

Compatibilization of Poly(vinyl chloride) and Polystyrene Blends with Poly(styrene-*co*-*n*-methylolacrylamide)

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ABSTRACT: In this work, the compatibilization of blends of plasticized polyvinyl chloride (PVC) and polystyrene (PS) with poly(styrene-*co*-*n*-methylolacrylamide) (PSnMA) was investigated. The PSnMA was synthesized by emulsion polymerization with different amounts of *n*-methylolacrylamide (nMA). Particle size and phase behavior was determined by scanning electron microscopy, and mechanical properties were determined in an Universal Testing Machine. Micrographs revealed that an appreciable size reduction of the dispersed phase was achieved when small

amounts of PSnMA were added to the blend, and as the amount of nMA was increased, particle size decreased. When the (PVC/PS/PSnMA) blend was subjected to solvent extraction to remove PS and unreacted PVC, the residue showed a single T_g . Tensile modulus and the ultimate strength of the blends increased with PSnMA content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 297–303, 2008

Key words: compatibilization; *n*-methylolacrylamide; morphology; blends

INTRODUCTION

In recent decades, there has been an increasing demand for polymeric materials with better properties. One way to respond to this demand is by blending polymers; however, most of the polymers are mutually incompatible when they are mixed. Physical, optical, and mechanical properties of incompatible polymer mixtures or blends can be improved by adding small amounts of a third component (compatibilizer) to induce compatibility.¹ The compatibilization must (i) stabilize the morphology against high stresses during formation and (ii) enhance adhesion between the phases in the solid state.^{1–3}

Typically, a mixture of two immiscible polymers produced by melt mixing exhibits low deformation capacity and poor mechanical properties, because when it is subjected to stress, the stress concentrates at the interface, which, for incompatible polymer pairs, is weak and it is unable to transfer the stress between the phases.^{4,5} Hence, one of the important roles of a compatibilizer is to transfer the stress between the continuous and disperse phases. Another role is to allow the formation of an extremely fine dispersion of one phase into the other by an emulsifying-like effect and to increase the

interfacial adhesion,^{6,7} which reduces the tendency of the dispersed phase to coalesce (more stable morphologies are obtained).^{8–11} Because of the increase in interfacial adhesion, there is an increase in the stress transfer between the continuous and dispersed phases, which improves the mechanical properties of the blend.^{12–14}

The motivation for blending PS and PVC is the development of a material that combines the properties of PS and PVC. PVC would improve the toughness and impact resistance to the resulting material and the PS could increase ultimate strength and moduli.¹⁵

In the literature, several publications^{15–20} have discussed some compatibilizers for PVC/PS blends. Copolymers based on poly(styrene-*block*-methyl methacrylate)^{15,16} refined the coarse morphologies and increased mechanical properties of the PS/PVC blends. When using copolymers of poly(styrene-*block*-butadiene),^{17,18} a superior adhesion between the PVC and the PS phases is reported. Zhong et al.¹⁹ reported the effectiveness of chlorinated polyethylene-*graft*-polystyrene (CPE-*g*-PS) as a polymeric compatibilizer for PVC/PS blends and their explanation was that although PVC is immiscible with the chlorinated polyethylene block of the CPE-*g*-PS, interactions between PVC and CPE can occur by polar–polar attractions, and the PS homopolymer is miscible with the PS block of CPE-*g*-PS. Recently, Abd-El-Messieh²⁰ reported that the addition of 10 and 20 wt %, of maleic anhydride to PVC/PS blends improved the compatibility of this blend. Haba and Narkis²¹ prepared PVC/PS blends through a

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reactive extrusion-polymerization method by the addition of styrene monomer, initiator, and a cross-linking agent to a commercial suspension-type porous polyvinyl chloride (PVC), forming a dry blend with a relatively high monomer content. These PVC/styrene dry blends were reactive extrusion polymerized in a twin-screw extruder and presented a single T_g transition and an increase in the thermostability of the PS phase. More recently, Kumaraswamy and Ranganathaiah²² prepared PVC/PS blends of different composition by the solution-casting technique and found by DSC that the polymers were mutually immiscible.

