

# Viscoelastic Properties of Blends of Poly(methyl methacrylate) and Poly(styrene-co-acrylonitrile) Having Various Acrylonitrile Contents

Yuji Aoki

Department of Polymer Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

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**ABSTRACT:** Dynamic viscoelastic properties of blends of poly(methyl methacrylate) (PMMA) and poly(styrene-co-acrylonitrile) (SAN) with various AN contents were measured to evaluate the influence of SAN composition, consequently  $\chi$  parameter, upon the melt rheology. PMMA/SAN blends were miscible and exhibited a terminal flow region characterized by Newtonian flow, when the acrylonitrile (AN) content of SAN ranges from 10 to 27 wt %. Whereas, PMMA/SAN blends were immiscible and exhibited a long time relaxation, when the AN content in SAN is less than several wt % or greater than 30 wt %. Correspondingly, melt rheology of the blends was characterized by the plots of storage modulus  $G'$  against loss modulus  $G''$ . Log  $G'$  versus log  $G''$  plots exhibited a straight line of slope 2 for the miscible blends, but did not show a straight line for the immiscible blends because of their long time relaxation mechanism. The plateau modu-

lus, determined as the storage modulus  $G'$  in the plateau zone at the frequency where  $\tan \delta$  is at maximum, varied linearly with the AN content of SAN irrespective of blend miscibility. This result indicates that the additivity rule holds well for the entanglement molecular weights in miscible PMMA/SAN blends. However, the entanglement molecular weights in immiscible blends should have "apparent" values, because the above method to determine the plateau modulus is not applicable for the immiscible blends. Effect of  $\chi$  parameter on the plateau modulus of the miscible blends could not be found. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2206–2210, 2008

**Key words:** polymer blend; rheological miscibility; plateau modulus; poly(methyl methacrylate); poly(styrene-co-acrylonitrile)

## INTRODUCTION

It is well-known that mixtures of poly(methyl methacrylate) (PMMA) and poly(styrene-co-acrylonitrile) (SAN) are miscible and the phase behavior of the blends is a function of the acrylonitrile (AN) content of the SAN.<sup>1–6</sup> According to Paul and coworkers, miscibility is observed in these blends for SAN with a AN content between  $\sim 9$  and 33 wt %.<sup>6</sup> In a previous article,<sup>7</sup> we studied viscoelastic properties of miscible PMMA/SAN blends with acrylonitrile of 18 and 27 wt %, and found that the zero-shear viscosity versus blend composition curves deviate positively from linear additivity for the blends at both constant temperature and free volume fraction and the plateau modulus varies linearly with blend composition. We concluded that the relaxation behavior of the miscible PMMA/SAN blends is similar to that of a blend consisting of homologous polymers and the entanglement molecular weights in

PMMA/SAN blends are identical with those in the component polymers.

Wu<sup>8–10</sup> and Han and Kim<sup>11,12</sup> studied linear viscoelastic properties of binary mixtures of miscible blends. They discussed compositional dependence of the plateau modulus and zero-shear viscosity of miscible blends in connection with the Flory-Huggins  $\chi$  parameter. They suggested that the  $\chi$  parameter influences the viscoelastic properties very much. Pathak et al.<sup>13</sup> reported the linear viscoelasticity of miscible PMMA/SAN blends in detail. They found that the blends are thermorheologically simple and these results are anticipated by a theory of concentration-fluctuation-induced dynamic heterogeneity<sup>14</sup> in miscible polymer blends.

Han and Chuang<sup>15</sup> proposed criteria for rheological miscibility of polymer blends. They found that plots of storage modulus  $G'$  against loss modulus  $G''$  give (a) temperature-independent correlation for both miscible and immiscible blend systems; (b) composition-independent correlations for miscible blends; (c) composition-dependent correlations for immiscible blends. It is of interest to know what correlation their plots have for the PMMA/SAN blends in which copolymer composition and consequently  $\chi$  parameter is varied.

Correspondence to: Y. Aoki (y.aoki@yz.yamagata-u.ac.jp).

