

# Binary and Ternary Polymer Blends Containing Poly(vinylidene chloride-co-acrylonitrile)

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**ABSTRACT:** Poly(vinylidene chloride-co-acrylonitrile) (Saran F), poly(hydroxy ether of bisphenol A) (phenoxy), poly(styrene-co-acrylonitrile) (PSAN), and poly(vinyl phenol) (PVPh) all have the same characteristic: miscibility with atactic poly(methyl methacrylate) (aPMMA). However, the miscibility of Saran F with the other polymer (phenoxy, PSAN, or PVPh) is not guaranteed and was thus investigated. Saran F was found to be miscible only with PSAN but not miscible with phenoxy and PVPh. Because Saran F and PVPh are not miscible, although they are both miscible with aPMMA, aPMMA can thus be used as a potential cosolvent to homogenize

PVPh/Saran F. The second part of this report focused on the miscibility of a ternary blend consisting of Saran F, PVPh, and aPMMA to investigate the cosolvent effect of aPMMA. Factors affecting the miscibility were studied. The established phase diagram indicated that the ternary blends with high PVPh/Saran F weight ratio were found to be mostly immiscible. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3068–3073, 2004

**Key words:** poly(vinylidene chloride-co-acrylonitrile) (Saran F); blends; miscibility; atactic; phase diagrams

## INTRODUCTION

A series of reports<sup>1–4</sup> was published by this laboratory dealing with the influence of the tacticity of poly(methyl methacrylate) (PMMA) when it is blended with a chemically different polymer. For the PMMA/poly(vinylidene chloride-co-acrylonitrile) (Saran F)<sup>1</sup> and PMMA/poly(vinyl phenol) (PVPh) blends,<sup>4</sup> isotactic and atactic PMMAs (denoted as iPMMA and aPMMA) were found to be miscible based on the transparency and/or a single glass-transition temperature ( $T_g$ ) of the films. However, syndiotactic PMMA (sPMMA) was immiscible with Saran F and PVPh because of the observations of two  $T_g$  values and opacity in most compositions of the blends. For the PMMA/poly(styrene-co-acrylonitrile) (PSAN) blends<sup>3</sup>, aPMMA and sPMMA were found to be miscible with PSAN. However, the iPMMA/PSAN blends were determined not to be miscible. Poly(hydroxyether of bisphenol A) (phenoxy)<sup>2</sup> was the only one in this series to be miscible with iPMMA, aPMMA, and sPMMA. In summary, Saran F, phenoxy, PSAN, and PVPh have the same characteristic: miscibility with aPMMA.

Saran F has its application as a transparent film. Studies of blending of Saran F with another polymer

are worthwhile. So the first part of this article is focused on the investigation of the miscibility of Saran F with phenoxy, PSAN, and PVPh, respectively. The second part of this research concentrated on using aPMMA as a cosolvent to homogenize Saran F/PVPh pairs. Factors influencing the miscibility of a ternary blend consisting of Saran F, PVPh, and aPMMA, such as the ratio between Saran F and PVPh and the amount of aPMMA, were investigated through calorimetry data.

## EXPERIMENTAL

### Materials

The vinylidene chloride-co-acrylonitrile copolymer (Saran F) used for this study contained 20 wt % acrylonitrile (AN) units was obtained from Polysciences (Warrington, PA). The  $M_w$  value for Saran F is approximately 260,000 g/mol. PVPh and aPMMA were also purchased from Polysciences. According to supplier information, the molecular weights ( $M_{ts}$ ) of PVPh and aPMMA are 30,000 and 100,000 g/mol, respectively. The estimation of meso ( $m$ ) and racemic ( $r$ ) fractions was reported previously. The calculated  $m$  and  $r$  fractions of aPMMA are 33.8 and 66.2%, respectively. The error of calculation was estimated to be about 5 to 8%. The poly(hydroxyether of bisphenol A) (phenoxy) was purchased from Scientific Polymer Products (Ontario, NY). The  $M_w$  value for phenoxy is 70,000 g/mol. The poly(styrene-co-acrylonitrile) (PSAN) copolymer containing 25 wt % of AN units

