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Colloidal scale blends of poly(p-benzamide) with sulfonated polystyrene and poly(vinyl acetate)

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Polymer composites containing the rigid poly(p-benzamide) (PBA) and the flexible sulfonated polystyrene (SPS) or poly(vinyl acetate) (PVA) are prepared using a two-step method. The SEM micrographs show that both PBA–SPS and PBA–PVA composites contain particles in the colloidal range, with sizes around 50 nm. The *FT*-i.r. spectra reveal that there are strong interactions between PBA and SPS; those between PBA and PVA are weaker. Two successive thermal scannings suggested that these colloidal scale dispersions are kinetically rather than thermodynamically stable. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Considerable attention was given in the last two decades to the preparation of molecular composites, in which rigid polymers are mixed at a molecular scale with flexible ones. Such a mixing had the goal of providing maximum reinforcement of the flexible polymers[1–3]. However, because of their thermodynamic incompatibility, it is difficult to obtain such composites. One route was to generate chemical bonding or specific interactions between the two polymers, which could overcome the aggregation tendencies of the molecules of the same kind[4,5]. Another route was to generate the rigid polymer *in situ* from the blend of its precursor with a flexible polymer[6–8].

Poly(p-benzamide) (PBA) is a fully aromatic polyamide, which is insoluble in organic solvents and does not melt even at high temperatures. Ogata *et al.*[9] prepared the PBA–polyarylate composites by the *in situ* direct polycondensation method; however, the properties of the composites were not satisfactory. Indeed, the tensile strength decreased with the PBA content and the aggregated PBA particles had a chain-like form with a diameter as large as 0.1 mm. Recently, colloidal scale blends of PBA–nylon 6(3)T[10] and PBA–poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl methacrylate) (PVVH)[11] were prepared by replacing the preceding one-step method by a two-step method. In the first step, a viscous PBA dispersion was generated by the direct polycondensation of p-aminobenzoic acid in N,N′-dimethylacetamide (DMAc); in the second step, the PBA dispersion was mixed with a solution of a flexible polymer in DMAc. A composite powder was collected by precipitation in a non-solvent. Semi-transparent thin films were obtained by the redispersion of the powders in DMAc, followed by casting. The obtained composite films contained spherical PBA particles, with sizes in the range 50–75 nm, dispersed in the flexible polymer matrices. The tensile and yield strengths, the Young modulus and the glass transition temperature increased with increasing PBA content. The interactions, particularly the hydrogen bonds, between the two polymers were responsible for the improved properties of the above colloidal composites.

In order to investigate more fully the colloidal scale composites and the effect of the interactions between the two polymers, we select the sulfonated polystyrene (SPS), the polystyrene (PS), or the poly(vinyl acetate) (PVA) as the flexible polymer and the PBA as the rigid one. The sulfonic groups of SPS are expected to generate strong interactions and the ester groups of PVA weak interactions with the amide groups of PBA. PS is expected to be completely incompatible with PBA.

EXPERIMENTAL

Materials

p-Aminobenzoic acid (99%, AB), triphenylphosphine (99%, TPP), hexachloroethane (99%, HCE), pyridine (anhydrous), N,N′-dimethylacetamide (anhydrous, DMAc), N,N′-dimethylformamide (anhydrous, DMF), poly(styrene) (PS, $M_w = 280\,000$), poly(vinyl acetate) (PVA, $M_n = 167\,000$) were used as received. All chemicals were purchased from Aldrich.

Preparation of sulfonated polystyrene (SPS)

The sulfonated polystyrene (SPS) was prepared by the sulfonation of PS in dichloroethane, following the method of Makowski *et al.*[12]. The sulfonation level was changed by altering the reaction time. The SPS was dissolved in a mixture of tetrahydrofuran and methanol (v/v = 9/1) to form a solution of 5 wt% concentration and the sulfonation level was determined by titration with methanolic NaOH using phenolphthalein as an indicator. Two sulfonated PS have been employed. They are denoted 7.1-SPS and 14.7-SPS, since they contain for every 100 mols of styrene 7.1 and 14.7 mols of sulfonic groups, respectively.

