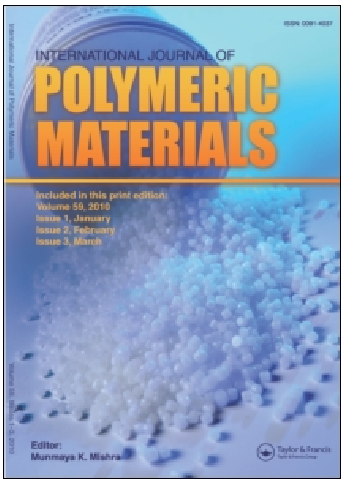

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Blends Containing Amphiphilic Polymers VI. Compatibilization of N-alkylitaconamic acid-co-Styrene Copolymers with Poly(hydroxypropyl methacrylate) and Poly(4-vinylphenol)

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Blends containing copolymers of N-alkylitaconamic acid (NAIA) with styrene (NAIA-co-S) of two copolymer compositions, that is, 80% and 50% styrene, with poly(hydoxypropyl methacrylate (PHPM) and poly(vinyl phenol) (PVPh) were studied by differential scanning calorimetry (DSC) and Fourier Transform Infrared spectroscopy (FT-IR). The phase diagrams of Tg against blend composition show one single Tg value, which are intermediate to those of the pure components. This is interpreted as miscibility over the whole range of compositions in both systems. The Calorimetric Analysis using Gordon Taylor, Couchman, and Kwei treatments allows one to conclude that interactions between the components is favorable to the miscibility. FT-IR spectra show important displacements in the wavenumber corresponding to the carbonyl groups of the itaconamic acid moiety. This behavior is atributed to strong interaction by hydrogen bonds formation, taking into account that PHPM and PVPh are interacting polymers. FTIR analysis of the blends suggests that the driving force for miscibility is hydrogen bonds formation. The variation of the absorptions of the carbonyl groups of PNAIA and the hydroxyl groups of P4VPh allows to attribute the miscibility to weak acid-base like interactions.

Keywords: amphiphilic polymers, functionalized polymers, hydrogen bonds, miscibility, phase behavior, poly(N-1-alkylitaconamic acids), polymer blends

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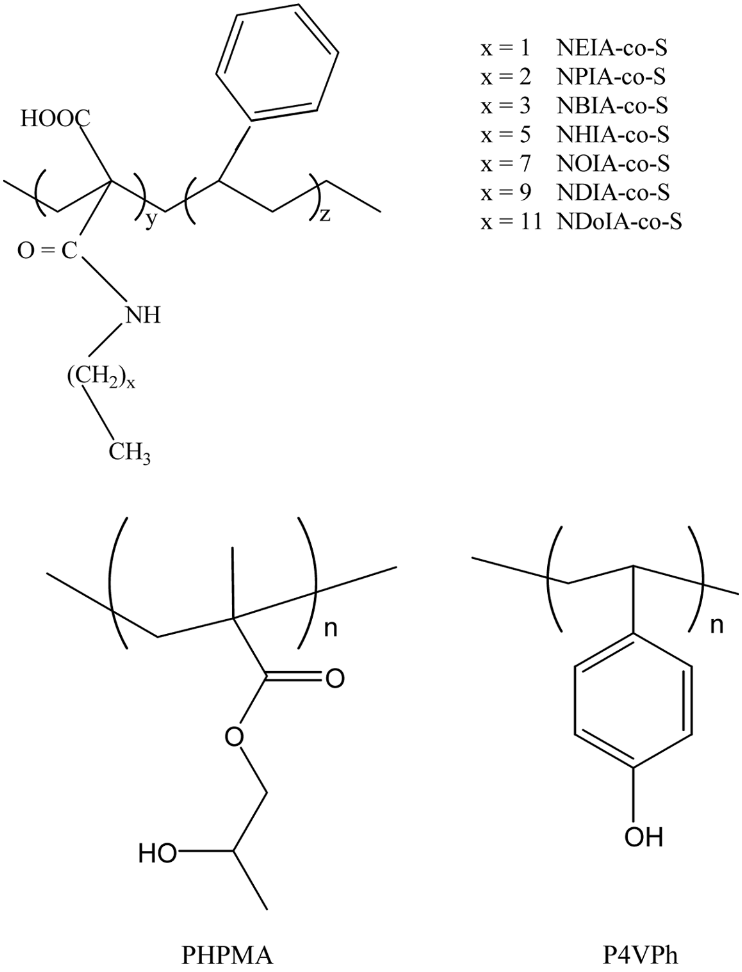
INTRODUCTION

