

# Rheological Behavior and Morphology of Blends of Copolymers of $\alpha$ -Methylstyrene-co-Acrylate with PVC

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## SYNOPSIS

The copolymers of poly( $\alpha$ -methyl styrene–methyl acrylate) (PMSMA) and poly( $\alpha$ -methyl styrene–ethyl acrylate) (PMSEA) were synthesized by emulsion polymerization. The compatibility of these copolymers with poly(vinyl chloride) (PVC) was estimated by the solubility parameter method and scanning electron microscopy (SEM). The rheological behavior was investigated by a flow tester. The mechanical properties, rheological behavior, and morphology of these blends show that these copolymers can be used as a processing aid for PVC. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The modification of poly(vinyl chloride) (PVC), (i.e., a “hard” polymer) by adding another polymer is a well-known method currently in practice. The number of polymers and copolymers applied as PVC modifiers is quite large. These modifiers may be divided into two basic groups: The first one involves rubberlike polymers added to PVC to improve its mechanical properties, in particular, its toughness. They are called resistant impact aids. The structure of the materials prepared in this way and the mechanism of the action of the modifiers have been for years the object of intensive investigations by numerous authors. The other group of modifiers involves polymers used for the modification of PVC under the general denomination of processing aids. While the mechanical properties of hard PVC are only insignificantly changed at room temperature by the addition of a modifier, the processing operations (milling, calendaring, extrusion, blow molding, and the like) in PVC melt are significantly facilitated.

Poly (methyl methacrylate) (PMMA) and a copolymer of an MMA type are usually used as processing aids of hard PVC.<sup>1–3</sup> The acrylic processing

aids are expensive commercially.  $\alpha$ -Methyl styrene (MS) has a low price commercially. The oligomers of poly( $\alpha$ -methyl styrene) (PMS) are also used as processing aids for various resins,<sup>4</sup> but copolymers of MS with acrylate are not used as processing aids for PVC to date.

It was the object and purpose of this article to suggest a synthesis of poly ( $\alpha$ -methyl styrene–methyl acrylate) (PMSMA) and poly( $\alpha$ -methyl styrene–ethyl acrylate) (PMSEA) and to investigate its use as a processing aid for PVC. The miscibility of PMSMA and PMSEA copolymer with PVC, its rheological behavior, morphology, and the mechanical properties of the mixtures of these aids with PVC were investigated.

## EXPERIMENTAL

### Materials

The monomers, methyl acrylate (MA) and ethyl acrylate (EA) were washed with aqueous sodium hydroxide to remove the inhibitor. The MA, EA, and MS were freshly distilled. Sodium dodecylsulfate (SDS) was used as an emulsifier. Potassium persulfate ( $K_2S_2O_8$ ) was used as an initiator. All monomers, SDS, and  $K_2S_2O_8$  were supplied by the Beijing Chemical Reagent Co. Solvents used to determine the solubility parameter  $\delta_p$  of copolymers and

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**Table I Recipes for Preparation of PMSMA and PMSEA**

Ingredients	Recipe I (g)	Recipe II (g)
MS	163	163
MA	112	0
EA	0	134
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.9	0.9
SDS	6	6
Water	450	450

Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18H<sub>2</sub>O, and Na<sub>3</sub>PO<sub>4</sub> were all of analytically pure grade. Distilled deionized water (DIW) was used in all polymerizations. PVC (Yanshan Chemical Co.), tribasic lead sulfate (TLS), dibasic lead phosphite (DLP), barium stearate (BS), and wax were all commercial grade and were supplied by Tianjin Chemical Co.

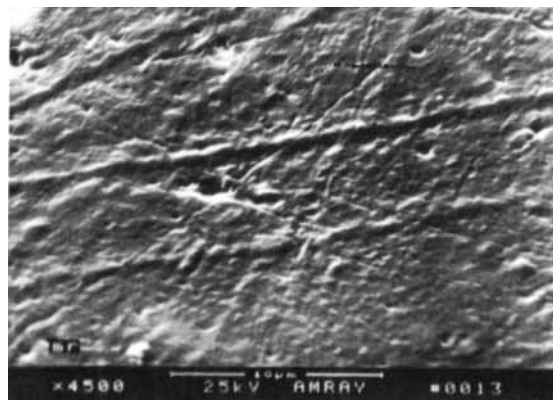
#### Synthesis of PMSMA and PMSEA Copolymer

The copolymers of PMSMA and PMSEA were synthesized by emulsion polymerization. The PMSMA and PMSEA copolymers were made using the recipes in Table I. All components were purged under N<sub>2</sub> for 10 min. The SDS and DIW were charged to a four-necked glass flask, followed by a part of the MA and MS mixture. The reaction vessel was then heated to 80°C and the mixture was stirred.