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**TABLE I**  
Glass-Transition Temperatures of Phenoxy/Saran F and PVPh/Saran F Blends

Blend	$T_g$ (°C)	$\Delta T$ (°C)
Phenoxy/Saran F (wt %)		
100/0	99.5	15
74.9/25.1	86.0,116.4	11, 13
49.7/50.3	71.4,115.0	5, 11
25.0/75.0	87.9	9
PVPh/Saran F (wt %)		
100/0	155.6	12
75.0/25.0	85.5,117.3	14, 12
50.0/50.0	84.4,116.6	16, 10
25.1/74.9	85.0,115.0	12, 13
0/100	58.8	10

( $M_w = 165,000$  g/mol) was obtained from Aldrich Chemical Company (Milwaukee, WI).

### Film preparation

Thin films of binary blends of phenoxy, PSAN, and PVPh with Saran F in different weight ratios were made by solution casting onto glass plates. The actual compositions of the binary blends are shown in Table I. 2-Butanone was used as solvent for all the blend compositions. 2-Butanone is ACS reagent purchased from Aldrich Chemical. Thin films of ternary blends of Saran F, PVPh, and aPMMA were made in several weight ratios. The weight ratios were designed in a way that the ratios between Saran F and PVPh were fixed at 3/1, 1/1, and 1/3; then the amount of aPMMA was added increasingly from 20 to 80% at a 20% interval. Because Saran F and its blends start to decompose at around 104–116°C, the final drying step for all the films occurred in a vacuum oven at 75°C for 15–23 h to avoid film degradation. Before 75°C, the oven temperature was slowly increased from room temperature. Also all the films were vacuumed continually. After thermal treatments the films were cooled to room temperature slowly by air to make as-cast samples, which were later used for DSC study. By the way, no solvent peak was detected in the related FTIR experiments (not reported here), confirming the complete removal of solvent.

### Differential scanning calorimetry

Glass-transition temperatures ( $T_g$ 's) of the polymer blends were determined by a DuPont 2000 thermal analyzer (DuPont, Boston, MA) coupled with a mechanical cooling system. According to our experimental results, Saran F had a higher thermal stability in a nitrogen environment than in vacuum. In repetitive test runs, we found that Saran F still maintained its thermal stability when the temperature was as high as

200°C. The reason for the observations is likely because the vacuum is not sufficiently low. Saran F is probably not stable in contact with air. The experiments for all the prepared samples were performed in two consecutive scans from 20 to 200°C in the ambient environment of nitrogen gas at a flowing rate of 100–110 mL/min. At the end of the first thermal scan, the samples were maintained at 200°C for 1 min. The samples were then cooled to 0°C at a cooling rate of 20°C/min and were scanned the second time. A heating rate of 20°C/min was used in each scan. Based on the observation, the annealing time was adequate for the determination of  $T_g$ . The inflection point of the specific heat jump of a second thermal scan was taken as the  $T_g$ . The cooling rate proved to be fast enough to produce virtually the same results as quenching.

## RESULTS AND DISCUSSION

For brevity, the thermal scans of the binary and ternary polymer blends are omitted in this presentation.

### Binary polymer blends

Table I presents the  $T_g$  values of the phenoxy/Saran F and PVPh/Saran F blends. For phenoxy/Saran F blends, two of three blend compositions showed two  $T_g$  values indicating immiscibility. The phenoxy/Saran F (25.0/75.0) blend had a single  $T_g$  and is therefore miscible. The high  $T_g$  values of the two immiscible blends are quite unusual to be even higher than phenoxy's  $T_g$ . Judging from the elevation of the low  $T_g$  of the two phase-separated blends, it can be concluded that phenoxy and Saran F are partially miscible. For PVPh/Saran F blends, the blends showed similar behavior regardless of composition. In view of the high  $T_g$  lower than PVPh's  $T_g$  and the low  $T_g$  higher than Saran F's  $T_g$ , PVPh and Saran F are also partially miscible. The glass-transition temperature regions ( $\Delta T$ ) (shown as the last column in Table I) were calculated as differences between the onset and end points of  $T_g$  and are included for reference.

