

Nanocomposites of rigid polyamide dispersed in flexible vinyl polymer

Eli Ruckenstein* and Yumin Yuan†

Department of Chemical Engineering, State University of New York at Buffalo, Amherst, NY 14260, USA

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Polymer composites consisting of a rigid poly(*p*-benzamide) (PBA) and a flexible poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) (PVVH) were prepared by a two-step method. A nanoscale level of mixing in the solid state was achieved. In the first step, a turbid, viscous PBA dispersion was obtained by the direct polycondensation of *p*-aminobenzoic acid in *N,N'*-dimethylacetamide (DMAc) under mild reaction conditions. In the second step, the PBA dispersion was mixed with a solution of PVVH in DMAc. A clear and homogeneous solution, which may be under certain conditions thermodynamically stable, was thus obtained, from which the polymer composite was recovered by precipitation in methanol. The composites could be re-dissolved in DMAc, generating slightly turbid solutions. The thin films prepared via casting exhibited rather good transparency. FTi.r. revealed the presence of hydrogen bonding between the two polymers. Scanning electron microscopy revealed the presence of uniformly dispersed PBA particles with sizes between 50 and 70 nm. The yield and tensile strengths and Young's modulus increased two- to three-fold, while the elongation decreased, when the PBA content increased from 0 to 25 wt%. Within the scanning range, a single T_g was identified in the composites by differential scanning calorimetry, which increased with increasing PBA content during the first thermal scanning; only the T_g of the PVVH was detected during the second scanning. The chemical resistance of PBA/PVVH composites was significantly enhanced compared to that of PVVH. The strong interactions between PBA and PVVH, which act as physical cross-linkers, are responsible for the behaviour of these composites. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polymer composites containing a rigid component have wide applications, typical examples being the structural materials, in which the rigid component reinforces the tensile strength and modulus of the polymer matrix. When the components are mixed at a molecular scale, a maximum reinforcing effect can be achieved theoretically; such a composite was called a 'molecular composite'^{1–3}. The conventional way to prepare a molecular composite is to dissolve the two components in a common solvent, followed by precipitation in a non-solvent^{3,4}. However, the rigid and the flexible polymers are usually thermodynamically incompatible and, as a result, the molecular composite undergoes phase separations during the preparation process or the end use. Much effort was expended to prevent phase separation, using the following procedures: (1) The linking of the rigid and flexible components by chemical bonding as graft or block copolymers^{5–8}; (2) the insertion of functional groups in the chains of the rigid and flexible components, which generate specific interactions between the two constituents^{9,10}; (3) the *in situ* generation of the rigid polymer from flexible precursor^{11–13}. For instance, regarding procedure (3), a composite film containing two flexible polymers,

poly(*p*-phenylene *m*-pyromellitimide diethyl ester) and poly(*p,p'*-oxydiphenylene oxydiphthalamic acid), was first prepared by solution casting. Subjecting the composite film to heating at 400°C, the former precursor was transformed into a rigid polyimide and the latter one into a flexible polyimide¹¹. Similarly, a pyromellitic dianhydride based flexible polyisoimide precursor, which is soluble in (and hence compatible with) an amorphous matrix or a thermosettable oligomer, was converted *in situ* into a rigid polyimide by heating^{12,13}.

Poly(*p*-benzamide) (PBA) is a fully aromatic polyamide, which can be synthesized via the triphenylphosphine mediated direct polycondensation of the *p*-aminobenzoic acid (AB) in a polar solvent, such as *N*-methyl-2-pyrrolidinone, under mild reaction conditions¹⁴. PBA has excellent solvent and heat resistant characteristics, since it is insoluble in organic solvents and does not melt even at high temperatures. For this reason, the preparation of PBA containing composites through the conventional solution or melting procedures is not possible. An approach to prepare polymer composites containing a rigid component such as PBA is to dissolve its monomer and the flexible polymer in a common solvent and then to obtain the rigid polymer *in situ*^{15,16}. Ogata *et al.*¹⁵ synthesized poly(*p*-benzoate) (PB)/poly(arylate) and PBA/poly(arylate) composites by this method, using methylene dichloride as solvent. The addition of a non-solvent (methanol) precipitated the composite. The dried powder was redispersed in

* To whom correspondence should be addressed

† Permanent address: Department of Material Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing, 100083, China

chloroform and a composite film was obtained by casting on a glass surface. In these composites, the rigid polymer was dispersed as fine particles within the poly(arylate) matrix. The composite films were opaque, because of the large particle size (1 μm), but no macrophase separation was observed. It is interesting to note that even intractable polymers became processable by this procedure. However, the tensile strength of the composite film decreased, while Young's modulus only slightly increased compared to those of the flexible polymer matrix.

