

The Compatibilizing Effect of Poly(styrene-*co*-4-vinylpyridine) Copolymers on the Polystyrene–Polyethylene-Based Ionomer Blends

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ABSTRACT: The compatibilizing effect of styrene-*co*-4-vinylpyridine (SVP) random copolymers on the immiscible polystyrene (PS)–polyethylene-based ionomer (Surlyn) blends was examined by means of scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and tensile test. For the binary SVP–Surlyn and ternary PS–Surlyn–SVP blends, the domain size of dispersed phase decreases dramatically with the increase in the vinyl pyridine (VP) content of the SVP copolymers. The mechanical properties are improved with increasing the VP content in copolymers. FTIR results suggest that the compatibilization in this blend system is attributed to the ion–dipole interaction between the polar VP groups of SVP copolymer and ionic groups of Surlyn. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 807–816, 1998

Key words: styrene-*co*-4-vinylpyridine copolymers; ionomer; ion–dipole interaction; compatibilization

INTRODUCTION

Among multicomponent polymeric materials, polymer blends have been of considerable interest as the simplest route for combining the outstanding properties of polymers.^{1–2} However, the well-known challenge confronting the development of polymer blends has been in relation to the thermodynamics of the system, which typically favors polymer pair immiscibility. In order to overcome this difficulty, in general, the presence of specific interactions between polymer components is needed. Many studies have been performed to enhance the miscibility of polymer blends through

incorporation of local centers capable of participating in strong interactions. Examples of specific attractive intermolecular interactions that have been used to develop miscible blends include hydrogen bonding,^{3,4} dipole–dipole interactions,⁵ ion–dipole interactions,^{6–10} acid–base interactions,¹¹ transition–metal complexation,¹² and charge–transfer complexation.¹³ Miscibility enhancement via ion–dipole interactions has been investigated widely. Eisenberg et al.¹⁴ have shown that a minimum of 5 mol % ionic groups along a polymer backbone is required for compatibilization of immiscible polystyrene (PS)–poly(ethyl acrylate) blends. Peiffer et al.¹⁵ examined the formation of transition metal complexes between the zinc and copper salts of sulfonated ethylene–propylene terpolymer (EPDM)–poly(styrene-*co*-4-vinylpyridine) (SVP) blends as a means of compati-

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bilizing and controlling the melt viscosity. Sakurai et al.¹⁶ also have examined transition metal complexes of zinc-neutralized sulfonated polystyrene–poly(ethyl acrylate-*co*-4-vinylpyridine) blends through spectroscopic study. Their results indicate that the pyridine group coordinates to the zinc ion upon blending. Other researchers studied the compatibilization of an immiscible polymer pair, poly(ethyl acrylate) and poly(ethylene terephthalate), by incorporating vinyl pyridine (VP) groups and zinc-neutralized sulfonate groups.^{17,18} The compatibility of this multiphase ionic blend resulted from the formation of a zinc–pyridine–sulfonate group coordination complex between polymer chains.

PS is widely used as an injection-molding and vacuum-forming material due to good dimensional stability, good moldability, low moisture absorption, good electrical insulation properties, and colorability, but the principal limitations of PS are its brittleness, inability to withstand the temperature of boiling water, and mediocre oil resistance. Surllyn is a random copolymer of ethylene and methacrylic acid containing less than 10 mol % methacrylic acid, which is neutralized with Zn^{2+} or Na^+ . It has thermoplastic properties at high temperatures and thermoset properties at low temperatures because of its ionic crosslinks, and it is soft, tough, and rather similar to rubber-like materials that have large elongation and low melt viscosity.¹⁹ Therefore, it is desirable to compromise the properties of these two polymers. However, the PS–Surllyn blend is a typical immiscible one; thus, a specific interaction is necessary to secure adequate overall mechanical behaviors of the blends.

In this study, the compatibilizing effect of SVP copolymers on the phase morphology and mechanical properties of PS–Surllyn blend is examined as a function of the VP content in SVP copolymer, and the origin of the enhancement of compatibility is characterized through infrared spectroscopy.

EXPERIMENTAL

Materials

PS and polyethylene ionomer (Surllyn 1653 SR-1) were supplied by Cheil Ind. (Euiwang 437-010, Korea) and du Pont, respectively, and used as received without further purification. SVP was synthesized