In this work, we report that the addition of small amounts of poly(styrene-*co*-*n*-methylolacrylamide) (PSnMA) to mixtures of a commercial PS and plasticized PVC induces an important decrease of the dispersed-phase size in the whole composition range, which indicates enhancement of the compatibility of PVC/PS by the presence of the PSnMA.

EXPERIMENTAL

The monomers used to synthesize the copolymer (PSnMA) were reagent-grade styrene (St) from Sigma-Aldrich (St Louis, MO) and an aqueous solution of *n*-methylolacrylamide (nMA) (60 wt %) from Tokio Kasei industries (Tokyo, Japan). The St was passed through a DTR-7 column (SPP) to remove the inhibitor, and the nMA was used as received. The copolymer was synthesized by emulsion polymerization, and the details on the synthesis and characterization of this copolymer are given elsewhere.²³ Copolymers (nMA-1, nMA-2, and nMA-3) containing 7, 11, and 14% weight of poly(*n*-methylolacrylamide) respectively, were obtained. PS (Resirene HF-777 from Resistol Lerma, Mexico) was used as received. The PVC was supplied from Mazatan Plastics, Guadalajara, Mexico, containing 27 wt % of dioctyl phthalate as the plasticizer.

Prior to a typical mixing experiment, PVC, PS, and PSnMA were dried under vacuum at 80°C overnight. Blends of different compositions from 10 to 90% of PVC in PS were prepared in a Haake Rheocord 9000 internal mixer with roller blade geometry, operating at 200°C and 40 rpm, and the blending time was 7 min. The PVC/PS/PSnMA blends were prepared in a Haake Rheocord 9000 internal mixer, operating at 200°C and 40 rpm, and the blending time was 7 min. The PVC/PS composition (30/70 wt/wt) remained constant, and the amount of compatibilizer was varied: 3, 5, and 10% with respect to the dispersed phase (PVC). First, master batches of mixtures of PS and PSnMA were prepared and then added to the PVC in the required quantities.

The morphologies of the freeze-fractured polymer samples with and without compatibilizer were

examined in a JEOL JSM-5400 LV scanning electron microscope (SEM) equipped with a quantum super dry detector. Potentials of 15–20 kV were employed. Samples were immersed in liquid nitrogen, fractured, and placed in a Baltec CE SCD004 golden evaporator to deposit a gold layer by electrodeposition. The average diameter of the dispersed phase in each mixture was determined from the SEM micrographs using an image-Pro Express analyser (Media Cybernetics). The number-average (D_n) and volume-average (D_v) diameters were calculated by

$$D_n = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

$$D_v = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (2)$$

Here n_i is the number of particles with diameter d_i . For these calculations, at least 300 particles were measured.

After blending, a portion of the PVC/PS/PSnMA blend was subjected to solvent extraction in a Soxhlet apparatus, using tetrahydrofuran (THF) to remove PS and unreacted PVC. The composition of the residue was analyzed by FTIR, and its glass transition temperature (T_g) was obtained in a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 10°C/min. Stress-strain properties were determined by using a Universal Testing machine UNITED SFM-100. The samples were cut in a type IV format according to ASTM D 638 norm.

RESULTS

Figure 1 shows the morphology of blends of PVC/PS of different composition. In Figure 1(a,b), it can be observed that when the PVC/PS ratio is 90/10, and 70/30 wt/wt, there are spherical particles (PS) imbedded in a continuous phase (PVC). When the PVC/PS ratio is modified to 60/40 and 50/50 wt/wt [Fig. 1(c,d)], the spherical particles disappear and it is not possible to differentiate which is the dispersed and the continuous phase, which indicates that phase inversion is occurring. If the PS content is increased (60–90%), it is again possible to observe spherical particles (PVC) imbedded in a continuous phase [Fig. 1(e,f)].