Miscibility in polymer blends results from the Gibbs free energy of mixing ΔG_m being negative. This term combines the effects of both entropy and enthalpy. Polymer-polymer miscibility is an enthalpically governed process because the entropic contribution is vanishingly small for high molecular weights. Therefore, in order to ensure a mixing process with only one phase material, the heat of mixing, which reflects the contact interactions between dissimilar components, must be negative or at least not significantly positive. For this reason, in the mixing process it is necessary to ensure interactions between the components of the blend [1]. This can be obtained through the combination of polymers with repeating units where specific interactions between the chains can exist, and the heat of mixing between components should be favorable. The functionalization by incorporation of interacting groups in the macromolecular chain is a way to reach this objective. Dipole-dipole, donor-acceptor, or acid-base interactions could take place. Basic polymers such as Poly(vinilpyridine)s are miscible with proton-donating polymers such as Poly(4-vinylphenol) (P4VPh) [2–3] Poly(acrylic acid) (PAA) [4–5] Poly(monoalkyl itaconates) (PMAI) [6]. Hydrogen bond formation has been considered as critical to enhancing the miscibility in these systems [6–8].

Poly(N-1-alkylitaconamic acids) (PNAIA) are a family of functionalized polymers derived from itaconic acid, containing a free carboxylic group and an amide group per repeating unit. These polymers can be multifunctionalized and also modified by inserting long side chains with different lengths as side groups, thus resulting in polymers with different hydrophobicity [9–11]. This structural characteristic is very useful when these polymers are used in different systems such as polymer blends [11–12]. Due to this interacting structure, PNAIA are interesting in the compatibilization process with weak basic and acidic polymers because they can interact by acid-base interaction through the free carboxylic group and/or the amidic carbonyl group. In a previous article we reported the compatibilization process of N-alkylitaconamic acid-co-Styrene (NAIA-co-S) copolymers of two different composition with several interacting homopolymers [13]. The miscibility behavior of these polymers depends on the composition of the copolymer and on the chemical structure of the homopolymers [13]. For weak interacting homopolymers phase separation is observed for copolymers with low NAIA composition and long side chains, which is attributed to steric hindrance of the long side chains. In the case of copolymers with higher NAIA moiety, miscibility over the whole range of composition is observed irrespective of the homopolymer counterpart.

The aim of the present work is the study of the compatibilization process of N-1-alkyl itaconamic acid-co-S containing ethyl (NEIA), propyl (NPIA), butyl (NBIA), hexyl (NHIA), octyl (NOIA), decyl (NDIA), and dodecyl (NDoIA) groups with two strongly interacting polymers like poly(2-hydroxypropyl methacrylate) (PHPMA) and poly(4-vinylphenol) (P4VPh); see Scheme 1. By this way it should be possible to get confidence about the nature of the strength of interaction between these pairs of polymers.



SCHEME 1 Chemical structures of N-alkylitaconic acids-costyrene copolymers, poly(hydroxypropyl methacrylate), and poly(4-vinylphenol)

EXPERIMENTAL

Monomers and Polymers Preparation

N-1-alkylitaconamic acids (NAIA) were synthesized by reaction of itaconic anhydride with the corresponding 1-alkylamine in chloroform, following procedures previously reported and improved by us [10–14].