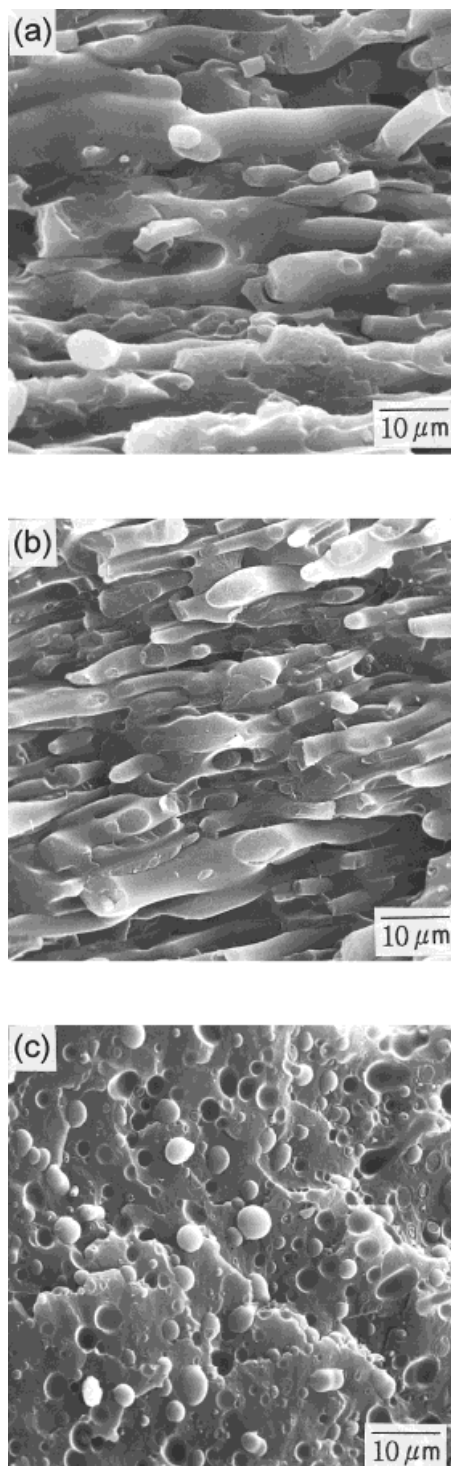


Figure 1 SEM micrographs of PS–Surllyn binary blends: (a) 7/3; (b) 5/5; (c) 3/7.

in a sealed glass ampule by bulk polymerization at 80°C using benzoyl peroxide as an initiator. The maximum degree of conversion was controlled to

Table I Polymer Characteristics

Polymers	$[\eta]$ (mL/g)	VP Content (wt %)	T_g^a (°C)	Source
Polystyrene	78.3	0	100.0	Cheil Ind.
SVP1	31.5	1.3	106.2	Synthesized
SVP3	37.7	3.1	107.0	Synthesized
SVP5	40.9	5.4	109.6	Synthesized
SVP7	42.0	6.8	109.9	Synthesized
SVP9	41.4	8.3	111.0	Synthesized
Polyethylene ionomer	—	—	—	du Pont

^a Measured by DSC.

approximately 30% to ensure reasonable compositional homogeneity of the copolymer. The reaction mixture was then diluted with toluene and poured into a large excess of methanol. The precipitated copolymer was filtered and dried in a vacuum oven at 70°C for 24 h. The VP content of the copolymer was determined by titration method, described by Tamikado.²⁰ The intrinsic viscosity was measured at 25°C in dilute toluene solution by extrapolating

to zero concentration. The characteristics of all the polymers are listed in Table I.

Preparation of the Blend Samples

Binary SVP–Surlyn and ternary PS–Surlyn–SVP blends were mechanically melt-blended at 200°C for 6 min and injection-molded into dumbbell-type specimen, using Mini-Max Molder (Model