**TABLE I**  
Molecular Characteristics of Samples

Polymer	AN (wt %)	$M_w$ ( $10^3$ )	$M_w/M_n$
PMMA-7	–	72	1.7
SAN-0 (PS)	0	113	2.2
SAN-10	9.6	151	1.9
SAN-15	14.7	138	2.5
SAN-18	18.4	136	2.1
SAN-20	20.1	145	2.0
SAN-23	23.2	131	2.3
SAN-27	27.0	84	2.4
SAN-30	28.6	78	2.1
SAN-33	31.8	56	2.4
SAN-37	36.5	74	2.0
SAN-40	38.7	63	2.1

AN (wt %): elementary analysis (Yanaco, CHN coder),  $M_w$ : light scattering (Otsuka Electronics, DSL-700),  $M_w/M_n$ : GPC (Waters Associates, ALC/GPC Model 150C), Tacticity:  $^1\text{H-NMR}$  (JEOL, EX-270 270 MHz).

There have been many studies of melt rheology of polymer blends. However, the effects of the  $\chi$  parameter on the viscoelastic properties have not been fully elucidated. In this article, we measure dynamic viscoelastic properties of blends of PMMA and SAN with various AN contents over wide range of temperatures and frequencies, and report the effects of  $\chi$  parameter on the linear viscoelastic properties for miscible and immiscible blends.

## EXPERIMENTAL

A PMMA sample supplied from Mitsubishi Rayon Co., PMMA-7, was used in this study. SAN samples having various AN contents were prepared by radical polymerization. Table I shows the molecular characteristics of the samples. The tacticity of PMMA was determined by  $^1\text{H-NMR}$  (JEOL, EX-270) using chloroform-d as solvent. The amounts of syndiotactic, heterotactic, and isotactic triads determined by integrating over peaks at 0.85, 1.02, and 1.21 ppm were 57.0, 38.1, and 4.9%, respectively. AN content of various SANs was measured by elementary analysis (Yanaco, CHN coder). The weight-average-molecular weight ( $M_w$ ) of the samples was determined by light scattering (Otsuka Electronics, DLS-700) and polydispersity index  $M_w/M_n$  by GPC (Waters Associates, ALC/GPC Model 150C) using tetrahydrofuran (THF) as solvent.

Blends of PMMA/SAN were prepared by casting films from THF solutions (5 wt %) at room temperature. The films were then dried thoroughly in a vacuum oven at 320–383 K for 2–3 days. The blend composition ratio of PMMA/SAN-18 was 0/100, 20/80, 40/60, 50/50, 60/40, 80/20, and 100/0 by weight. The composition ratio of other PMMA/SANs blends

was 50/50 by weight. In a previous article,<sup>7</sup> we found that the blends of PMMA/SAN = 50/50 have bigger effects on the rheological properties. For this reason, we prepared the composition of only 50/50 by weight for other blends.

It was found that the blend films were opaque for PMMA/SAN-0 (polystyrene, PS), SAN-30, SAN-33, SAN-37, and SAN-40 blends and transparent for PMMA/SAN-10, SAN-15, SAN-18, SAN-23, SAN-27 blends. Accordingly, we can conclude that PMMA is miscible with SANs when the AN wt % of SAN range from 10 to 27 wt %. Therefore, it is clear that the  $\chi$  parameter of PMMA/SAN blends changes among the PMMA/SAN blends, from positive values for the immiscible blends (PMMA/SAN-0 (PS), SAN-30, SAN-33, SAN-37, and SAN-40), about zero for the blends of a margin of miscibility (PMMA/SAN-10 and SAN-27), and negative values for the miscible blends, PMMA/SAN-15 to SAN-23 blends.