Figure 2 shows average particle size (D_n and D_v) of the dispersed phase of blends of PVC/PS as a function of PS composition. At low PS concentration (left side on the graph), the PS should be the dispersed phase. When the PS concentration is increased, particles size increases until a composition above 30% and below 60% PS, where it is not possible to distinguish which is the dispersed or the continuous phase [Fig. 1(c,d)]. By increasing the PS concentration to

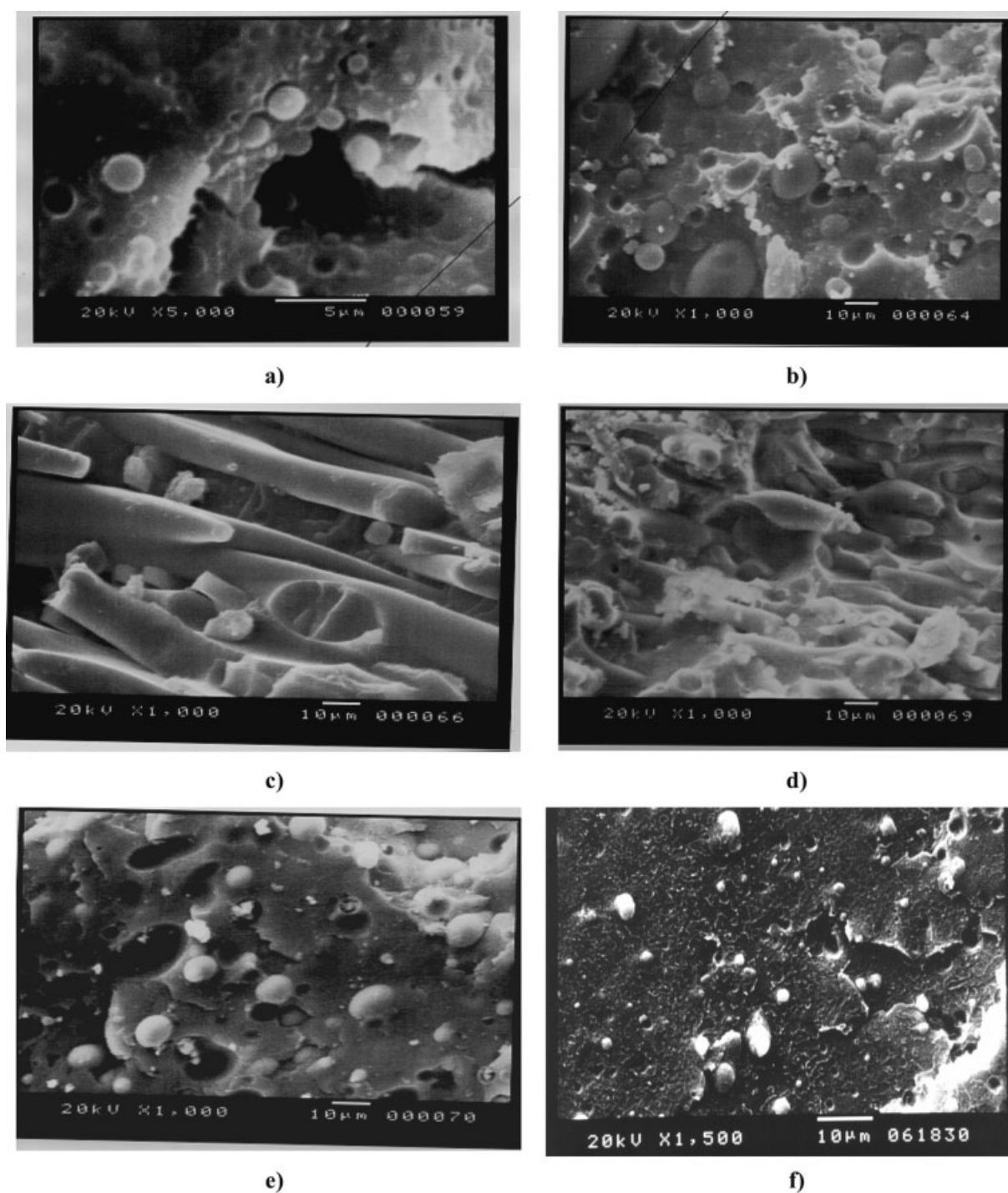


Figure 1 Micrographs of PVC/PS blends of different composition PVC/PS wt/wt: (a) 90/10, (b) 70/30, (c) 60/40, (d) 50/50, (e) 40/60, and (f) 10/90.