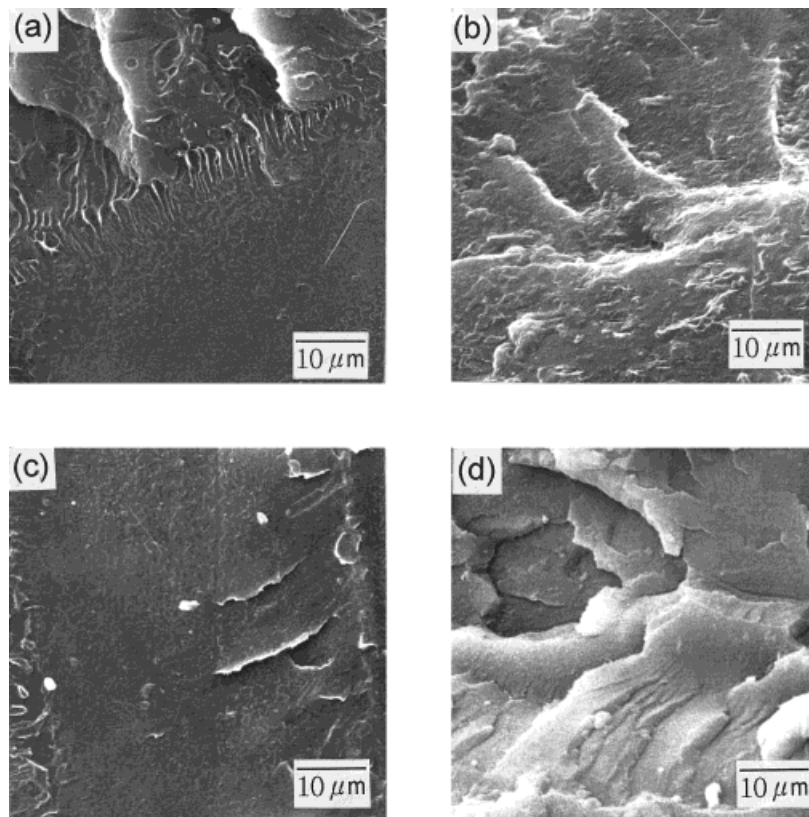


Figure 2 SEM micrographs of PS–SVP 7/3 binary blends: (a) PS–SVP1; (b) PS–SVP3; (c) PS–SVP7; (d) PS–SVP9.

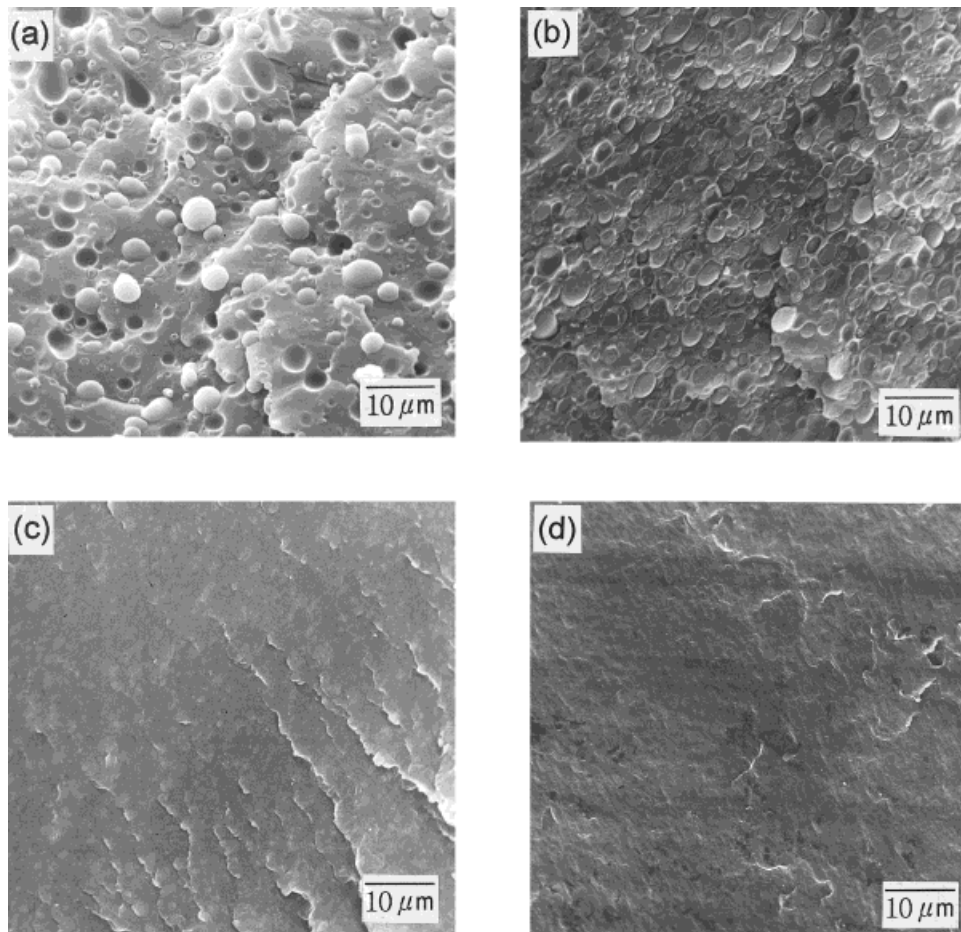


Figure 3 SEM micrographs of SVP-Surlyn 3/7 binary blends: (a) PS-Surlyn; (b) SVP1-Surlyn; (c) SVP3-Surlyn; (d) SVP9-Surlyn.

CS-183 MMX, Custom Scientific Instrument, Inc.). All polymers were completely dried under vacuum before mixing.

Morphological Observation

The morphology of the blends was investigated with scanning electron microscope (SEM, JEOL JSM-35) at an accelerating voltage of 25 kV. The samples were prepared by cryogenic fracture after immersion in liquid nitrogen, and the fracture surface was coated with gold for enhanced conductivity.

Infrared Spectroscopy

Infrared spectroscopy was used to examine the interaction in the blends. Infrared spectra were obtained with Fourier transform infrared spec-

trometer (FTIR, Perkin-Elmer 1760X). The samples were compression-molded into thin films using hot press.