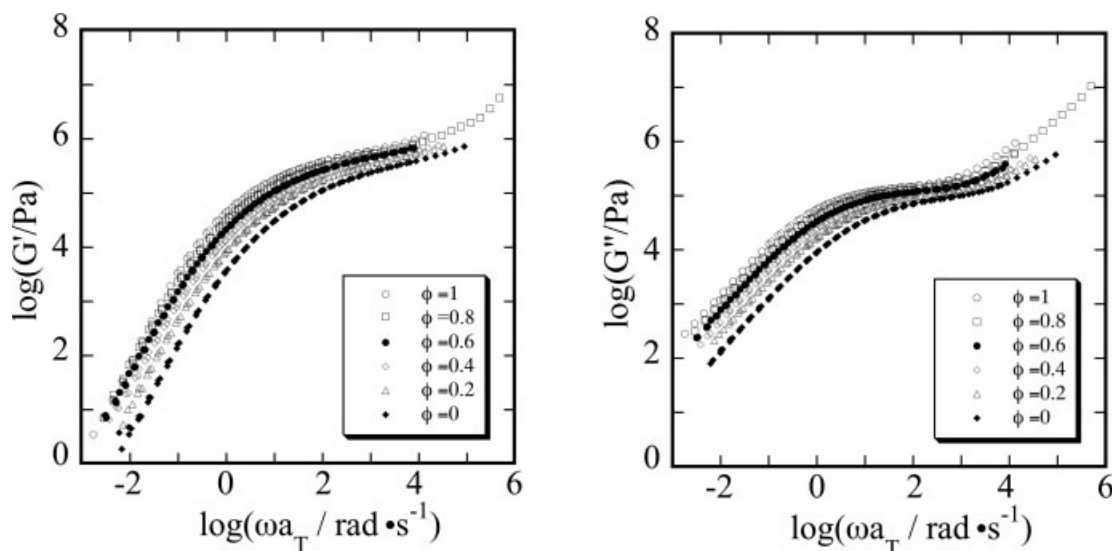
Viscoelastic measurements were carried out with a Rheometrics ARES-2KFRTN1 with parallel-plate geometry (25 mm diameter plates and 1–2 mm gap heights). The storage modulus  $G'$  and loss modulus  $G''$  were measured as a function of frequency  $\omega$ . Measurements were taken at different temperatures in order to investigate the temperature dependence of the viscoelastic properties. The frequency-dependence curves of  $G'$  and  $G''$  at various temperatures were superimposed onto the master curves at 200°C according to the time-temperature superposition. All measurements were performed under nitrogen so as to minimize oxidative degradation at high temperature.

## RESULTS AND DISCUSSION

The  $G'$  and  $G''$  for the component (co)polymers and blends were measured as a function of  $\omega$ . Measurements were taken at different temperatures to investigate the temperature dependence of the viscoelastic properties. The frequency-dependence curves of  $G'$  and  $G''$  at various temperatures were superimposed onto the master curves at 200°C. The temperature dependence of the shift factors  $a_T$  became slightly steep with an increase in PMMA content, as the glass transition temperature  $T_g$  increases. When the reference temperatures  $T_s$  were chosen at 138, 145, and 152°C for PMMA/SAN = 0/100, 50/50, and 100/0, all the curves could be expressed in a single WLF equation denoted by eq. (1).

$$\log a_T = -c_1(T - T_s)/(c_2 + T - T_s) \quad (1)$$

where  $T$  is the temperature,  $T_s$  is the reference temperature,  $c_1 = 8.86$ , and  $c_2 = 101.6$ . Provided that data are taken over a sufficiently wide temperature range, this procedure determines  $T_s$  to within  $\pm 1$  K. These facts are consistent with our previous results.<sup>7</sup>