In this paper, PBA is selected as the rigid component and poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) (PVVH) as the flexible polymer matrix, and a two-step method is suggested to prepare composites with higher yield and tensile strengths and Young's modulus than the flexible polymer. In the first step, PBA is obtained, via direct polycondensation, starting from a solution of the monomer AB and activators (triphenylphosphine, pyridine and hexachloroethane) in dimethylacetamide (DMAc). By using high concentrations of reactants a fast polymerization rate results, which leads to a highly viscous solution. This prevents the precipitation of the formed PBA, which is insoluble in the solvent. In the second step, the solution containing the dispersed PBA particles is mixed with a solution of PVVH in DMAc.

The purpose of this work is to prepare PBA/PVVH polymer composites using the two-step method and to investigate the effect of the PBA content on the structure and properties of the polymer composites.

EXPERIMENTAL

Materials

The monomer *p*-aminobenzoic acid (99%) (AB), the activators triphenylphosphine (99%) (TPP), hexachloroethane (99%) (HCE) and pyridine (anhydrous), the solvent *N,N'*-dimethylacetamide (anhydrous) (DMAc) and poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) (M_w 33 000, vinyl chloride 81 wt%, vinyl acetate 4 wt% and 2-hydroxypropyl acrylate 15 wt%) (PVVH) were used as received. All chemicals were purchased from Aldrich.

Preparation of PBA/PVVH polymer composites

In the first step, the AB monomer (1.73 g, 12.6 mmol) and TPP (4.0 g 15.2 mmol) were dissolved in 15 ml DMAc and 8 ml pyridine and the mixture was stirred at 60°C for 15 min. After it was cooled down to 40°C, HCE (4.2 g, 17.7 mmol) was added with vigorous magnetic stirring. The direct polycondensation took place immediately, accompanied by a colour change (from slight yellowish to red yellowish), heat release and viscosity increase. Since PBA is insoluble in DMAc, the solution became turbid as the reaction continued. In the second step, a part of the colloidal dispersion of PBA was mixed with PVVH solutions in DMAc, so as to obtain final composites with PBA contents of 8, 15 and 25 wt%. Another part was poured into methanol to generate a PBA powder. When the turbid PBA solution was mixed with the PVVH solution under stirring, a clear and homogeneous system was obtained. The polymer composite was collected by pouring the viscous solution into methanol, filtering, washing the precipitate repeatedly with methanol, and finally drying in a vacuum oven at

Table 1 PBA/PVVH composites

Abbreviation	Yield (%)	PBA content (wt%)	Appearance of thin film
PVVH	—	0	transparent
PBA8	99	8	semitransparent
PBA15	99	15	semitransparent
PBA25	99	25	semitransparent

60°C. This was followed by the re-dispersion of the composite in DMAc, and the obtained slightly turbid solution was used to prepare a film by casting.

FT i.r. analysis

Thin film samples for FT i.r. analysis were prepared by casting the solutions of the composites onto aluminium pans at 50°C, followed by vacuum drying at 60°C to remove the solvent. A Perkin-Elmer 1760X instrument was employed.

Tensile testing

Thin films with good transparency were obtained by casting the DMAc solutions of the composites onto glass plates and evaporating the solvent at 50°C. The thin films were cut into dumbbell-shaped specimens, as required by ASTM D. 638–58T, after which they were thoroughly dried in a vacuum oven at 50°C overnight to remove the residual high boiling point solvent, DMAc. 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.

Thermal transition determinations

The glass transition temperature (T_g) was determined with a Du Pont 910 differential scanning calorimeter (d.s.c.). The composite powders were dried under vacuum at 50°C before scanning, and the samples were scanned under nitrogen, from 30 to 150°C, with a heating rate of 10°C min⁻¹. T_g was defined as the midpoint of the transition range.

Scanning electron microscopy (SEM)

The morphology of the PBA/PVVH composite films was examined by SEM (Hitachi S-800). The films were fractured under liquid nitrogen and the fractured surfaces were coated with a thin layer of carbon before scanning.