60%, the dispersed phase becomes the PVC and large particles are obtained, further increase of PS concentration causes a decrease in PVC particle size.²⁴⁻²⁶

It has been reported²⁴ that when using a compatibilizer the blends are prepared by a two-step mixing process and that the migration of the modifier to the interface is facilitated when it is initially mixed with one of the components.²⁵ For this reason, in this

work to determine the compatibilizer effect of PSnMA, previously obtained blends of PSnMA/PS of different composition were mixed with PVC to obtain blends containing 30% of PVC. This blend composition, where PVC is the dispersed phase, was chosen because the compatibilizer is richer in PS and the PVC particles are large, which facilitates the observation of changes in particle size.

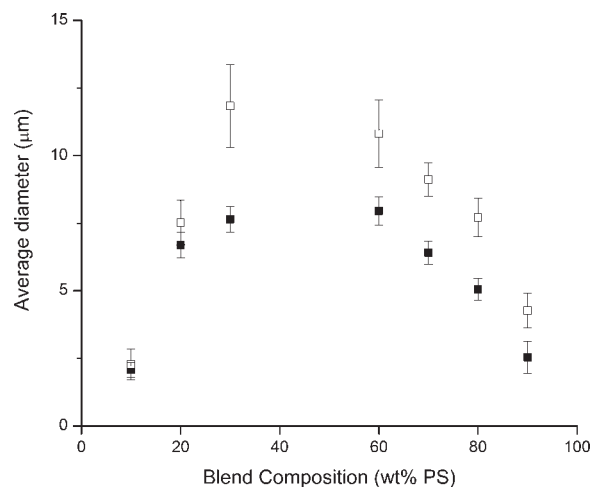


Figure 2 Average particle size (D_n ■, D_v □) of the dispersed phase as a function of blend composition.

Figure 3 shows a micrograph of mixtures of PVC/PS, with a ratio of 30/70 wt/wt, and one of the mixtures does not have PSnMA [Fig. 3(a)] and the others contain 5% of PSnMA [Fig. 3(b–d)]. It can be clearly observed that particle size decreases

by the presence of the PSnMA, and as the PSnMA has a higher content of PnMA, the particle size is smaller.

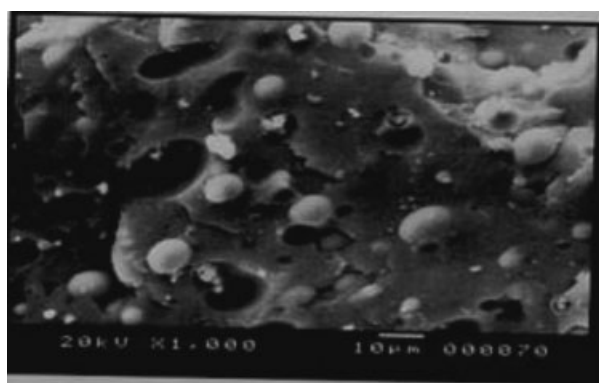
Figure 4 shows the average diameter (D_n and D_v) of the dispersed phase as a function of the PSnMA composition. Average particle size decreases by the presence of any of the PSnMA compositions used, and as the amount of PSnMA is increased, the particle size decreases. It has been reported that compatibilizers decrease particle size because they reduce interfacial tension.^{24,25}

Figure 5 shows that D_n and D_v decrease when increasing the amount of PnMA in the blend until at a content of 0.2% of PnMA, where a further increase in PnMA does not modify particle size.

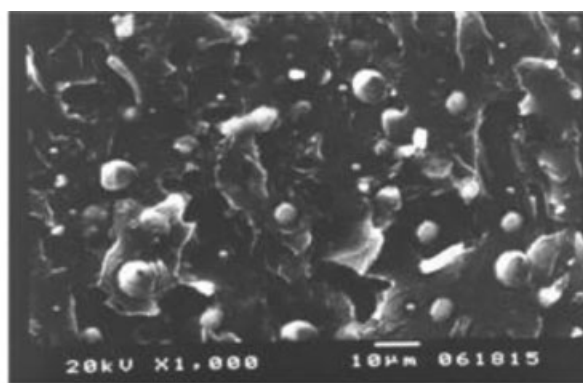
The (PVC/PS/PSnMA) blend was subjected to solvent extraction to remove PS and unreacted PVC. The infrared spectra of the insoluble residue showed characteristic bands of the three polymers (Fig. 6).