The K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution and the remainder of the MA-MS mixture was added over the course of 1.5 h under a nitrogen atmosphere. The reaction was then held at 80°C for an additional 2 h. The Na<sub>3</sub>PO<sub>4</sub> solution was used to control the pH of the reaction system at 6–7. The copolymer was precipitated by the Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution and purified by washing with warm DIW, then dried *in vacuo*. The conversion was measured gravimetrically, usually at 89–95%. The

**Table II The Recipes of Components About Experimental Specimens**

	Specimens (Wt)					
	0	1	2	3	4	5
PVC	100	100	100	100	100	100
TLS	3	3	3	3	3	3
DLS	2	2	2	2	2	2
Wax	0.2	0.2	0.2	0.2	0.2	0.2
BS	2	2	2	2	2	2
Copolymer	0	2	4	6	8	10

**Figure 1** SEM graph of mixture of PMSMA copolymer with PVC in a 10/100 ratio.

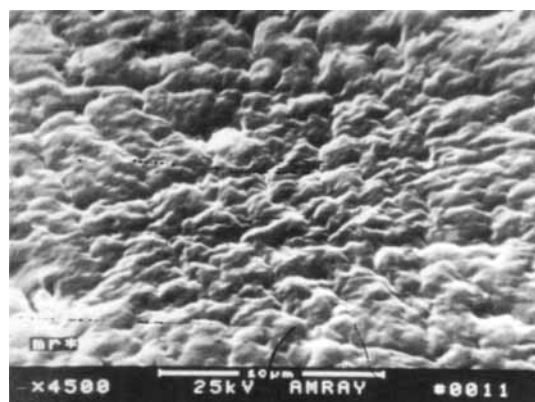
PMSEA was synthesized with the monomers of MS and EA by the same method.

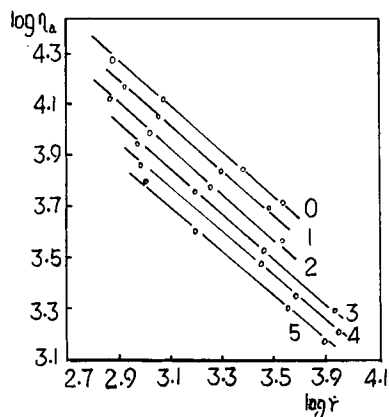
#### Determination of Solubility Parameter

The solubility parameter of PMSMA and PMSEA copolymers was determined by the method of turbidity titration.<sup>5</sup> The copolymer was dissolved in acetone and then titrated by some precipitating agents. The volume fraction of solvents in these systems was calculated.

#### Electron Microscopy

The morphology of polymer mixtures of PVC with PMSMA and with PMSEA were studied by scan-

**Figure 2** SEM graph of mixture after it was put into acetone for 8 h.



**Figure 3** Apparent viscosity  $\eta_a$  of the mixture melt vs. shear rate  $\dot{\gamma}$  for the mixture of PMSMA copolymer with PVC at 180°C (specimens 0–5).

ning electron microscopy (SEM) using the method of Zelinger.<sup>2</sup> The same samples were put in acetone for 8 h, then analyzed by SEM. The broken surfaces of samples by impact and tension were also analyzed by SEM.

#### Preparation of Samples

PVC was mixed with a determined quantity of copolymer (in wt %), and a lubricant and a stabilizer were then added to this mixture (recipes in Table II). All components were first mixed in a mixer and then milled on a laboratory two-roll mill at a temperature of 155–175°C for 10 min. Two millimeter-thick plates were pressed at temperatures of 170–190°C. After cooling in a cooling press, the plates were tempered for a period of 12 h at 90°C. Dumb-bell-shaped samples for tensile tests were cut out from the plates. The samples for notch impact tests and hardness tests were all 120 × 15 × 5 mm.

#### Determination of Rheological Behavior

The rheological behavior of mixtures of copolymers with PVC were investigated by a Shimadzu Koka flow tester.<sup>6,7</sup> The fixed temperature method was used. The nozzle diameter was 1 mm, and the nozzle length was 2.38 mm. The weight of the test specimen was 1.5 g.

