Miscibility and Rheological Properties of Poly(vinyl chloride)/Styrene–Acrylonitrile Blends Prepared by Melt Extrusion

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ABSTRACT: Styrene–acrylonitrile (SAN) with acrylonitrile (AN) concentrations of 11.6–26 wt % and α-methylstyrene acrylonitrile (αMSAN) with a wide range of AN concentrations are miscible with poly(vinyl chloride) (PVC) through solution blending. Here we examine the rheological properties and miscibility of PVC/SAN and PVC/αMSAN blends prepared by melt extrusion for commercial applications. We have investigated the rheological properties of the blends with a rheometer and a melt indexer. The PVC/SAN and PVC/αMSAN blends have a low melting torque, a long degradation time, and a high melt index, and this means that they have better processability than pure PVC. The miscibility of the blends has been characterized with differential scanning calorimetry, dynamic mechanical thermal analysis, and advanced rheometrics expansion system analysis. The miscibility of the blends has also been characterized with scanning electron microscopy. The SAN series with AN concentrations of 24–31 wt % is immiscible with PVC by melt extrusion, whereas αMSAN with 31 wt % AN is miscible with PVC, even when they are blended by melt extrusion, because of the strong interaction between PVC and αMSAN. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 95–101, 2007

Key words: blends; melt; miscibility; poly(vinyl chloride) (PVC); rheology

INTRODUCTION

One of the practical limitations of poly(vinyl chloride) (PVC) lies in its low service temperature. Commercially available rigid PVC shows low heat-distortion temperatures in the range of 75–80°C, which give rise to inappropriate modulus and creep-compliance values above these temperatures. Many industrial accessories, such as electrical and electronic appliances, require suitable mechanical properties at relatively high temperatures. Furthermore, new control norms are currently required for tubes and pipes, making evident the limitations of PVC at high temperatures.

To achieve better properties, different polymers can be blended to use the physical characteristics of both polymers.[1–3] However, because of the relatively low entropy of mixing, most polymer pairs are immiscible. Because of the formation of a separated phase between the two polymer phases, a coarse phase morphology and poor mechanical properties are obtained.[2–5]

To increase the heat-deflection temperature of PVC, styrene–acrylonitrile (SAN) copolymer series are openly blended with PVC. It is well known that PVC is not miscible with either polystyrene or polyacrylonitrile; however, SAN series are miscible with PVC via solution blending in some range of acrylonitrile (AN) concentrations, especially 11.5–26 wt %.[6–8] The intramolecular repulsion between the different segments of SAN accounts for the miscibility of this blend system.[8–13] Moreover, SAN containing about 25 wt % AN is miscible with PVC and enhances the compatibility between PVC and SAN containing about 35 wt % AN, which is immiscible with PVC by itself.[14]

The interaction between SAN and PVC is influenced by the AN concentration in SAN because of the self-association of polar AN groups and steric effects. Figure 1(a) shows the interaction between PVC and SAN. Two interactions exist: an induced dipole interaction between the aromatic quadrupole (benzene ring) of SAN and halogen (chlorine) of PVC and hydrogen bonding between AN and the α-hydrogen of PVC. At high AN concentrations, the self-association of the AN groups reduces the miscibility with PVC. Even with low AN concentrations, SAN shows limited miscibility with PVC because of the easy rotation of SAN, which helps the self-association of AN and reduces AN exposure (steric effect).
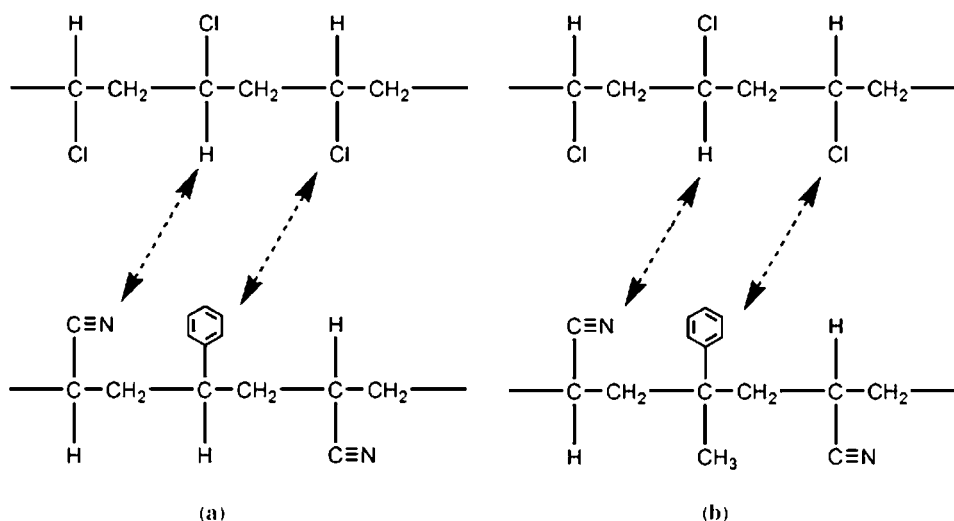
Figure 1 Interactions between PVC and (a) SAN and (b) αMSAN.