The DSC thermograph of the residue of the solvent extraction exhibited only one T_g (114°C).

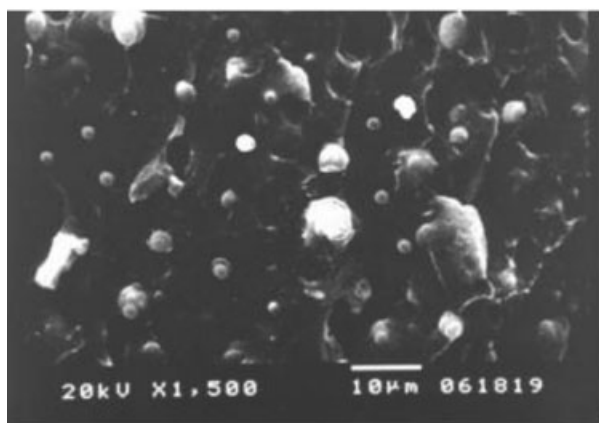
Figures 7 and 8 show that the tensile modulus and the ultimate strength of the blends increase as the amount of PSnMA increases, and the higher the



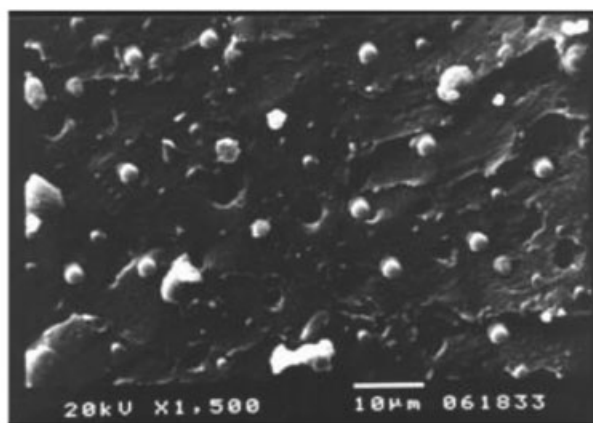
a)



b)



c)



d)

Figure 3 Micrographs of PVC/PS (30/70 by weight) blends containing 5% of PSnMA with respect to the minor phase: (a) without PSnMA, (b) nMA-1, (c) nMA-2, and (d) nMA-3.

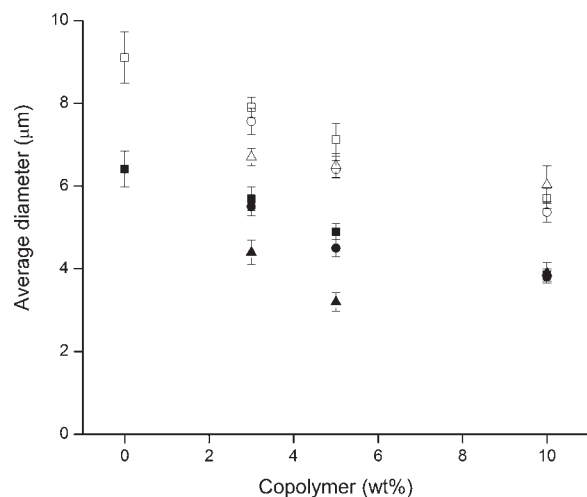


Figure 4 Average particle size (D_n ■, D_v □) of the dispersed phase in PVC/PS (30/70 wt/wt) blends containing different amounts of PSnMA: (nMA-1 ■, nMA-2 ●, nMA-3 ▲).

concentration of PnMA in the compatibilizer the higher the tensile modulus and ultimate strength.

DISCUSSION

PVC and PS are rigid thermoplastic resins, each having wide commercial application. The resins differ markedly in polarity, and the high chlorine content makes PVC much more polar than PS. For this reason, the resins are not miscible,²² and when blending, the domains adhere poorly to one another, which results in brittle, low-strength materials.