#### Determination of Mechanical Properties

Tensile strength testing was performed using an electronic tensile tester. Tests were conducted at an extension rate of 12.0 mm/min at 25°C and 50%

relative humidity. The notch impact tests and hardness tests were carried out on an X CJ-40 impact tester and a Brinell hardness tester, respectively.

## RESULTS AND DISCUSSION

### Compatibility of Copolymer with PVC

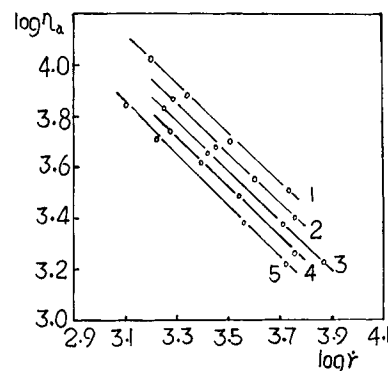
The compatibility of the PMSMA copolymer with PVC can be estimated by the determination of the solubility parameter. To determine the compatibility of PMSMA with PVC, the solubility parameter of PMSMA was determined by the method of turbidity titration.<sup>5</sup> The sample was dissolved in acetone ( $\delta_s = 20.4$ ), then titrated by a precipitating agent. The solubility parameter  $\delta_{sm}$  of the mixed solvent was calculated by the following equation:

$$\delta_{sm} = \Phi_1\delta_1 + \Phi_2\delta_2 \quad (1)$$

where  $\Phi_1$ ,  $\Phi_2$  and  $\delta_1$ ,  $\delta_2$  are the volume fraction and solubility parameter of solvents 1 and 2, respectively. If the water ( $\delta_s = 47.7$ ), methanol ( $\delta_s = 29.6$ ), cyclohexane ( $\delta_s = 16.7$ ), and hexane ( $\delta_s = 14.9$ ) were used as the precipitating agent, the solubility parameter of the PMSMA copolymer may be calculated in following equation:

$$\delta_p = \frac{1}{2n} (\delta_{sm}h_1 + \delta_{sm}h_2 + \dots + \delta_{sm}l_n + \delta_{sm}l_n) \quad (2)$$

From the experimental of turbidity titration, we obtained the solubility parameter  $\delta_p$  of the PMSMA copolymer as 19.18  $J^{1/2}/cm^{3/2}$ . The solubility pa-



**Figure 4** Apparent viscosity  $\eta_a$  of the mixture melt vs. shear rate  $\dot{\gamma}$  for the mixture of PMSEA copolymer with PVC at 180°C (specimens 1–5).

**Table III Impact Strength, Tensile Strength, and Hardness of Improved PVC**

Property	Species						
		0	1	2	3	4	5
Impact strength (N/cm <sup>2</sup> )	I	80.4	86.0	92.4	100.8	115.2	120.4
	II		82.4	84.8	100.8	112.4	120.8
Tensile strength (N/cm <sup>2</sup> )	I	4032	3926	3895	3858	3762	3513
	II		3910	3593	3481	3366	2946
Hardness (kg/mm <sup>2</sup> )	I	20.41	20.04	18.51	16.29	15.71	14.98
	II		19.58	16.83	15.27	14.54	12.89

The species are similar as in Table II. I is the blend samples of PMSMA with PVC. II is the blend samples of PMSEA with PVC.

parameter  $\delta p$  can be calculated from molar attraction constant of the constitutive group:

$$\delta P = \frac{\sqrt{\sum F_{pi}^2}}{\sum V_{pi}} \quad (3)$$

where  $F_{pi}$  is the molar attraction constant of molecular constitutive group, and  $V_{pi}$ , the molar volume of the constitutive group. From eq. (3), we obtained  $\delta p$  as  $19.61 J^{1/2}/cm^{3/2}$ . These  $\delta p$  values are approximated to the solubility parameter for PVC:  $19.2\text{--}22 J^{1/2}/cm^{3/2}$ ; therefore, PMSMA is compatible with PVC.

In the same method, we can obtain the solubility parameter of PMSEA: It is  $20.10 J^{1/2}/cm^{3/2}$ . From these data, it is shown the PMSEA is also compatible with PVC.