Studies of blends containing a modified copolymer of SAN, including α-methylstyrene acrylonitrile (αMSAN), have also been reported.[8,15–17] Kim et al.[9] found that blends of αMSAN with 30 wt % AN and PVC showed a single glass-transition temperature (T_g) for all compositions and that phase separation on heating did not occur before 250°C, which is beyond the normal processing range for PVC. Gan and Paul[18] also found that blends of αMSAN with 11.9–30 wt % AN and PVC showed a single T_g. Kim et al.[14] reported that αMSAN containing approximately 16–51 wt % AN was miscible with PVC, whereas it was immiscible outside this range.

The interaction between αMSAN and PVC is also influenced by the AN contents in αMSAN. The intramolecular repulsion between different segments of αMSAN and the additional interaction between the α-hydrogen of PVC and AN of αMSAN account for the miscibility of this blend system. Figure 1(b) shows the interaction between PVC and αMSAN. Two interactions exist: an induced dipole interaction between the aromatic quadrupole (benzene ring) of αMSAN and halogen (chlorine) and hydrogen bonding between AN and the α-hydrogen of PVC. Methyl groups in αMSAN inhibit chain rotation and help with AN exposure. Compared with SAN, αMSAN shows improved miscibility with PVC over a wide range of AN concentrations because of the gauche conformation of the chain, which helps with hydrogen bonding between AN and the α-hydrogen of PVC.

However, these studies have been conducted mainly with samples prepared by solution blending. The preparation method of a blend is a very important factor in determining its final homogeneity.[8,9] Solution blending is an easy method but has two disadvantages. One is that the result in terms of the miscibility of the blend depends not only on the thermodynamic

miscibility of the blend but also on the sample preparation method, such as solvent casting, coprecipitation, or freeze drying, as well as the choice of the solvent, casting temperature, and rate of solvent evaporation. The other disadvantage is that solution methods do not exactly mimic real situations, such as melt extrusion and melt injection, which are common processes for industrial thermoplastic blends. In a proper solution, the miscibility of two polymers depends on their thermodynamic behavior. If the heat of mixing of the two polymers is negative and the other conditions are good, they are easily mixed to the molecular level. However, in practical blend systems such as melt extrusion and injection, it is very difficult to mix two different long-chain polymers at the molecular level.

In this article, we investigate the rheological properties and miscibility of blends of commercial SAN and αMSAN with PVC through melt-extrusion blending. These investigations should provide practical data for the PVC industry for improving the heat resistance of PVC and the processability of PVC.

TABLE I
Characteristics of the Polymers

Resin	AN (%)	M_w[b]	T_g (°C)	MI (g/10 min)	Source
PVC 1000[a]	—	140,000	74.5	9.8[c]	LG Chemical
SAN24	24	140,000	106.5	29[d]	LG Chemical
SAN27	27	110,000	106.8	35[d]	LG Chemical
SAN31	31	110,000	108.5	35[d]	LG Chemical
αMSAN	31	95,000	119.5	14[d]	BASF

[a] The T_g and MI values of PVC 1000 were evaluated from the rigid PVC composition (P1).
[b] Weight-average molecular weight.
[c] Measured at 210°C under a 12.5-kg load.
[d] Measured at 220°C under a 10-kg load.

