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Effect of α-MSt content in α-MSAN copolymer on the miscibility of PVC/α-MSAN blends

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Summary

A series of α-methylstyrene, styrene and acrylonitrile(α-MSAN) copolymers with different α-methylstyrene (α-MSt) content were synthesized by altering α-MSt and St ratios with emulsion copolymerization method. By melt blending these copolymers with PVC resin and di-isooctyl phthalate (DOP), PVC/α-MSAN and PVC/α-MSAN/DOP blends were prepared. The miscibility and morphology of the blends were investigated by dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). The miscibility of PVC/α-MSAN blends is substantially improved with the increasing α-MSt content in α-MSAN copolymer containing identical AN content and the blends show homogeneous morphology as the α-MSt content in α-MSAN copolymer is up to 22.5wt%. α-MSAN copolymer containing 37.5wt% α-MSt is fully miscible with PVC throughout the whole composition range. When DOP was introduced into the PVC/α-MSAN blends, a single Tanδ peak over room temperature in DMA detection is found as α-MSt content in α-MSAN copolymer is from 15 to 75 wt%, and morphology result also shows that the PVC and α-MSAN copolymer is miscible under the influence of DOP.

Keywords

PVC blend, α-MSAN copolymer, miscibility, plasticizer, α-methylstyrene content

Introduction

Miscibility is unusual in blend systems of high molecular weight polymer for the very small combinatorial entropy [1]. However, a great number of systems in which at least one component is a random copolymer show miscibility over a range of copolymer compositions, even though combinations of the corresponding homopolymers are immiscible. Such as, the miscibility of SAN/PMMA shows this behavior [2]. Polymer blends of SAN/PCL are compatible in a limited range of AN content in SAN copolymers [3-5]. This phenomenon has been attributed to the mutual repulsion between the constituents of the copolymer prevails over other interactions and the repulsion in the copolymer leads to miscibility in the homopolymer-copolymer pair [6-8]. It is well known that the PMMA/α-MSAN is a typical miscible blend system, owing to the mutual repulsion which is different from the interactions such as hydrogen bonding present between the molecules [9-11]. In the case of PVC/SAN blends, no interaction is found by infrared spectroscopy [12]. Kim et al. have reported that intermolecular repulsion between styrene and acryonitrile units in SAN is the cause of miscibility of PVC/SAN blends [13].

Many studies on the miscibility behavior of ternary blend made by the addition of a low molecular weight ester have been reported in the literatures. The plasticizer is one of the most important formulating ingredients as a polymer modifier [14]. For example, Paul et al. has found that the addition of DMP first lowered the cloud point for the PMMA/SAN blend system but further addition caused the cloud point to increase [15]. The miscibility behavior of DOP/CPE48/PVC and DOP/PVC/CPVC67 ternary blends was influenced by the DOP concentrations [16]. So far, no study has been reported on the use of DOP as plasticizing agent for PVC/α-MSAN blend system to our knowledge.

The present work attempts to investigate the effectiveness of α-MSt content in α-MSAN copolymer on the miscibility of PVC/α-MSAN blend via DMA and SEM methods. Besides that, the miscibility behavior of ternary blends made by the addition of DOP to the mixture of PVC and α-MSAN or SAN polymers was also investigated.

Experimental

Materials

A series of α-MSAN copolymers with different α-MSt contents were synthesized by changing α-MSt and St ratios. The AN content was set at 25wt% and the α-MSt content was changed systematically from 0wt% to 75wt%. When α-MSt content was 0wt%, the copolymer is consisted of St and AN monomers and it is referred to by SAN. The emulsion polymerization was performed in 1L glass reactor under nitrogen at 62°C. An oil-soluble initiator, cumene hydroperoxide(CHP), was used in combination with a redox system. The redox initiator system was consisted of cumene hydroperoxide(CHP), sodium pyrophosphate(SPP), dextrose(DX), and iron(II)sulfate(FeSO4). Sodium abietate aqueous solution was used as surfactant. First, the water, initiator and KOH were added to the glass reactor and stirred five minutes and then the mixture of monomers were added continuously into the reactor in 5 hours. The α-MSAN and SAN powder were isolated from the emulsion by coagulation and dried in a vacuum oven at 60°C for 24h before being used.