The morphology of mixtures of PMSMA and PMSEA with PVC show that the compatibility is good. Although the particles of dried copolymers are usually larger than 1 mm (diameter), the morphology of the mixtures is uniform. The morphology of the mixture of PMSMA with PVC is shown in Figure 1. Although PMSMA and PMSEA can be dissolved by acetone, the holes did not appear on the surface of mixture samples after it was put into acetone for 8 h (Fig. 2). The samples of the mixture and PVC were all swollen by acetone, and the original plane shapes disappeared.

#### Rheological Behavior of Mixtures of PMSMA and PMSEA with PVC

The experimental specimens were made using the recipes shown in Table II. The experimental tem-

perature was fixed at 180°C, with experimental loads of 85, 95, 110, and 130 kg, respectively. The apparent shear stress  $\tau_w$ , apparent shear rate  $\dot{r}_w$ , and apparent viscosity  $\eta_a$  were calculated using the following equations: The effective shear stress at wall of nozzle is given by

$$\tau_w = \frac{Pr}{2L} \quad (4)$$

where  $P$  is the applied pressure (kg/cm<sup>2</sup>);  $r$ , the nozzle radius (cm); and  $L$ , the nozzle length (cm). The efflux rate is given by

$$Q = \frac{h \cdot s}{t} \quad (\text{cm}^3/\text{s}) \quad (5)$$

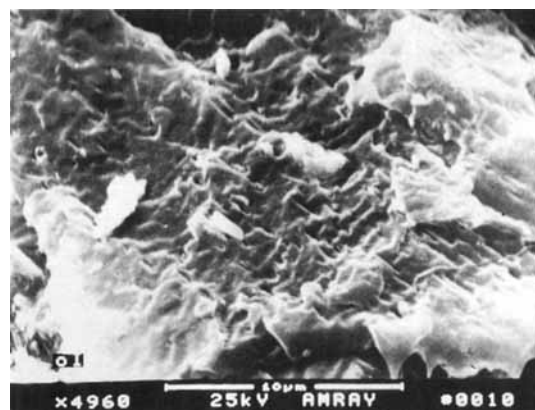
where  $h$  is the downward displacement of the plunger (cm);  $s$ , the area of the plunger (cm<sup>2</sup>); and  $t$ , the effluent time of melt (s). The apparent shear rate at the wall of the nozzle is calculated by

$$\dot{r}_w = \frac{4Q}{\pi r^3} \quad (\text{s}^{-1}) \quad (6)$$

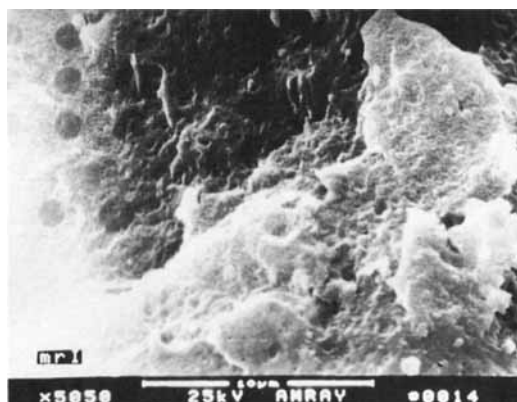
The apparent viscosity is given by

$$\eta_a = \frac{\tau_w}{\dot{r}_w} \cdot 9.8 \times 10^5 \quad (\text{poise}) \quad (7)$$

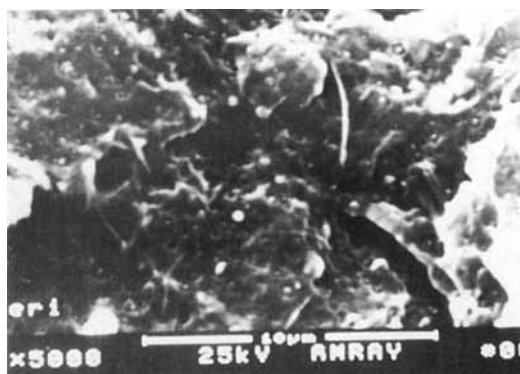
A plots of  $\log \eta_a$  vs.  $\log \dot{r}_w$  are given in Figures 3 and 4. As seen from these figures, the apparent viscosity  $\eta_a$  decreases with increasing shear rate and the contents of the copolymers. For example, the



(a)



(b)

