

# Effect of the Composition of $\alpha$ -MSAN Copolymer on the Miscibility of PVC/ $\alpha$ -MSAN Blends

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**ABSTRACT:** A series of  $\alpha$ -methylstyrene, styrene, and acrylonitrile ( $\alpha$ -MSAN) copolymers with different acrylonitrile (AN) contents were synthesized by altering  $\alpha$ -MSt, St, and AN ratios with emulsion copolymerization method. By melt-blending these copolymers with PVC resin and di-isooctyl phthalate (DOP), PVC/ $\alpha$ -MSAN, and PVC/ $\alpha$ -MSAN/DOP blends were prepared. The miscibility and morphology of the blends were investigated by dynamic mechanical analysis (DMA) and scanning electron microscopy. The PVC is immiscible with SAN by melt-mixing, whereas PVC is miscible with  $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) if AN weight percent is within the window range of 20–25 wt %, and  $\alpha$ -MSAN (not containing St) with 35 wt % AN is miscible with PVC even when they are blended by melt-mixing. Replacement of styrene with  $\alpha$ -methylstyrene widens the miscibility window with PVC. The miscibility

of PVC/ $\alpha$ -MSAN blends is substantially improved with the increasing  $\alpha$ -MSt content in  $\alpha$ -MSAN copolymer containing identical AN content. When DOP was introduced into the PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) blends, a single  $\tan \delta$  peak over room temperature in DMA detection is found as AN content in  $\alpha$ -MSAN copolymer is within the range of 15–25 wt %, and SEM observation also shows that the blends are homogeneous. When the AN content in  $\alpha$ -MSAN copolymer is over 35 wt %, the presence of DOP causes the phase domain extended. The phase domain size of the PVC/ $\alpha$ -MSAN/DOP blends intensively depends on AN content in  $\alpha$ -MSAN copolymer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3016–3023, 2008

**Key words:** poly(vinyl chloride); blends; miscibility; morphology

## INTRODUCTION

Miscibility in polymer blends has received substantial attention during the last decades, and considerable effort has been devoted to investigate the factors which have an effect on their miscibility. Such as, the miscibility of SAN/PMMA and SAN/PCL blends has been extensively covered in various literatures.<sup>1–4</sup> In our previous article,<sup>5</sup> the miscibility of SAN/PVC blend was reported. Miscibility occurs in a range of copolymer compositions that has been observed in binary blend systems, whose constituents involved at least one copolymer. According to Kamboor et al.,<sup>6–8</sup> this phenomenon has been attributed to the so-called copolymer effect. The “copolymer effect” suggests that mutual repulsion between the constituents and the repulsion in the copolymer leads to miscibility in the homopolymer–copolymer pair. It is well-known that the PMMA/ $\alpha$ -MSAN is a typical miscible blend system, owing to the so-called copolymer effect which is different from the interactions such as hydrogen bonding present between the molecules.<sup>9–11</sup>

Gan and Paul<sup>12</sup> have made a comprehensive examination of  $\alpha$ -MSAN/PVC blend systems. It was found that the completely substitution  $\alpha$ -methylstyrene for styrene made the miscibility window of  $\alpha$ -MSAN/PVC to be broadened compared with the SAN/PVC system. They prepared a series of PVC/SAN blends with different acrylonitrile (AN) contents via solution-precipitation technique. Consequently, they found that the miscibility occurred between PVC and SAN copolymers containing AN from 11.5 to 28 wt %, and a single glass transition was observed. The interactions between monomer unit pairs accounts for the miscibility of these blend systems.<sup>12–15</sup> However, we have found PVC/SAN blends which had two  $T_g$  values via melt-mixing method, and Moon et al. have found SAN series with AN concentrations of 24–31 wt % is immiscible with PVC by melt-extrusion.<sup>5,16</sup>

Besides that, there are a number of reported instances in the literature where different miscibility windows have been reported, although the blends had the same constituent.<sup>17</sup> It is believed that there are various reasons for it. This may be due to the use of different methods of blend preparation (e.g., solution vs. melt-mixing). It is also possible that the presence of low-molecular weight fractions in the blend polymers, techniques of measurement, or

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TABLE I  
Characterization of  $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) Copolymers