Copolymerization of the NAIA monomers with styrene were carried out by radical polymerization in bulk a 354–388 K according to the procedure previously reported [13].

Poly(2-hydroxypropyl) (P2HPMA) and Poly(4-vinylphenol) (P4VPh) both with weight average molecular weight $\overline{M_w} = 20.000$ were commercial samples from Aldrich.

Preparation of the Blends

Blends of different compositions were prepared by solution casting using THF as solvent and then evaporated at room temperature and vacuum dried at 298 K for 120 h. The polymer concentration in the solution was about 2% w/w.

DSC Measurements

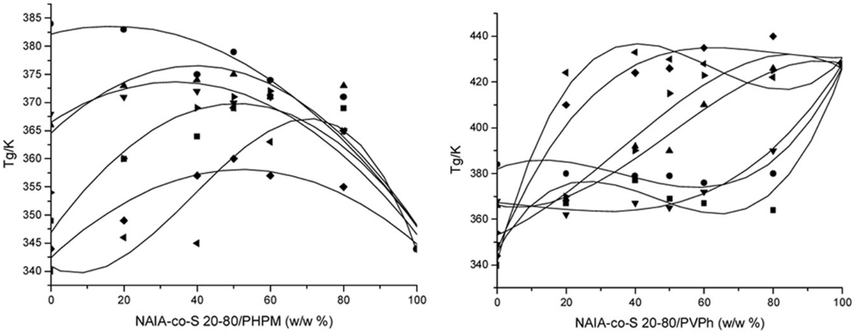
The glass transition temperatures (Tg) of the pure polymers and blends were measured witha Mettler 821 calorimetric system using the STAR^e program. Polymer samples were dried under reduced pressure in a vacuum oven prior measurements. Dry nitrogen was used as purge gas and thermograms were measured in the range 308 to 523 K at a scan rate of 20° min^{-1}.

FTIR Measurements

Infrared spectra of pure polymers, copolymers, and blends were recorded on a Vector 22 Bruker Fourier Transform Infrared (FT-IR) spectrophotometer. The spectra were recorded with a resolution of 1 cm^{-1}. The samples were prepared directly in KBr pellets.

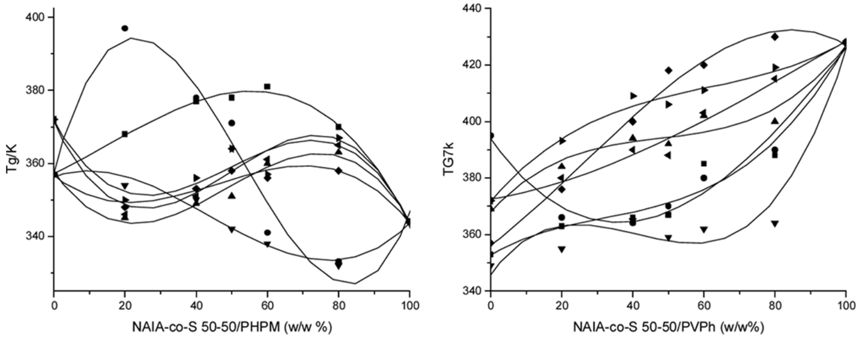
RESULTS AND DISCUSSION

Copolymers of NAIA-co-S, that is, NEIA-co-S, NPIA-co-S, NBIA-co-S, NHIA-co-S, NOIA-co-S, NDIA-co-S, and NDoIA-co-S of two different compositions (80% and 50% Styrene) were selected for the present study. PHPMA and P4VPh were blended with each of the copolymers. Different blend compositions were obtained in order to analyze the whole range of blend composition. Dry blends of NAIA-co-S with PHPM and P4VPh were transparent and show thermograms exhibiting a distinct single glass transition temperatures (Tg). Figures 1a and 1b, show the variation of Tg with the composition for blends of NAIA-co-S (20/80) with PHPM and P4VPh with the seven different NAIA-co-S considered for this study. A continuous variation of Tg, which values are intermediate between the Tg of the pure components is observed. This behavior would indicate miscibility over the whole range of composition irrespective of the NAIA-co-S considered in the blends, and whether the blend contains PHPM or P4VPh. However, there are differences in the shape of the curves and the degrees of curvature are rather different for the systems analyzed. In the case of blends with PHPMA, curves can be observed over the weight values of Tg between the pure components and an S-shape curve for NDIA-co-S. Figure 1b shows different shapes of curves although all of them are continuous and with an important degree of curvature. In fact, it is possible to observe curves over and below the weighed values of the pure components. For the blends containing ethyl and propyl moieties an S-shape curve is observed. Figures 2a and 2b show the variation of Tg with blend composition for copolymers containing 50% of NAIA. From a qualitative point of view, curves corresponding to blends containing