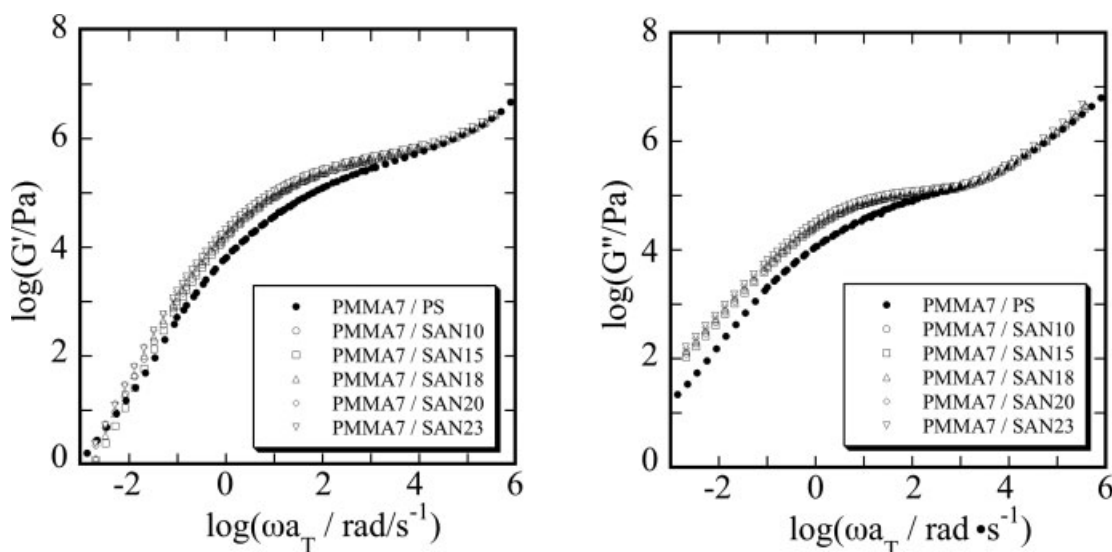
**Figure 1** Master curves of the storage modulus  $G'$  (left) and loss modulus  $G''$  (right) reduced to 200°C for the PMMA-7/SAN-18 blends.

We reported that miscible PMMA/SAN blends were thermorheologically simple.<sup>7</sup> The reasons may be due to dynamic symmetry of PMMA and SAN, as already explained by Pathak et al.<sup>13</sup> The temperature dependence of  $a_T$  for these blends are essentially same as that for the PMMA/SAN blends.

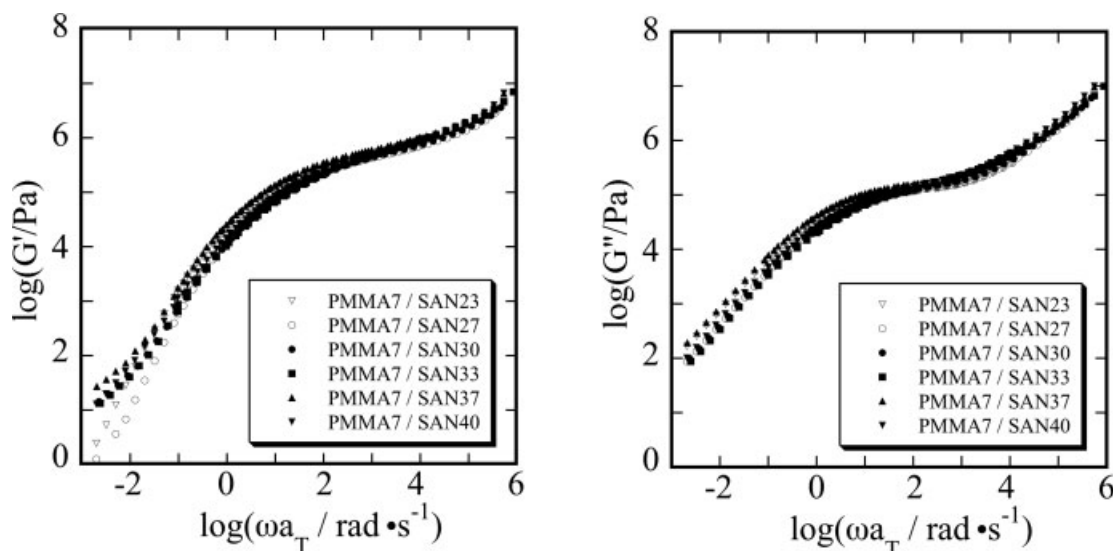
Figure 1 shows the master curves of  $G'$  and  $G''$  for the PMMA/SAN-18 blends and the component polymers, respectively, as a function of the reduced angular frequency  $\omega a_T$  at reference temperature of 200°C. They show the terminal zone at low frequencies, the plateau zone at intermediate frequencies, and entry into the transition zone at higher frequencies. At low frequencies,  $G'$  is proportional to  $(\omega a_T)^2$

and  $G''$  to  $\omega a_T$  for each sample. In the terminal zone the dynamic viscosity  $\eta' = G''/\omega$  is independent of frequency. Therefore, the zero-shear viscosity  $\eta_0$  can be obtained from these data. The terminal relaxations of PMMA and SAN-18 are too close to resolve clearly.