Sample	$\alpha$ -MSAN Composition (St) ( $\alpha$ -MSt)/AN (wt/wt/wt)	$M_n$ (g/mol)	$M_w$ (g/mol)	$T_{g\alpha\text{-MSAN}}$ (°C)
$\alpha$ -MSAN-15	42.5/42.5/15	71,051	159,976	112.8
$\alpha$ -MSAN-20	40/40/20	64,429	149,775	115.5
$\alpha$ -MSAN-25	37.5/37.5/25	55,336	110,302	113.4
$\alpha$ -MSAN-30	35/35/30	68,722	159,569	117.2
$\alpha$ -MSAN-35	32.5/32.5/35	82,072	184,432	117.5
$\alpha$ -MSAN-40	30/30/40	74,201	183,914	117.9
$\alpha$ -MSAN-50	25/25/50	110,020	263,114	118.5

other factors which have not been accounted for adequately.<sup>18</sup>

The plasticizer is one of the most important formulating ingredients as a polymer modifier.<sup>19</sup> Many studies on the miscibility behavior of ternary blend made by the addition of a low-molecular weight ester have been reported in the literature. For example, Paul and coworkers have found that the addition of DMP first lowers the cloud point for the PMMA/SAN blend system, but further addition causes the cloud point to increase.<sup>20</sup> The miscibility behavior of DOP/CPE48/PVC and DOP/PVC/CPVC67 ternary blends was influenced by the di-isooctyl phthalate (DOP) concentrations.<sup>21</sup> So far, no study has been reported on the use of DOP as plasticizing agent for PVC/ $\alpha$ -MSAN blend system.

This work attempts to investigate the compatibility between PVC and  $\alpha$ -MSAN copolymers via dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) methods. The effectiveness of the AN and  $\alpha$ -MSt content on the miscibility of PVC/ $\alpha$ -MSAN blends were examined. Besides that, the miscibility behavior of ternary blends made by the addition of DOP to the mixture of PVC and  $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) polymers was investigated.

## EXPERIMENTAL

### Materials

Two series of  $\alpha$ -MSAN copolymers with different AN contents were synthesized by copolymerizing various ratio of  $\alpha$ -MSt, St, and AN. The first series of  $\alpha$ -MSAN copolymers contain St,  $\alpha$ -MSt, and AN monomers. The ratio of St and  $\alpha$ -MSt was set at 1 : 1,

TABLE II  
Characterization of SAN Copolymers

Sample	St/AN (wt/wt)	$M_n$ (g/mol)	$M_w$ (g/mol)	$T_{g\text{SAN}}$ (°C)
SAN-25	75/25	93,464	203,120	107.8
SAN-35	65/35	89,159	201,320	115.8
SAN-50	50/50	103,507	225,358	117.5

and the AN content was changed systematically from 15 to 50 wt %. The second series of  $\alpha$ -MSAN copolymers contain  $\alpha$ -MSt and AN monomers. The AN contents were 25, 35, and 50 wt %, separately. For comparing purpose a series of SAN copolymers containing different AN contents were synthesized.

The emulsion polymerization was performed in 1-L glass reactor under nitrogen at 62°C. The redox initiator system consisted of cumene hydroperoxide (CHP), sodium pyrophosphate (SPP), dextrose (DX), and iron(II) sulfate (FeSO<sub>4</sub>). Sodium abietate aqueous solution was used as surfactant. First, the water, initiator, and KOH were added to the glass reactor and stirred 5 min, and then the mixture of monomers was added continuously into the reactor in 5 h. The  $\alpha$ -MSAN and SAN powder were isolated from the emulsion by coagulation and dried in a vacuum oven at 60°C for 24 h before being used.

The molecular weights of  $\alpha$ -MSAN and SAN copolymers were estimated by gel permeation chromatography (GPC, Waters-410). The analysis was calibrated with polystyrene standards. These measurements were performed in THF at 35°C and a flowing rate of 1 mL/min. The characterization results of  $\alpha$ -MSAN and SAN copolymers are listed in Tables I-III. Commercial grades of PVC resin (*K* value = 57) was supplied by JILIN Chemical Company of Jilin, China in the form of powder. Di-isooctyl phthalate and other accessory ingredient were supplied by HUATAI Chemical Company of Hangzhou, China.

### Blend preparation

Blend samples of PVC/ $\alpha$ -MSAN, PVC/SAN, and PVC/ $\alpha$ -MSAN/DOP were prepared by melt-blend-

TABLE III  
Characterization of  $\alpha$ -MSAN  
(not containing St) Copolymers

Sample	$\alpha$ -MSt/AN (wt/wt)	$M_n$ (g/mol)	$M_w$ (g/mol)	$T_{g\alpha\text{-MSAN}}$ (°C)
$\alpha$ -MSAN-25	75/25	79,037	151,804	116.4
$\alpha$ -MSAN-35	65/35	127,167	269,347	120.7
$\alpha$ -MSAN-50	50/50	127,840	288,321	117.2

**TABLE IV**  
 **$T_g$  of PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) (50/50) Blends**

Sample of blends	$T_{gPVC}$ (°C)	$T_{g\alpha\text{-MSAN}}$ (°C)	$\Delta T_g$ (°C)
PVC/ $\alpha$ -MSAN-15	81.8	112.4	30.6
PVC/ $\alpha$ -MSAN-20	104.6	104.6	–
PVC/ $\alpha$ -MSAN-25	104.8	104.8	–
PVC/ $\alpha$ -MSAN-30	95	108.2	13.2
PVC/ $\alpha$ -MSAN-35	91.4	117.5	26.1
PVC/ $\alpha$ -MSAN-40	87.9	118.8	30.9
PVC/ $\alpha$ -MSAN-50	83.5	118.2	34.7

ing these materials in two-roll milling at 170°C for about 5 min and press-molding at 185°C for about 3 min. To prevent the degradation of PVC, 2 wt % lead sulfate was added as a heat stabilizer. The lubricant (1 wt % calcium stearate) was also added to reduce the friction between the powder particles and the mixing roll.