TABLE II
Blend Ratios and MIs

Sample	Blend ratio	MI (g/10 min)
P1	100 wt % PVC DP 1000 and additives	9.8
P12430	30 wt % SAN24/70 wt % P1	19.2
P12730	30 wt % SAN27/70 wt % P1	19.0
P13130	30 wt % SAN31/70 wt % P1	22.7
P1A3	30 wt % αMSAN31/70 wt % P1	14

EXPERIMENTAL

Materials

Commercially available PVC and SAN samples (24, 27, and 31 wt % AN) were obtained from LG Chemical Co. (Seoul, Republic of Korea); αMSAN (31 wt % AN) was obtained from BASF (Ludwigshafen, Germany). Each was used as received. The physicochemical properties are listed in Table I.

To prepare the basic PVC powder compound (P1), the PVC resins and additives were mixed thoroughly in a turbo mixer at 800 rpm until it reached 120°C, and they were cooled to 60°C. In P1, some additives were added. To prevent the degradation of PVC, 2 wt % tin maleate was added as a heat stabilizer. Internal lubricants (0.5 wt % calcium stearate and 0.5 wt % fatty alcohol) and external lubricants (0.5 wt % stearic acid and 0.5 wt % oxidized polyethylene wax) were also added to improve the gelation of the PVC matrix and to reduce the friction between the powder particles and the extruder wall. SAN series pellets were mixed by hand with the prepared PVC powder compound (P1). The blend ratios, names, and MI data are listed in Table II.

Melt-extrusion blending

The blend compounds were extruded with a Buss (Prattein, Switzerland) MDK46 kneader extruder (length/diameter = 5/11) with a zone temperature profile of 170–190°C and at 700 rpm. The extrudates were quenched in water, pelletized with a cutter, and dried in a dry oven.

Characterization

A Haake (Karlsruhe, Germany) model 600 rheometer was used to study the melt rheology of the blends for the prediction of the processing properties.[19–25] The melting torque and equilibrium melting torque were measured with this device. They were determined at 180°C and 30 rpm. The degradation time was also measured at 210°C and 30 rpm.

A melt indexer (model F-B01, Toyoseiki, Tokyo, Japan) was used to study the melt rheology of the blends for the prediction of the processing properties. The melt index (MI) was measured with this de-
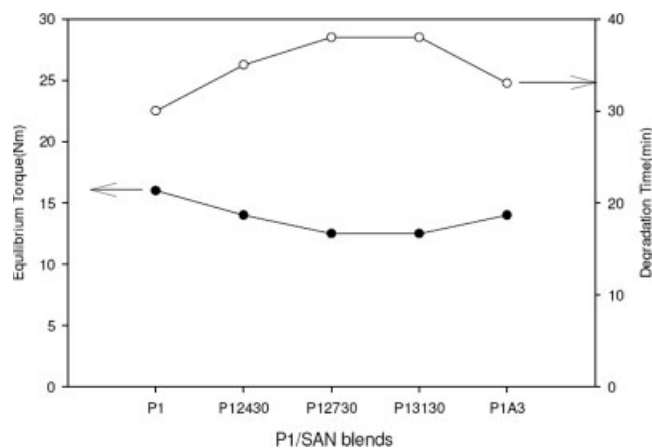
Figure 2 Equilibrium torque and degradation time of P1 and P1/SAN blends.

vice. It was determined at 210°C under a 12.5-kg load after 5 min of preheating.

The T_g values were determined with a differential scanning calorimeter (model 910, Du Pont, Wilmington, USA). A heating rate of 10°C/min was used. Each sample was first heated to 200°C and then rapidly quenched until it reached −20°C. The transition behavior was recorded during a second heating, with the midpoint of the transition defined as T_g of the blend. Dynamic mechanical thermal analysis (DMTA; model MK-II, Polymer Laboratories, Shropshire, UK) was performed to determine T_g of the blends. The scans were performed in the bending mode from 0 to 150°C at a heating rate of 3°C/min and at frequencies of 1 and 10 Hz. The sample dimensions were 45 mm × 12 mm × 3 mm: these bars were obtained by injection molding of the extruded material at 200°C.

