

# Miscibility and Esterification in the Poly(styrene-*co*-maleic anhydride)/Phenoxy Blends

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**ABSTRACT:** The “miscibility” and esterification in poly(styrene-*co*-maleic anhydride) (PSTMA)/phenoxy blends were investigated by DSC and FTIR. The blends prepared by casting exhibited a single composition-dependent but broad  $T_g$  during the first scanning. The broadness of the  $T_g$  transition range is due to the presence of microphases in the blends, which acquired some stability because of the hydrogen-bonding interactions with the continuous phase. However, the blends displayed two distinct  $T_g$ s during the second scanning, which can be attributed to phenoxy-rich and PSTMA-rich phases dispersed one in another at a scale larger than the initial one. To investigate the effect of esterification, the samples subjected previously to two scannings have been additionally heat-treated several times between 30 and 220°C and annealed each time at 220°C for increasing periods of time. During the additional scannings, the two  $T_g$ s identified during the second scanning increased with increasing annealing time but remained distinct. The fact that the fraction soluble in tetrahydrofuran decreased with increasing annealing time indicates that crosslinking due to esterification has occurred in both phases. The two phases generated after the first scanning were stabilized by the esterification reaction at the interfaces. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 913–919, 1998

**Key words:** miscibility; esterification; differential scanning calorimetry; Fourier transform infrared spectroscopy

## INTRODUCTION

The nature of the miscibility of the two polymers of a blend has been examined for several decades. Although a number of miscible polymers were identified, only a few of them have attracted commercial interest. Most of the polymer blends in practical use are multiphase materials. However, such systems can have stability only if the interface between the two phases is compatible. This compatibility can be achieved by adding interfacially active agents, such as graft or block copolymers, which reduce the interfacial tension between the two phases<sup>1</sup> or by using the reactive

blend method in which a “compatibilizer” is generated *in situ* during the process.<sup>2</sup> One typical example of the reactive blend is the introduction of polar maleic anhydride moieties into a nonpolar polymer, such as polyethylene or polypropylene, the mixing of the obtained copolymer with the polar polyamide, and their melting.<sup>3,4</sup> The reaction between the anhydride moieties and the amide groups generates the compatibilizer. Another example is the transesterification of polyesters, which by randomizing the polymer chain sequences may lead even to a single homogeneous phase.<sup>5</sup> Recently, the reactive blends of poly(styrene-*co*-maleic anhydride) (PSTMA) and poly(ethylene-*co*-vinyl alcohol) were investigated regarding the effect of the blend composition and processing conditions on the mechanical and thermal properties.<sup>6</sup> The interfacial reaction and the

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interdiffusion in the blend of PSTMA and bis-(amine)-terminated low molecular weight polytetrahydrofuran were also studied by FTIR spectroscopy and microscopy.<sup>7</sup> Various methods to prepare tough, compatibilized blends, which employ concentrated emulsions of monomers as precursors, were developed in this laboratory.<sup>8–11</sup>

In this article, the “miscibility” and its dependence on the interactions between PSTMA and phenoxy were investigated. These two polymers possess functional groups, maleic anhydride in PSTMA and hydroxyl in phenoxy, which can provide intermolecular hydrogen bonding and/or can lead to intermolecular esterification.

## EXPERIMENTAL

### Materials

Poly(styrene–maleic anhydride) ( $M_w = 50,000$ , PSTMA, St/MA = 50/50 w/w) and poly(hydroxyl ether of bisphenol A) ( $M_w = 86,000$ , phenoxy) were purchased from Scientific Polymer Products. PSTMA was slightly hydrolyzed, because hydroxyl groups could be identified in the FTIR spectrum. All chemicals were used as received.

### Blend Preparation

Blends with different compositions (PSTMA/phenoxy 0/100, 20/80, 30/70, 40/60, 50/50, 70/30, 80/20, and 100/0 w/w) were prepared by casting at room temperature from tetrahydrofuran (THF) solutions. The thin films were thoroughly dried in a vacuum oven at 50°C.