Swelling and insoluble species content measurements

Prewighted composite films prepared as for mechanical testing were immersed in chloroform at room temperature for 12 h. The swollen films were retrieved, weighted and then dried to remove the solvent. The swelling and insoluble species content are defined as the ratios between the weights of the swollen and dried specimen to the original weight, respectively, multiplied by 100.

RESULTS AND DISCUSSION

Table 1 summarizes some characteristics of the two-step method and shows that the PBA/PVVH composites have a high yield (percentage of the theoretical amount of composite), even for a PBA content as low as 8 wt%. The conversion of AB (near 100%) is much higher than that

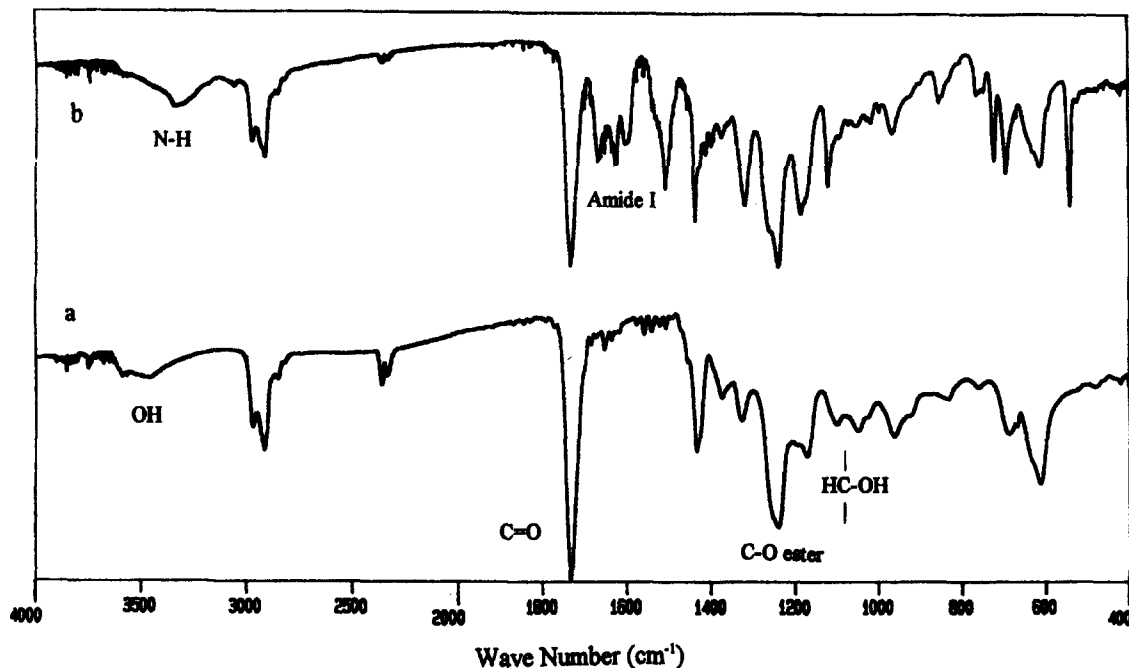


Figure 1 FTIR spectra: (a) PVVH; (b) PBA/PVVH (8 wt% PBA)

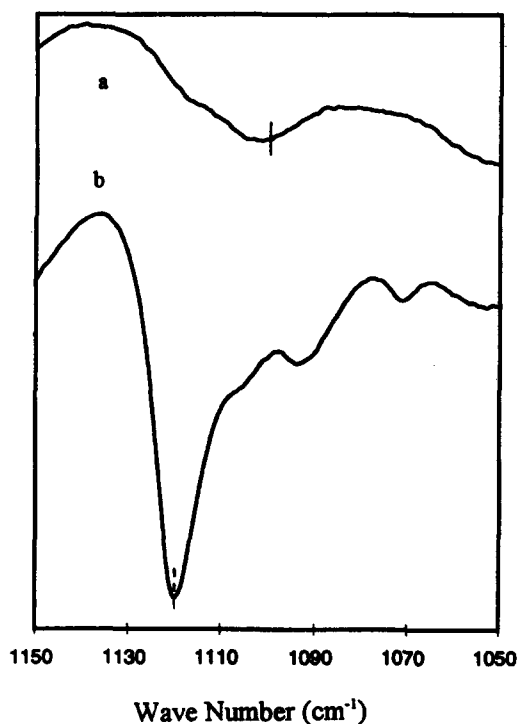


Figure 2 C-O stretching of the secondary alcohol: (a) PVVH; (b) PBA/PVVH (8 wt% PBA)