### Dynamic mechanical analysis

The dynamic mechanical properties of the blends were characterized using DMA. The measurements were carried out on a Diamond-DMA using rectangular samples. The scans were carried out in tensile mode. The samples were sized 30 × 10 × 1 mm<sup>3</sup>, and test were carried out in temperature range of 50–150°C at a frequency of 1 Hz and a heating rate of 3°C/min with the amplitude of 5  $\mu$ m.

### Morphological characterization

The disperse morphology was characterized by SEM (model Japan JSM-5600). The sample surface was cut at room temperature with a glass knife to generate clean and flat surface. Contrast between the phases was achieved by immersing each sample in CrO<sub>3</sub> · H<sub>2</sub>SO<sub>4</sub> solution for 8 min to remove the  $\alpha$ -MSAN at the surface. Surface of the samples were coated with a thin layer of gold before the observations.

## RESULTS AND DISCUSSION

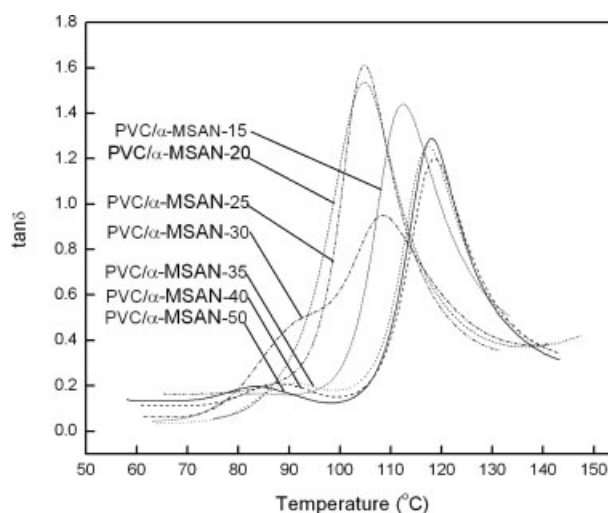
### Dynamic mechanical analysis

Miscibility of polymer blends can be determined from the viscoelastic data obtained by DMA. Our previous studies showed that SAN copolymers containing 5, 25, 35, and 50 wt % AN content were immiscible with PVC, and two  $T_g$  values were found for these blends. The interaction between SAN and PVC was influenced by the AN concentration in SAN.<sup>5</sup> This observation has been reported to be due to the self-association of polar AN groups and steric effects.<sup>16</sup> At high AN concentrations, the self-association of the AN groups reduces the miscibility with

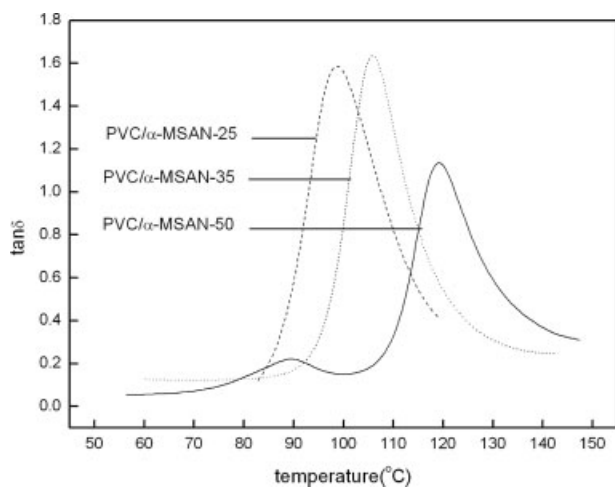
PVC. Even with low AN concentrations, SAN shows limited miscibility with PVC because of the easy rotation of SAN, which helps the self-association of AN and reduces AN steric effect. In this article, the miscibility of PVC and  $\alpha$ -MSAN with different AN contents were investigated. The results listed in Table IV shows the tendency that the  $T_g$ s of PVC phase increase first and then decrease with the increase of AN content in  $\alpha$ -MSAN copolymers. On the contrary, the  $T_g$ s of  $\alpha$ -MSAN decrease with the AN content and then increase.

