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Effect of copolymer composition on the miscibility of poly(styrene-*co*-acetoxystyrene) with phenolic resin

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Abstract

The miscibility behavior and specific interaction of phenolic/polystyrene-*co*-acetoxystyrene, (PS-*co*-PAS) blends by varying acetoxystyrene contents of the PS-*co*-PAS copolymer were investigated by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR). A miscibility window was found when the acetoxystyrene fraction in the copolymer is higher than 45 mol% in phenolic/PS-*co*-PAS = 50/50 blend system. Painter–Coleman Association Model (PCAM) is able to predict the miscibility window at 150°C compared with our experimental results based on DSC analyses. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymer blend; Hydrogen bonding; Miscibility window

1. Introduction

It is well known that most polymer blends are immiscible due to a high degree of polymerization. Therefore, the entropy term becomes vanishingly small and the miscibility is increasingly dependent on the nature of the enthalpic term contribution. As a result, phase behavior of polymer blends is strongly affected by intermolecular association. To enhance the formation of a one-phase system in polymer blends, it is necessary to ensure that favorable specific intermolecular interaction exists between two base components of the blend. Ideally, one polymer possesses donor sites and the other acceptor sites on the chain, such as hydrogen bonding [1–7]. The miscibility of an immiscible blend can be enhanced by introducing a functional group to one component capabling of forming intermolecular association with another component [8]. In our previous study, on the role of intermolecular association in miscibility enhancement, we found that the incorporation of a small amount of hydrogen bonding acceptor (such as acetoxystyrene) into the polystyrene chain renders the modified polymer to be miscible with phenolic resin, a well known hydrogen bonding donor [9]. The purposes of this study are (1) to investigate blends of phenolic resin with PS-*co*-PAS, (2) to provide evidence of specific intermolecular association by using Fourier transform infrared spectroscopy and (3) to predict whether a miscibility window exists for the PS-*co*-PAS blend by using the Painter–Coleman Association Model [10] (PCAM). Experimental data obtained using the PCAM result in successful prediction of the miscibility behavior.

2. Experimental

2.1. Samples

The novolac type phenolic resin (Fig. 1) was synthesized by condensation reaction using sulfuric acid as catalyst and the average molecular weights of $M_n = 500$ and $M_w = 1200$ were obtained.

The poly (styrene-*co*-acetoxystyrene) copolymer (PS-*co*-PAS, Fig. 1) was obtained through radical polymerization of styrene and *p*-acetoxystyrene monomers (AS) using AIBN initiator (1 wt% based on monomer) at 60°C under nitrogen atmosphere. The product was dissolved in benzene, and then poured into excess methanol under vigorously agitation to precipitate the copolymer. The copolymers were characterized by Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

2.2. Blend preparation

Blends of phenolic/PS-*co*-PAS = 50/50 were prepared by solution blending. Tetrahydrofuran solution containing

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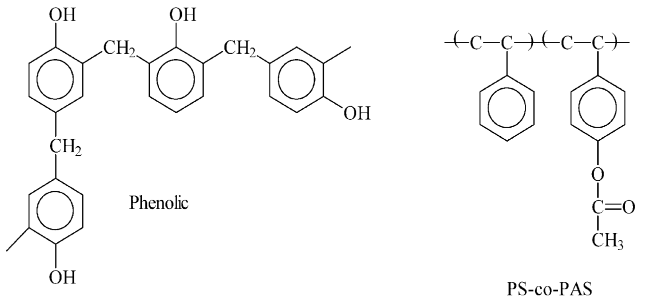

Fig. 1. Chemical structures of phenolic and PS-*co*-PAS.

5 wt% polymer mixture was stirred for 6–8 h, and the solution was allowed to evaporate slowly at room temperature for 1 day. The blend film was then dried at 50°C for 2 days.

3. Characterizations

3.1. Differential scanning calorimetry

T_gs of polymer blend films were determined by a DSC from Du-Pont (DSC-9000). The scan rate was 20°C min^{-1} within the temperature range of 30–150°C and held at 150°C for 10 min to ensure complete remove of the residual solvent. The measurement was carried out using 5–10 mg sample on a DSC sample cell after the sample was quickly cooled to −50°C from the melt of the first scan. The glass transition temperature is at the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glass lines.