The information about α-MSAN and SAN copolymers used in this study was listed in Table1. Commercial grades of PVC resin (K value=57) was supplied by JILIN Chemical Company of China in the form of powder. Di-isooctyl phthalate and other accessory ingredient were supplied by HUATAI Chemical Company.

Blend preparation

Blend samples of PVC/α-MSAN and PVC/α-MSAN/DOP were prepared by melt blending 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, 2wt% lead

Table 1. Composition of α-MSAN copolymers

Sample of blends	Composition of α-MSt/St/AN(wt/wt/wt)
α-MSAN-0(SAN)	0/75/25
α-MSAN-7.5	7.5/67.5/25
α-MSAN-15	15/60/25
α-MSAN-22.5	22.5/52.5/25
α-MSAN-30	30/45/25
α-MSAN-37.5	37.5/37.5/25
α-MSAN-52.5	52.5/22.5/25
α-MSAN-75	75/0/25

sulfate was added as a heat stabilizer. The lubricant (1wt% calcium stearate) was also added to reduce the friction between the powder particles and the mixing roll.

Dynamic mechanical analysis (DMA)

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^3 and test were carried out in temperature range of 50~150°C at a frequency of 1Hz and a heating rate of 3°C/min.

Morphological characterization

The disperse morphology was characterized by scanning electron microscopy (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 $CrO_3 \cdot H_2SO_4$ solution for 8min to remove the α-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

In the present paper, the miscibility of PVC and α-MSAN with different α-MSt content was investigated. In order to gain more insight into the miscibility behavior of PVC/α-MSAN, DMA has been used to characterize. The results list in Table 2 shows the Tgs of PVC and α-MSAN phases. The temperature dependence of the Tanδ peak for PVC/α-MSAN blends with different α-MSt content is given in Figure1. It shows that there are two separate glass transition of the PVC-rich phase and the SAN-rich/α-MSAN-rich phase, as α-MSt content in the α-MSAN copolymers is less than 15wt%. When the α-MSt content is over than 22.5wt%, only a single glass transitions for the blends of PVC/α-MSAN exists. It is well supported by the qualitative evidences obtained from SEM examination as will be reported later. This indicates that the introduction of α-MSt improves the miscibility of the blends since the α-MSt unit interacts more favorably with PVC units than styrene does. Kim et al. [17] have

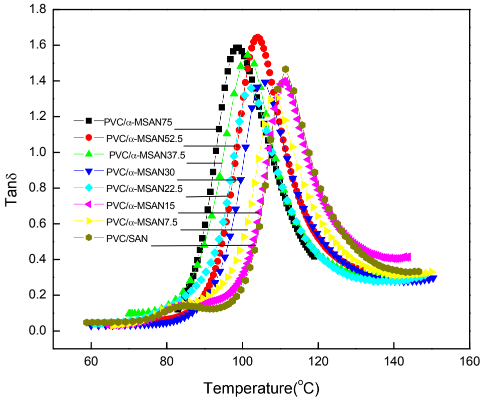

Figure 1. Temperature dependence of the Tanδ for PVC/α-MSAN(50/50) blends

Table 2. Tg of PVC/α-MSAN (50/50) blends

Sample of blends	Tg_{PVC} (°C)	$Tg_{\alpha\text{-MSAN}}$ (°C)	ΔTg (°C)
PVC/α-MSAN-0(SAN)	84.5	111.4	26.9
PVC/α-MSAN-7.5	80.9	104.7	23.8
PVC/α-MSAN-15	85.1	110.7	25.6
PVC/α-MSAN-22.5	102.3	102.3	0
PVC/α-MSAN-30	105	105	0
PVC/α-MSAN-37.5	101.4	101.4	0
PVC/α-MSAN-52.5	104.1	104.1	0
PVC/α-MSAN-75	100.3	100.3	0

reported that PVC/α-MSAN blends showed higher LCST behavior comparing with PVC/SAN blends. The value of LCST increased as the strength of interaction between the component polymers increases [18].

