Elongational Viscosity for Miscible and Immiscible Polymer Blends. I. PMMA and AS with Similar Elongational Viscosity

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ABSTRACT: The effects of miscibility and blend ratio on uniaxial elongational viscosity of polymer blends were studied by preparing miscible and immiscible samples at the same composition by using poly(methyl methacrylate) (PMMA) and poly(acrylonitrile-*co*-styrene) (AS). Miscible polymer blend samples for the elongational viscosity measurement were prepared by using three steps: solvent blends, cast film, and hot press. A phase diagram of blend samples was made by visual observation of cloudiness. Immiscible blend samples were prepared by maintaining the prepared miscible samples at 200°C, which is higher than cloud points using a LCST (lower critical solution temperature) phase diagram. The phase structure of immiscible blends was observed by an optical microscope. The elongational viscosity of all samples was measured at 145°C, which is lower than the cloud-point temperature at all blend ratios. The elongational viscosity of PMMA and AS was similar to each other. The strain-hardening property of miscible blends in the elongational viscosity was only slightly influenced by the blend ratio, and this was also the case with immiscible blends. The strain-hardening property was only slightly influenced, whether it was miscible or immiscible at each blend ratio. Polydispersity in molecular weight for blend samples was not changed by GPC (gel permeation chromatography) analysis. Almost no change in the polydispersity of the molecular weight for blends and the similarity of elongational viscosity between PMMA and AS resulted in little influence of the blend ratio and miscibility on the strain-hardening property. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 757–766, 1999

Key words: elongational viscosity; miscible polymer blends; immiscible polymer blends

INTRODUCTION

Melt rheology of miscible and immiscible polymer blends have been extensively studied in linear viscoelastic region under shear deformation.[1–5] In miscible blends, Wu reported that the melt viscosity was influenced by the reduction of entanglement, the increase of the friction between dissimilar chains, and the change of free volume.[1] Miscible blends resulted in a reduction of melt viscosity in most cases. Saito et al.[2,3] reported that the relaxation behavior of miscible blends of dissimilar polymers is different from that of homologous mixture because of a constraint caused by interaction. They also reported the evidence of locally ordered chains in miscible blends of dissimilar polymers.[2,3] Aoki[4] reported that relaxation behavior of miscible blends is similar to that of a blend consisting of homologous polymers. In immiscible blends, linear rheological behavior was interpreted with an emulsion model by Scholz et al.[5] in recent years. A comprehensive review up to 1988 was published by Utracki.[6]

It is very difficult to predict nonlinear melt viscoelasticity of miscible and immiscible

blends from their linear viscoelasticity, because polymer behavior and phase structures are dramatically changed by large deformation. Nonlinear melt viscoelasticity has been most frequently investigated under uniaxial elongational deformation.[7–20] Elongational rheology studies of polymer blends are classified into two groups. One is acrylonitrile–butadiene–styrene (ABS) polymers,[7–12] and the other is polyethylene-based blends.[13–20]

Elongational viscosity of ABS polymer melts, which are immiscible blends, have already been studied by some researchers.[7–12] Munstedt has found yielding of ABS-containing agglomerated butadiene particles.[7] Saito[8–10] reported that nonlinear properties depend on the degree of aggregation of butadiene particles, their size, and M_w of matrix AS. Li et al.[11] suggested that the effect of well-dispersed butadiene particles appeared on the time-independent linear elongational viscosity, and it was not seen for the strain-hardening property. We[12] have reported the effect of hardness and content of well-dispersed butadiene particles on the strain-hardening property. The strain-hardening or softening property was strongly correlated with the degree of butadiene particle deformation.[12] The increase of hardness and content changed the strain-hardening property to a strain-softening property.[12]

Elongational viscosity of polyethylene-based blends have been studied to improve processability and mechanical property.[13–20] All of the blends were prepared by melt mixing. Miscibility was determined by dynamic shear measurement, and most of the works were immiscible blends. In some immiscible blends, a compatibilizer was also blended.[17,18,20] The addition of a compatibilizer reduced the strain-hardening property.[17,18,20]

Until now, the effect of blend ratios on the elongational viscosity was reported. However, the effect of miscibility at each blend ratio on elongational viscosity was not reported before, because it was difficult to prepare both miscible and immiscible blends at the same blend composition. Here, a method to make miscible and immiscible samples at the same composition is established using a combination of PMMA and AS. The miscibility is determined by the observation of whether it is transparent or opaque. In this report, the effects of miscibility and blend ratio on uniaxial elongational viscosity of polymer blends are presented.

EXPERIMENTAL

Preparation of Miscible and Immiscible Samples

Melt compounding is one way to prepare polymer blends. The melt mixing method has concern about the variation on degree of dispersion and molecular characteristics by melt mixing condition for the immiscible state. The reason is that a slight change in the degree of dispersion and molecular weight might affect elongational viscosity. A slow extrusion on a single extruder has been used in previous works[21–23] to obtain uniform rod-like samples for elongational measurement. At least 1 kg is require for a sample preparation when using a single extruder. Here, a new method was introduced to eliminate such concerns to prepare miscible and immiscible samples.

Poly(methyl methacrylate) (PMMA 60N) and poly(acrylonitrile-co-styrene) (AS 783, 30 wt % of AN) from Asahi Chemical Industry Co., Ltd., were used for the present study. The blend weight ratios of PMMA and AS were 9 : 1, 8 : 2, 7 : 3, 6 : 4, 5 : 5, 4 : 6, 3 : 7, 2 : 8, and 1 : 9. Two samples, PMMA and AS, as received, were dried in a vacuum oven at 80°C for overnight. The dried samples were blended at the desired blend ratios in tetrahydrofuran (THF, dehydrated, stabilizer free, from Kanto Chemical Co., Inc.) solvent as received. The concentration of THF solution was 5 wt %, and the solution was stirred on a magnetic stirring table for 1 day. Table I summarizes the molecular characteristics of PMMA, AS, and their blends.