The results of the PSAN/Saran F blends are shown in Figure 1. A single  $T_g$  was observed in all the studied blend compositions and therefore miscibility was detected in the PSAN/Saran F blends. An elevation of  $T_g$  above weight average is likely attributable to dipole-dipole interaction between AN units existing both in PSAN and Saran F.

Several empirical equations have been proposed to describe the composition dependency of the  $T_g$  of miscible blends that involve strong specific interactions. Because there are data from three blends, the following two equations were chosen to describe the experimental data.

First, the simplified Kwei equation<sup>6</sup>:

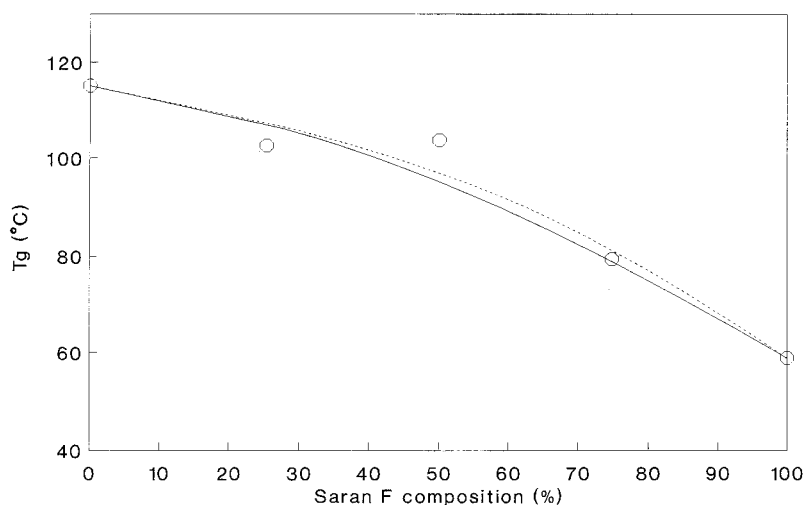


Figure 1 Glass-transition temperatures of PSAN/Saran F blends.

$$T_g = w_1T_{g1} + w_2T_{g2} + qw_1w_2 \quad (1)$$

where  $w_1$  and  $w_2$  denote the weight fractions of components 1 and 2, respectively;  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the glass-transition temperatures of a blend and polymers 1 and 2, respectively; and  $q$  is a parameter that depends on the net polymer-polymer interaction. A  $q$  value of 36.6 (shown as the solid line in Fig. 1) was obtained to describe the experimental data qualitatively.

Second, the Gordon-Taylor equation<sup>7</sup>:

$$T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2) \quad (2)$$

All the symbols except  $k$  have the same meaning as in eq. (1). Here  $k$  is used as a fitting parameter.  $T_{g1}$  is designated as the low  $T_g$  value. The Gordon-Taylor equation with a  $k$  value of 2.28 (presented as the dash

line) was found to represent the  $T_g$  data qualitatively. Based on the large  $q$  value and  $k > 1$ , the interaction between PSAN and Saran F can be characterized as strong.

### Ternary polymer blends and phase diagram

Table II presents the glass transition temperatures of the ternary blends. Five of the 12 studied blends showed a single  $T_g$  value, indicating miscibility.  $\Delta T$  values are included in Table II for reference. Some  $\Delta T$  values of miscible blends do show broadening and this is quite common in the multicomponent system.

For polymer blends with weak or no interaction, the Fox equation<sup>8</sup> seems to predict the glass-transition temperature quite well. The Fox equation extended for a ternary mixture is shown as follows:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} + w_3/T_{g3} \quad (3)$$