In order to testify the influence of composition on miscibility, blend samples of PVC/α-MSAN-37.5（75/25,50/50 and 25/75）are prepared. It is expected that the miscibility of the α-MSAN-37.5/PVC blends would be very good in the whole composition, and DMA experiment was adopted to verify this assumption. Figure2

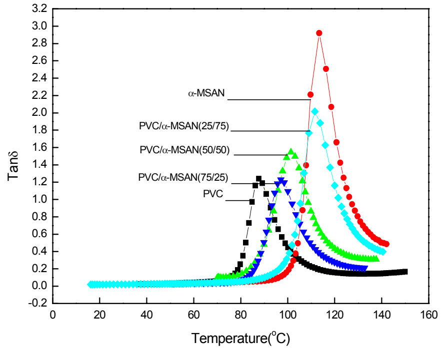

Figure 2. Temperature dependence of the Tanδ for PVC/α-MSAN-37.5 blends

Table 3. Tg of PVC/α-MSAN/DOP blends

Sample of blends	PVC/α-MSAN/DOP(45/45/10) $Tg_{\alpha\text{-MSAN}} \backslash Tg_{PVC}$ (°C)	PVC/α-MSAN/DOP(40/40/20) $Tg_{\alpha\text{-MSAN}} \backslash Tg_{PVC}$ (°C)
PVC/α-MSAN-0(SAN)	96.5/77.7	83.5/52.2
PVC/α-MSAN-15	87.5	66.1
PVC/α-MSAN-22.5	81.6	64.2
PVC/α-MSAN-37.5	80.8	66.5
PVC/α-MSAN-75	70.4	59.5

shows the temperature dependence of the Tanδ for PVC/α-MSAN-37.5 blends with different compositions. As shown in Figure2 only a single glass transition is observed. This observation identifies that the PVC/α-MSAN-37.5 blend system is a miscible system in the whole composition. The intermolecular repulsion between different segments of α-MSAN and the additional interaction between the α-hydrogen of PVC and AN of α-MSAN account for the miscibility of this blend system [19].

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 viscoelastic behavior of the PVC/α-MSAN blends with 10wt% and 20wt% DOP as plasticizer, evaluated by means of DMA, are summarized in Table 3. It is obvious that there are two glass transitions of the blends as the copolymer not containing α-MSt even when DOP are added. According to Utraki [20], the appearance of one or two Tg 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 [21]. So it is needed to examine the morphology of the blend to verify this assumption.

In addition, it can be seen from Table 3 that the ternary blends exhibit only a single Tg value when the α-MSt content in α-MSAN copolymer is up to 15wt%. The miscibility of PVC/α-MSAN-15 blend is improved by introducing DOP. The PVC/α-MSAN/DOP blends containing 10~20wt% DOP exhibit only a single Tg. Therefore, comparing with PVC/SAN/DOP system, a high miscibility is maintained even when the 20wt%DOP are added, which suggests that there is strong interaction between DOP and nitrite group of α-MSAN. The Tg of the blends shifts to lower temperature with the increase of DOP content. The decrease of Tg is due to a substantial increase in the free volume of the blends. Plasticizer disperses in both phases molecularly and changes the viscoelastic behavior of the blends.

Morphology

Figure3 shows the morphology of the PVC/α-MSAN (50/50) blends. Figure3 (a) and (b) show that cluster is formed in the PVC matrix when the α-MSt content in α-MSAN copolymer is 0 and 15wt%, respectively. Figure3(c) and (d) show the homogeneous morphology of PVC/α-MSAN blends when the α-MSt content in α-MSAN copolymer is more than 22.5wt%. It is founded that the size of the dispersed phase decreases with increase of α-MSt content in α-MSAN copolymer until homogeneous morphology formed. This attributes to the fact that the α-MSt unit interacts more favorably with the PVC unit than styrene. The interaction of which increases with the increase of α-MSt content in α-MSAN copolymer.