Tensile Testing

Tensile properties were measured on an Instron Tensile Tester (Model 4204, Instron Co.). The crosshead speed was 1 mm/min for PS matrix blends and 6 mm/min for Surlyn matrix blends, respectively. All mechanical properties were determined by averaging the results of 6 out of 8 specimens.

RESULTS AND DISCUSSION

Morphological Analysis of Binary Blends

Interfacial adhesion between phases and melt viscosities of blends are the key parameters govern-

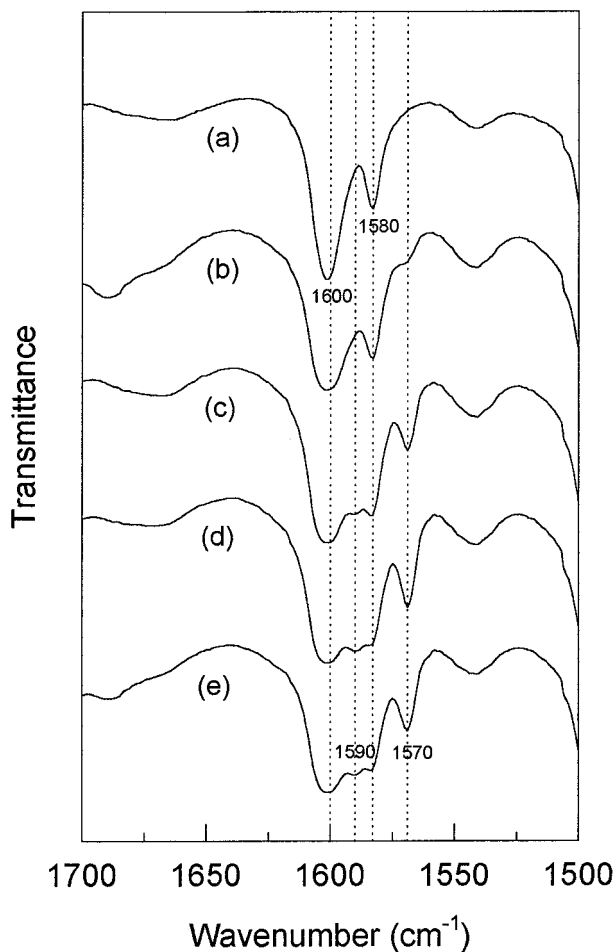


Figure 4 FTIR spectra of SVP copolymers: (a) PS; (b) SVP1; (c) SVP3; (d) SVP7; (e) SVP9.

ing the degree of dispersion of dispersed phase and its stability against coalescence or stratification. Prior to investigate the interfacial activity of the SVP copolymer on the immiscible PS–Surlyn blend, the morphologies of the binary blends of the component polymers were examined first.

Figure 1 shows the morphologies of PS–Surlyn blends with blend ratio from 7/3 to 3/7. These show the typical morphology of immiscible blend at all the blend ratios. Figure 2 shows the effect of the VP content in SVP copolymer on the morphology of PS–SVP binary blends. The overall homogeneity is still retained up to 9 wt % VP content in SVP copolymer. Figure 3 shows the morphological change of SVP–Surlyn 3/7 blends. As the VP content in SVP copolymer increases, the dispersed domain size is reduced, and a more uniform particle size distribution is produced. This result suggests that some specific interaction between SVP

copolymer and Surlyn exist and only about 3 wt % of VP content is enough to attain compatibility of SVP–Surlyn blend. The similar phase behavior is observed at all the blend ratios of SVP–Surlyn blends.

Infrared Spectroscopy of Binary Blends

Figure 4 shows the FTIR spectra of PS and SVP copolymers in the range of 1500–1700 cm^{-1} . PS