obtained by the *in situ* direct polycondensation method¹⁵, for which it was as low as 50 wt%. While PBA does not dissolve in organic solvents, the turbid PBA dispersions in DMAc mixed with PVVH/DMAc solutions led to clear and homogeneous solutions, even for a PBA content in the composite as high as 25 wt%. The obtained composite powders could be re-dissolved in DMAc, but the solutions were slightly turbid. The films obtained by solution casting exhibited a slight colour and a rather good transparency, indicating a rather small particle size of the PBA dispersion in PVVH. When the turbid PBA dispersion in DMAc was poured into methanol, a

yellowish powder was generated, which could not be dissolved in DMAc, confirming that AB was converted to PBA. One possible explanation for the formation of clear solutions after mixing PVVH solutions with turbid PBA dispersions, is that the PVVH chains are grafted to the surface of PBA particles, via the coupling of the OH groups of PVVH with the carboxyl acid terminated PBA molecules. However, the concentration of the latter group is very low and the concentration of OH groups in PVVH is only 8 mol%. The more likely explanation is that PVVH molecules are adsorbed upon the surface of the colloidal particles of PBA, thus increasing the compatibility between particles and solvent.

FTIR analysis

The FTIR spectra of PVVH and a PBA/PVVH composite are present in Figure 1. The characteristic absorptions of PBA are in the 3200–3450 cm^{-1} (N-H stretching) and 1630–1670 cm^{-1} (amide I bands) ranges as well as at 1603 cm^{-1} (aromatic C=C stretching). The characteristic absorptions of PVVH are at 3450 and 3600 cm^{-1} (OH stretching vibrations), 1730 cm^{-1} (C=O stretching), 1240 cm^{-1} (ester C-O stretching) and 1100 cm^{-1} (secondary alcohol C-O stretching). The hydroxyl group of the 2-hydroxypropyl acrylate moiety of the pure PVVH generates two peaks, at 3450 and 3600 cm^{-1} , the lower wave number peak being due to the hydrogen-bonded-OH and the higher wave number one to the hydrogen-bond-free-OH¹⁶. When 8 wt% PBA was incorporated, the absorption due to the OH stretching was overlapped by the strong absorption due to the N-H stretching and could not be used to identify the presence of hydrogen bonding. However, the C-O stretching of a secondary alcohol, usually located in the range 1075–1150 cm^{-1} , is sensitive to environmental changes and is shifted toward higher wavenumbers if hydrogen bonding occurs¹⁸. Figure 2 depicts the C-O stretching of the secondary alcohol moieties of PVVH before and after blending with PBA, and shows that it is shifted from 1100 cm^{-1} for pure PVVH to 1120 cm^{-1} for