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Preparation of PBA–SPS and PBA–PVA composites

In the first step, PBA was synthesized by the direct polycondensation of AB in DMAc at 40°C, in the presence of pyridine–TPP–HCE as activators. A transparent and viscous solution was obtained which became turbid as the reaction continued, owing to the formation of colloidal PBA particles. In the second step, the PBA dispersion was mixed with SPS in DMAc to obtain composites with a PBA content of 7.5, 10 and 15 wt%, respectively. The composite powders were precipitated by pouring the viscous solutions into water–methanol mixtures (v/v = 1/1); this was followed by filtering and washing the precipitates repeatedly with water–methanol. The PBA–PS composite was prepared as follows. PS was dissolved in toluene and DMF was added to the solution in order to increase its polarity. Subsequently, a PBA–DMAc dispersion was added slowly to the PS solution whilst stirring. The PBA–PS blend was precipitated by pouring the mixture into methanol and recovered by filtering, washing with methanol and drying. The same procedure was employed to prepare the PBA–PVA composites.

Thin films preparation

The composite powders were redispersed in DMF at 50°C with stirring; slightly turbid dispersions were thus obtained. Semi-transparent thin films of PBA–SPS were prepared by casting the dispersions onto aluminium pans at 50°C. These films have been too brittle to perform tensile testing. For the PBA–PVA composites, the thin films were prepared also by casting, but at room temperature. When the PBA content in the PBA–PVA composites was over 10 wt%, the films became too brittle to conduct tensile testing.

Tensile testing

The PBA–PVA thin films with a PBA content less than 10 wt% were cut into dumbbell-shaped forms, as required by ASTM D. 638-58T, after which they were dried in a vacuum oven at room temperature. The tensile testing was performed with an Instron universal testing instrument (model 1000) at room temperature, with an elongation rate of 10 mm min^{-1}.

***FT*-i.r. analysis**

Thin film samples of SPS, PVA and their composites with PBA were prepared by casting their DMF solutions onto aluminium pans at 50°C, followed by vacuum drying. A Perkin-Elmer 1760X instrument was employed. The number of *FT*-i.r. scannings was 50 with a resolution of 2 cm^{-1}.

Thermal transition determinations

The glass transition temperature (T_g) was determined with a Du Pont 910 differential scanning calorimeter (d.s.c.). The T_g was taken as the midpoint of the thermal transition. The PBA–SPS powders, dried under vacuum at 60°C, were scanned under nitrogen, from 30 to 200°C, with a heating rate of 20°C min^{-1}. The PBA–PVA powders, dried under vacuum at room temperature, were scanned from − 20 to 100°C with a lower heating rate of 10°C min^{-1}, because the T_g of PVA is close to the starting temperature.

Scanning electron microscopy (SEM)

The morphology of the PBA composite films was examined with a Hitachi S-800 scanning electron microscope. The films were fractured under liquid nitrogen and the fractured surfaces were coated with a thin layer of carbon before scanning.

RESULTS AND DISCUSSION

PBA–SPS blends

***FT*-i.r. analysis.** *Figure 1* presents the *FT*-i.r. spectra ofSPS and of the 15 wt% PBA–SPS composite in the stretching vibration range of the sulfonic anion SO_3^-. The absorption of SPS at 1036 cm^{-1} can be attributed to the symmetric stretching vibration of S–O and that at 1126 cm^{-1} to the in-plane bending vibration of the sulfonated-phenyl ring. Both are sensitive to the local environment of the sulfonic group[13,14]. Indeed, Weiss *et al.*[14] noted that these absorptions were shifted to lower wavenumbers when nylon 6 was blended to the zinc