### FTIR Characterization

The blends were dissolved in THF and cast onto sodium chloride plates. The thin films were thoroughly dried in a vacuum oven at 50°C. The FTIR analysis was carried out using a Perkin–Elmer 1760X Instrument under nitrogen purging. The scanning number was 64 with a resolution of 2  $\text{cm}^{-1}$ .

### Differential Scanning Calorimeter (DSC) Characterization

The thermal behavior of the samples was examined using a DuPont 910 differential scanning calorimeter (DSC) under nitrogen. The samples were scanned from 30 to 220°C at a heating rate

of 20°C/min. After cooling, the samples were scanned several times and held at 220°C for increasing periods of time.  $T_g$  is defined as the midpoint of the heat capacity change ( $\Delta C_p$ ) and the width of  $T_g$  ( $\Delta T_g$ ) as the difference between the end and the onset of the  $C_p$  transition range.

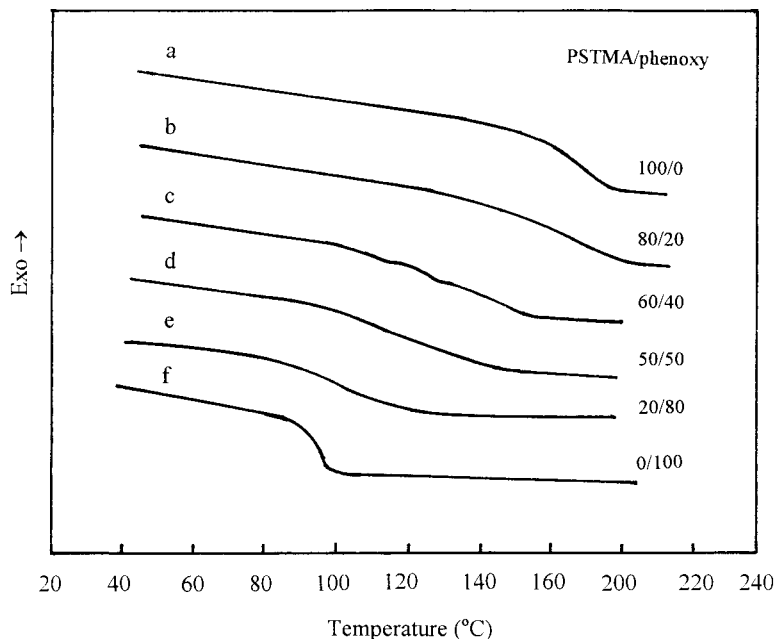
### Solvent Extraction

Two samples of the blend containing 20 wt % PSTMA were annealed at 200°C under nitrogen for 10 and 20 min, respectively; then, they were subjected to THF extraction in a Soxhlet extractor for 24 h. The insoluble fraction remained as a gel. A filter paper was used to remove the extra THF from the surface of the gel and then the gel was quickly weighed. This was followed by THF evaporation in air and drying in an oven at 120°C. The weight of THF in the gel was calculated as the weight difference between the gel and the dried solid. The THF content in the gel was calculated by dividing the amount of THF in the gel by the weight of the dried solid. The insoluble fraction of the annealed blends was calculated as the ratio between the weight of the dried insoluble solid and the initial weight of the blend. The soluble fraction was determined by evaporating the solvent.