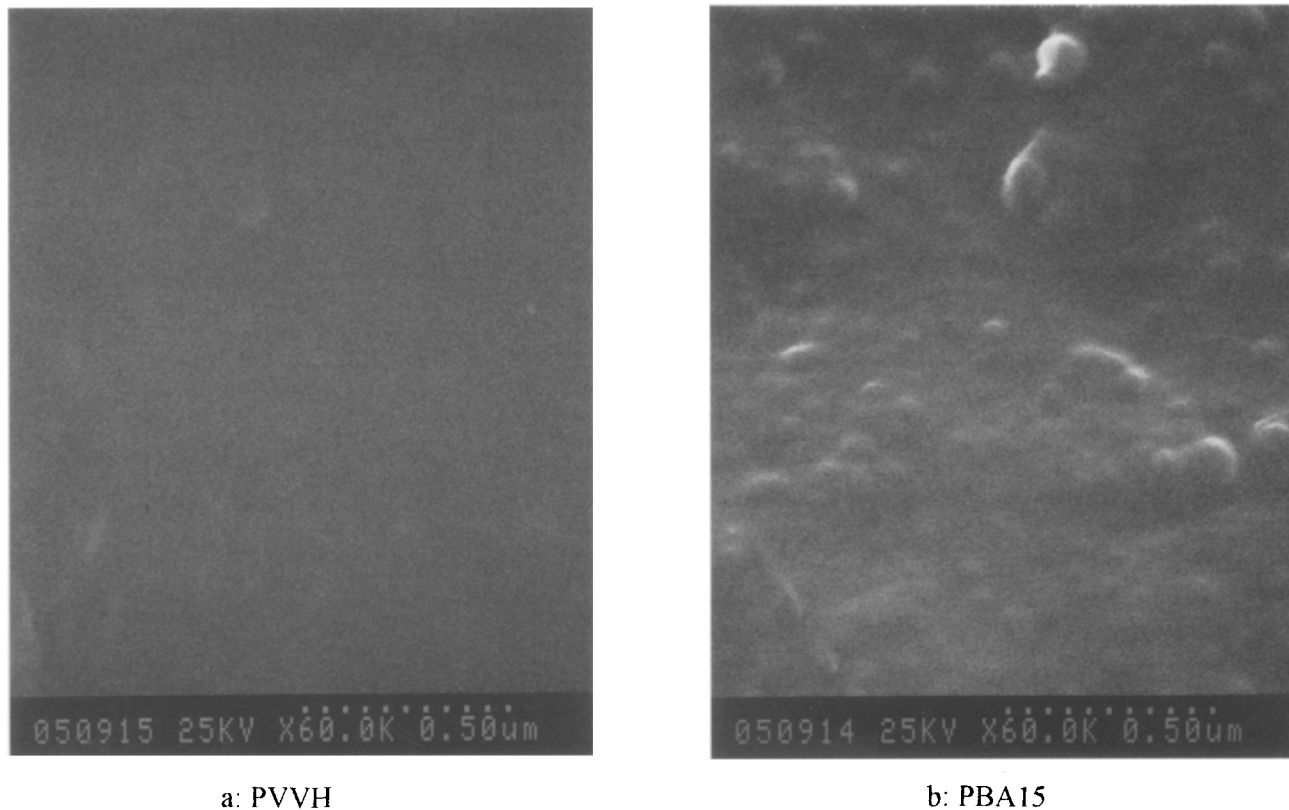


Figure 3 SEM micrographs of the fractured surfaces of PVVH and PBA/PVVH composites: (a) PVVH; (b) 15 wt% PBA

the PBA/PVVH composite. This occurs because the secondary OH groups of PVVH are hydrogen-bonded to the C=O of the amide groups of PBA. Because of the hydrogen bonding and other interactions between various polar groups, the PVVH chains are strongly adsorbed on the surface of the PBA colloidal particles, thus increasing the compatibility between the colloidal particles and solvent. This explains why the mixture obtained by mixing the turbid dispersion of PBA in DMAc with the solution of PVVH in DMAc became

clear and homogeneous. The clear solution might be even thermodynamically stable, for the following reasons:

The entropy of dispersion of the colloidal particles provides a negative contribution to the free energy of the system. Similarly, the adsorption of the PVVH chains on the surface of the colloidal particles decreases the concentration of PVVH in the solvent, thus decreasing its chemical potential but increasing the chemical potential of the solvent; since the concentration of PVVH is changed much more than that of the solvent, this

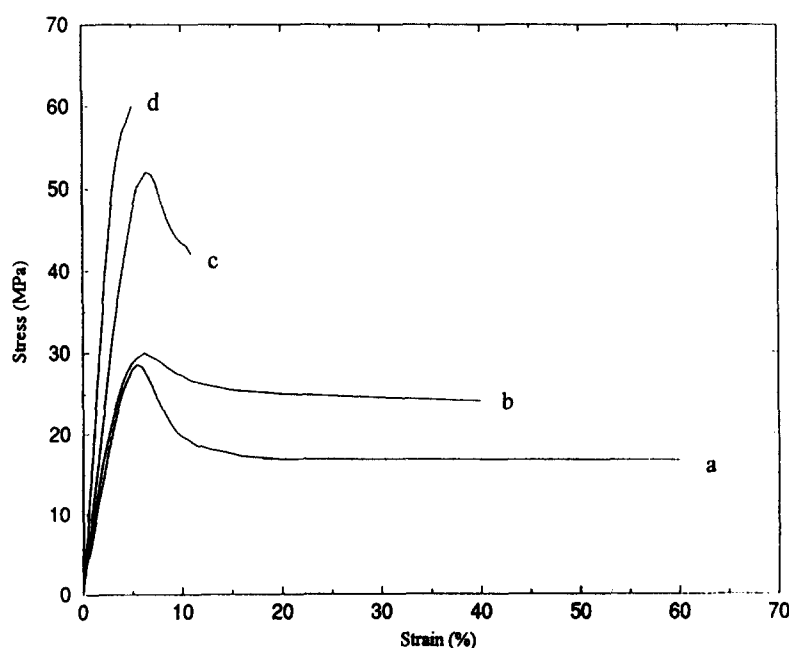


Figure 4 Stress-strain curves of PVVH and PBA/PVVH composites: (a) PVVH; (b) 8 wt% PBA; (c) 15 wt% PBA; (d) 25 wt% PBA