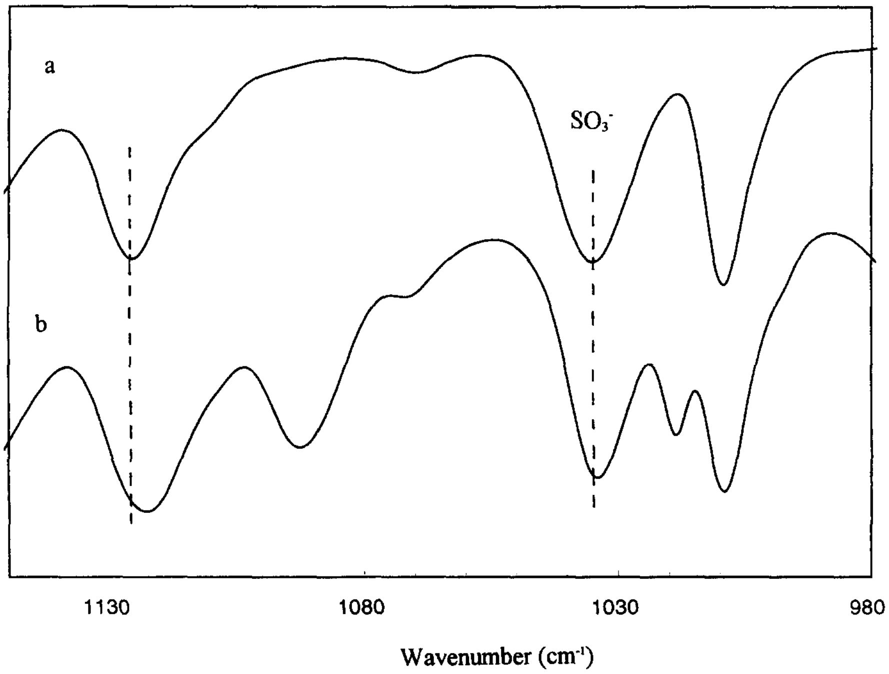

Figure 1 *FT*-i.r. spectra of 14.7-SPS (a) and 15 wt% PBA/14.7-SPS composite (b).

neutralized sulfonated PEEK (poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene)), by 3 and 5 cm^{-1}, respectively. Similar shifts to lower wavenumbers were observed when SPS was blended with PBA. The absorption at 1026 cm^{-1} was downshifted by 1.5 cm^{-1} and that at 1126 cm^{-1} by 3 cm^{-1}. Although the shift of the 1036 cm^{-1} band is lower than the resolution (2 cm^{-1}), its trend is in the same direction as the latter. The larger shifts observed for the system nylon 6–Zn-PEEk[14] are probably due to the larger proportion of Nylon (at least 30 wt%), to their molecular miscibility and to the stronger ionic interactions. The shifts for the PBA–SPS system are smaller because the two polymers are miscible only at the colloidal scale, the amount of PBA is much smaller and the ionic interactions weaker. The increased dissociation of the sulfonic groups, owing to the binding of the cation to the rigid polyamide and the interactions between the opposite charges, is most likely responsible for the behaviour of the above composites.

D.s.c. determinations. The T_gs of PS, SPS and their composites with different PBA contents during two successive thermal scannings are listed in *Table 1*. The T_g of SPS increases with sulfonation level; for the pure PS, T_g is 100°C, while for the 7.1- and 14.7-SPS, the T_g increases to 115 and 131°C, respectively. For all PBA–SPS composites, a single, broad and composition-dependent T_g, which increases linearly with increasing PBA content, was obtained during the first thermal scanning (*Table 1*). However, only the T_g of SPS was found during the second scanning, at about 115°C for the PBA–7.1-SPS composite and at about 130°C for the PBA–14.7-SPS composite. The interactions between the SPS and PBA hinder the movements of the SPS chains, thus increasing the T_g of the composite. However, as soon as the temperature was raised above the T_g, the SPS segments became free to move and the PBA particles and SPS chains segregated. For this reason, only the T_g of the pure SPS could be detected during the second scanning (the T_g of PBA could not be detected within the scanning range employed). The thermal behaviour of the PBA–SPS composites is similar to those of the PBA–nylon 6(3)T[10] and PBA–poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl methacrylate) (PVVH)[11] composites. In the latter two cases, the hydrogen-bonding played an important role. For the composites considered in this paper, the T_g increases with increasing sulfonation level of SPS. The T_g of the PBA–7.1-SPS composite increases by about 2.3°C, while that of the PBA–14.7-SPS composite by about 3.0°C, for each increase by 1 wt% of the PBA content (*Figure 2*). This occurs because a higher PBA content and a higher sulfonation level of SPS result in stronger interactions. In contrast, for the PBA–PS composites containing 10 and 15 wt% PBA only the T_g of PS was detected during both the first and second scanning, regardless of the PBA content. This takes place because there are no specific interactions between PBA and PS. It is of interest to note that the T_g of the PBA–polyarylate composite containing 29 wt% PBA was only 6°C higher than that of the pure polyarylate[9]. This occurred because the PBA particles were large (elongated with about 0.1 mm diameter) and therefore their interactions with the matrix weak. The behaviour of the colloidal scale composites during the two successive thermal scannings suggests that they are kinetically rather than thermodynamically stable.