Mixtures of PS with plasticized PVC were prepared, and their morphology was studied as a function of composition. From preliminary blend experiments, we found that after 3 min the torque values become constant and particle size did not

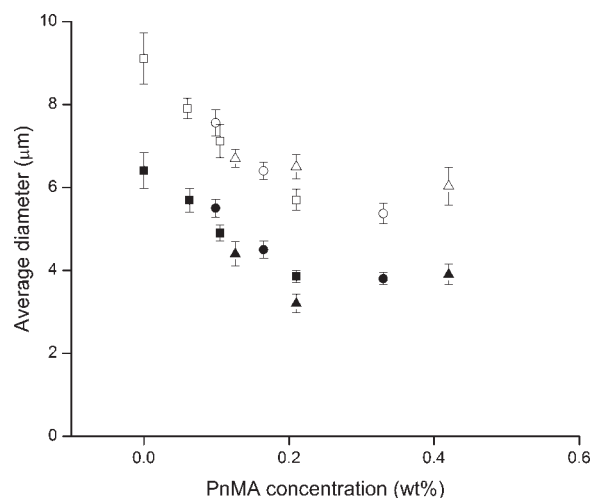


Figure 5 Average particle size (D_n ■, D_v □) of the dispersed phase in PVC/PS (30/70 wt/wt) blends as a function of the PnMA content: nMA-1 ■, nMA-2 ●, nMA-3 ▲.

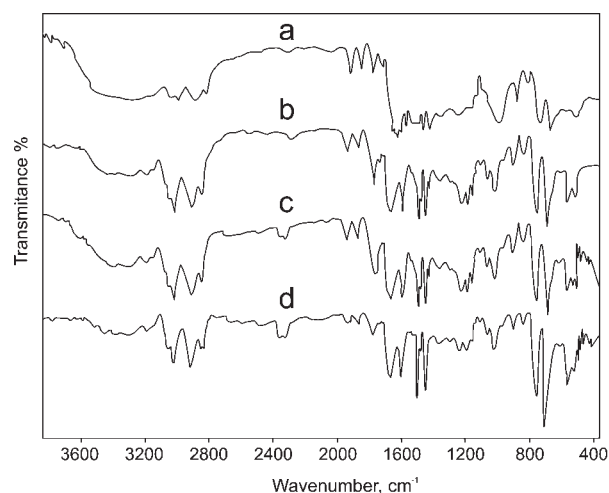


Figure 6 Infrared spectra. PsnMA before being blended: (a) Residues of the solvent extraction of (PVC/PS/PsnMA) blends containing different amounts of PSnMA with respect to dispersed phase (PVC): (b) 3%, (c) 5%, and (d) 10%.

change; for this reason, we decided to blend the components for 7 min. Figure 2 shows average particle size as a function of blend composition. At low PS content, the PS should be the dispersed phase, and the particles are almost spherical [Fig. 1(a,b)]. As the PS concentration is increased, particles grow (Fig. 2) and elongate, until a composition is reached (between 40 and 50%), where it is no longer possible to distinguish which is the continuous and the dispersed phase [Fig. 1(c,d)]. Increasing the PS concentration further causes the PVC now to become the dispersed phase [Fig. 1(e)]. Further increase in PS concentration gives the formation of smaller spherical PVC particles [Figs. 2 and 1(f)].

The viscosity ratio (p) plays an important role in particle size and morphology of blends of polymers mutually immiscible.^{24,25} In our case, the viscosity

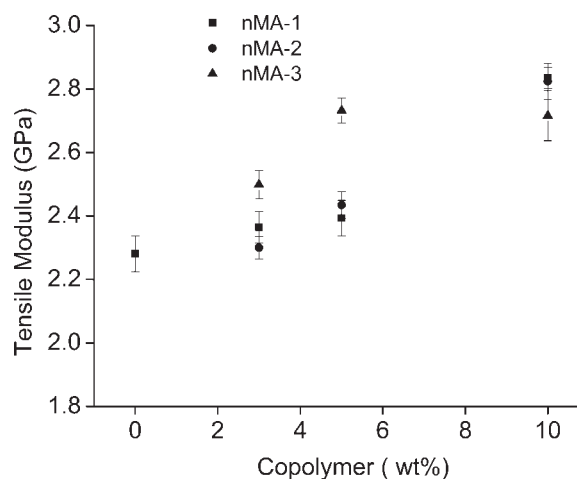


Figure 7 Tensile modulus of PVC/PS (30/70 wt/wt) blends as a function of copolymer content.

