transition breadth is not listed in this table for comparison. Apparently, within some experimental deviation, the T_g results for separated phases in these two systems are reasonably comparable, indicating the LCST behaviour and phase

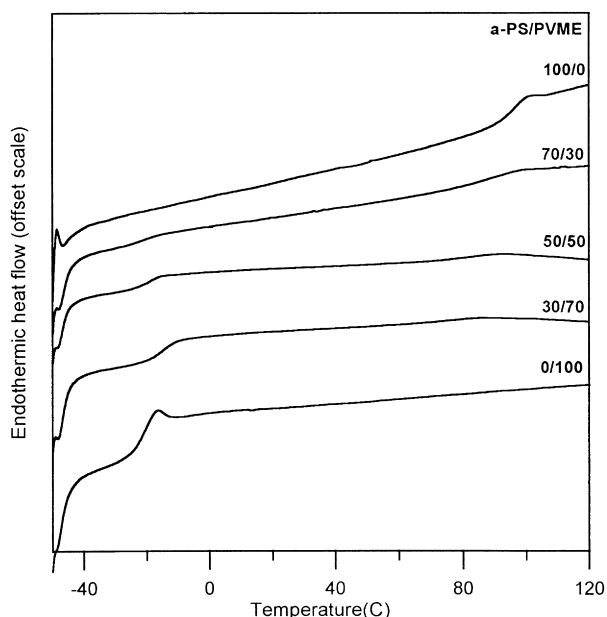


Fig. 5. DSC thermograms showing two phases in a-PS/PVME blends after being quenched from 300°C.

structure following LCST-induced phase separation in the s-PS/PVME blend system are similar to those in the classical a-PS/PVME.

To investigate reversibility of the LCST phase separation, two s-PS/PVME samples (70/30) were prepared. One sample was prepared by heating a virgin cast blend of s-PS/PVME (70/30) to above LCST at 300°C then fast quenched ($320^{\circ}\text{C min}^{-1}$) to -50°C . The other sample was prepared by heating the same blend of s-PS/PVME (70/30) to above LCST at 300°C, but, then slowly cooled (at $1^{\circ}\text{C min}^{-1}$) down to -50°C . These two samples (fast quenched and slowly cooled) were then scanned, respectively, at $20^{\circ}\text{C min}^{-1}$ from -50°C to 300°C to reveal their glass transition behaviour. Fig. 6 (Curves *b* and *c*) shows the DSC thermograms of these two samples of

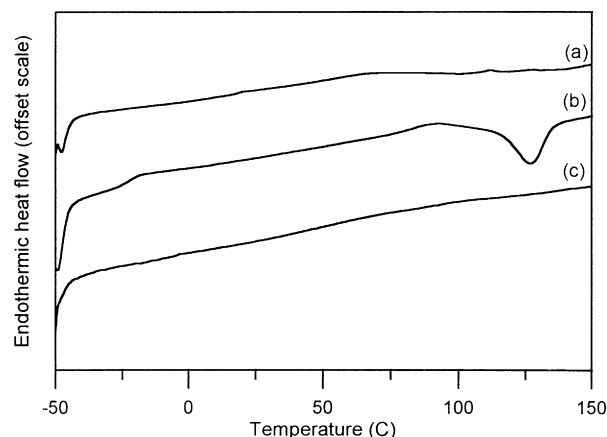


Fig. 6. DSC thermograms of s-PS/PVME (70/30): (a) virgin solution-cast sample; (b) quenched sample; and (c) heated to 300°C and slow-cooled sample.

s-PS/PVME (70/30) in comparison to DSC Curve-*a* of a virgin solution-cast sample of the same composition (70/30). Curve-*b* (quenched sample) shows clearly two T_g 's (-30 and 80°C , respectively), indicating two separated phases being 'frozen' as a result of quick cooling from above LCST. Curve-*c* (slow-cooled sample) is similar to the virgin cast-sample and shows only one broad T_g (onset at about 25°C). Apparently, two phases are 'frozen' as a result of quick cooling and remain to be in a state of phase separation as the temperature is quickly lowered below LCST. Kinetically, this two-phase morphology is preserved at below LCST upon fast cooling because the chain mobility is not quick enough to respond to thermodynamic driving force induced by lowering the temperature. On the other hand, upon cooling at slow rates, the polymer chains can gradually re-organize and eventually return to the original phase structure below LCST. Thus, at slow cooling, the phase-separated morphology can be reversed to an original molecular state of aggregation that is represented by a single, but broad T_g .