(a) (b)

FIGURE 1 Variation of the glass transition temperature (Tg) for blends of: (a) (N-alkyl itaconamic acids-co-Styrene (NAIA-co-S) 20/80 with Poly(2-hydroxypropyl methacrylate) (■) PNEIA-co-S/PHPMA; (•) PNPIA-co-S/PHPMA; (▲) PNBIA-co-S/PPHPMA; (▼) PNHIA-co-S/PHPMA; (◆) PNOIA-co-S/PHPMA; (◀) PNDIA-co-S/PHPMA; (▶) PNDoIA-co-S/PHPMA and (b) PNAIA-co-S 20/80 with Poly(4-vinylphenol) (P4VPh). (■) PNEIA-co-S/ P4VPh; (•) PNPIA-co-S/ P4VPh; (▲) PNBIA-co-S/ P4VPh; (▼) PNHIA-co-S/ P4VPh; (◆) PNOIA-co-S/ P4VPh; (◀) PNDIA-co-S/ P4VPh; (rtrif;) PNDoIA-co-P4VPh.



(a) (b)

FIGURE 2 Variation of the glass transition temperature (Tg) for blends of: (a) (N-alkyl itaconamic acids-co-Styrene (NAIA-co-S) 50/50 with Poly(2-hydroxy-propyl methacrylate) (■) PNEIA-co-S/PHPMA; (●) PNPIA-co-S/PHPMA; (▲) PNBIA-co-S/PPHPMA; (▼) PNHIA-co-S/PHPMA; (◆) PNOIA-co-S/PHPMA; (◀) PNDIA-co-S/PHPMA; (▶) PNDoIA-co-S/PHPMA and (b) PNAIA-co-S 50/50 with Poly(4-vinylphenol) (P4VPh). (■) PNEIA-co-S/ P4VPh; (●) PNPIA-co-S/ P4VPh; (▲) PNBIA-co-S/ P4VPh; (▼) PNHIA-co-S/ P4VPh; (◆) PNOIA-co-S/ P4VPh; (◀) PNDIA-co-S/ P4VPh; (▶) PNDoIA-co- P4VPh.

PHPMA are rather different in shape from those of Figure 1a. However, curves in Figures 1b and 2b for blends containing P4VPh are very similar. Nevertheless, the general behavior indicates that all the blends are compatible over the whole range of compositions.

In order to analyze in a quantitative way the variation of Tg with the blend composition for these systems, the Gordon Taylor [15] (GT) and Couchman [16] (Cou) treatment of the data were used. These procedures are based on Eqs. 1 and 2, respectively.

$$\mathrm{Tg} = \frac{\mathrm{w_1 tg_1 + w_2 tg_2}}{\mathrm{w_1 + k_{GT} w_2}} \tag{1}$$

$$\mathrm{LnTg} = \frac{\mathrm{LnTg_1 + (k_{Cou} w_2/w_1) LnTg_2}}{\mathrm{1 + (k_{Cou} w_2/w)}} \tag{2}$$

where Tg is the Glass transition of the blend, $\mathrm{Tg_i}$ the glass transition of the blends, and $\mathrm{w_1}$ and $\mathrm{w_2}$ represent the weight fraction of the components.