The morphology of the polymer mixtures of PVC with the SAN series and αMSAN was observed with scanning electron microscopy (SEM; JSM 5610, JEOL Co., Tokyo, Japan). The samples were prepared with two methods: cryogenic fracturing of specimens prepared by a compression-molding method and impact fracturing of specimens prepared by injection molding.

To investigate the miscibility in a molten state, the rheological properties of the blends were measured with an Advanced Rheometrics Expansion System (ARES; Rheometric Scientific, Leatherhead, UK). For the melt-property measurements, a plate-and-plate

TABLE III
T_g and Tan δ of P1/SAN Blends from DSC and DMTA

| Sample	T_g from DSC (°C)	Tan δ from DMTA (°C)
P1	76.1	79.5
P12430	78.4, 102.9	82, 101
P12730	79.1, 95.6	81, 97.5
P13130	78.3, 105.3	81, 104
P1A3	97.6	91
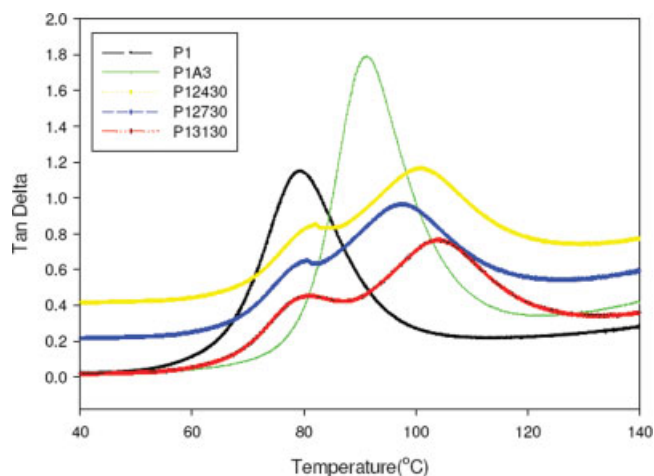
Figure 3 Tan δ of P1 and P1/SAN blends from DMTA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fixture and a press-molded disk specimen were used. The frequency sweep was performed at 200°C and 10% strain, which was the upper limit at which the linear viscoelastic behavior was maintained.