The temperature dependence of the tan  $\delta$  peak for PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) blends with different AN content is given in Figure 1. It shows that there are two separate glass transitions of the PVC-rich phase and the  $\alpha$ -MSAN-rich phase, as AN content in the  $\alpha$ -MSAN copolymers are 15, 35, 40, and 50 wt %. The occurrence of a shoulder in the tan  $\delta$ -T curve of the blend confirms partial miscibility as  $\alpha$ -MSAN copolymer containing 30 wt % AN content. When the AN content is in the range of 20–25 wt %, only a single glass transition for the blends of PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) exists. It is well-supported by the qualitative evidences obtained from SEM examination, as will be reported later. This indicates that the introduction of  $\alpha$ -MSt improves the miscibility of the blends. The interaction between  $\alpha$ -MSAN and PVC is also influenced by the AN contents in  $\alpha$ -MSAN. The intermolecular repulsion between different segments of  $\alpha$ -MSAN, and the additional interaction between the  $\alpha$ -hydrogen of PVC and AN of  $\alpha$ -MSAN accounts for the miscibility of this blend system.<sup>16</sup>

It is expected that the miscibility of the blends would be improved after the complete substitution of St by  $\alpha$ -MSt monomer, and DMA experiment was adopted to verify this assumption. Figure 2 shows the



**Figure 1** Temperature dependence of the tan  $\delta$  for PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) (50/50) blends.



**Figure 2** Temperature dependence of the  $\tan \delta$  for PVC/ $\alpha$ -MSAN (not containing St) (50/50) blends.

temperature dependence of the  $\tan \delta$  for PVC/ $\alpha$ -MSAN (not containing St) blends with different AN contents. As shown in Figure 2 only a single glass transition is observed when the AN content of  $\alpha$ -MSAN is 35 wt %. This observation further identifies the truth that the introduction of  $\alpha$ -MSt makes the miscibility windows expanded. Similar improvements in miscibility were also reported by other researchers.<sup>12,16</sup> According to Moon et al., the methyl groups in  $\alpha$ -MSAN inhibit chain rotation and help to AN exposure (steric effect). Compared with SAN,  $\alpha$ -MSAN shows improved miscibility with PVC over a range of AN concentrations because of the gauche conformation of the chain, which helps with hydrogen bonding between AN and the  $\alpha$ -hydrogen of PVC.<sup>16</sup>

Plasticizers act as solvents for amorphous regions of polymer, and the polymer chains are softened by the introduction of plasticizer. It induces the glass transition temperatures shift to lower temperature. The decrease of  $T_g$  is due to a substantial increase in the free volume of the blends. Plasticizer dispersed in both phases molecularly and changes the viscoelastic behavior of the blends.

The viscoelastic behavior of the PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) blends with 10 and 20 wt % DOP as plasticizer has been measured, and the  $T_g$  values of the blends were given in Tables V and VI. It is obvious that there is only one glass transition of the

blends when the AN content of  $\alpha$ -MSAN copolymer is in the range of 15–25 wt %. There is strong interaction between DOP and nitrite group of  $\alpha$ -MSAN when AN content is low. DOP distributes much more into the  $\alpha$ -MSAN phase causes the  $T_g$  of  $\alpha$ -MSAN phase shifts to lower temperature in a large range. The  $T_g$  of PVC phase also shifts to lower temperature under the influence of DOP; however, the range is smaller than that of  $\alpha$ -MSAN phase. So the glass transitions of the two phases overlap showing only one  $T_g$ . However, according to Utraki,<sup>22</sup> the appearance of one  $T_g$  is not a proof of miscibility but only a proof of a state of fine dispersion. The presence of a single or dual glass transition could depend on the particle size of dispersed phase in phase-separated blends.<sup>23</sup> So it is needed to examine the morphology of the blend to verify this assumption that the introduction of DOP improve the miscibility of the blend in this AN content range.