3.2. Infrared spectroscopy

Infrared spectra of polymer blend films were determined by using the conventional NaCl disk method. The THF solution containing the blend was cast onto NaCl disk and dried under condition similar to that used in the bulk preparation. The film used in this study was sufficiently thin to obey the Beer–Lambert law. FT-IR measurement was recorded on a Nicolet Avatar 320 FT-IR spectrophotometer and 32 scans were collected with a spectral resolution 1 cm^{-1}. Samples containing hydroxyl groups are water sensitive; a pure nitrogen gas was used to purge the IR optical box in order to maintain sample film dry.

4. Results and discussion

4.1. Copolymer analyses

Fig. 2 shows scale expanded infrared spectra recorded in the region from 1550 to 1900 cm^{-1} for neat PS, neat PAS and various PS-*co*-PAS copolymers at room temperature. The carbonyl group absorption is at 1763 cm^{-1} and the absorption at 1600 cm^{-1} is related to the C=C stretching vibrations of the benzene ring. The intensity of the carbonyl increases with the increase of the PAS content in the PS-*co*-PAS copolymer as would be expected. This simply reflects the stoichiometry from the quantitative measurement by Beer's–Lambert law. Fig. 3 shows the DSC curves of PS-*co*-PAS copolymers from 60 to 160°C. The glass transition temperature increases with the increase of the PAS content

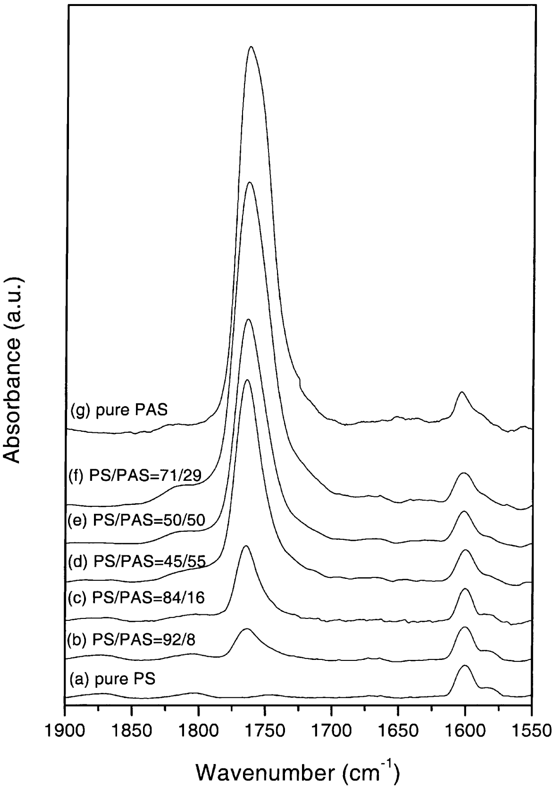

Fig. 2. The IR spectra at 1550–1900 cm^{-1} of pure PS, pure PAS and PS-*co*-PAS copolymers with different PAS contents at room temperature.

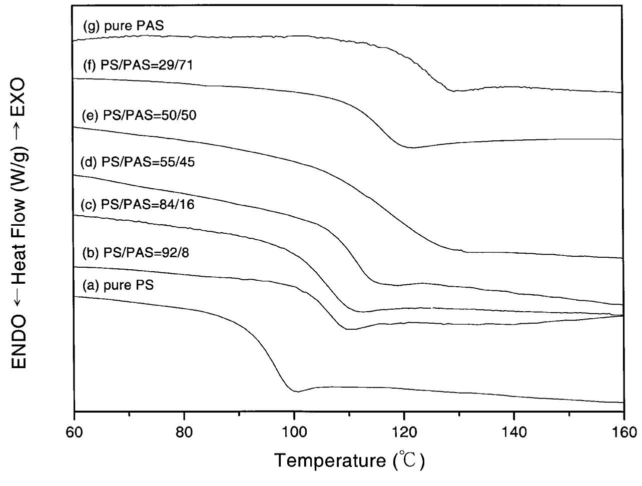

Fig. 3. DSC thermograms of pure PS, pure PAS and PS-*co*-PAS with different PAS contents: (a) pure PS (b) PAS8 (c) PAS16 (d) PAS45 (e) PAS50 (f) PAS71 (g) pure PAS.