Table 2

Temperature (onset) of glass transition of separated phases in s-PS/PVME mixtures after quenching from above LCST in comparison with classical a-PS/PVME mixtures

Composition	$T_{g,1}$ ($^{\circ}\text{C}$)	$T_{g,2}$ ($^{\circ}\text{C}$)
s-PS/PVME		
0/100	-29	—
30/70	-23.7	79
50/50	-24	69
60/40	-26	75
70/30	-25	73
80/20	-24	76
100/0	—	97
a-PS/PVME		
0/100	-29	—
30/70	-23	71
50/50	-24.4	72
70/30	-24.5	79
100/0	—	90

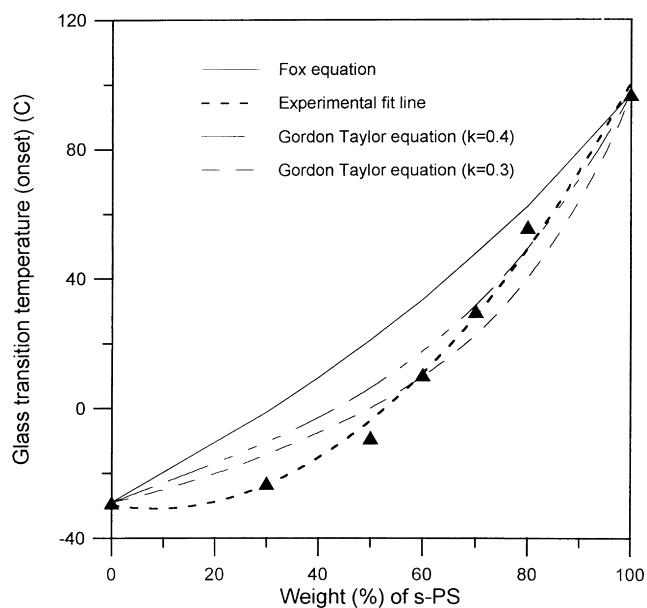


Fig. 7. Asymmetric dependence of T_g of s-PS/PVME blend on composition.

3.5. Interactions and T_g -composition relationship

Fig. 7 shows the T_g data of the s-PS/PVME blend plotted as a function of composition (weight % of s-PS in blend). The asymmetry in the relationship suggests a probable uneven contribution of the individual polymer components to blend's T_g . The upper portion of the curve (s-PS-rich compositions) represents characteristics of approaching molecular-scale miscibility, while the lower portion (compositions of PVME-rich) probably indicates a larger scale of homopolymer molecular aggregation leading to a borderline miscibility. A few other miscible blend systems containing one crystalline polymer can also exhibit such behaviour of asymmetric T_g -composition relationships [16,17]. Note that the classical a-PS/PVME (completely amorphous) also exhibits such characteristics [2], therefore, initial crystallinity in this s-PS/PVME is not a factor leading to an asymmetry relationship of T_g versus composition.

Apparently, the Fox equation [18] does not fit the T_g relationship. Additionally, because of the asymmetry, even the Gordon–Taylor equation [19] with a best-fitted k parameter will not describe the entire composition range, but over-predict the lower portion (PVME-rich) while under-predict the upper portion (s-PS rich). Nevertheless, if the lower portion (PVME-rich) is ignored and a best fit is performed on the portion of data of s-PS rich blend compositions (upper portion) with the Gordon–Taylor equation [19]:

$$T_g = (\omega_1 T_{g1} + k \omega_2 T_{g2}) / (\omega_1 + k \omega_2) \quad (1)$$

where ω_i is the mass fraction of component i and $k = \Delta C_{p2} / \Delta C_{p1}$, i.e. ratio of heat capacity change of PVME polymer (the low- T_g component, $T_{g1} = -30^\circ\text{C}$) to the change of s-PS (the high- T_g component, $T_{g2} = 95^\circ\text{C}$) at T_g .