Table 2 Mechanical properties of PBA/PVVH composites

PBA content (wt%)	Yield strength (MPa)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation (%)
0 (PVVH)	28.6	16	700	60
8	30	24	800	40
15	52	43	1060	11
25	—	60	1500	8

Table 3 T_g of PBA/PVVH composites

PBA content (wt%)	T_g during the 1st scanning (°C)		T_g during the 2nd scanning (°C)	
	Onset	Midpoint	Onset	Midpoint
0 (PVVH)	68	72	68	72
8	82	88	68	73
15	86	102	65	72
25	100	120	68	72

'dilution effect' decreases the free energy of the system. Finally, the adsorption of PVVH upon the surface of the particles decreases the interfacial tension between the latter and the liquid. While the free energy due to the interfacial tension provides a positive contribution to the free energy, the decreased interfacial tension makes this contribution relatively small. It is, therefore, possible for the first two negative contributions to compensate for the latter positive contribution and a thermodynamically stable system to be generated.

The variation of the Gibbs free energy of the system is given by the expression:

$$dG = \mu_s dn_s + \mu dn + \gamma dA + d\Delta G \quad (1)$$

where μ_s and μ are the chemical potentials of the solvent and PVVH, n_s and n the corresponding number of moles, γ is the interfacial tension at the surface of the particles, A is the area of the particles and ΔG the free energy due to the entropy of dispersion of the colloidal particles in the liquid. The area A at thermodynamic equilibrium is given by the minimum of G with respect to A , at constant n_s and n . Since ΔG is a function of the number of particles m and their radius R , and $A = 4\pi mR^2$, at equilibrium:

$$\gamma = -\frac{1}{8\pi mR} \frac{\partial \Delta G}{\partial R} \quad (2)$$

As shown later, the particles encountered in this paper have a size of the order of 10^2 nm. For such large particles, the entropy of dispersion is expected to be small. For this reason on the basis of equation (2), one can conclude that, at equilibrium, γ is also very small. This may indeed happen in the present case, since the chains of PVVH adsorbed on the surface of the particles provide an atmosphere compatible with the solution of PVVH in the solvent, and the solvent is no longer in direct contact with the particle but with the atmosphere that surrounds it. Equation (2) is very similar to that derived previously for microemulsions¹⁹, with the difference that the number of particles is this time given. Expressions for the entropy of dispersion have been derived²⁰, but information about γ is not yet available. In principle, if expressions for ΔG and γ are introduced in equation (2), the latter can be used to calculate the equilibrium radius of the particles. If the initial radius of the PBA particles is smaller than the equilibrium radius, they can grow in size, via the adsorption of PVVH, to

Table 4 Swelling and insoluble species content (ISC) of PBA/PVVH composites

PBA content (wt%)	Appearance in chloroform	Swelling (wt/wt, %)	ISC (wt/wt, %)
0 (PVVH)	collapsed	dissolved	0
8	original	480	35
15	original	360	50
25	original	200	70

acquire the equilibrium value. If the initial radius of the PBA particles is larger, no thermodynamic equilibrium can be achieved. However, even if the thermodynamic equilibrium is not achieved, the system can have kinetic stability with a long life, because the compatibility between the PBA particles covered by adsorbed PVVH molecules and solvent prevents coagulation.

Morphology

The SEM micrographs of the fractured surfaces of PVVH and PBA/PVVH composite films are presented in *Figure 3*. The pure PVVH film has a homogeneous structure. In the PBA/PVVH composites, a two-phase structure can be identified, in which PBA particles, with a narrow size distribution between 50 and 70 nm, are uniformly dispersed in the PVVH continuous phase. This observation indicates that a colloidal level of mixing is achieved between the two polymers. In contrast, the PB particle size in PB/poly(arylate) composite, determined with a cross-optical microscope, was much larger, about 1000 nm¹⁵.