The morphology of the PVC/α-MSAN-37.5 blend system can be seen from Figure 4. It can be seen that the dispersed phase disperse uniformly in the matrix. Interestingly, Figure 4(c) shows that the particle size of α-MSAN etched by CrO_3/H_2SO_4 aqueous solution is very small even though the fraction of α-MSAN in the blend is up to 75wt%, namely, the α-MSAN phase is the matrix. It indicates that full miscibility exits in PVC/α-MSAN-37.5 blend system within the range of composition examined.

The introduction of DOP to PVC/α-MSAN blends is expected to have an important effect on the morphology of these blends. Firstly, the effect of DOP on the morphology of PVC/SAN blend is investigated and the morphology is illustrated in Figure5 (a) and (e) which suggests that the size of the PVC/SAN/DOP domains is much smaller than that of PVC/SAN as shown in Figure3 (a).

When DOP is introduced into the PVC/α-MSAN-15 blend, as shown in Figure5 (b) and (f), homogeneous structure is observed. It is obvious that the size of the dispersed phase is much smaller in comparison with the Figure3 (b). This suggests that the presence of DOP obviously increases the miscibility of the PVC/α-MSAN-15 blend. Figure5 (c), (d), (g) and (h) exhibits homogeneous structure of the PVC/α-MSAN/DOP blends as the α-MSt content in α-MSAN copolymer is higher. Consequently, the effect of DOP on the morphology of the blends depends on the α-MSt content in α-MSAN copolymer.

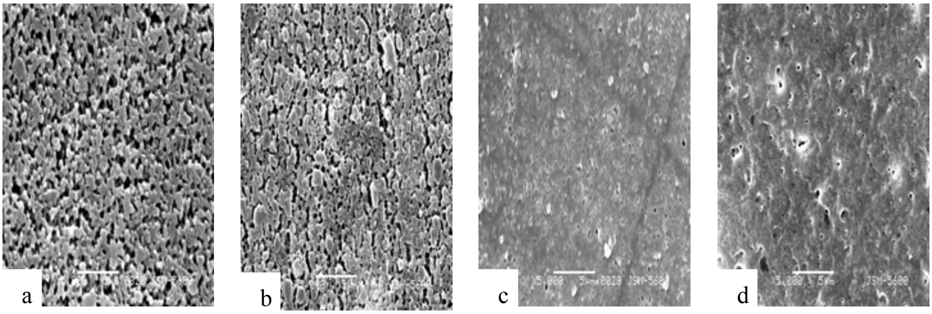

Figure 3. SEM images of PVC/α-MSAN blends etched by CrO_3/H_2SO_4 aqueous solution.
The composition of the blends for a) PVC/SAN, b) PVC/α-MSAN-15, c) PVC/α-MSAN-22.5, d) PVC/α-MSAN-75

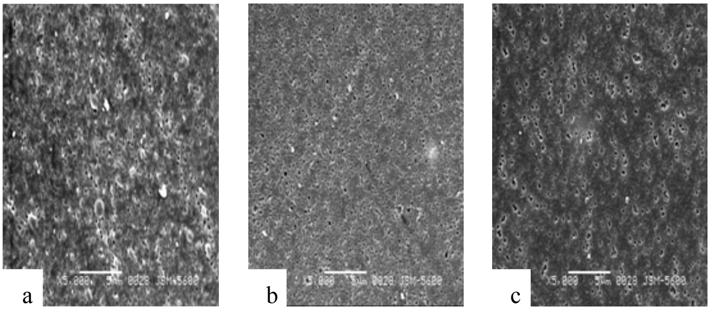

Figure 4. SEM images of PVC/α-MSAN-37.5 blends etched by CrO_3/H_2SO_4 aqueous solution.
The blends for a) PVC/α-MSAN(75/25), b) PVC/α-MSAN(50/50), c) PVC/α-MSAN(25/75)