Note that $k = 1.0$ in the Gordon–Taylor model leads to a

limiting case of linear relationship of mixture T_g versus composition, indicating systems with excellent or perfect intermolecular interactions. The parameter (k) in the Gordon–Taylor equation was suggested to correlate with the intensity of interaction forces between the constituent molecular segments [20]. The best fitted k value was about 0.4 for the PS-rich compositions, while an even lower value of k (0.1–0.2) was roughly acceptable for describing the lower portion (PVME-rich) of the T_g -composition data. Thus, the PS/PVME blend of entire composition range might be miscible, but the intermolecular forces between the PVME-PS pair in the PVME-rich compositions are generally lower than those between the same pair within the PS-rich compositions. Another possibility is that the molecular aggregation phenomenon is more significant for the PVME-rich compositions, leading to borderline miscibility for the polymer mixtures within these compositions.

Hsu et al. [21] conducted a detailed spectroscopy study on classical a-PS/PVME blends in compatible or non-compatible state and concluded that the vibrations most sensitive to change in molecular environments of compatibility are the CH out-of-plane bending (700 cm^{-1}) in PS and C–O–CH₃ stretching (1100 cm^{-1}) of PVME. The change, either in terms of wavenumber for the 700 cm^{-1} peak or intensity for the 1100 cm^{-1} peak, is relatively minor. All this suggests that interactions, if any, between the PS and PVME molecular segments are rather weak. Regardless of the difference in tacticity in s-PS and a-PS, similar weak interactions may be expected to occur between s-PS and PVME, leading to similar phase behaviour for s-PS/PVME and a-PS/PVME alike.

4. Conclusion

Solvent-blended samples of s-PS/PVME were investigated using thermal analysis (T_g), optical microscopy (LCST) and scanning electron microscopy (phase structure). This study provides comprehensive information to suggest that the miscibility and phase behaviour in the syndiotactic s-PS/PVME mixtures are similar to those in classical a-PS/PVME. The miscibility state in s-PS/PVME is equivalent to that in a-PS/PVME. In this study on s-PS/PVME, the difference in tacticity of the polymer chains was not a factor influencing the phase behaviour. Polymer miscibility is generally in the amorphous domain of polymer mixtures. In the amorphous domains, polymer chains of a particular tacticity are not likely to display a fixed spatial order to affect molecular interactions.

Similar to the behaviour already reported in the literature regarding the classical amorphous a-PS/PVME, this semi-crystalline s-PS/PVME system exhibits similar scales of molecular aggregation depending on composition. The changing intermolecular mixing versus homopolymer aggregation lead to a single T_g but with asymmetric composition dependence and with various extents of broadening

that reflect corresponding homopolymer aggregation scales. At intermediate compositions, more significant homopolymer aggregation of either polymer (s-PS or PVME) results in still a single T_g but with distinct broadening. In addition to the broadening, another peculiar behaviour is the asymmetry dependence of T_g on composition. The s-PS/PVME blends of compositions richer in s-PS exhibit a miscibility state closer to prediction by the Fox equation or Gordon–Taylor. This can be interpreted that the molecules of PVME, as a minor component in the mixtures, more intimately mingle with the s-PS molecules. Thus, less homopolymer aggregation of PVME molecules leads to a single T_g representing a phase structure approaching better inter-molecular mixing. The asymmetry also points out that the T_g of the mixtures rich in PVME is more depressed from what would be predicted by the Fox equation. The maximum deviation occurs at compositions with PVME contents ranging from 80 to 50 wt%. An interesting characteristic in this system is that the T_g of the mixtures with PVME contents between 100 and 80 wt% is relatively insensitive to the increasing contents of s-PS. This can be interpreted that the molecules of PVME, as a major component in the mixtures, may aggregate among the homopolymer more readily than they would mingle with the s-PS molecules. Thus, more significant aggregation of PVME molecules leads to a T_g that is relatively insensitive to the presence of still minor s-PS contents. Note that similar behaviour has also been observed and discussed by Bank et al. for classical a-PS/PVME [2]. The phase behaviour of s-PS/PVME agrees mostly with that of a-PS/PVME, indicating that the tacticity does not influence the interactions between PS and PVME molecules.

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