Stress-strain curves

The stress-strain curves of PVVH and PBA/PVVH composites are presented in *Figure 4*, which shows that as the PBA content increases, the materials change from thermoplastic to brittle. Curve a for PVVH has a typical thermoplastic behaviour, since it exhibits a yield point at about 6% strain. Curve b, with a PBA content of 8 wt%, has a similar stress-strain behaviour as curve a. Curve c shows that for a PBA content of 15 wt%, the specimen breaks during stress softening. In curve d, which is for the 25 wt% PBA composite, the material breaks before the yield point is reached.

Mechanical properties

The mechanical properties of PVVH and PBA/PVVH composites are listed in *Table 2*, which shows that, with increasing PBA content, both the yield and tensile strengths and Young's modulus increase, while the elongation decreases. Compared to pure PVVH, the yield and tensile strengths and Young's modulus are enhanced up to two- to three-fold, indicating that the PBA reinforces the flexible PVVH matrix. This tensile behaviour is very different from that of PBA/poly(arylate) composites¹⁵, in which the tensile strength decreased about 27% and Young's modulus increased only 17% at 23°C, as the PBA content increased from 0 to 29 wt%.

D.s.c. measurement

The T_g data of the PBA/PVVH composites are listed in Table 3. The PVVH powder became black at temperatures over 150°C, indicating that thermal degradation occurred. For this reason, the scanning range was selected between 30 and 150°C. The PVVH had a narrow T_g at about 72°C and the PBA powder did not exhibit thermal transitions within the above scanning range. All the PBA/PVVH composites exhibited a single, broad and composition-dependent T_g , which increased with increasing PBA content, during the first scanning. These composites displayed the T_g of the pure PVVH during the second scanning. Usually a single and composition-dependent T_g implies a miscible blend. In the present case, SEM reveals that the PBA and PVVH blends are miscible at the colloidal scale. The fact that the composites exhibit a single, composition-dependent T_g indicates that the movements of the PVVH chains are hindered by the nanoscaled PBA particles, due to the interactions between the two. However, once the temperature was raised above the T_g of the composites, PBA and PVVH segregated, and only the T_g of the pure PVVH could be detected during the second scanning, regardless of the PBA content in the composite. For comparison, a PBA/Poly(styrene) (PSt) composite with a PBA content of 30 wt% was prepared by *in situ* direct polycondensation in chloroform. A single T_g was detected at 105°C during the first and second scanning, which is the T_g of the pure PSt. This happens because there are no strong interactions between PBA and PSt and therefore, the movements of PSt chains were not hindered by PBA.

Swelling and insoluble species content

PVVH dissolved rapidly in chloroform at room temperature, while the composite films dissolved only partially after 12 h. The swelling and the insoluble species content (in chloroform) are listed in Table 4. The PBA/PVVH thin films kept their original shape, but their swelling decreased and the insoluble species content increased with increasing PBA content. It should be noted that no cross-linkers were added to the PBA-PVVH systems, hence no chemical cross-linking occurred in the composites. The significant resistance to chloroform of the PBA/PVVH thin films can be attributed to the strong interactions between the two constituents. These interactions, acting as physical cross-linkers, inhibit the complete dissolution and collapse of the composite films. For comparison purposes, the behaviour of a PBA/PSt composite thin film with a PBA content of 30 wt% was also tested. This thin film collapsed within minutes when it was immersed in chloroform. This clearly indicates that there are relatively weak interactions between PBA and PSt. Once the continuous phase, PSt, was dissolved by the solvent, the whole film collapsed.

CONCLUSIONS

A two-step method was developed to prepare polymer

composites consisting of the rigid poly(*p*-benzamide) (PBA) and the flexible poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) (PVVH). As revealed by SEM, a nanoscale level of mixing between PBA and PVVH was achieved in the solid composites. The stress-strain behaviour of the composites indicates that the materials change from thermoplastic to brittle as the PBA content increases. The yield and tensile strengths and Young's modulus were enhanced several fold, while the elongation decreased, as the PBA content increased. This indicates that PBA reinforces efficiently the flexible PVVH matrix. The T_g of the composite increased with increasing PBA content, indicating that the movements of the PVVH segments are hindered by the PBA particles. The PBA/PVVH composites exhibited a significant solvent-resistance to chloroform; while their swelling was relatively high, they dissolved only partially after 12 h. FTi.r. revealed the presence of hydrogen bonding between the secondary OH group of PVVH and the amide group of PBA. The strong interactions, which act as physical cross-linkers, explain the behaviour of PBA/PVVH composites.

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