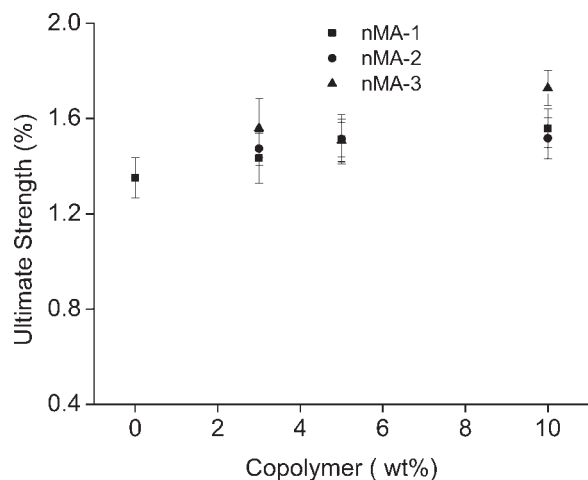


Figure 8 Ultimate strength of PVC/PS (30/70 wt/wt) blends as a function of copolymer content.

ratio (p) was calculated as a ratio of the torques of the styrene (1.16 N m) and plasticized PVC (2.72 N m) measured at the same processing conditions as those used to prepare the blends;

$$p = \frac{\eta_d}{\eta_m} = \frac{TQ_d}{TQ_m} \quad (3)$$

where η_d and η_m are, respectively, the viscosity of the dispersed and continuous phase and TQ_d and TQ_m are the torque of the dispersed and the continuous phases. Because of the differences in the amount of stress transferred when the viscosity of the continuous phase is lower than the viscosity of the dispersed phase, larger particles are obtained compared with the particles obtained when the viscosity of the continuous phase is larger than the viscosity of the dispersed phase.²⁴

When comparing average particle size of the dispersed phase at the same concentration (Fig. 1), it can be observed that when the PS is the dispersed phase ($p = 0.43$), it disintegrates into smaller particles (D_v) because the matrix (PVC) is a more viscous material, which causes larger stress transfer between the continuous and dispersed phases, than when PVC is the dispersed phase ($p = 2.34$).⁸⁻¹¹ Similar results were reported by Favis and Chalifoux²⁶ when comparing, at the same ratio of dispersed phase/continuous phase, blends of polypropylene/polycarbonate, where smaller particle size was obtained for the lower p value. Wu²⁷ found that for blends of nylon 66/ethylene-propylene rubber the minimum particle size is obtained when $p = 1$. At higher or lower p values, the particle size is bigger.

Figure 1(b) shows a microphotography of the blend when the PVC/PS ratio is 70/30 wt %; particles are small and have an almost spherical shape. If PS concentration is increased, the particles grow until a composition is reached, where it is no longer possible to differentiate which is the dispersed or

continuous phase [Fig. 1(d)]. If the amount of PS is increased further, spherical particles dispersed in a continuous phase are obtained [Fig. 1(f)].

Copolymers of PSnMA prepared in our laboratory were used as a compatibilizer for the PS-PVC mixtures. It has been reported²³ that, when this copolymer is prepared by emulsion polymerization, because of the high water solubility of the nMA the polymerization starts in the aqueous phase incorporating mainly nMA, and when the radical enters the particle, the monomer which is now mainly added is the styrene, which would give as a result a polymer with a composition that resembles that of a block copolymer.²³ These copolymers because of their composition can position at the interface of the PS-PVC domains. The PS-rich portion of the PSnMA will be oriented toward the PS phase, and the polar nMA rich portion toward the PVC phase, where under the blending conditions (high temperature), nitrogen or oxygen of the nMA could be displaced by nucleophilic substitution the chlorine atom of the PVC to obtain a better compatibilizing effect.²⁸⁻³⁰

Figure 3 shows microphotographies of mixtures of PVC/PS (30/70 wt/wt) with and without compatibilizer. It can be observed that particle size decreases by the presence of the PSnMA, and as the compatibilizer has a higher content of PnMA [Fig. 3(c)], the particle size is smaller.