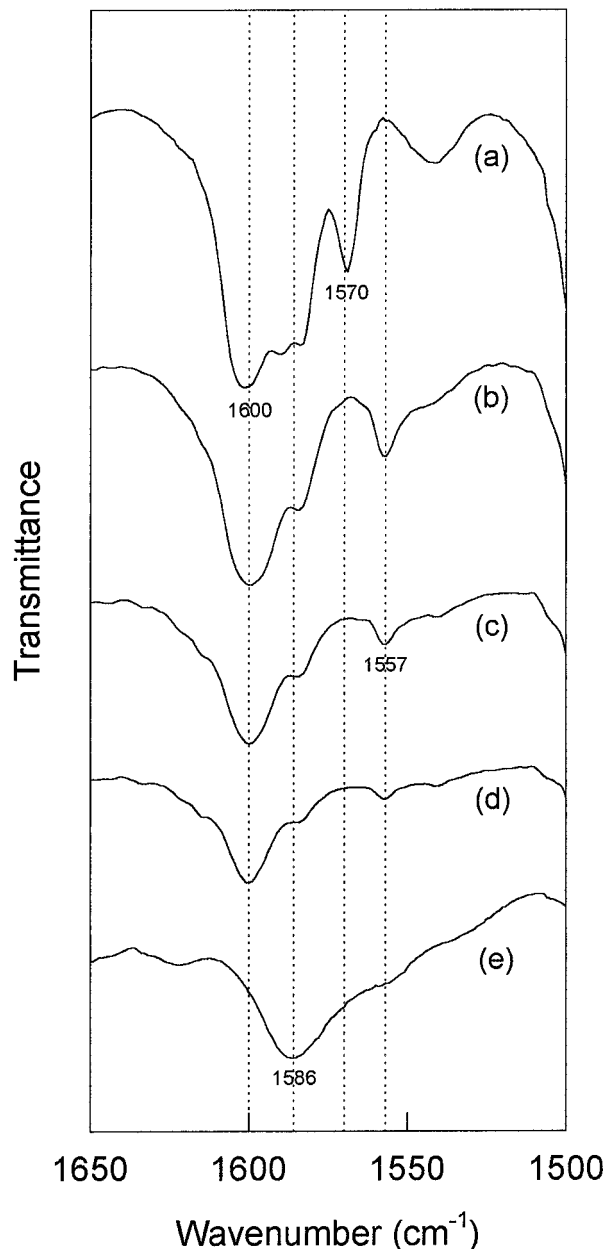


Figure 5 FTIR spectra of SVP9–Surlyn binary blends: (a) 10/0; (b) 7/3; (c) 5/5; (d) 3/7; (e) 0/10.