## RESULTS AND DISCUSSION

### Miscibility of PSTMA and Phenoxy

Figure 1 shows typical DSC thermograms during the first scanning of the PSTMA/phenoxy blends prepared by casting from THF solutions at room temperature. All the blends exhibit a single, composition-dependent, broad  $T_g$ . It is usually considered that the occurrence of a single, composition-dependent  $T_g$  in blends indicates miscibility, while the occurrence of two  $T_g$ s, immiscibility. However, the presence of a single  $T_g$  does not mean necessarily that the blends are miscible at the molecular scale. As the authors demonstrated,<sup>12</sup> miscibility at the colloidal level can also provide a single, somewhat broader and composition-dependent  $T_g$ . Indeed, a colloidal-scale, uniform dispersion of particles, below 100 nm in size, of poly(*p*-benzamide) (PBA) in Nylon 6(3)T was prepared which had a single  $T_g$  during the first scanning. The existence of a single  $T_g$  was attributed to the hydrogen-bonding interactions between the particles and nylon. During the second



**Figure 1** DSC thermograms of PSTMA, phenoxy, and the as-prepared PSTMA/phenoxy blends during the first scanning.

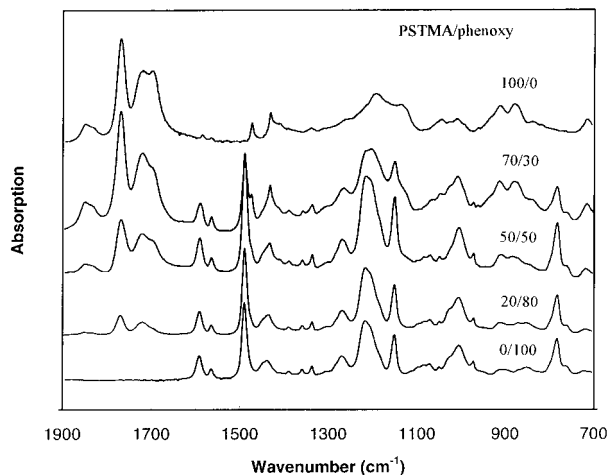
scanning, only the  $T_g$  of the nylon was detected (that of PBA outside the scanning range could not be identified). This was thought to happen because the hydrogen bonding becomes negligible at high temperatures, and as a result, the PBA particles aggregate to larger particles. A similar behavior was noted for PBA colloidal dispersions in a vinyl copolymer<sup>13</sup> and in sulfonated polystyrene.<sup>14</sup> Similarly, Song and others noted<sup>15</sup> that the presence of a single broad  $T_g$  does not indicate molecular miscibility. As is well known,  $\Delta T_g$  is relatively small for pure polymers and for the blends miscible at the molecular scale. However, for the blends miscible at the colloidal or even at the supracolloidal scale,  $\Delta T_g$  can be large, and of course, larger for the supracolloidal scale. The

**Table I**  $T_g$  and  $\Delta T_g$  of the PSTMA/Phenoxy Blends (°C)

PSTMA/Phenoxy (w/w)	$T_g$	$\Delta T_g$	Appearance
0/100	97	9	Transparent
20/80	105	40	Opaque
30/70	113	30	Opaque
50/50	125	50	Opaque
60/40	130	65	Opaque
80/20	160	45	Opaque
100/0	166	18	Transparent

broad  $\Delta T_g$  is due to the microphase separation in the blend.

Table I lists the  $T_g$  and  $\Delta T_g$  for the PSTMA/phenoxy blends and shows that  $\Delta T_g$  is large (30–65°C) for all of them. This indicates that the PSTMA/phenoxy blends are not miscible at the molecular scale. In addition, these amorphous thin films are opaque, which reveals that a microphase at a scale larger than the wavelength of light is present. All the blends investigated exhibited two distinct  $T_g$ s, representing the phenoxy- and PSTMA-rich phases during the second scanning. (The traces for the first and the second scanning are presented in Figure 4, where the effect of esterification is investigated.) Consequently, the miscibility of the PSTMA and phenoxy blends depends on the thermal history. The DSC thermograms of the blends during the first thermal scanning reflect the phase behavior of the blends prepared via casting, while those during the second scanning reflect the phase behavior after the first scanning. The PSTMA/phenoxy blends prepared by casting at room temperature are mixed at a scale for which a single broad  $T_g$  is present. When the blends were subjected to the second scanning, two  $T_g$ s were exhibited, indicating that PSTMA and phenoxy were much more segregated after the first scanning. We propose that this happened because at the temperatures above  $T_g$  the hydrogen-bonding interactions at the interface of the



**Figure 2** FTIR spectra of PSTMA, phenoxy, and PSTMA/phenoxy blends in the range of 700–1900  $\text{cm}^{-1}$  wavenumbers.