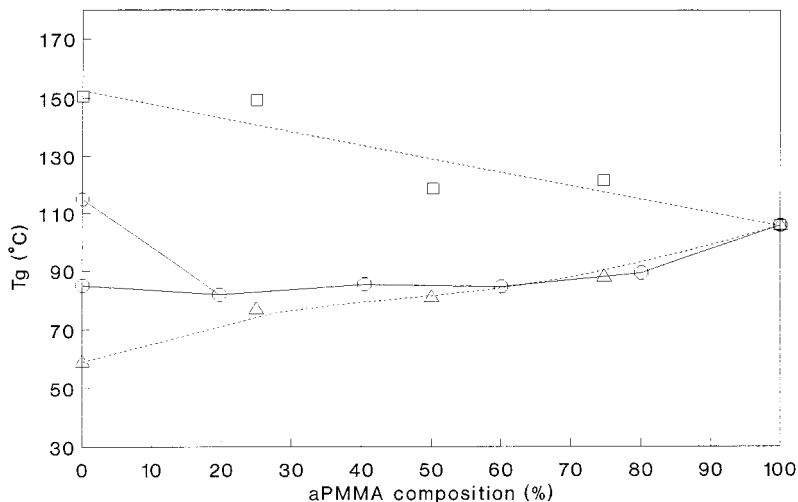
where  $T_g$  is the glass-transition temperature of a blend,  $T_{gi}$  and  $w_i$  are the glass-transition temperature and the weight fraction of polymers  $i$ , respectively ( $i = 1, 2, 3$ ). The  $T_g$  values of Saran F, PVPh, and aPMMA

TABLE II  
Glass-Transition Temperatures of Ternary Blends

Saran F/PVPh/aPMMA (wt %)			
Blend	Ratio	$T_g$ (°C)	$\Delta T$ (°C)
1	0/0/100	102.7	18
2	15.0/5.0/80.0	89.3	20
3	10.1/10.0/79.9	87.7	27
4	5.2/14.9/79.9	85.6, 110.6	13, 11
5	30.1/9.9/60.0	84.7	14
6	19.9/19.9/60.2	83.5, 121.8	14, 16
7	9.9/30.0/60.1	86.4, 108.4	18, 10
8	44.7/14.9/40.4	85.4	15
9	29.7/29.7/40.6	81.5, 117.8	15, 16
10	15.2/44.8/40.0	84.2, 130.7	15, 18
11	60.3/20.0/19.7	81.9	13
12	40.1/40.0/19.9	81.0, 116.6	13, 18
13	19.9/59.5/20.6	81.2, 149.2	15, 13

TABLE III  
Glass-Transition Temperatures of Ternary  
Blends by Fox Equation Prediction

Saran F/PVPh/aPMMA (wt %)			
Blend	Ratio	$T_g$ (°C)	$T_{gF}$ (°C)
2	15.0/5.0/80.0	89.3	97.6
3	10.1/10.0/79.9	87.7	102.3
5	30.1/9.9/60.0	84.7	92.6
8	44.7/14.9/40.4	85.4	88.0
11	60.3/20.0/19.7	81.9	83.1

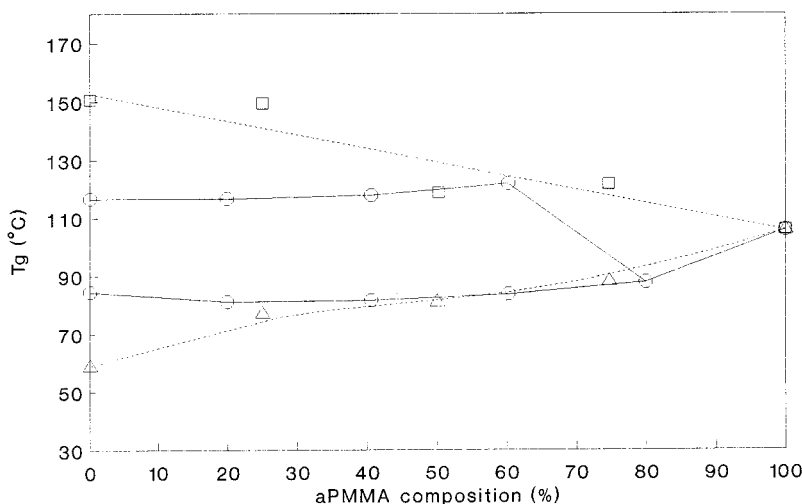


**Figure 2** Change of  $T_g$  of the ternary blends with aPMMA composition (PVPh/Saran F wt ratio = 1/3).  $\circ$ : data point;  $\triangle$ : Saran F/aPMMA;  $\square$ : PVPh/aPMMA (curves drawn for viewing).