Table 1
Information on poly (styrene-*co*-acetoxystyrene) in this study

Polymer	Monomer feed (mol%)		Polymer composition (mol%)		T_g	M_n
	Styrene	AS	Styrene	AS		
PS	100	0	100	0	96.90	24500
PAS8	93.97	6.03	91.77	8.23	106.36	22600
PAS16	91.27	8.73	83.67	16.33	107.33	19850
PAS45	69.79	30.21	54.22	45.78	112.27	26400
PAS50	60.90	39.10	49.48	50.52	116.37	25400
PAS71	34.18	65.82	28.60	71.40	118.16	23200
PAS	0	100	0	100	122.20	21500

in the PS-*co*-PAS copolymer. The properties of synthesized PS-*co*-PAS copolymers are summarized in Table 1. Table 1 lists the monomer feed ratio and resultant copolymer compositions from which reactivity ratios were calculated using the methodology of Kelen and Tudos [11–12]. The Kelen–Tudos equation is given by Eq. (1)

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \tag{1}$$

where

$$\eta = \frac{G}{(\alpha + F)} \qquad \text{and} \qquad \xi = \frac{F}{(\alpha + F)}$$

F and G can be obtained by the quantities of x and y, where $x = M_1/M_2$ is the ratio of molar concentration of monomer 1 and 2, and $y = dM_1/dM_2$ is the mole ratio of these monomers in the copolymer, $F = x^2/y$ and $G = x(y-1)/y$. Parameter α is suitably obtained by Eq. (2)

$$\alpha = \sqrt{F_m F_M} \tag{2}$$

where F_m and F_M are the lowest and highest F from the experimental data. Plotting of η versus ξ, we can obtain r_2 and r_1 from the intercept and slope. The results are shown in Fig. 4 from which values of $r_{ps} = 0.72$ and $r_{pas} = 2.34$ are calculated.

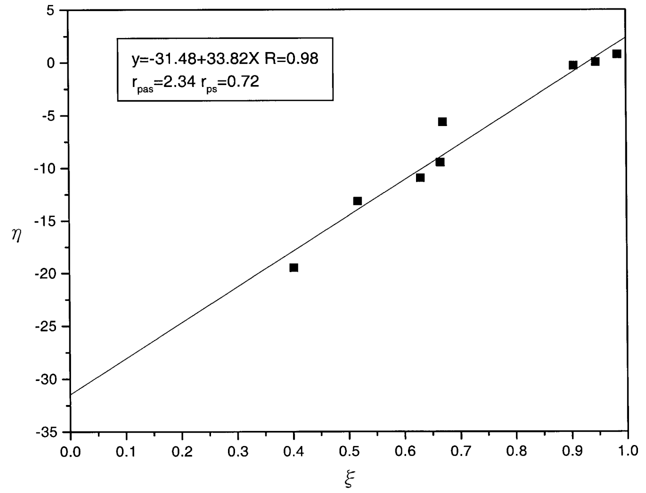

Fig. 4. Kelen–Tudos plot for PS-*co*-PAS copolymers.

4.2. Thermal analyses

Glass transition behaviors for blends of phenolic with the various PS-*co*-PAS were examined by DSC and the results as shown in Fig. 5. Fig. 5 shows typical results for selected PS-*co*-PAS with a wide range of PAS levels while Table 2 summarizes whether one or two T_g values were noted for all phenolic/PS-*co*-PAS = 50/50 blends. Blends of the phenolic with PS-*co*-PAS containing 45 or higher mol% of PAS exhibit a single glass transition, which indicates complete miscibility within this window of PAS contents.

4.3. FT-IR analyses

FT-IR spectroscopy has been successfully applied in polymer blends possessing intermolecular interaction through hydrogen bonding [13–16]. Fig. 6 shows the infrared spectra measured at 25°C ranging from 1680 to 1820 cm^{-1} for various phenolic/PS-*co*-PAS = 50/50 blends containing different PAS contents in PS-*co*-PAS copolymers. The carbonyl stretching of these blends is split into two bands, absorption by free and hydrogen-bonded carbonyl groups at 1763 and 1735 cm^{-1}, respectively. Quantitative analyses of these carbonyl bands can provide a direct