RESULTS AND DISCUSSION

Rheological properties

In the rigid PVC industry, a PVC polymer with an average of 1000 vinyl chloride monomer units is termed PVC DP 1000 and is normally used for extrusion molding. PVC DP 800 is normally used for injection molding and calendaring, but a PVC polymer with a high number of vinyl chloride monomer units, such as PVC DP 1300 or chlorinated poly(vinyl chloride) (CPVC), is very difficult to use because of its high processing viscosity. Moreover, it easily burns because of its short degradation time under high
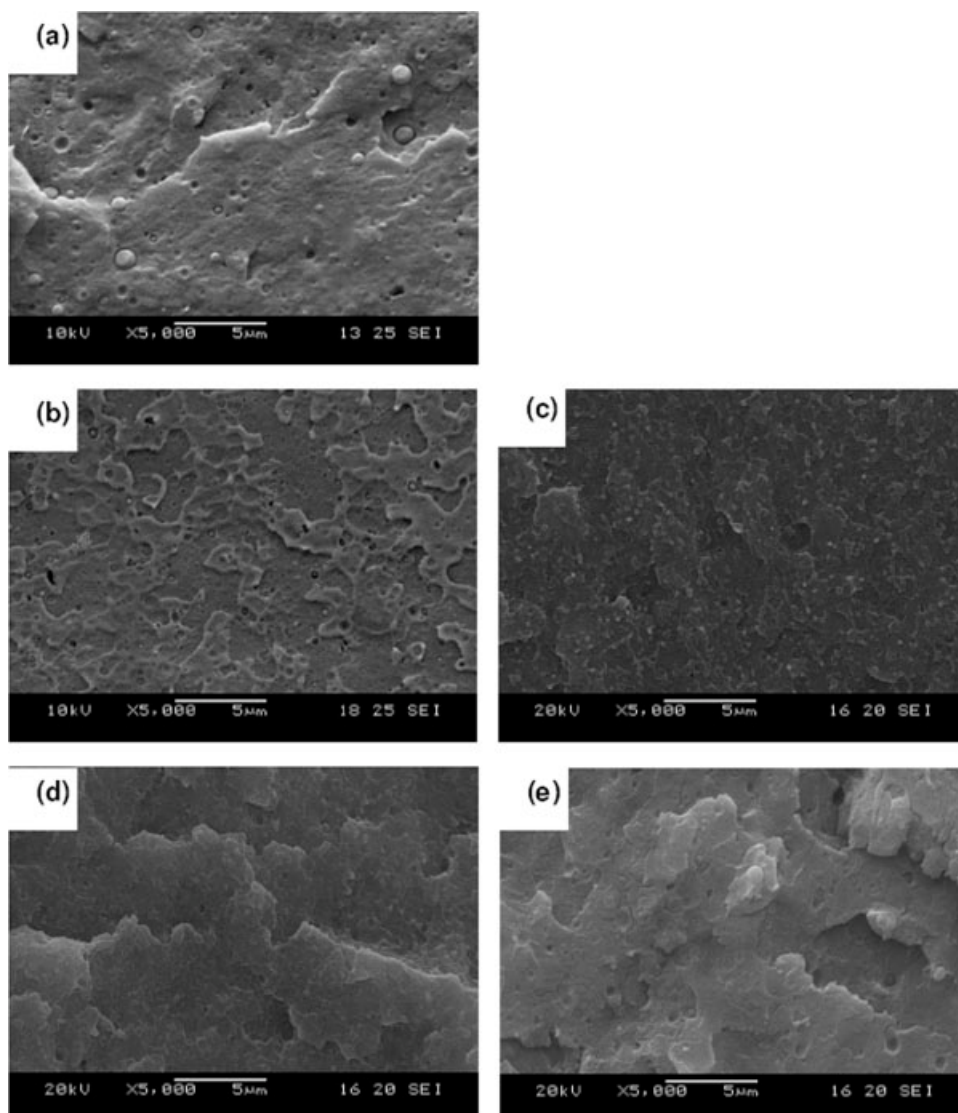
Figure 4 SEM images of cryogenically fractured surfaces of blend samples by compression molding: (a) P1, (b) P1A3, (c) P12430, (d) P12730, and (e) P13130.
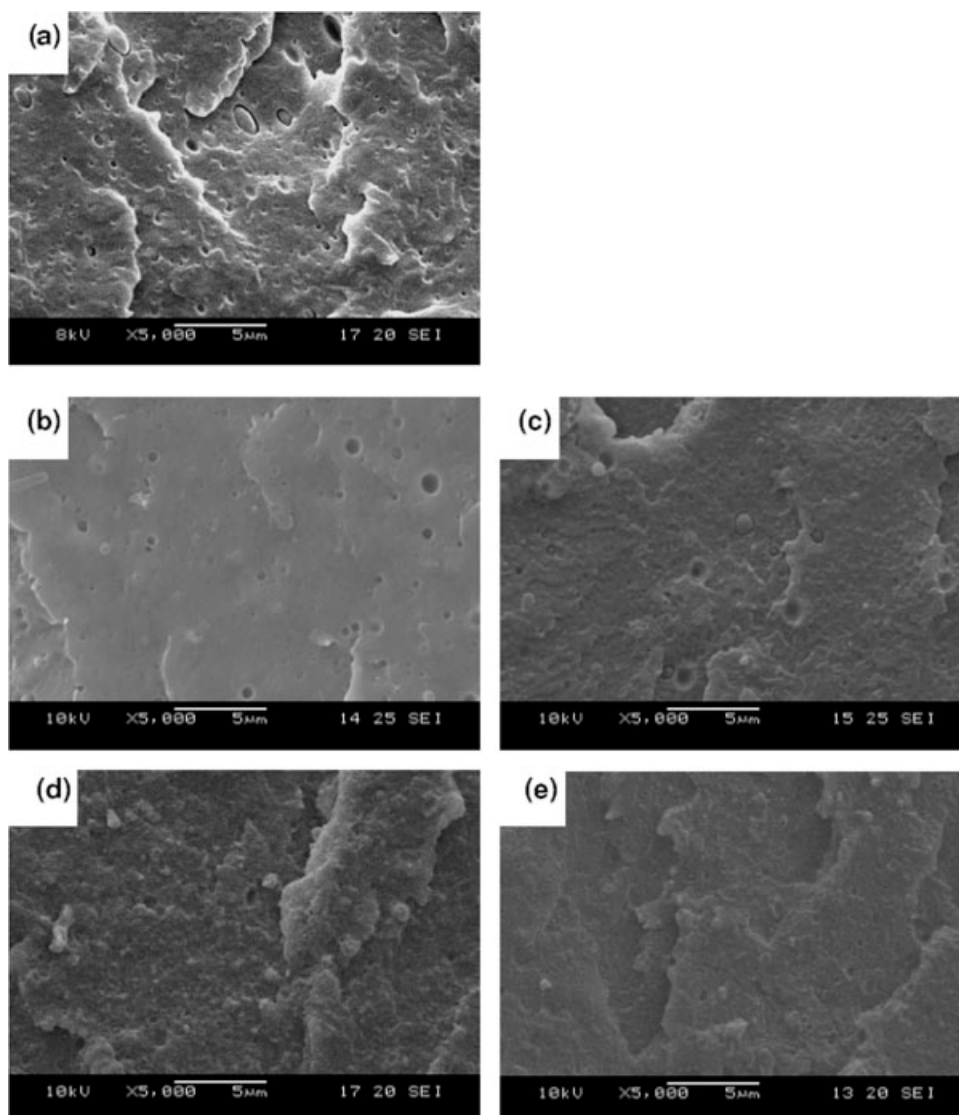
Figure 5 SEM images of impact-fractured surfaces of blend samples by injection molding: (a) P1, (b) P1A3, (c) P12430, (d) P12730, and (e) P13130.