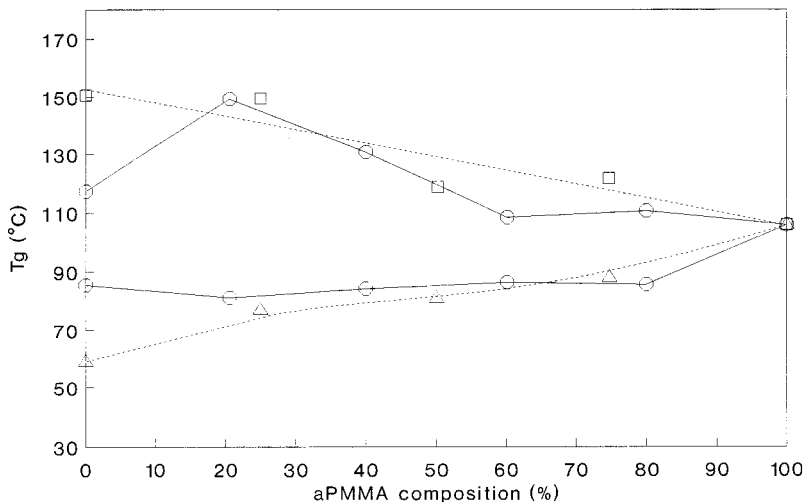
were used in eq. (3) to estimate the  $T_{gF}$  (Fox prediction) values of the miscible ternary blends. As shown in Table III, the  $T_{gF}$  values are always larger than experimental values. However, there seems to be a qualitative relation between  $T_g$  (experimental) and  $T_{gF}$  (Fox prediction) values, given that  $T_g$  increases with increasing  $T_{gF}$ . For compositions 8 and 11, the Fox prediction agrees quite well with experimental results.

For the purpose of illustrating the cosolvent effect of aPMMA, the  $T_g$  values of the ternaries with Saran F/PVPh wt ratios 1 : 3, 1 : 1, and 3 : 1 are plotted in Figures 2, 3, and 4, respectively. Previous results of the corresponding binaries with Saran F<sup>1</sup> and PVPh<sup>4</sup> (shown as the dashed lines in Figs. 2–4) are also presented for comparison. Because the  $T_g$  difference between Saran F/aPMMA and PVPh/aPMMA blends

with approximately the same aPMMA composition is always  $>30^\circ\text{C}$ , the single  $T_g$  criterion for miscibility seems to be justified in our ternary system. For PVPh/Saran F (1 : 3) ternaries (as shown in Fig. 2), the addition of 20% of aPMMA is sufficient to produce a miscible ternary. The  $T_g$  values of the miscible ternaries are located between corresponding binaries with the same aPMMA composition but are close to low  $T_g$  binaries. For the ternaries with PVPh/Saran F (wt ratio = 1 : 1) (as demonstrated in Fig. 3), addition of 80 wt % aPMMA is able to drive the ternaries toward miscibility. The  $T_g$  values of the immiscible ternaries in Figure 3 are still located between those corresponding binaries. It is interesting to observe that from 20 to 60% aPMMA, the ternaries are not so different from the PVPh/Saran F (50/50) binary. For the ternaries



**Figure 3** Change of  $T_g$  of the ternary blends with aPMMA composition (PVPh/Saran F wt ratio = 1/1).  $\circ$ : data point;  $\triangle$ : Saran F/aPMMA;  $\square$ : PVPh/aPMMA (curves drawn for viewing).