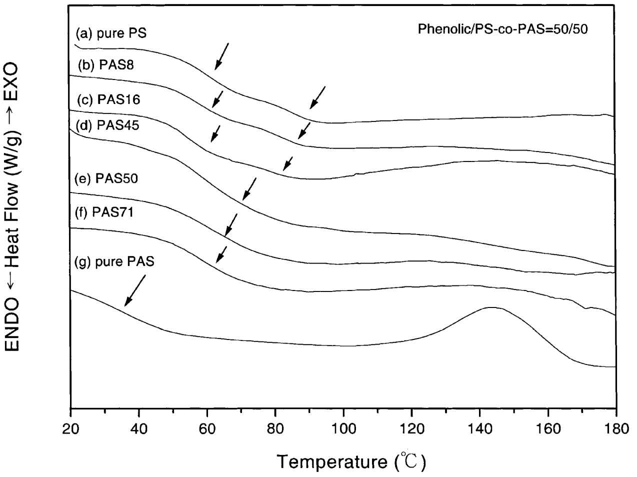

Fig. 5. The DSC curves of phenolic/PS-*co*-PAS = 50/50 blends containing different contents (a) pure PS (b) PAS8 (c) PAS16 (d) PAS45 (e) PAS50 (f) PAS71 (g) pure PAS.

Table 2
The DSC thermograms of phenolic/PS-*co*-PAS = 50/50 for various PAS contents

Compositions		T_g	
Phenolic/PS	60.74		84.83
Phenolic/PAS8	59.61		81.35
Phenolic/PAS16	53.16		75.73
Phenolic/PAS45		59.73	
Phenolic/PAS50		60.22	
Phenolic/PAS71		57.61	
Phenolic/PAS		34.51	

measure of the degree of mixing in these polymer blends. Therefore, these bands can be readily decomposed into two Guassian peaks, with areas corresponding to the free carbonyl (1763 cm^{-1}) and the hydrogen-bonded carbonyl (1735 cm^{-1}) absorptions. Knowing the respective absorptivity coefficients, we can calculate from the relative intensities of these two bands. The fraction of the hydrogen-bonded carbonyl group [10] can be calculated by Eq. (3)

$$f_{\mathrm{b}}^{\mathrm{C=O}} = \frac{A_{\mathrm{b}}/1.5}{A_{\mathrm{b}}/1.5 + A_{\mathrm{f}}} \tag{3}$$

A_{b} is the peak area of the hydrogen-bonded carbonyl absorption, A_{f} is the peak area of the free carbonyl absorption. The conversion coefficient of 1.5 is the ratio of these two bands, 'free' and 'hydrogen bonded' carbonyl groups, in an ester group [10]. The curve fitting results are summarized in Table 3. The hydrogen bonded fraction of the carbonyl group increases with the increase of the PAS content in the PS-*co*-PAS copolymer.

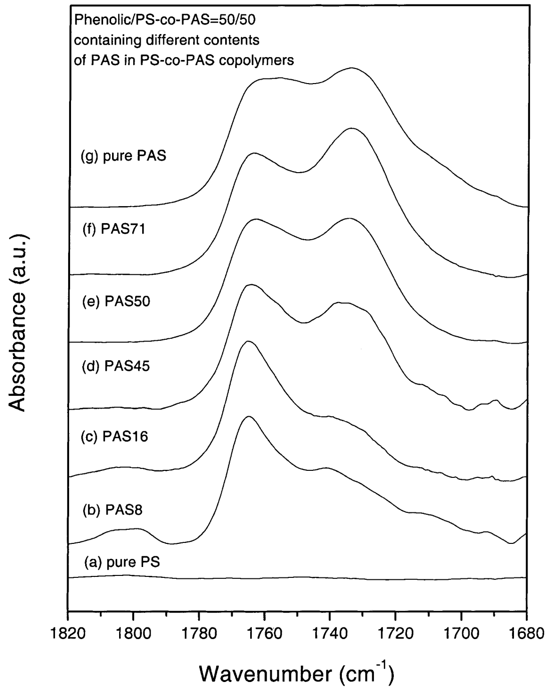

Fig. 6. The IR spectra at 1680–1820 cm^{-1} of Phenolic/PS-*co*-PAS = 50/50 blends containing different PAS contents (a) pure PS (b) PAS8 (c) PAS16 (d) PAS45 (e) PAS50 (f) PAS71 (g) pure PAS.