These parameters have been considered as a semiquantitative measure of the strength of the interaction between the interacting groups of the polymeric components [16]. The $\mathrm{K_{GT}}$ and $\mathrm{K_{Cou}}$ values compiled in Table 1 would indicate that the interaction between the polymeric components is sufficient to favor polymer-polymer miscibility.

TABLE 1 Gordon Taylor (k_{GT}), Couchman (k_{cou}) and k_{wei} (k_{kw} and q) Constants for Blends of 80% and 50% Styrene (S) Copolymers of NAIA-co-S with PHPM and PVPh

	PHPMA				PVPh			
	k_{GT}	k_{Cou}	k_{Kw}	q	k_{GT}	k_{cou}	k_{kw}	q
NAIA-co-S (80% S)								
NEIA-co-S	0.09	0.08	0.15	1.2	0.45	0.40	0.2	1.0
NPIA-co-S	0.03	0.04	0.18	1.5	0.08	0.09	0.2	2.0
NBIA-co-S	0.04	0.05	0.20	1.8	0.03	0.04	0.09	1.0
NHIA-co-S	0.20	0.14	0.22	2.0	0.26	0.22	0.3	3.0
NOIA-co-S	0.20	0.30	0.21	5.0	0.41	0.40	0.2	2.0
NDIA-co-S	0.21	0.15	0.22	11.0	0.95	0.87	0.4	4.0
NDoIA-co-S	0.20	0.25	0.22	23.0	0.35	0.42	0.3	5.0
NAIA-co-S (50% S)								
NEIA-co-S	0.01	0.06	0.1	1.0	0.02	0.03	0.1	1.0
NPIA-co-S	0.15	0.17	0.2	2.0	0.05	0.07	0.1	1.5
NBIA-co-S	0.16	0.17	0.2	2.0	0.14	0.15	0.2	2.5
NHIA-co-S	0.11	0.11	0.15	1.5	0.38	0.36	0.4	3.0
NOIA-co-S	0.45	0.38	0.5	1.0	0.38	0.49	0.5	4.0
NDIA-co-S	0.55	0.33	0.6	5.0	0.26	0.32	0.3	3.0
NDoIA-co-St	0.38	0.35	0.5	1.0	0.36	0.37	0.4	4.0

However, the aforementioned procedures are not the best fitting methods because they cannot describe S-shaped curves. For the case of S-shaped curves exhibited in Figure 1a and 1b it can be commonly fitted by the Kwei [17] equation:

$$Tg = \frac{(w_1Tg_1 + k_{kw}w_2Tg_2)}{(w_1 + k_{kw}w_2)} + qw_1w_2 \tag{3}$$

From these procedures it is possible to estimate the strength of the interaction through the values of the corresponding constants k_{GT}, k_{Cou}, and k_{kw}, respectively. Table 1 summarizes the k_{GT}, k_{Cou}, and k_{kw} for all the systems studied.

The values of k_{kw} and q obtained by this procedure are in good agreement with those reported for other systems. By this way it is possible to assume that there is an important interaction between the components of the blends that is responsible for the compatibility [18,19]. On the other hand, annealed blends show one single enthalpy relaxation peak what is indicative of miscibility.

To obtain further information about the interactions involved, FT-IR measurements were performed. Intra- and inter-molecular association in NAIA moieties cannot be disregarded because of the carboxylic and amide groups. Three main absorptions were considered in order to analyze the displacements due to interactions between polymers, that is, the acidic carbonyl group at 1775 cm^{-1}, the amidic carbonyl group at 1700 cm^{-1}, and the absorption of the amidic –NH group at 3450 cm^{-1}. As a general behavior the region of the vibration of the carbonyl shows small but significant displacements that can

TABLE 2 FT-IR Absorptions for the Different Functional Groups con PNAIA-co- S Copolymers and Homopolymers. Displacements of Acidic Carbonyl Group, Amidic Carbonyl Group and –NH Amidic Group with the Blend Composition for Blends Containing Copolymers of 80% and 50% S with PHPMA