Table 1 T_gs of PS, SPS, PBA–PS and PBA–SPS composites

Polymer	PBA content (wt%)	T_{g1} (°C)^a	T_{g2} (°C)^a
PBA	100	N^b	N^b
PS	0	102	102
	10	102	102
	15	105	102
7.1-SPS	0	115	115
	7.5	138	110
	10	140	112
	15	150	115
14.7-SPS	0	131	134
	7.5	150	130
	10	162	131
	15	175	127

$^a T_{g1}$ and T_{g2} represent the T_gs obtained from the first and second scannings, respectively.
^{b}N: not detected.

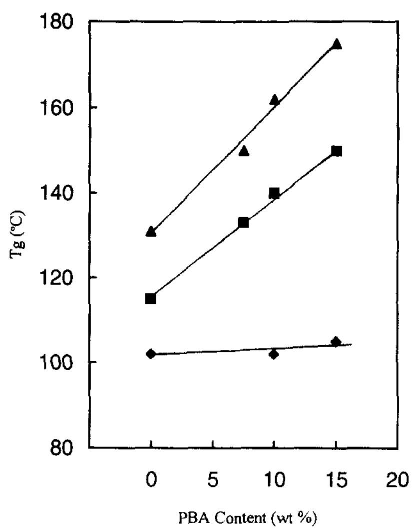

Figure 2 Effects of sulfonation level of SPS and PBA content on T_g of the PBA–SPS composites: (▲) 14.7-SPS; (■) 7.1-SPS; (◆) PS.

Morphology. The SEM micrographs of the fractured surfaces of SPS and PBA–SPS composites are shown in *Figure 3*. The pure SPS exhibits a two-phase structure with nanoscale particles dispersed in a continuous phase. The particles, which have sizes around 75 nm, may be attributed to the clustering of the polymer molecules. The PBA–SPS composites also contain particles; they have, however, average sizes of about 50 nm which are smaller than those observed for SPS. The interactions between the sulfonic groups of SPS and the amide groups of PBA, which were revealed by the *FT*-i.r. spectra, probably lead to the adsorption of SPS upon the surface of the colloidal particles of PBA, which are generated during the first step, forming PBA core–SPS shell particles. Such a structure is the reason for the colloidal scale redispersion of the composite powders in the DMF solvent, it prevents the aggregation of PBA particles during casting and, finally, it is responsible for the increase of the T_g of the composites with increasing PBA content. Of course, some of the particles may contain only SPS.

PBA–PVA blends

***FT*-i.r. analysis.** The *FT*-i.r. spectra of PVA and of the PBA–PVA thin films near the wavenumbers 1740 (C=O stretching) and 1250 cm^{-1} (C–O stretching) are shown in *Figure 4*. There is no shift in the peak position and shape