Figure 4 shows that, when using any PSnMA composition, the particle size decreases. Also, increasing the amount of compatibilizer causes a decrease in particle size. When comparing blends containing the same amount of compatibilizer, particle size is smaller when the PSnMA has higher PnMA content. A plot of the PnMA content in the blend versus particle size is shown in Figure 5. In this figure, it can be observed that, as the PnMA concentration increases, the particle size decreases until a PnMA composition (around 0.2%), and here a further increase of PnMA concentration does not cause a change in particle size. The behavior shown in Figures 4 and 5 is typical of emulsification curves. The compatibilizer reduces interfacial tension between the dispersed phase and the matrix causing a decrease in particle size^{6,7} and the degree of particle size reduction depends on compatibilizer type and processing conditions.^{9,11} The decrease in particle size by the presence of PSnMA indicates that it is acting as a compatibilizer. Because the compatibilizer reported here is a copolymer of PS and PnMA, the increase in compatibility (because of the emulsifier effect) when increasing PSnMA content indicates that an interaction between the nMA portion of the compatibilizer and the PVC occurs. Liang et al.³¹ reported a reduction on particle size in mixtures of LLDPE/PVC when using a compatibilizer containing a nitrogen group poly(isoprene-4-vinylpyridone)

(PIP-P4VP), because a strong adsorption exists between the basic P4VP segment in PIP-P4VP copolymer and the acidic PVC. Polyisoprene is not acidic, and hence no possibility exists for strong acid-base interaction between it and LLDPE.

Further evidence for interactions between the PnMA portion of the compatibilizer and the PVC is that the infrared spectra [Fig. 6(b-d)] of the residues of the solvent extraction of the (PVC/PS/PnMA) blends shows characteristic bands of the three polymers. The broad band at 3200–3600 cm^{-1} is due to the OH and NH groups of the nMA and the peaks at 1700–2000 are characteristic of the aromatic ring.³² Evidence of the presence of PVC in the residue of the solvent extraction can be found by comparing their spectra [Fig. 6(b-d)] with that of the PnMA before being blended with PVC [Fig. 6(a)]. In the spectra of the residues can be observed an increase of the two peaks at around 1450 cm^{-1} , because of the CH_2 and CH groups of the PVC. In Figure 6(b-d), a new small band at around 1200 cm^{-1} can also be observed because of the new C–N bond.³² Then, it is proposed that under the blending conditions the –NH of the PnMA reacts with the chlorine of the PVC forming a C–N bond and HCl; this reaction is known as ammonolysis of halides.²⁸ The HCl produced reacts with the secondary thermal stabilizers present in the PVC.^{33,34}

The presence of only one T_g demonstrates that the residue of the solvent extraction is a single polymer, and not a blend. The infrared spectra (Fig. 6) combined with the presence of only a T_g (114°C), which is higher than that of the PVC and PS, indicates a reaction between the PnMA and PVC.

Figure 7 shows that the tensile modulus of the blends increases as the amount of PnMA increases, and a higher concentration of PnMA in the compatibilizer yields a higher tensile modulus. This indicates that there is better distribution of the stresses by the presence of PnMA. It has been reported that mechanical properties of incompatible polymer mixtures or blends can be improved by adding small amounts of a third component (compatibilizer) to induce compatibility.^{1–3} Zhong et al.¹⁹ using CPE-g-PS as a polymeric compatibilizer for PVC/PS blends found that the tensile modulus is substantially enhanced. In the case of ultimate strength (Fig. 8), a slight increase in its value is observed. Similar results are reported by Fisch.³³

CONCLUSIONS

The copolymer of PnMA is an effective compatibilizer of mixtures of PVC/PS.

The PnMA has the capacity to reduce the size of the dispersed phase and to increase the ultimate strength and ultimate modulus of the blend.

The smaller particle size (increase in compatibility) when increasing PnMA content and the presence of only a T_g observed when the ternary blend was subjected to a treatment in a Soxhlet apparatus using THF to remove PS and unreacted PVC indicates that an interaction between the nMA portion of the compatibilizer and the PVC occurs.

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