		PHPMA						
Signal	Blend composition	NEIA	NPIA	NBIA	NHIA	NOIA	NDIA	NDoIA
	20/80 w/w copolymers of NAIA-co-S							
Acidic carbonyl (C=O) group 1775 cm^{-1}	20/80	0.9	6.2	1.7	3.6	1.6	3.5	0.1
	40/60	1.0	5.3	0.8	4.4	2.5	3.6	0.8
	50/50	1.1	4.5	0.6	4.2	3.3	4.6	0.9
	60/40	2.4	1.7	0.5	5.1	4.3	4.5	0.8
	80/20	—	—	—	7.3	—	—	—
Amidic carbonyl (C=O) group 1700 cm^{-1}	20/80	0.9	0.3	1.7	1.2	0.8	1.6	0.5
	40/60	1.8	1.3	2.7	0.8	1.3	1.5	0.8
	50/50	1.8	2.1	3.3	0.6	1.8	1.3	1.3
	60/40	3.6	2.4	4.3	0.4	2.9	1.6	1.4
	80/20	7.0	—	8.4	—	3.3	1.6	2.5
Amidic-NH group 3448 cm^{-1}	20/80	1.3	27.2	2.3	0.8	2.6	4.7	3.0
	40/60	1.3	22.5	5.0	4.7	5.2	10.7	4.4
	50/50	1.4	27.0	7.9	3.8	7.1	8.2	9.0
	60/40	7.9	26.0	7.9	6.0	10.1	9.7	10.4
	80/20	6.8	23.0	1.0	5.2	12.8	9.2	12.3
	50/50 w/w copolymer of NAIA-co-S							
Acidic carbonyl (C=O) group 1775 cm^{-1}	20/80	0.3	2.6	0.6	0.6	0.7	0.4	1.3
	40/60	0.9	3.4	1.3	0.3	1.4	0.8	2.5
	50/50	0.8	2.3	2.6	0.6	2.8	1.4	2.1
	60/40	0.5	1.5	5.7	1.3	2.1	2.0	3.0
	80/20	—	—	—	—	—	—	—
Amidic carbonyl (C=O) group 1699 cm^{-1}	20/80	0.1	0.8	0.4	1.0	0.7	0.2	2.2
	40/60	0.9	0.5	0.6	0.2	1.9	0.2	2.5
	50/50	8.1	1.8	1.5	0.5	1.6	0.5	3.0
	60/40	2.3	2.8	6.4	0.9	2.2	7.0	3.4
	80/20	—	6.2	6.3	2.9	4.3	1.2	4.4
Amidic-NH group 3448 cm^{-1}	20/80	2.0	1.0	6.0	1.2	9.0	0.2	58.7
	40/60	3.0	9.0	6.0	1.4	2.1	3.4	54.4
	50/50	4.0	2.0	4.0	4.4	1.9	7.5	64.4
	60/40	5.7	5.2	6.0	1.3	2.8	8.3	67.8
	80/20	–	3.6	5.2	1.9	2.5	10.9	97.7

be considered as an effect of the interaction between the polymers. However, the most important displacement of the absorptions in the IR is observed al 3450 cm^{-1} corresponding to the vibration of the amidic –NH group. This effect is more pronounced in blends containing P4VPh than in the case of blends with PHPMA. Tables 2 and 3 compile

TABLE 3 FT-IR Absorptions for the Different Functional Groups con PNAIA-co-S Copolymers and Homopolymers. Displacements of Acidic Carbonyl Group, Amidic Carbonyl Group, and NH Amidic Group with the Blend Composition for Blends Containing Copolymers of 80% and 50% S with P4VPh