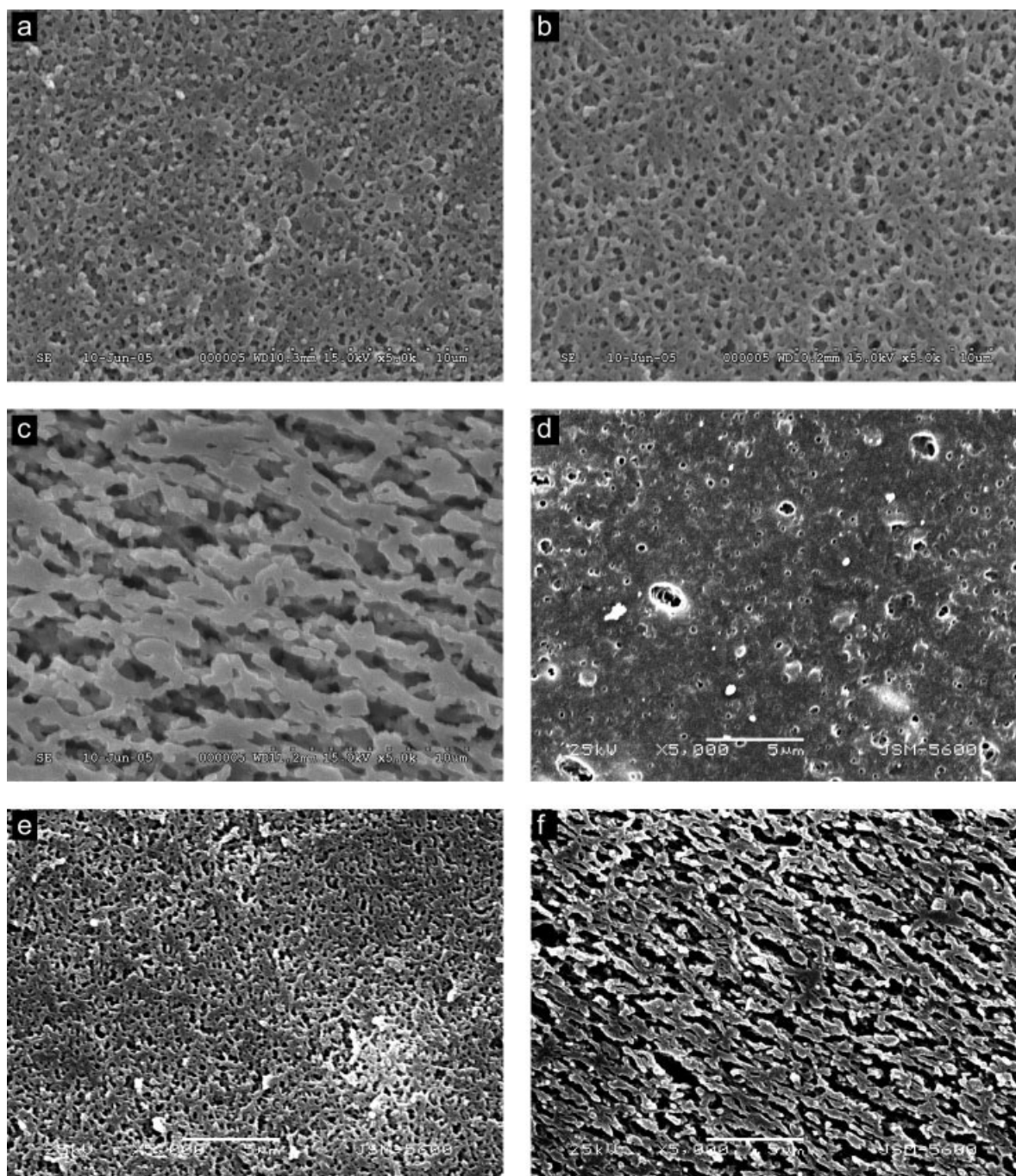
As shown in Table V, two distinct glass transitions of the blends are observed when AN contents in  $\alpha$ -MSAN copolymer are more than 35 wt %. The magnitude of  $\Delta T_g$  (distance of two glass transition regions) of PVC/ $\alpha$ -MSAN/DOP(45/45/10) blends (41–51.6°C in Table V) is larger than that of PVC/ $\alpha$ -MSAN blends (30.9–34.7°C in Table IV). This observation suggests that there is obviously different distribution of DOP between the two phases. With the increase of DOP content, the magnitude of  $\Delta T_g$  of PVC/ $\alpha$ -MSAN/DOP (40/40/20) blends (59.6–81.5°C in Table VI) is larger than that of PVC/ $\alpha$ -MSAN/DOP (45/45/10) blends. This observation suggests that the extent of phase separation increased rapidly with the increasing fraction of DOP in the blend. According to Zeman and Patterson,<sup>24</sup> the asymmetry in the polymer–solvent interactions ( $x_{12} \neq x_{13}$ ) strongly accelerates the phase separation of ternary systems. As shown in Tables V and VI, when AN content in  $\alpha$ -MSAN copolymer is more than 35 wt %, the  $T_g$  value of PVC phase obviously decreased with increasing DOP content, while the  $T_g$  value of  $\alpha$ -MSAN phase did not change obviously. The observation indicates that the interaction between DOP and PVC phase is stronger than that between DOP and  $\alpha$ -MSAN phase, and DOP mainly disperses in the PVC phase. As a consequence, the  $\Delta T_g$  values of the two phases in the blend systems become larger.