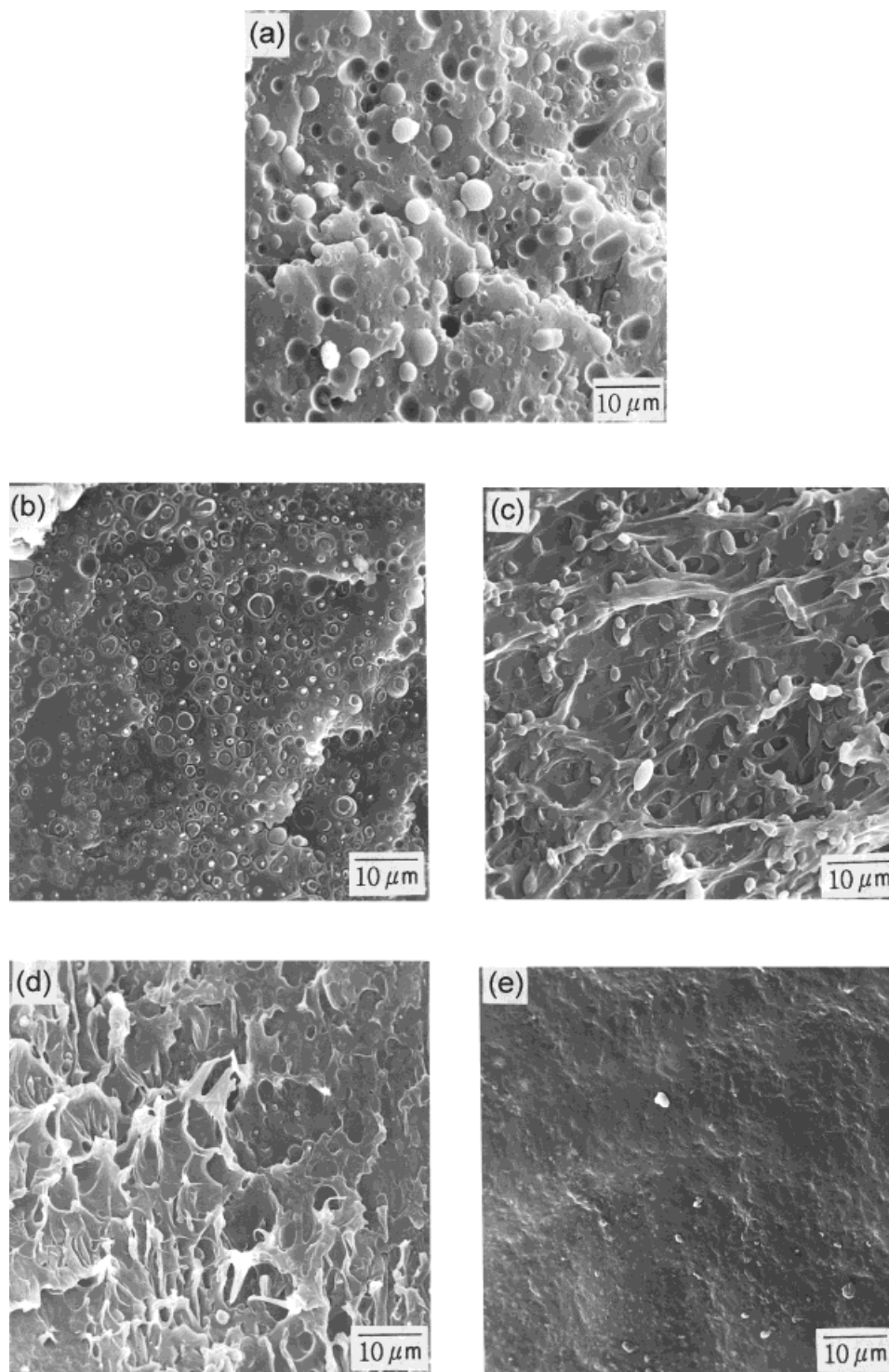


Figure 6 SEM micrographs of PS–Surlyn 3/7 blends containing 5 wt % SVP copolymers: (a) without SVP; (b) SVP1; (c) SVP3; (d) SVP5; (e) SVP7.

exhibits double peaks at 1600 and 1580 cm^{-1} corresponding to the stretching bands of phenyl ring, while SVP copolymers have additional two peaks

at 1590 and 1570 cm^{-1} . The intensities of these additional peaks grow as the VP content in SVP copolymer increases. Hence, the peaks can be as-

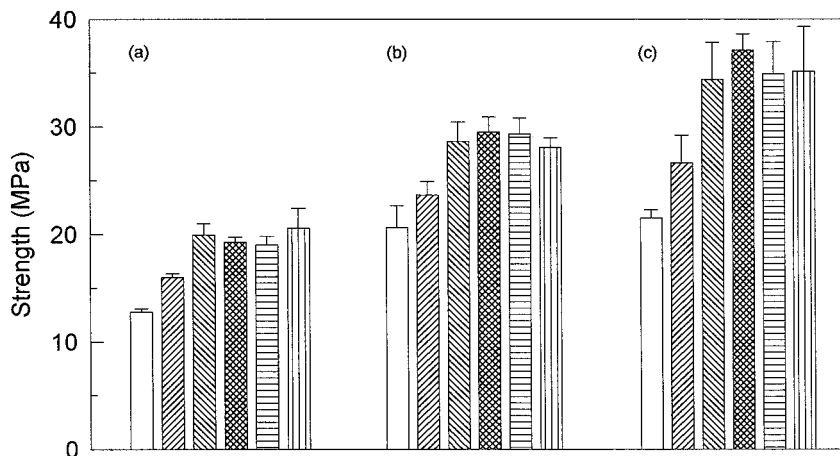


Figure 7 Strength of SVP-Surlyn binary blends (a) 3/7, (b) 5/5, and (c) 7/3: (□) PS-Surlyn; (▨) SVP1-Surlyn; (▩) SVP3-Surlyn; (▤) SVP5-Surlyn; (▥) SVP7-Surlyn; (▧) SVP9-Surlyn.

signed as the coupled C=C and C=N stretching vibrational bands in the pyridine ring.

Figure 5 shows the FTIR spectra of SVP9-Surlyn binary blends. Surlyn has a peak at 1586 cm^{-1} due to the C=O stretching in carboxylate salt. For the blend samples, the 1570-cm^{-1} band in SVP9 copolymer shifts to lower frequency of 1557 cm^{-1} , while a shift of the 1590-cm^{-1} band in SVP copolymer can be hardly observed because the band is overlapped by the other adjacent bands. This lower shift is seen in all the blend ratios. From these results, it is believed that the origin of the specific interaction in this blend system comes from the ion-dipole interaction between the polar

C=N groups of VP unit of SVP copolymer and zinc carboxylate ionic groups in Surlyn.

Morphological Analysis of Ternary Blends

Figure 6 shows the morphological change in PS-Surlyn 3/7 blend with the addition of 5 wt % SVP copolymers. As the VP content in SVP copolymer increases, the domain size of dispersed phase decreases, and the blend shows nearly homogeneous morphology above approximately 7 wt % VP content in SVP copolymer. This tendency was confirmed at the other blend ratios. This result means that the SVP copolymer plays a proper role as an