Figures 2 and 3 show the master curves of  $G'$  and  $G''$  for the PMMA/SAN = 50/50 blends as a function of the reduced angular frequency  $\omega a_T$  at reference temperature of 200°C. The  $G'$  and  $G''$  values lie between those of the constituent components, PMMA and SANs, as shown in Figure 1. All the blends show the terminal zone at low frequencies, the plateau zone at intermediate frequencies, and



**Figure 2** Master curves of the storage modulus  $G'$  (left) and loss modulus  $G''$  (right) reduced to 200°C for the PMMA-7/SAN-0, SAN-10, SAN-15, SAN-18, SAN-20, and SAN-23 blends.

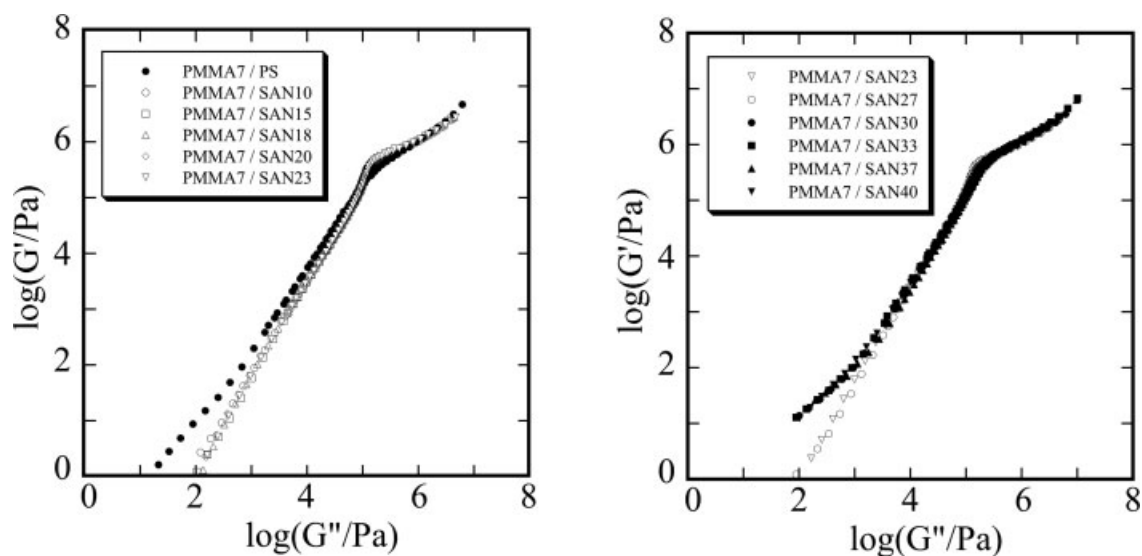


**Figure 3** Master curves of the storage modulus  $G'$  (left) and loss modulus  $G''$  (right) reduced to 200°C for the PMMA-7/SAN-23, SAN-27, SAN-30, SAN-33, SAN-37, and SAN-40 blends.