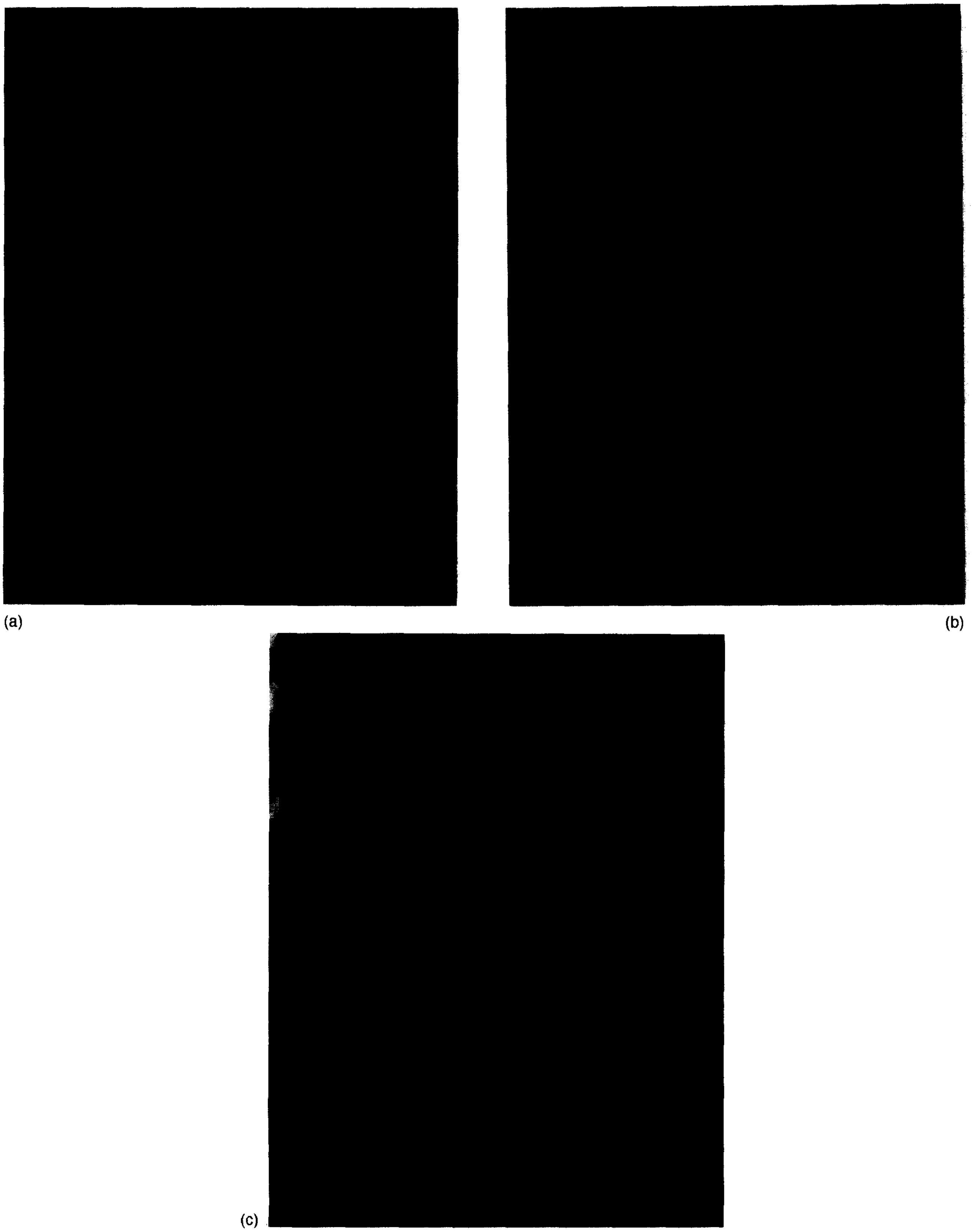

Figure 3 SEM micrographs of SPS and PBA–SPS composites: (a) 14.7-SPS; (b) 7.5 wt% PBA; (c) 15 wt% PBA.

for the C=O stretching vibration when the spectra of the composite and the pure PVA are compared. This indicates that there is no significant hydrogen-bonding between the C=O groups of PVA and the amide groups of PBA. Similarly, there is no shift in the peak position of the C–O stretching of PVA; however, the peak becomes broader. The broadening may be attributed to some intermolecular interactions between the PBA particles and the PVA chains, which lead to some conformational changes of the PVA molecules[15].