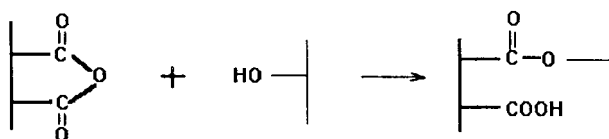
dispersed particles were destroyed and the particles acquired higher mobility. The higher segregation achieved then would make the blends exhibit two  $T_g$ s during the second scanning.

#### FTIR Analysis

Figure 2 presents the FTIR spectra of PSTMA, PSTMA/phenoxy blends, and phenoxy in the range of 700–1900  $\text{cm}^{-1}$ . The characteristic absorptions of PSTMA, due to the maleic anhydride moiety, are at 1780 and 1860  $\text{cm}^{-1}$ , respectively. The characteristic absorptions of phenoxy are at 1515 (*para*-substituted benzene ring stretching), 1250 (ester group), and 829  $\text{cm}^{-1}$  (two adjacent aromatic CH wag vibrations). The intensity ratio of the anhydride C=O stretching to the aromatic CH wag vibration ( $I_{1780}/I_{829}$ ) increases with increasing PSTMA content  $x$  (wt %) in the blends. A linear relationship,  $I_{1780}/I_{829} = 2.8x$ , could be established between  $I_{1780}/I_{829}$  and the PSTMA content, when the latter is less than 50 wt %. The stretching vibration at about 1045  $\text{cm}^{-1}$  of the hydroxyl groups of phenoxy is sensitive to the local environmental changes.<sup>16</sup> Indeed, as shown in Figure 3, the peak position is shifted to high wavenumbers with increasing PSTMA content, indicating the presence of intermolecular hydrogen-bonding interactions between the hydroxyl groups and the anhydride groups. These hydrogen-bonding interactions at the interfaces between the two microphases are responsible for the single and broad  $T_g$  that occurs during the first scanning.

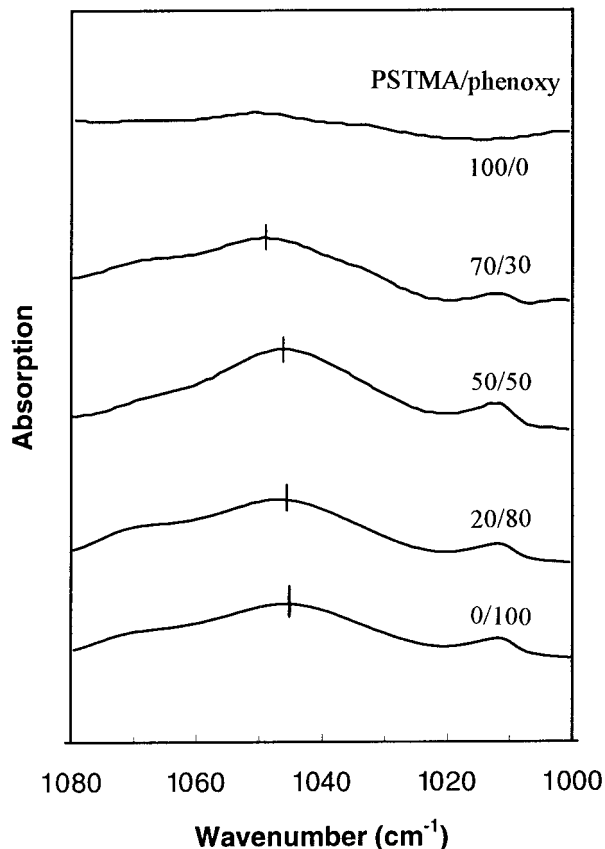
#### Effect of Esterification

To investigate the effect of intermolecular esterification on the thermal behavior of the blends, the samples prepared by casting were subjected to several scanings from 30 to 220°C (with a rate of 20°C/min). After each scanning, they were kept at 220°C for various lengths of time. The following interchain esterification reaction occurs at high temperatures between the anhydride and the hydroxyl groups:

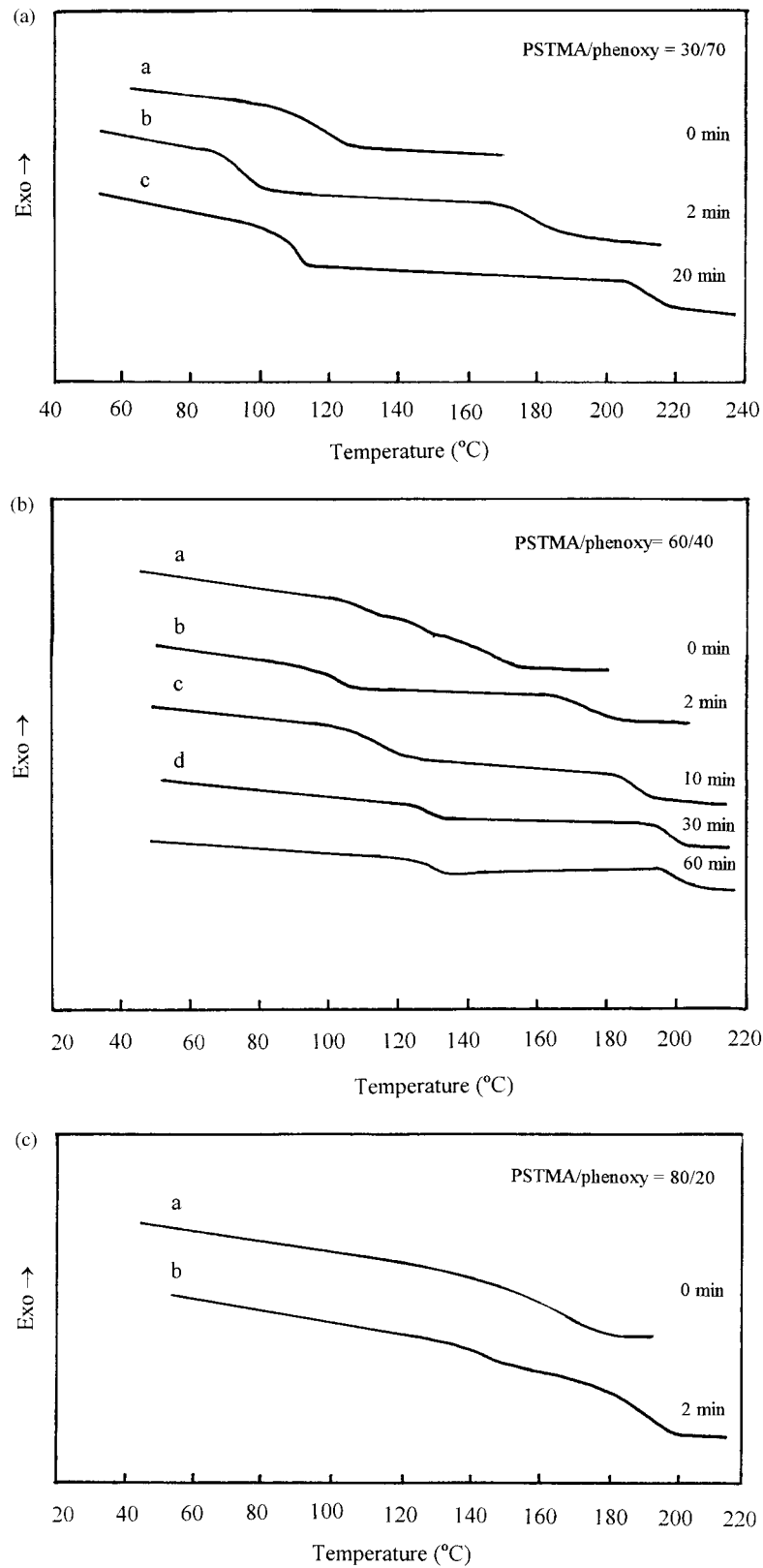


This reaction generates crosslinking in both phases.