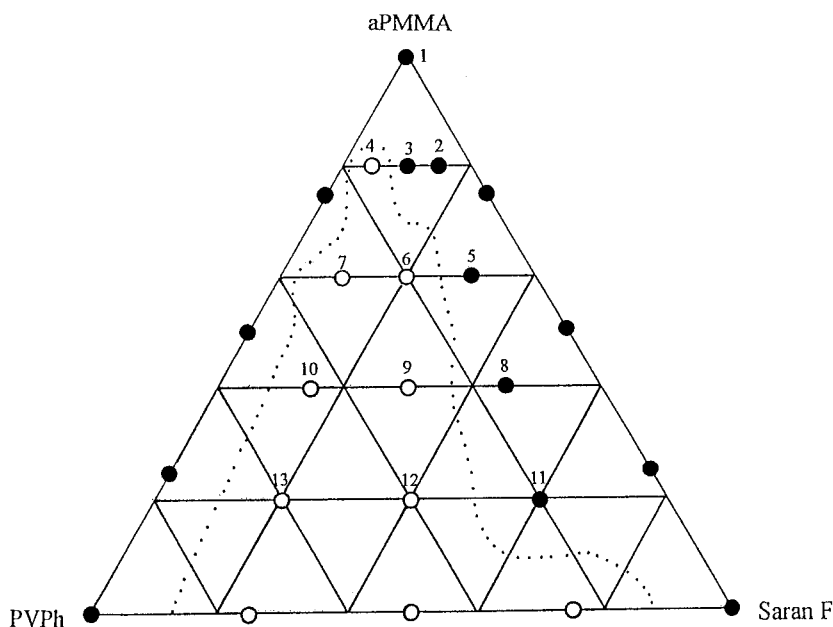


**Figure 4** Change of  $T_g$  of the ternary blends with aPMMA composition (PVPh/Saran F wt ratio = 3/1).  $\circ$ : data point;  $\triangle$ : Saran F/aPMMA;  $\square$ : PVPh/aPMMA (curves drawn for viewing).

with PVPh/Saran F wt ratio = 3 : 1 in Figure 4, the ternaries were found to be immiscible regardless of the compositions of aPMMA. However, increasing aPMMA concentration in the ternary seems to cause the two  $T_g$ 's of the ternary blends to become closer in value, indicating slight improvement toward miscibility. The two  $T_g$  values of the ternaries are still located mostly between those of the respective binary.

Using the single  $T_g$  as the criterion for miscibility, the phase diagram of the ternary blends composed of Saran F, PVPh, and aPMMA is shown in Figure 5. A postulated phase boundary (shown as the dotted line

in Fig. 5) was established for reference by connecting through middle points between miscibility and immiscibility data. Inside the figure the solid circles represent a single  $T_g$  and the empty circles symbolize two  $T_g$  values. An asymmetric immiscibility region is clearly observed in Figure 5. The reason for the ternaries with high PVPh concentration to exhibit immiscibility is likely attributable to stronger interaction between aPMMA and PVPh than that between aPMMA and Saran F. No definite detection of interaction between aPMMA and Saran F was observed according to a previous publication.<sup>1</sup> However, aPMMA is



**Figure 5** Phase diagram of Saran F/PVPh/aPMMA blends:  $\bullet$ : miscible;  $\circ$ : immiscible;  $\cdots$ : estimated immiscible region; numbers in the figure indicate the same compositions as in Table II.

known to form strong hydrogen bonds with PVPh.<sup>4</sup> Therefore a strong interaction of aPMMA/PVPh excludes Saran F, which leads to immiscibility in the ternary region of a high PVPh concentration. When the composition of PVPh is higher than that of Saran F in ternaries, addition of aPMMA cosolvent does not produce miscibility.

### CONCLUSIONS

Saran F was found to be miscible with PSAN likely because of dipole–dipole interaction between AN units existing in both polymers. However, Saran F and phenoxy are not miscible because two  $T_g$  values were observed. Saran F formed partially miscible mixtures with PVPh. Using aPMMA as a cosolvent to cosolubilize PVPh/Saran F pairs was successful when the PVPh content in the ternary blend was lower than 25%. The reason for immiscibility observed in the ternary phase diagram is because the interaction be-

tween aPMMA and PVPh is stronger than that between aPMMA and Saran F. Therefore when the PVPh concentration was higher than (or equal to) 50%, aPMMA associated more with PVPh and less with Saran F. Phase separation was thus observed.

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