shear. In this study, the equilibrium torque (16 Nm), degradation time (30 min), and MI data of PVC compound P1 (i.e., PVC DP 1000 mixed with additives) is taken as a guide line for the evaluation of the rheological properties of the blend systems.

The equilibrium torque and degradation time of P1 and the P1/SAN blends are shown in Figure 2. Compared with P1, the P1/SAN and P1/αMSAN blends show a decreased equilibrium torque and a longer degradation time. The MI data are listed in Table II. Compared with P1, the P1/SAN and P1/αMSAN blends have high MI data because of the low melt viscosity of the SAN series and αMSAN copolymer.

This means that the PVC/SAN and PVC/αMSAN blends have low melt viscosities and good processing properties. It also means that a PVC with a high number of vinyl chloride monomer units (high molecular weight) or CPVC can be blended with the SAN series and αMSAN for further improvements to the mechanical and physical properties of the PVC/SAN and PVC/αMSAN blends.

Miscibility

T_g of the P1/SAN and P1/αMSAN blends from melt-extrusion blending was investigated with differential scanning calorimetry (DSC). Table III indicates that the P1/αMSAN blends have one T_g, whereas the P1/SAN blends have two T_g values that are independent of the AN concentration of SAN. T_g of the blends was also investigated with DMTA. Table III and Figure 3 indicate that the P1/αMSAN blends have a single tan δ; however, the P1/SAN blends have two tan δ values with the various AN concentrations of SAN. This is consistent with the results of the DSC measurements.
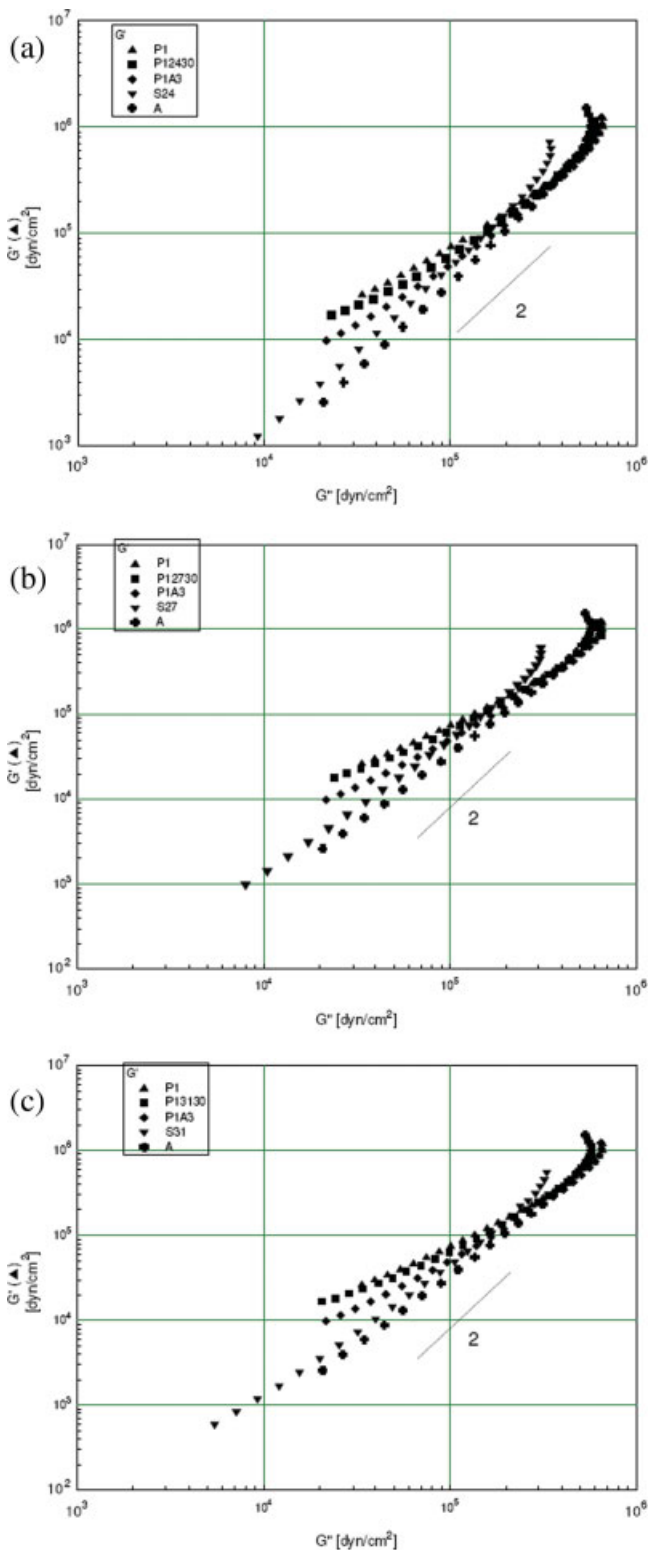
Figure 6 G' and G'' of the polymers and blends: (a) P1, αMSAN (A), SAN24 (S24), P1A3, and P12430; (b) P1, A, SAN27 (S27), P1A3, and P12730; and (c) A, SAN31 (S31), P1A3, and P13130.

These results indicate that it is very difficult to mix completely with low interaction levels between two different polymers, PVC and SAN, by extrusion

blending. However, these thermal analyses of the P1/αMSAN blend show a single T_g, and this indicates that αMSAN has sufficient interaction to mix completely with PVC, even through extrusion blending. αMSAN has a steric effect on α-methyl groups in the styrene units. The steric effect causes the copolymer chain to become more rigid, inhibits the self-association of polar AN segments within the copolymer, and enables additional interaction between the α-hydrogen of PVC and AN of αMSAN.

Figure 4 shows SEM images of the cryogenically fractured surfaces of P1, P1/SAN blends, and P1/αMSAN blends. Figure 5 shows SEM images of the impact-fractured surfaces of P1, P1/SAN24 blends, and P1/αMSAN blends. The P1/αMSAN blends show a homogeneous morphology in comparison with P1 and the P1/SAN blends.