Figure 4(a–c) provides DSC traces of the blends with 30, 60, and 80 wt % PSTMA, respectively. Two  $T_g$ s are identified during the second and the additional successive scanings (the time



**Figure 3** FTIR spectra of the secondary alcohol stretching of phenoxy.



**Figure 4** DSC traces of PSTMA/phenoxy blends annealed at 220°C for various lengths of time: (a) PSTMA/phenoxy = 30/70 (w/w); (b) PSTMA/phenoxy = 60/40 (w/w); (c) PSTMA/phenoxy = 80/20 (w/w).

**Table II Insoluble Content of PSTMA/Phenoxy Blends (20/80 w/w) Annealed at 200°C**

Time (min)	Initial Weight (g)	Insoluble Gel (g)	Insoluble Solid (g)	Solvent Content (wt %)	Insoluble Content (wt %)
0	0.210	0	0	0	0
10	0.218	2.20	0.122	960	57
20	0.212	1.80	0.180	100	88

marked in the figures represents the total time of annealing). The lower  $T_g$  represents the phenoxy-rich phase, and the higher one, the PSTMA-rich phase. Both  $T_g$ s increase with increasing total annealing time. For polyesters and/or polycarbonates, the transesterification at high temperatures between the two polymers generates a copolymer which compatibilizes the parent polymers. Consequently, the two initial  $T_g$ s shift closer to each other, and, eventually, the entire blend acquires a single intermediate  $T_g$ , corresponding to a single phase.<sup>17,18</sup> In the present case, the intermolecular reactions between PSTMA and phenoxy result in crosslinked polymers. The two phases generated after the first scanning (identified during the second scanning) are stabilized by the esterification reaction, which is crosslinking the two polymers particularly in their interfacial region but also, to a smaller extent, in the bulk phases. With increasing annealing (reaction) time, both  $T_g$ s increase but remain distinct, indicating that the crosslinking density has increased.

### Solvent Extraction

Table II lists the insoluble content of the PSTMA/phenoxy (20/80) blends after annealing at 200°C for various lengths of time. The insoluble content and its THF swelling reflect the crosslinking density (i.e., the extent of reaction in the blends). As expected, the insoluble content increases, while its THF swelling decreases with increasing annealing time.

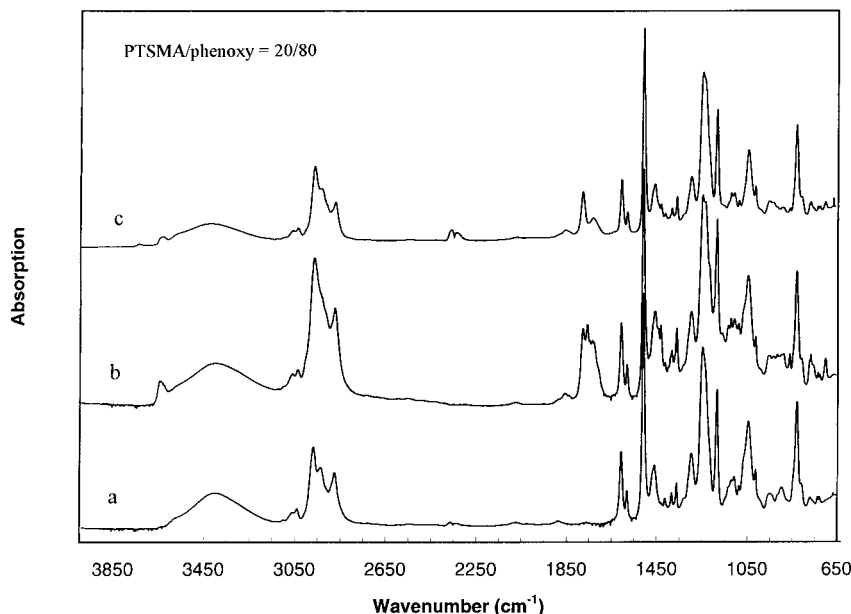
Figure 5 presents the FTIR spectra of the THF-soluble fractions of the PSTMA/phenoxy blends before and after annealing. The established linear relationship between the intensity ratio  $I_{1780}/I_{829}$  and the PSTMA content  $x$  (wt %) can be used to estimate the PSTMA content in the blends. For the blend which was not subjected to heat treatment, the two polymers are soluble in THF and the intensity ratio  $I_{1780}/I_{829}$  is 0.505 (corresponding to 20 wt % PSTMA). However, the intensity ratio  $I_{1780}/I_{829}$  in the soluble fraction decreases