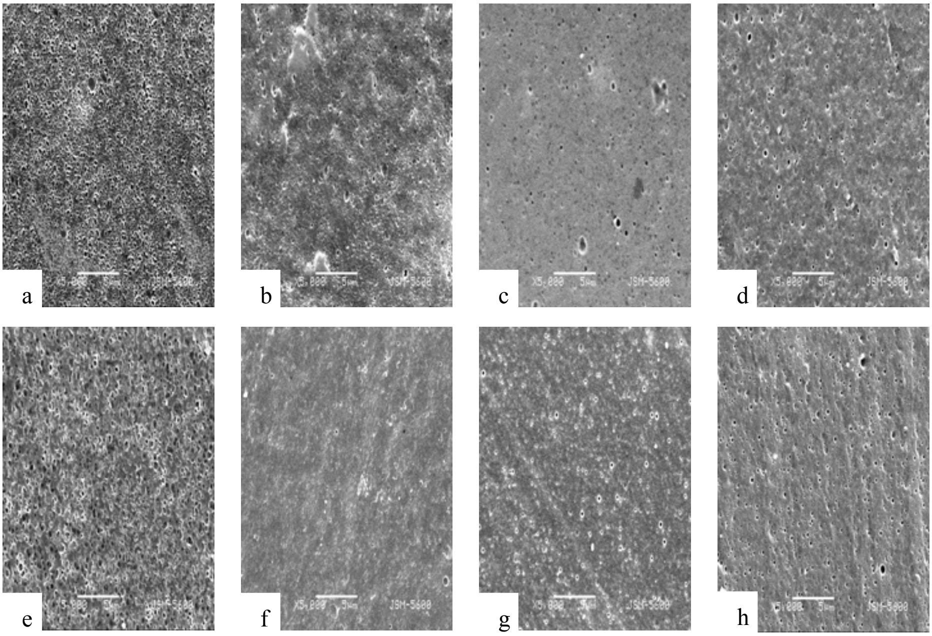

Figure 5. SEM images of PVC/α-MSAN/DOP blends etched by CrO_3/H_2SO_4 aqueous solution. The composition of the blends for a) PVC/SAN/DOP(45/45/10), b) PVC/α-MSAN-15/DOP (45/45/10), c) PVC/α-MSAN-37.5/DOP(45/45/10), d) PVC/α-MSAN-70/DOP(45/45/10), e) PVC/SAN/DOP(40/40/20), f) PVC/α-MSAN-15/DOP(40/40/20), g) PVC/α-MSAN-37.5/DOP(40/40/20), h) PVC/α-MSAN-70/DOP(40/40/20)

Conclusions

The miscibility behavior of PVC/α-MSAN blends depends on the α-MSt content in α-MSAN copolymer. The PVC is immiscible with α-MSAN as the α-MSt content in α-MSAN is less than 15wt% by melt mixing. However, the miscibility of PVC/α-MSAN blends is substantially improved with the increase of α-MSt content in α-MSAN copolymer containing identical AN content, and it develops homogeneous morphology when the α-MSt content in α-MSAN is more than 22.5wt%. So the miscibility of PVC/α-MSAN blends depends not only on the AN content in α-MSAN copolymer but also on the different α-MSt content in α-MSAN copolymer. The miscibility of PVC/α-MSAN-37.5 blends has been investigated by changing the composition of the blends. It was found that the PVC/α-MSAN-37.5 blend system is a miscible system in the whole composition.

The presence of plasticizer has a substantial effect on the blends. A high miscibility is founded in PVC/α-MSAN/DOP blends when 10~20wt% DOP are added, and SEM pictures show a true homogeneous phase.

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