In this study, SEM sample were prepared by injection molding with the melt-extrusion pellets and by compression molding with the melt-extrusion pellets. PVC is very weak under high shear and at a high temperature. From the results of the testing of the rheological properties, the P1/SAN and P1/αMSAN blends are a little more stable than a pure PVC compound (P1), but these blends are also weak under high shear and at a high temperature. This means that the processing conditions of the PVC/SAN and PVC/αMSAN blends are similar to those of a pure PVC compound. Injection molding and compression molding are some of the hardest processing conditions in the PVC industry. If the blends are not miscible under these conditions, it is impossible to obtain improvements in the properties of the blends with general processing equipment.

As shown by the cryogenically fractured surfaces of the blend samples by compression molding (Fig. 4), P1 has a clear-cut surface and has a nongelling part appearing as a small, round particle. The surface of the P1/SAN series blend is very rough and shows phase separation in comparison with P1 and the P1/αMSAN blend. The surface of the P1/αMSAN blend is clearer than those of the P1 and P1/SAN blends.

As shown by the impact-fractured surfaces of the samples by injection molding (Fig. 5), P1 has a clear-cut surface and has a nongelling part appearing as a small, round particle. The surfaces of the P1/SAN blends are not as clear-cut and are somewhat coarse compared with those of P1 and the P1/αMSAN blend. The surface of the P1/αMSAN blend is very clear compared with those of P1 and the P1/SAN blends. This shows that αMSAN has good miscibility with PVC in comparison with the SAN series and PVC; for that reason, the PVC/αMSAN blends show a homogeneous morphology compared with that of the PVC/SAN blends under PVC processing conditions such as injection molding and compression molding.

To investigate the miscibility in a molten state, the rheological properties of the P1/SAN and P1/αMSAN blends were measured with an ARES. The blends were characterized by the storage modulus (G') and loss modulus (G'') as functions of the frequency. The results for the blends of P1 with the SAN series and αMSAN are shown in Figure 6.

The ARES results indicate that the P1/αMSAN blends show miscible behavior in comparison with the P1/SAN blends in a molten state. If two polymers are miscible or homogeneous, the slope of G'/G'' is close to 2, whereas if the blend is immiscible or heterogeneous, the slope is lower than 2.[26] Figure 6 shows that the slope of the P1/αMSAN blend is close to 2 in comparison with the P1/SAN series blends. The slope of P1 shows that PVC is not homogeneous in comparison with the SAN copolymer and αMSAN copolymer. This may be caused by the existence of nongelling particles of the PVC domain in the PVC matrix.

CONCLUSIONS

The rheological properties of the PVC/SAN and PVC/αMSAN blends have been studied. The PVC/SAN and PVC/αMSAN blends have a low melting torque, a long degradation time, and a high MI in comparison with the pure PVC compound. This suggests that all the PVC/SAN and PVC/αMSAN blends have good processing properties.

The miscibility of the PVC/SAN and PVC/αMSAN blends has been studied with DSC and DMTA. The results indicate that the PVC/αMSAN blends have a single T_g, whereas the PVC/SAN blends have two T_g values that are independent of the AN concentrations of the SAN series. The miscibility of the PVC/SAN and PVC/αMSAN blends has also been studied with SEM. The cryogenically fractured surface and impact-fractured surface show that the PVC/αMSAN blends are blended more homogeneously than the PVC/SAN blends. The miscibility of the PVC/SAN and PVC/αMSAN blends has been studied with ARES. The slope of G'/G'' shows that the PVC/αMSAN blends are miscible in comparison with the PVC/SAN blends.

In conclusion, SAN samples with AN concentrations of 24–31 wt % are immiscible with PVC by melt extrusion. On the other hand, because of the strong interaction between PVC and αMSAN, αMSAN with 31 wt % AN is miscible with PVC even if blended by melt extrusion. This suggests that αMSAN can be easily blended with PVC by an industrial extruder and can improve the thermal properties of PVC without adverse effects regarding any processing problems.

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