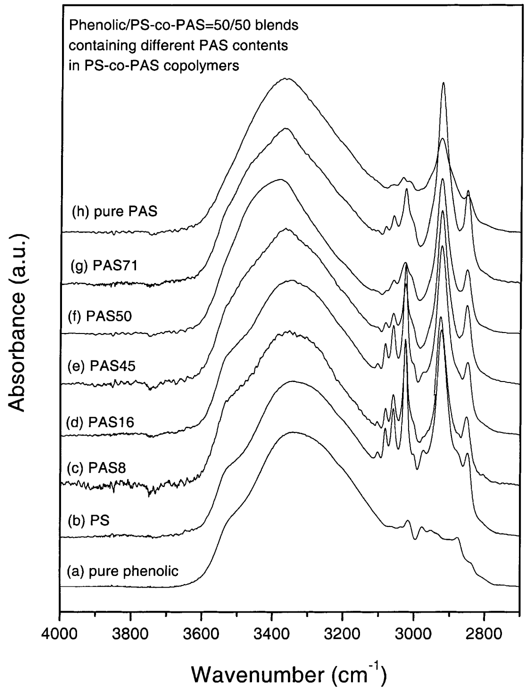

Fig. 7. The IR spectra at 2700–4000 cm^{-1} of pure phenolic and phenolic/PS-*co*-PAS = 50/50 blends containing different PAS contents (a) pure phenolic (b) pure PS (c) PAS8 (d) PAS16 (e) PAS45 (f) PAS50 (g) PAS71 (h) pure PAS.

A comprehensive understanding of the changes occurring in the hydroxy stretching region is important to investigate the phase behavior of polymer blends. Therefore, we now turn our attention to focus on the hydroxy stretching region. Fig. 7 shows the absorption region between 2700 and 4000 cm^{-1} of the pure phenolic and various phenolic/PS-*co*-PAS blends. As shown in Fig. 7(a), the pure phenolic polymer exhibits two bands in the hydroxy stretching region of the infrared spectrum. The free hydroxyl group absorption is located at 3525 cm^{-1}, while the hydrogen-bonded hydroxyl gives a broad absorption at 3350 cm^{-1} due to wide distribution of hydrogen-bonded hydroxyl groups. As also shown in Fig. 7, the intensity of the free hydroxy absorption (3525 cm^{-1}) decreases as the PAS content in the PS-*co*-PAS copolymer is increased from 8 to 100 mol%. The self-association band of the hydroxyl group of in the phenolic shifts into higher frequency at the vicinity of 3380 cm^{-1}, due to shifting from the hydroxyl–hydroxyl bonding to the hydroxyl–carbonyl bonding. We may therefore assign the band at 3380 cm^{-1} to the hydroxyl groups that are hydrogen-bonded to carbonyl groups. Therefore, the blend containing higher PAS content in the PS-*co*-PAS copolymer has greater amount of hydrogen bonding than that of the lower PAS content to form one phase system more preferably. The presence of a significant fraction of hydrogen bonding may give a well-mixed system, but it does not necessarily imply the existence of a thermodynamically

Table 3
Curve fitting results of Phenolic/PS-*co*-PAS = 50/50 at room temperature

PAS content	Free C=O			H-bonded C=O			F_b (%)
	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_f (%)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_b (%)	
8PAS	1763.8	14.85	52.93	1738.8	22.96	47.07	37.21
16PAS	1764.7	13.76	52.70	1742.5	26.41	47.30	37.43
45PAS	1763.9	15.85	39.66	1735.8	25.98	60.34	50.35
50PAS	1762.9	17.76	39.23	1735.0	24.81	60.77	50.80
71PAS	1763.3	16.69	35.23	1734.3	24.31	64.77	55.06
100PAS	1762.5	17.14	34.24	1735.4	27.78	65.76	56.14

miscible blend [16]. Fortunately, we can use the PCAM to calculate and define the miscibility window. However, this model requires the knowledge of molar volume, molecular weight, solubility parameter, degree of polymerization and equilibrium constants including self-association and inter-association equilibrium constants and we will discuss this in more detail in Section 4.4.

4.4. Painter–Coleman association model analyses

Painter and Coleman [18] suggested adding an additional term accounting for the free energy of the hydrogen bonding formation into a simple Flory–Huggins expression for the free energy of mixing of two polymers as Eq. (4)

$$\frac{\Delta G_N}{RT} = \frac{\Phi_1}{N_1}\ln \Phi_1 + \frac{\Phi_2}{N_2}\ln \Phi_2 + \Phi_1\Phi_2\chi_{12} + \frac{\Delta G_H}{RT} \qquad (4)$$

where Φ and N are the volume fraction and the degree of polymerization, χ is the 'physical' interaction parameter and subscripts 1 and 2 refer to the blend components. ΔG_H is the free energy change contributed by the hydrogen bonding between two components, which can be estimated by FT-IR [19]. This equation ignores the free volume change and other complications [20,21]. All parameters required estimating the miscibility window for the homopolymer–copolymer blend by the PCAM are listed in Table 4.