		P4VPh						
Signal	Blend composition	NEIA	NPIA	NBIA	NHIA	NOIA	NDIA	NDoIA
	20/80 w/w copolymer of NAIA-co-S							
Acidic carbonyl (C=O) group 1775 cm^{-1}	20/80	0.7	0.2	4.7	0.1	0.6	3.4	0.2
	40/60	0.2	0.3	4.0	0.2	0.7	4.0	0.3
	50/50	0.2	0.7	2.1	4.0	1.1	4.4	0.3
	60/40	0.7	1.2	3.8	3.7	1.6	4.9	0.2
	80/20	0.9	0.3	1.5	1.5	2.6	3.9	0.5
Amidic carbonyl (C=O) group 1700 cm^{-1}	20/80	0.1	1.6	0.4	0.7	0.1	0.2	o.3
	40/60	0.3	2.2	0.9	0.9	0.5	0.3	0.3
	50/50	0.4	2.1	1.5	2.3	0.9	0.6	0.3
	60/40	0.9	2.7	1.6	2.4	1.2	1.2	0.7
	80/20	—	1.8	5.9	1.5	1.8	1.2	0.8
Amidic-NH group 3448 cm^{-1}	20/80	1.3	29.1	2.7	1.6	53.3	63.5	59.8
	40/60	64.6	35.0	24.1	67.7	60.3	53.9	43.7
	50/50	62.0	15.0	34.7	92.7	69.0	67.5	64.7
	60/40	64.8	6.0	70.9	96.6	67.0	67.5	67.9
	80/20	60	5.3	69.8	96.7	96.4	33.2	66.3
	50/50 w/w copolymers of NAIA-co-S							
Acidic carbonyl (C=O) group 1775 cm^{-1}	20/80	1.0	2.8	1.9	0.4	1.0	0.2	1.2
	40/60	0.4	2.5	5.2	0.2	0.7	0.5	1.3
	50/50	1.1	0.9	3.5	0.4	1.2	0.7	1.6
	60/40	1.9	—	6.8	1.0	2.0	0.9	2.0
	80/20	—	—	—	0.9	3.5	1.9	2.9
Amidic carbonyl (C=O) group 1699 cm^{-1}	20/80	1.0	1.9	1.5	1.1	1.2	1.7	2.2
	40/60	1.2	4.8	6.1	1.6	1.2	1.8	2.5
	50/50	1.0	5.5	4.6	1.6	1.4	2.5	3.0
	60/40	1.7	7.1	6.7	1.7	1.9	3.0	3.4
	80/20	1.2	8.3	3.0	1.9	2.3	3.7	4.4
Amidic-NH group 3448 cm^{-1}	20/80	12.3	26.4	38.0	5.6	50.7	63.0	58.7
	40/60	44.5	34.7	60.0	51.8	27.5	61.3	54.4
	50/50	32.9	59.2	51.0	62.7	60.4	70.4	64.4
	60/40	60.3	66.8	63.0	68.7	72.1	70.4	67.8
	80/20	64.8	66.1	57.0	66.9	95.1	—	97.7

the displacements observed in the FT-IR spectra in the three absortion regions analyzed. These results suggest that the interaction between the polymers can be attributed to hydrogen-bonding formation, which is stronger for blends containing P4VPh. This result can be explained in terms of the freedom and the acidity of the –OH group in PHPMA and P4VPh. In fact, P4VPh is a more acidic polymer than PHPMA. On the other hand, the degree of freedom of the -OH group in PHPMA is lower than in P4VPh due to the esteric hindrance. These results would be indicative of interaction between the carboxylic group of NAIA moiety with the −OH of PHPMA and the phenolic one of P4VPh.

CONCLUSIONS

Both DSC and FTIR were used to investigate the phase behavior of blends containing NAIA-co-Styrene with PHPMA and P4VPh. Miscibility over the whole range of composition is found. In both systems hydrogen bonding interaction between the components seems to be responsible for the miscibility. Differences are observed in the phase behavior of blends containing PHPMA and P4VPh, which can be attributed to the different acidity of the polymers. Therefore, a weak acid–base interaction can be considered as the driving force for miscibility.

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