**TABLE V**  
 $T_g$  of PVC/ $\alpha$ -MSAN/DOP (45/45/10) Blends

Sample of blends	$T_{gPVC}$ (°C)	$T_{g\alpha-MSAN}$ (°C)	$\Delta T_g$ (°C)
PVC/ $\alpha$ -MSAN-15	84.8	84.8	–
PVC/ $\alpha$ -MSAN-25	80.8	80.8	–
PVC/ $\alpha$ -MSAN-35	62.6	103.6	41
PVC/ $\alpha$ -MSAN-50	60.5	112.1	51.6

**TABLE VI**  
 $T_g$  of PVC/ $\alpha$ -MSAN/DOP (40/40/20) Blends

Sample of blends	$T_{gPVC}$ (°C)	$T_{g\alpha-MSAN}$ (°C)	$\Delta T_g$ (°C)
PVC/ $\alpha$ -MSAN-15	61.2	61.2	–
PVC/ $\alpha$ -MSAN-25	66.5	65.5	–
PVC/ $\alpha$ -MSAN-35	37.8	97.4	59.6
PVC/ $\alpha$ -MSAN-50	29.5	111.0	81.5

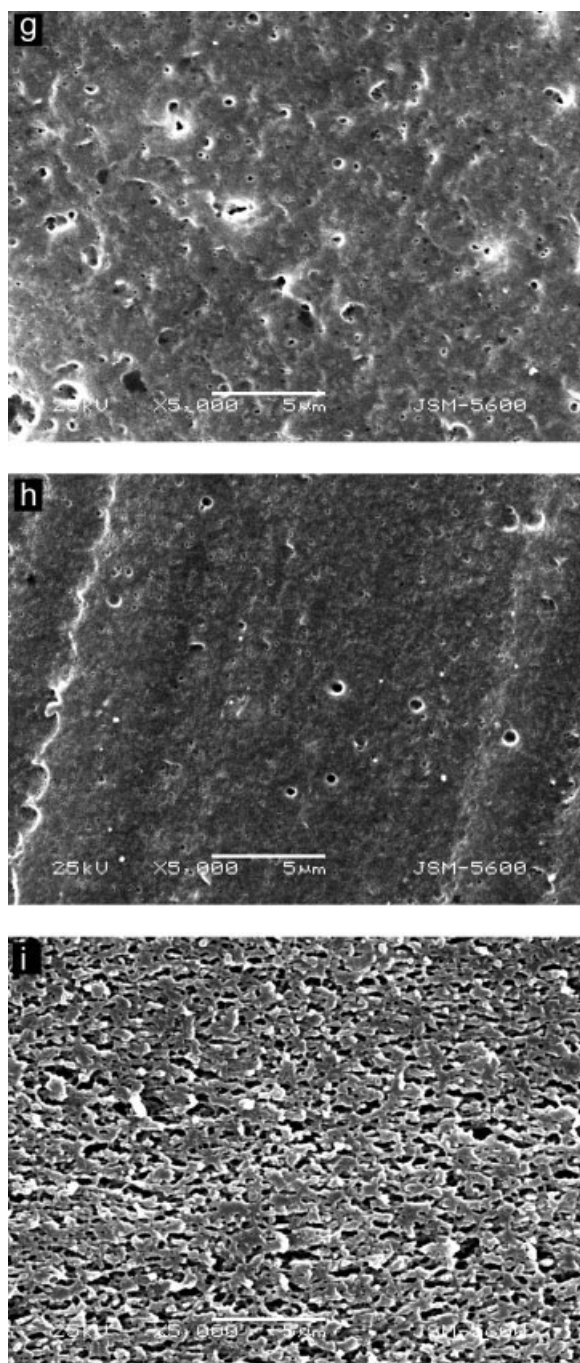


**Figure 3** SEM images of PVC/SAN (50/50), PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) (50/50) and PVC/ $\alpha$ -MSAN (not containing St) (50/50) blends etched by  $\text{CrO}_3/\text{H}_2\text{SO}_4$  aqueous solution. (a) PVC/SAN-25, (b) PVC/SAN-35, (c) PVC/SAN-50, (d) PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1)-25, (e) PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1)-35, (f) PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1)-50, (g) PVC/ $\alpha$ -MSAN-25, (h) PVC/ $\alpha$ -MSAN-35, and (i) PVC/ $\alpha$ -MSAN-50.

### MORPHOLOGY

The morphology of the PVC/SAN (50/50) blends can be seen from Figure 3(a–c). It can be seen that cluster is formed in the PVC matrix, and the size of the dispersed phase changes with different AN content in SAN copolymer. A co-continuous phase structure develops at around 50 wt % AN content in the SAN copolymer. Figure 3(d–f) shows the mor-

phology of PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) blends. It is obvious that the size of the dispersed phase is much smaller in comparison with the PVC/SAN blends. When the AN content in the  $\alpha$ -MSAN copolymer is up to 25 wt %,  $\alpha$ -MSAN forms finely dispersed droplets in the PVC matrix [Fig. 3(d)]. The particle size of the dispersed phase become smallest compared with Figures 3(e–f), and it suggests that the miscibility between the two phase are best.