with increasing annealing time, indicating that PSTMA is involved in the crosslinking reaction with phenoxy and, hence, that less PSTMA than phenoxy has been extracted. The estimated PSTMA content in the soluble fractions after annealing at 200°C for 10 and 20 min is about 17 and 14 wt %, respectively.

It is of interest to note that the FTIR spectra revealed that non-hydrogen-bonded hydroxyl groups are present in the soluble fraction. Three kinds of hydroxyl stretching vibrations are usually present: a broad one centered at about 3435  $\text{cm}^{-1}$ , which can be assigned to the multi-hydrogen-bonded OHs; a shoulder at 3550  $\text{cm}^{-1}$ , which can be attributed to the OH dimers; and a sharp absorption at about 3630  $\text{cm}^{-1}$ , which can be assigned to the non-hydrogen-bonded OH groups. The FTIR spectra indicate that all the OH groups in the pure phenoxy and the PSTMA/phenoxy blend (20/80) without any heat treatment are hydrogen-bonded. However, in the soluble fraction of the sample annealed for 10 and 20 min, a sharp absorption at 3630  $\text{cm}^{-1}$  is present, indicating the presence of non-hydrogen-bonded hydroxyl groups. The soluble fractions are expected to consist of unreacted phenoxy, unreacted PSTMA, and the PSTMA-grafted phenoxy copolymer. Probably, the grafting of PSTMA to phenoxy generates a steric impediment to the association of the OH groups of phenoxy among themselves.

### CONCLUSIONS

The miscibility and intermolecular esterification of poly(styrene–maleic anhydride) (PSTMA) and phenoxy were studied by DSC, FTIR, and solvent extraction. A single composition-dependent broad  $T_g$  was detected during the first DSC scanning. The broadness of  $T_g$  indicates that the blends prepared by casting were not miscible at the molecular scale at room temperature. Two distinct  $T_g$ s were identified during the second scanning, indicating that the blends were increasingly phase-



**Figure 5** FTIR spectra of the THF-soluble fractions of PSTMA/phenoxy (80/20, w/w) blends before and after annealing at 200°C for 10 and 20 min, respectively: (a) without annealing; (b) annealed for 10 min; (c) annealed for 20 min.

separated upon heating. The intermolecular hydrogen-bonding interactions are likely responsible for the single  $T_g$ s during the first scanning. At high temperatures, these interactions are destroyed and a larger-scale phase separation occurs. This explanation is consistent with the observation that two  $T_g$ s were present during the second scanning. Intermolecular esterification between the anhydride groups of PSTMA and the hydroxyl groups of phenoxy occurred upon annealing at 220°C for various lengths of time, and two  $T_g$ s, corresponding to PSTMA-rich and phenoxy-rich phases, with various extents of cross-linking, were identified.

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