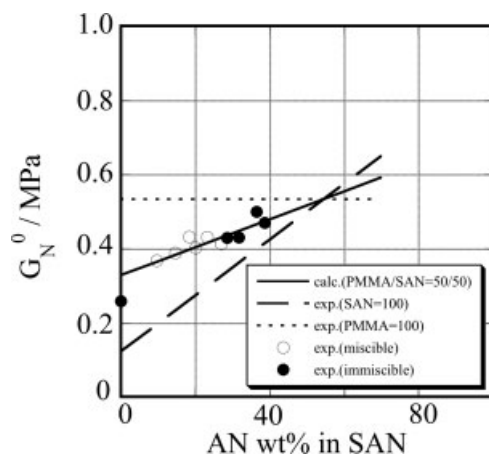
entry into the transition zone at higher frequencies. At low frequencies, the PMMA/SAN-10, SAN-15, SAN-18, SAN-20, SAN-23, and SAN-27 blends exhibit a Newtonian flow; the dynamic viscosity  $\eta' = G''/\omega$  is independent of frequency and  $G'$  is proportional to  $(\omega a_T)^2$ . The blends are miscible and exhibit almost the same master curves. It should not be surprising to observe such behavior. Because, SAN-10, -15, -18, -20, -23, and -27 are almost the same rheological behavior. While, the PMMA/SAN-0, SAN-30, SAN-33, SAN-37, and SAN-40 blends show a long time relaxation. This relaxation should arise from an inhomogeneous structure, because of immiscibility of these blend systems which form two

phases. On the contrary, the immiscible PMMA/SAN blends were also thermorheologically simple.

Figure 4 show plots of  $G'$  against  $G''$  for the PMMA/SAN = 50/50 blends at five temperatures, 140, 160, 180, 200, and 220°C. It was found that plots of  $G'$  versus  $G''$  give temperature-independent correlations for both miscible and immiscible blends, as already shown by Han and Chuang.<sup>15</sup> It was also seen that for the miscible blends (open symbols) such plots yield correlations which become independent of AN wt % of SAN with slope of 2. On the contrary, for immiscible blends (closed symbols) the slopes become slower at low  $G'$  and  $G''$  region. These results indicate that the  $G'$  versus  $G''$  plot is a



**Figure 4** Log  $G'$  versus log  $G''$  plot for the various PMMA-7/SAN blends.



**Figure 5** Plot of plateau modulus  $G_N^0$  against AN wt % in SAN for the various PMMA-7/SAN blends.

very useful tool for determining polymer–polymer miscibility.

Figure 5 shows change in plateau modulus  $G_N^0$  with AN wt % in SAN for various PMMA/SAN blends. Here, the plateau modulus  $G_N^0$  was determined as the storage modulus  $G'$  in the plateau zone at the frequency where  $\tan \delta$  is at a minimum from the master curves. The  $G_N^0$  value of SAN was found to be a linear function of AN wt % in SAN. The solid line in the figure denotes a straight line calculated by assuming the additivity of the plateau modulus of component polymers. Most interesting results seen in Figure 5 are that the  $G_N^0$  shows a linear function of AN wt % in SAN irrespective of polymer miscibility. The entanglement molecular weight in immiscible blends should have “apparent” values, because the above method to determine the plateau modulus is meaningless for the immiscible blends.

The effects of shear flow on the phase behavior of PMMA/SAN blends were reported.<sup>16–19</sup> The shear effect is an important and interesting phenomena. However, we did not evaluate the flow effects on the miscibility of PMMA/SAN blends, because we thought that the effects of AN contents of SAN on the miscibility are larger than the flow effect.

## CONCLUSIONS

Dynamic viscoelastic properties of blends of PMMA and SAN with various AN contents have been measured. It was found that PMMA/SAN blends are

miscible when the AN content of SAN ranges from 10 to 27 wt % and are immiscible when the AN content in SAN is less than 10 wt % or greater than 30 wt %. Melt rheology of the blends was characterized by the plots of  $G'$  against  $G''$ . Log  $G'$  against log  $G''$  plots exhibited a straight line of slope 2 for the miscible blends, but did not show a straight line for the immiscible blends. These facts suggest that  $G'$  versus  $G''$  plots can be used for determination of rheological miscibility of polymer blend systems.  $G_N^0$  determined as the  $G'$  at the frequency where  $\tan \delta$  is at maximum, varied linearly with the AN content of SAN irrespective of blend miscibility. This result indicates that the additivity rule holds well for the entanglement molecular weights in miscible PMMA/SAN blends. However, the entanglement molecular weights in immiscible blends should have “apparent” values, because the above method to determine the plateau modulus is meaningless for the immiscible blends.

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