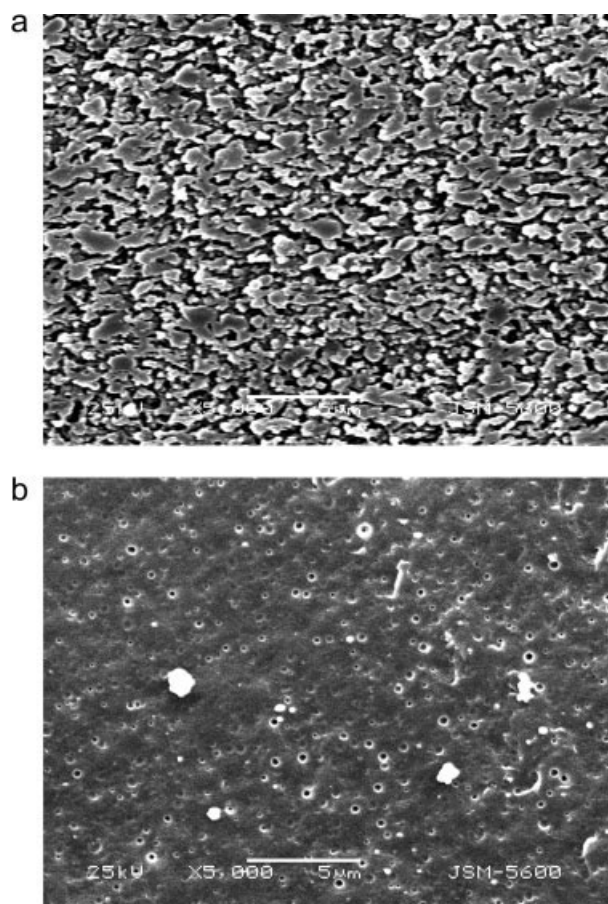


**Figure 3** (Continued from the previous page)

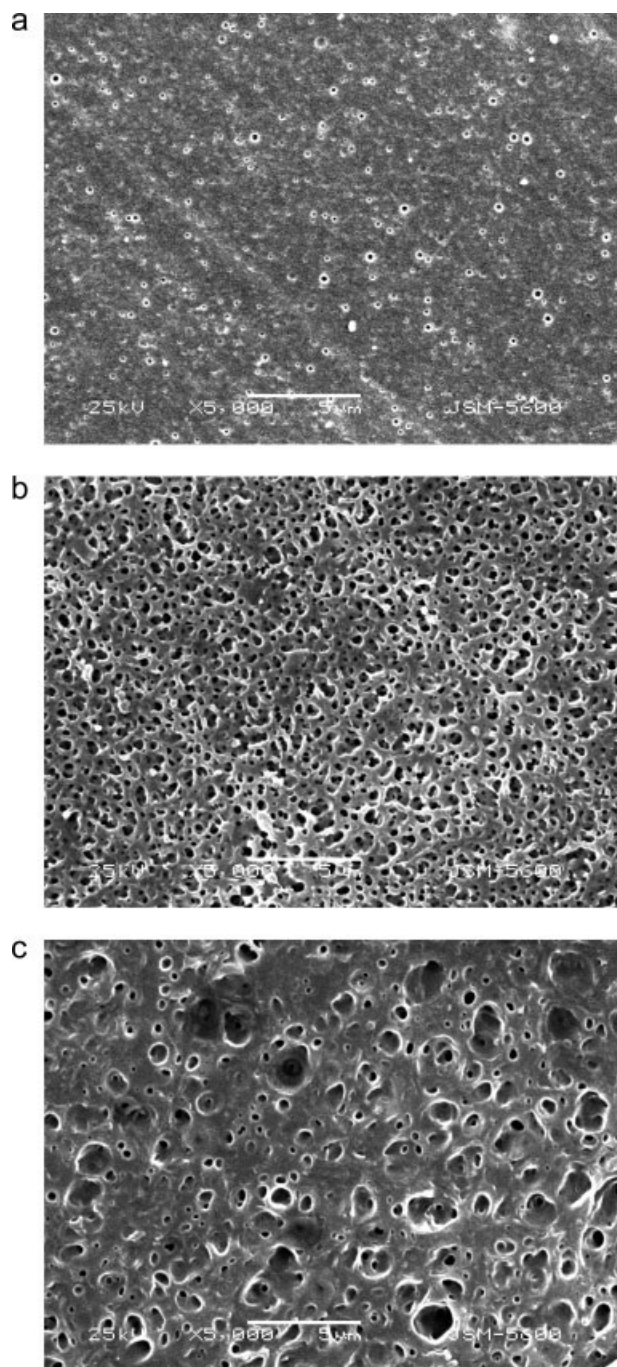
Figure 3(e) indicates that the cluster for  $\alpha$ -MSAN containing 35 wt % AN content is formed. With the continuously increasing AN content, co-continuous phase structure develops [Fig. 3(f)]. The SEM micrograph in the Figure 3(g-i) presents the morphology of the PVC/ $\alpha$ -MSAN (not containing St) blends. We note that the PVC/ $\alpha$ -MSAN35 blend shows a homogeneous morphology [Fig. 3(h)], and this result is in accordance with the DMA characterization that only a single glass transition is observed.