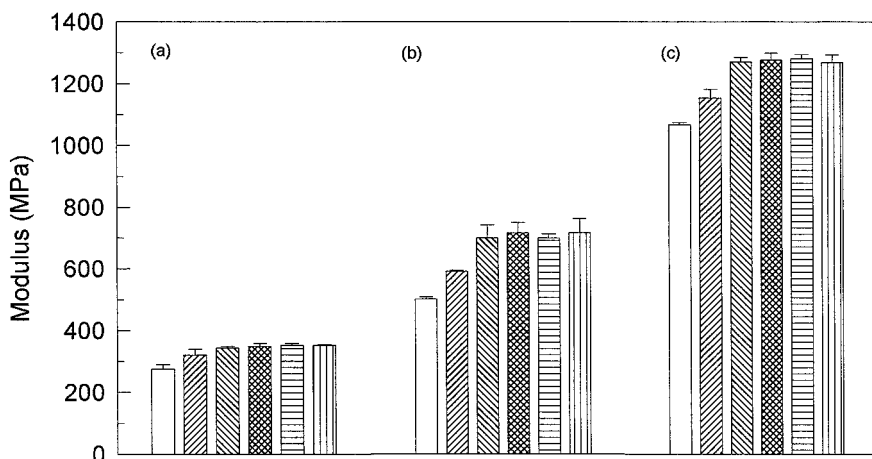


Figure 8 Modulus of SVP-Surlyn binary blends (a) 3/7, (b) 5/5, (c) 7/3: (□) PS-Surlyn; (▨) SVP1-Surlyn; (▩) SVP3-Surlyn; (▤) SVP5-Surlyn; (▥) SVP7-Surlyn; (▧) SVP9-Surlyn.

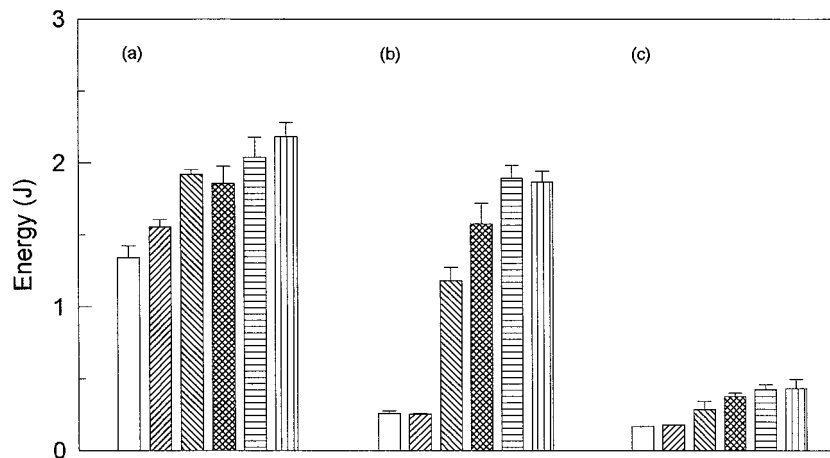


Figure 9 Fracture energy of SVP-Surlyn binary blends (a) 3/7, (b) 5/5, (c) 7/3; (□) PS-Surlyn, (▨) SVP1-Surlyn; (▩) SVP3-Surlyn; (▧) SVP5-Surlyn; (▯) SVP7-Surlyn; (▮) SVP9-Surlyn.

interfacial agent in this blend system, and the compatibilization can be achieved by adding only 5 wt % SVP copolymers containing more than 7 wt % VP groups. Unlike the binary system, 7 wt % of VP content in SVP copolymer is necessary to compatibilize the blends, and this is reasonably understood considering the fact that the total amount of VP groups are larger in the binary system.

Mechanical Properties of Blends

The strength, the modulus, and the fracture energy of SVP-Surlyn binary blends are shown in

Figures 7, 8, and 9, respectively. The fracture energy was calculated by integration of the stress-strain curve. On the whole, the trends of these properties are quite similar over all the blend composition. The mechanical properties increase dramatically with increasing the VP content in SVP and then level off at approximately over 3 wt % of VP content. Similarly, the mechanical properties for PS-Surlyn-SVP's ternary blends enhance as the VP content in SVP copolymer increases gradually and show leveling off behavior, as shown in Figures 10, 11, and 12. The introduction of VP group to PS-Surlyn blends enhances the phase dispersion and the interfacial adhesion,

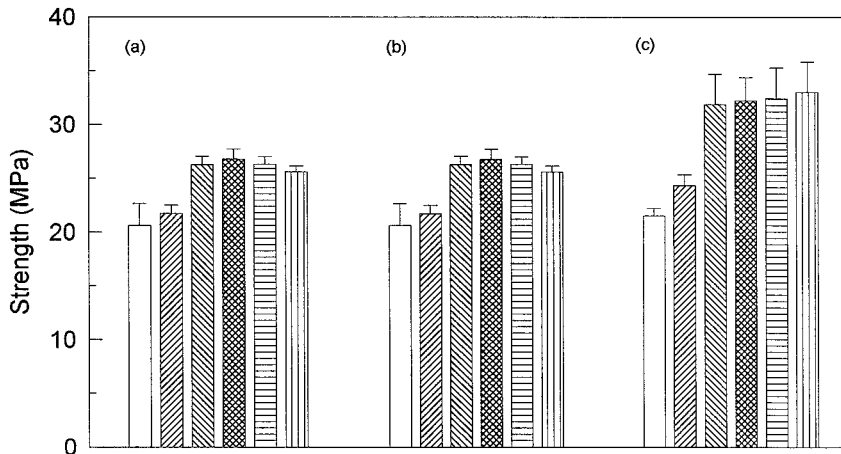


Figure 10 Strength of PS-Surlyn-SVP ternary blends when 5 wt % SVP copolymers are added to blends (a) 3/7, (b) 5/5, and (c) 7/3: (□) without SVP; (▨) SVP1; (▩) SVP3; (▧) SVP5; (▯) SVP7; (▮) SVP9.