According to the Painter–Coleman Eq. (4), two major factors are responsible for this increase in the miscibility window. Firstly, when the difference in the solubility parameters of two polymer components of the blend decrease, the value of χ will decrease. Therefore, incorporation of poly (acetoxystyrene) (10.29 cal cm^{-3}) into polystyrene (9.48 cal cm^{-3}) will decrease its solubility parameter difference with the solubility parameter of phenolic (12.05 cal cm^{-3}). Secondly, the strength of inter-association over self-association increases with the increase of the PAS content in the PS-*co*-PAS copolymer that tends to enhance the favorable contribution from the $\Delta G_H/RT$ term in Eq. (4) and results in a favorable trend for miscibility. Fig. 8 shows the theoretical predicted miscibility window for phenolic/PS-*co*-PAS blends at 150°C by the PCAM. We choose 150°C to compare the theory with experiment data because this temperature is above the glass transition temperature and the DSC curves were experimentally obtained by quenching the sample from this temperature. Therefore, it

Table 4
Parameters for estimating the critical composition of homopolymer–copolymer blend by using the Painter–Coleman equation

	Equilibrium constant K (25°C)	Enthalpy, Δh (kcal/mole)
Self-association[a]		
Dimer formation K_2	23.29	−4.246
Multimer formatin K_B	52.31	−6.110
Inter-association between phenolic and PAS[b]	64.60	−3.875

Polymer	Molar volume (ml mol^{-1})	Molecular weight (g mol^{-1})	Solubility parameter (cal ml^{-1})$^{0.5}$	Degree of polymerization (DP)
Phenolic[a]	84	105	12.05	6
PAS[c]	128.60	162.20	10.29	132
PS[c]	93.90	104.15	9.48	235

[a] Ref. [22].
[b] Ref. [9].
[c] Estimated by using a group contribution method proposed by Coleman et al. [10].

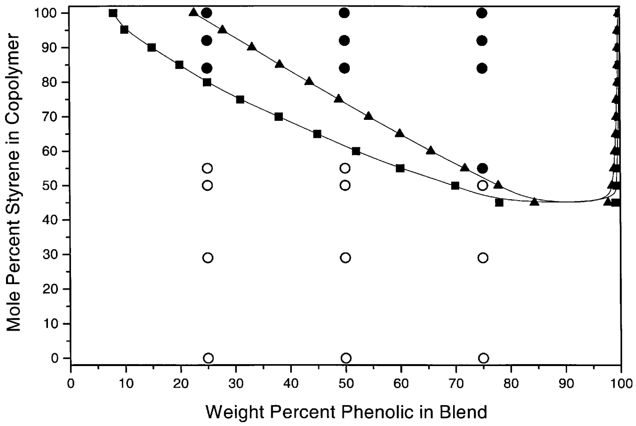

Fig. 8. The theoretical miscibility window of phenolic/PS-*co*-PAS blends from the PCAM (▲) spinodal curve (■) binodal curve and experimental data (●) two phase system (○) one phase system.

is reasonable to calculate miscibility window by quenching from 150°C that the equilibrium conditions is retained. As also shown in Fig. 8, the x-axis is the weight fraction of phenolic resin in the blend, and the y-axis is the mole percent styrene in the PS-*co*-PAS copolymer. The phenolic resin is predicted to be completely miscible with phenolic/PS-*co*-PAS = 50/50 blends with the PAS content higher than 40 mol%. The model gives a precise prediction of the miscibility window at 150°C compared with our experimental results based on DSC analyses.

5. Conclusions

We have ascertained that the incorporation of acetoxystyrene monomer into the polystyrene chain can enhance the miscibility with phenolic, because the value of χ decreases and the inter-association increases between the hydroxyl group in phenolic and the carbonyl group in PAS of PS-*co*-PAS copolymers.

Phenolic was found to be miscible with PS-*co*-PAS copolymers having an acetoxystyrene content higher than 45 mol% in phenolic/PS-*co*-PAS = 50/50 blend system. Furthermore, the PCAM used predicts miscibility of this blend system successfully.

Acknowledgements

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