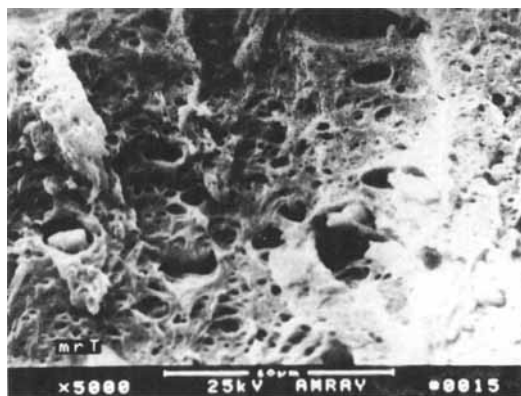


(c)

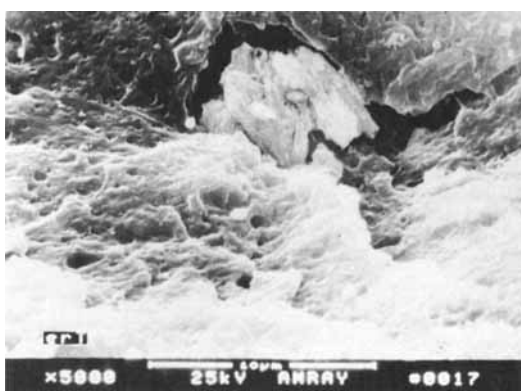
**Figure 5** SEM graphs of impact breaking surface for samples: (a) PVC; (b) PVC-PMSMA; (c) PVC-PMSEA.

apparent viscosity of hard PVC is  $2.42 \times 10^4$  (poise) under the experimental load of 85 kg at 180°C, but it dropped to  $1.38 \times 10^4$  and  $1.14 \times 10^4$  when 4 and 6 parts of PMSMA were added, respectively. It is shown that the flow behavior of these mixtures in

the melt is the behavior of a pseudoplastic liquid. When the copolymers of PMSMA and PMSEA are used as a processing aid for PVC, it can drop the melt viscosity and the processing temperature for hard PVC.



(a)



(b)

**Figure 6** SEM graphs of tensile breaking surface for samples: (a) PVC-PMSMA; (b) PVC-PMSEA.

### Mechanical Properties and Morphology

The notch impact strength, tensile strength, and hardness for improved PVC by PMSMA and PMSEA are shown in Table III. As seen from Table III, the notch impact strength increases with an increasing amount of PMSMA and PMSEA. Therefore, these copolymers not only drop the processing temperature of hard PVC and  $\eta_a$ , but they can also increase the impact strength of hard PVC. The properties of these copolymers are not the same as a general commercial resistant impact aid for PVC, which is to increase the impact strength of hard PVC, but the processing viscosity  $\eta_a$  is also increased.<sup>6</sup>

Figure 5 shows the SEM graphs of the impact fractured surface for the PVC/PMSMA and PVC/PMSEA blend systems. As seen from Figure 5, hard PVC has a clear-cut impact fracture surface and exhibited a stress focus. It is a brittle material and

exhibited a brittle break. The fracture behaviors of the modified PVC showed some toughness characteristics. The fracture surface is not so clear-cut and appear as so many fine holes.

The PMSMA and PMSEA are a pliable component in these systems. They have good compatibility with PVC. When these materials are subjected to impact, these copolymer particles become centers of stress, and crazes or shear bands occur and absorb significant amounts of energy in this region. On the other hand, these pliant particles can confine the development of crazes and prevent the break of materials.<sup>8,9</sup>

The tensile strength and hardness for modified PVC by PMSMA and PMSEA decrease with an increasing amount of the copolymer. This result is similar to the general commercial processing aid and resistant impact aid.<sup>2,6</sup> Figure 6 shows the SEM graphs of the tensile fracture surface of these samples.

As seen from Figure 6, holes appeared on the tensile fracture surface of blends. They exhibit a tensile fracture feature of toughness materials.

## CONCLUSIONS

1. The copolymers of PMSMS and PMSEA have a good compatibility with PVC; their solubility parameters are close to the solubility parameter of PVC.
2. The PMSMA and PMSEA copolymers can be used as processing aids for hard PVC, which can decrease the processing temperature and melt flow viscosity of hard PVC, but also can increase its impact strength.
3. When these copolymers were mixed with PVC, the tensile strength and hardness decreased, i.e., the blend is softer than is PVC. The added amount of copolymers was approximately 3–6%.

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