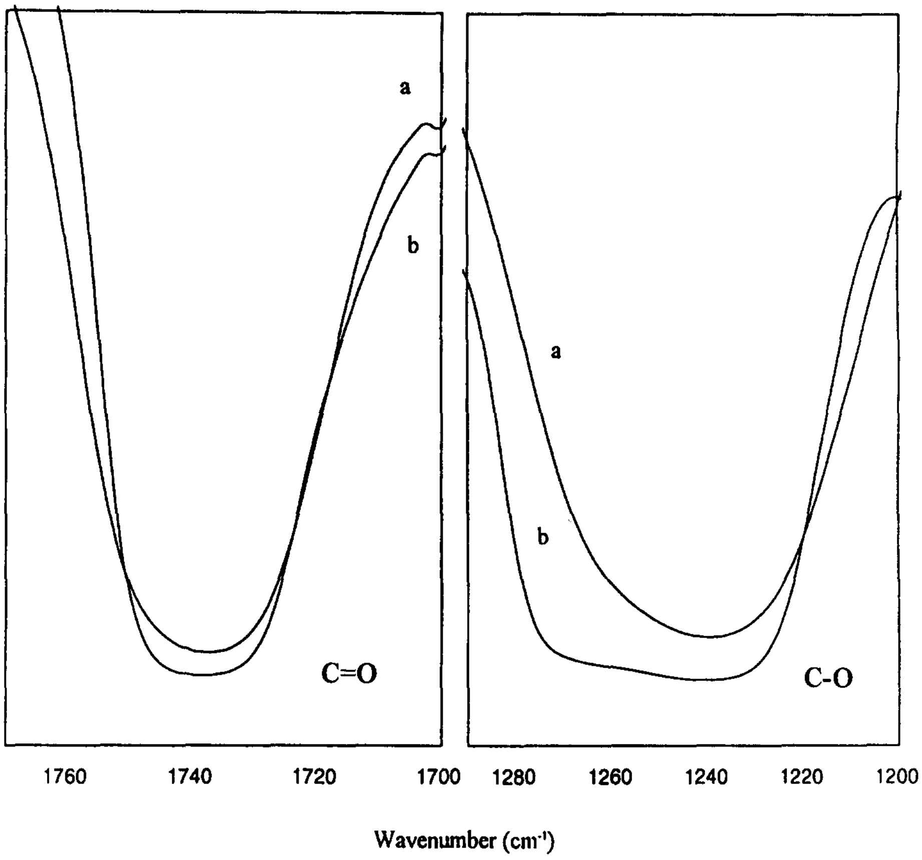

Figure 4 *FT*-i.r. spectra of PVA (a) and 10 wt% PBA–PVA composite (b).

D.s.c. measurements. The pure PVA and the PBA–PVA composites with 10, 15 and 20 wt% PBA were investigated by d.s.c. and the results are listed in *Table 2*. The pure PVA exhibited a T_g at 24°C, while the PBA–PVA composites displayed, during the first scanning, two distinct T_gs: a lower one, at about 24°C, which can be assigned to the PVA matrix, and a higher one, which increases with increasing PBA content and can be attributed to the PBA–PVA microdomains. During the second scanning, the samples with 10 and 15 wt% PBA exhibited a single broad T_g at about 30°C, which is higher than that of the pure PVA. The sample with 20 wt% still exhibited two T_gs, a lower one at 24°C and a higher one, downshifted to 57°C. The above results indicate that PBA and PVA were not completely segregated during the first scanning. The thermal behaviours of the PBA–SPS (single T_g) and PBA–PVA composites (two T_gs) are different, because the interactions between PBA and SPS are stronger than those between PBA and PVA. The stronger interactions in the former composites raise the T_g of the entire material, while the weaker ones in the latter enhance the T_g of some microdomains, and the material displays two T_g values.

Morphology. The SEM micrographs of the fractured surfaces of PVA and PBA–PVA composites are presented in *Figure 5*. PVA, which is an amorphous polymer, has a homogeneous structure [*Figure 5*(a)]. However, the PBA–PVA composites contain small particles of about 50 nm. Because their number is very large, it is likely that most of them are of PVA and the other ones are either PBA particles or PBA core–PVA shell particles. All the particles have sizes in the colloidal range.

Table 2 T_gs of PVA and the PBA–PVA composites (°C)

PBA content (wt%)	First thermal scanning		Second thermal scanning	
	T_{g1}	T_{g2}	T_{g1}	T_{g2}
0 (PVA)	24	—	24	—
10	23	45	30	—
15	24	55	30	—
20	24	75	24	57

Mechanical properties. The mechanical properties of PVA and PBA–PVA composites are listed in *Table 3*. The tensile and yield strengths and the Young modulus are low and the elongation is high for pure PVA because its T_g (about 24°C) is close to the testing temperature (room temperature). With increasing PBA content, the yield and tensile strengths and the Young modulus increase, indicating that PBA reinforces the flexible PVA matrix. The elongation is, however, reduced dramatically, demonstrating that the materials change from thermoplastic to brittle with increasing PBA content. The sample with 7.5 wt% PBA has a low tensile strength, since it is so brittle (elongation 2%) that it breaks before a yield stress is reached.

CONCLUSION

Colloidal scale blends of a rigid polymer, poly(p-benzamide) (PBA), with sulfonated polystyrene (SPS) and with poly(vinyl acetate) (PVA) were prepared using a two-step method. The effect of the interactions between the two polymers on the morphology and thermal properties was investigated. For the PBA–SPS composites, a single T_g was detected during the first scanning, which increased with increasing PBA content and sulfonation level; only the T_g of SPS was detected during the second scanning. The PBA–PVA composites exhibited two T_gs during the first scanning.