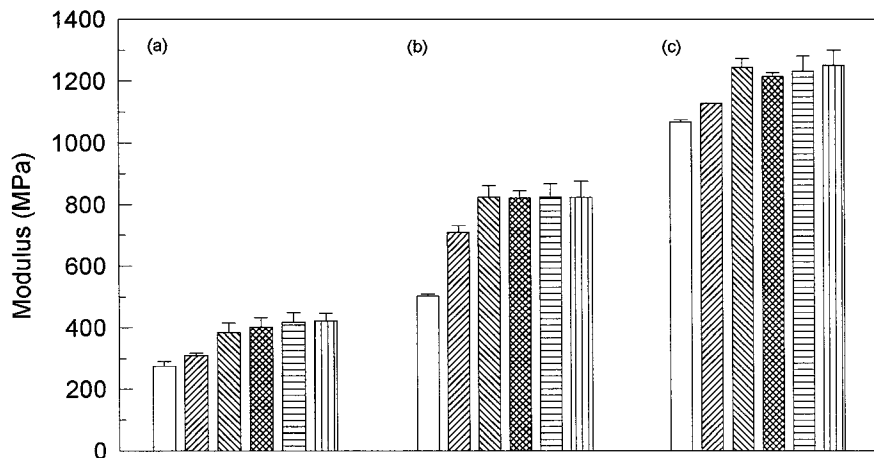


Figure 11 Modulus of PS-Surlyn-SVP ternary blends when 5 wt % SVP copolymers are added to blends (a) 3/7, (b) 5/5, and (c) 7/3: (□) without SVP; (▨) SVP1; (▩) SVP3; (▤) SVP5; (▥) SVP7; (▧) SVP9.

which results in the improvement of the mechanical properties.

CONCLUSIONS

SVP copolymers were synthesized, and their compatibilizing effects on the immiscible PS-Surlyn blend were investigated. From SEM photographs, more regular and finer dispersions of SVP-Surlyn binary blends are observed when small amounts of VP groups are introduced into the PS part as a comonomer. The significant compatibilizing effect is observed when the VP content in

SVP copolymers is larger than 3 wt %. With further addition of SVP copolymers, the morphology shows leveling-off behavior. In the ternary blend, the addition of 5 wt % SVP7 copolymer led to a nearly homogeneous morphology in the PS-Surlyn blend system.

The mechanical properties are improved with the introduction of VP groups in the system and level off when the VP content in SVP copolymer reaches a certain amount. The morphological and mechanical results show that the SVP copolymers can be used as a compatibilizer in the immiscible PS-Surlyn blends.

From the FTIR investigation, it is believed that

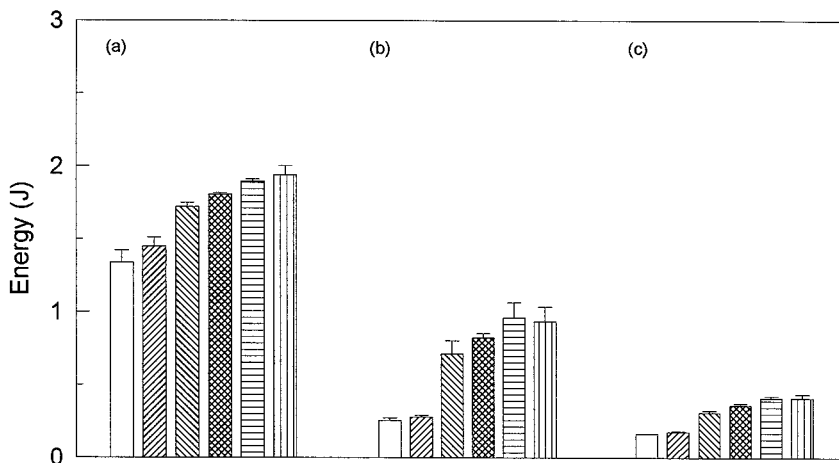


Figure 12 Fracture energy of PS-Surlyn-SVP ternary blends when 5 wt % SVP copolymers are added to blends (a) 3/7, (b) 5/5, and (c) 7/3: (□) without SVP; (▨) SVP1; (▩) SVP3; (▤) SVP5; (▥) SVP7; (▧) SVP9.

the specific interaction in this system comes from the ion–dipole interaction between the VP groups in SVP copolymer and the zinc ion-substituted carboxylate groups in Surlyn. This interaction could be ascertained by shifting to lower frequency of a pyridine band of SVP copolymer in the blend system with respect to that in the original SVP copolymer.

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