Figure 3 schematically illustrates the structure of the blends, and the size of the dispersed phase substantially becomes smaller with the decreasing AN content in the copolymers. It is found that the incorporation of  $\alpha$ -MSt in polymers improves the miscibility of the blends very well. This result is verified by using SEM and DMA techniques. The miscibility of PVC/ $\alpha$ -MSAN blends strongly depends on the  $\alpha$ -MSt content in  $\alpha$ -MSAN copolymer, and the miscibility is substantially improved with the increase of  $\alpha$ -MSt content in  $\alpha$ -MSAN copolymer containing identical AN content.

The introduction of DOP to PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) blends is expected to have an important effect on the morphology of these blends. First, the effect of DOP on the morphology of the blend is investigated as  $\alpha$ -MSAN copolymer containing lower AN content, and the morphology is illustrated in Figure 4. The morphology of PVC/ $\alpha$ -MSAN15 blend, as indicated in Figure 4(a), suggests that the size of the  $\alpha$ -MSAN domains is relatively large as for the  $\alpha$ -MSAN containing 15 wt % AN content. When DOP



**Figure 4** SEM images of PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) and PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1)/DOP blends etched by  $\text{CrO}_3/\text{H}_2\text{SO}_4$  aqueous solution. (a) PVC/ $\alpha$ -MSAN-15 = 50/50, (b) PVC/ $\alpha$ -MSAN-15/DOP = 40/40/20.



**Figure 5** SEM images of PVC/ $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1)/DOP blends etched by  $\text{CrO}_3/\text{H}_2\text{SO}_4$  aqueous solution. (a) PVC/ $\alpha$ -MSAN-25/DOP = 40/40/20, (b) PVC/ $\alpha$ -MSAN-35/DOP = 40/40/20, (c) PVC/ $\alpha$ -MSAN-50/DOP = 40/40/20.

is introduced, as shown in Figure 4(b), homogeneous structure is observed. This suggests that the addition of DOP obviously improves the miscibility of PVC/ $\alpha$ -MSAN15 blend. Figure 5 shows the morphology of PVC/ $\alpha$ -MSAN/DOP blends with higher AN content. Figure 5(a) exhibits homogeneous structure in the blend as the AN content in  $\alpha$ -MSAN copolymer is 25 wt %. However, there is a poor dispersion of  $\alpha$ -

MSAN particles in PVC matrix when the AN content in  $\alpha$ -MSAN copolymer is more than 35 wt % by comparing Figure 5(b,c) with Figure 3(e,f). It is further indicated that the presence of plasticizer causes the phase domain extended. Consequently, the effect of DOP on the morphology of the blends depends on the AN content in  $\alpha$ -MSAN copolymer.

## CONCLUSIONS

The miscibility of PVC/ $\alpha$ -MSAN blends has been investigated by changing the composition of  $\alpha$ -MSAN copolymer. It was found that the miscibility behavior of blends depend on the AN and  $\alpha$ -MSt content in  $\alpha$ -MSAN copolymer. PVC is miscible with  $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) if AN weight percent in  $\alpha$ -MSAN ( $\alpha$ -MSt/St = 1/1) is within a window range of 20–25 wt %. From the SEM micrograph, the size of the dispersed phase changes with composition. The diameter of dispersed droplets is smaller than 1  $\mu\text{m}$  when AN content of  $\alpha$ -MSAN copolymer is in the range of 20–25 wt %.  $\alpha$ -MSAN (not containing St) copolymer with 35 wt % AN is miscible with PVC even when they are blended by melt-mixing. The miscibility window was further expanded by complete substitution of  $\alpha$ -methylstyrene for styrene in  $\alpha$ -MSAN copolymer. The miscibility of PVC/ $\alpha$ -MSAN blends is substantially improved with the increasing  $\alpha$ -MSt content in  $\alpha$ -MSAN copolymer containing identical AN content.

The presence of plasticizer has a substantial effect on the blends. The different distribution between the two phases of DOP induces the glass transition shift to lower temperature and form a single  $T_g$  peak, as AN content in  $\alpha$ -MSAN copolymer is within the range of 15–25wt %. When the AN content in  $\alpha$ -MSAN copolymer is over 35 wt %, the distance of two glass transition regions extends, and SEM micrographs extended phase domain is obtained.

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