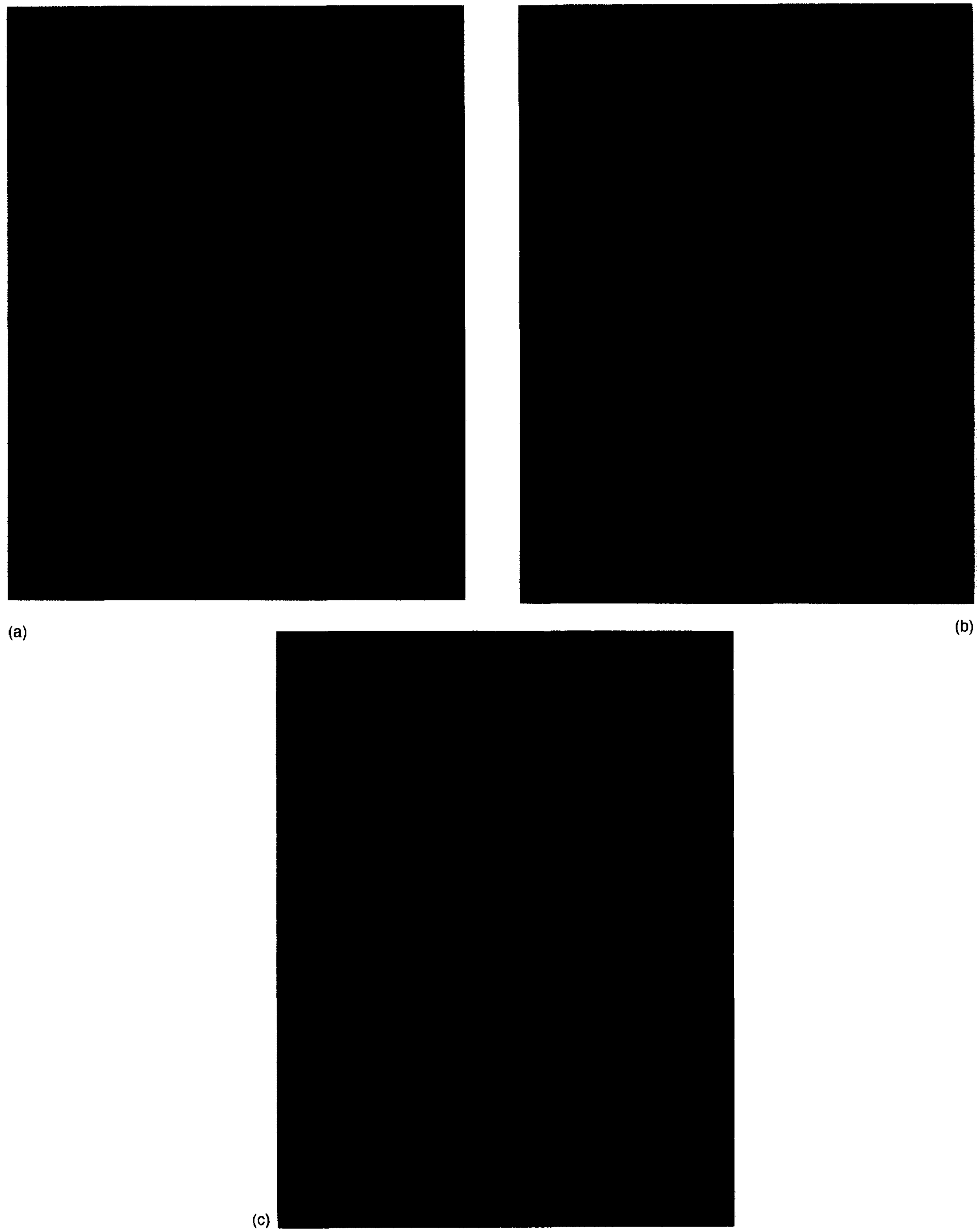

Figure 5 SEM micrographs of PVA and PBA–PVA Composites: (a) PVA; (b) 2.5 wt% PBA; (c) 7.5 wt% PBA.

Table 3 Mechanical properties of PVA and the PBA–PVA composites

PBA content (wt%)	Yield strength (MPa)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation (%)
0	11	9	235	200
2.5	16	14	400	160
5.0	44	34	700	20
7.5	—	24	860	2

The lower one was assigned to the PVA matrix and the higher one, which increased with increasing PBA content, to the PBA–PVA microdomains; only the T_g of PVA was found in most cases during the second scanning. *FT*-i.r. revealed the existence of interactions between the sulfonic groups of SPS and the amide groups of PBA. For PBA–PVA composites, only weak interactions between PVA and PBA were noted. The SEM micrographs revealed blends containing particles of colloidal size. For the PBA–PVA composites, the tensile strength and Young's modulus increased and the elongation decreased with increasing PBA content, indicating that PBA particles reinforce the flexible PVA matrix.

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