Blends solution was poured into several pans, and they were dried at room temperature for 2 days. The obtained cast films were dried in a vacuum oven at 120°C for 3 days to eliminate THF solvent completely. A sheet of transparent plate (15 × 15 mm, 2 mm thickness) was made by hot-press method at 140°C for 15 min. Miscible bar samples for elongational measurement were made by cutting the transparent plate into bars (2 × 3 mm cross-section, 150 mm long).

Cloud-point measurement for PMMA/AS blends at various blend ratios were carried out by eye observation. The cloud points were determined by immersing bar samples (2 × 2 mm cross-section, 20 mm long) in the heated silicone oil of an elongational rheometer for 30 min. The heated silicone oil in the bath was well stirred, and the precise oil temperature was measured by a thermocouple. This cloud-point evaluation con-

Table I Molecular Characteristics of Tested Samples

Weight Ratio PMMA : AS	M_n	M_w	M_z	M_w/M_n	M_z/M_n
10 : 0	76,200	146,000	254,000	1.92	3.33
9 : 1	85,500	162,000	272,000	1.90	3.18
8 : 2	93,400	182,000	308,000	1.94	3.30
7 : 3	101,000	199,000	339,000	1.97	3.36
6 : 4	107,000	213,000	358,000	1.98	3.34
5 : 5	112,000	217,000	356,000	1.94	3.18
4 : 6	120,000	231,000	377,000	1.93	3.15
3 : 7	127,000	241,000	387,000	1.90	3.05
2 : 8	133,000	253,000	409,000	1.90	3.07
1 : 9	138,000	255,000	404,000	1.85	2.92
0 : 10	142,000	259,000	406,000	1.82	2.86

dition came from the practical fact that elongational measurement was performed and completed within 30 min after immersing samples in the heated silicone oil. Figure 1 shows the phase diagram of the tested PMMA/AS blend samples. At 140°C, all blend samples were transparent, suggesting a miscible state. The temperature (140°C) of the hot-press condition was determined from the phase diagram.

Figure 1 also suggests that all miscible samples became immiscible with holding samples at 200°C for 10 min. Thus, immiscible samples were made with pressing miscible samples at 200°C. Figure 2 illustrates the preparation method of miscible and immiscible samples at each blend ratio, which we have established for the present elongational viscosity study.

Optical Microscope Observation

Optical microscope observation was carried out for all samples. Thin transparent miscible samples were prepared first, and the opaque immiscible samples were obtained by keeping them at 200°C for 10 min.

Figure 1 Cloud point measurements for PMMA/AS blends at various blend ratios. Transparency was checked by immersing 2 × 3 × 20-mm bar samples in heated silicone oil for 30 min: (○) transparent; (■) translucent; (●) opaque.

Figure 2 Illustrated schemes for preparation methods of PMMA/AS blends in the miscible and immiscible stage.

Elongational Measurement

Measurements of uniaxial elongational viscosity at constant strain rates were carried out using our home-made elongational rheometer at 145°C. The measurement temperature of 145°C was selected from the fact that miscible or immiscible blends do not change their miscible or immiscible states, transparent or opaque, within the measurement time. A detailed description and a discussion of the reliability of the elongational rheometer were given in previous articles.[21,22] Bar samples were pretreated in a vacuum oven at 80°C for 1 day just before measurement. No void generation of the samples in the heated silicone oil was checked by eye. Because bar samples slightly shrank in the heated silicone oil, 10 min of equilibration time was allowed before measurement. The actual strain rates were calculated from measuring actual width, which is obtained from recording the width change of bar by a video. A homogeneous elongation along the bar was also confirmed with eye observation.

RESULTS AND DISCUSSION

Optical Microscope Observation

Figure 3 shows optical microscope photographs of PMMA and AS. They were completely transparent, and nothing was observed for PMMA and AS. We have also observed an optical microscope of various miscible blends. They were also completely transparent, and nothing was detected for the miscible blends with the optical microscope. Figures 4, 5, and 6 give optical microscope photographs of PMMA/AS blends at a series of blend ratios. In a 9 : 1 ratio PMMA/AS blends, an island–sea-type distinct two-phase structure was seen. Many AS particles with a diameter range of 1 to 5 microns existed. As AS weight percentage increased, the two-phase structure changed into an interpenetrated cocontinuous network structure. In the 7 : 3 and 6 : 4 PMMA/AS blends, a clear interpenetrated cocontinuous network structure was seen. The width of each phase was about 10 microns. As AS increased more, it was changed into an vague island–sea-type structure. In the 7 : 3 and 6 : 4 PMMA/AS blends, the difference between the cloud point and 200°C, the temperature to make the immiscible sample, was larger than in other blend ratios. Thus, the phase-separated structure was highly developed in the 7 : 3 and 6 : 4 PMMA/AS blends.

Figure 3   Optical micrographs of PMMA and AS.

Elongational Viscosity

The preparation method of the samples illustrated in Figure 2 was a new way for the elongational viscosity study. We have checked the influences of heat history, residual THF, and sample shape before going into the measurement of blend samples. The reason to check these factors came from the fact that the rod-like samples made through a slow melt extrusion have been used until now. Samples of PMMA for elongational measurement were prepared in three ways. One way was direct preparation of a sheet from PMMA pellets by hot press. Another way was based on the procedure in Figure 2 using THF solvent. The other way was making rod-like samples through a slow melt extrusion. The molecular characteristics of PMMA in Table I were hardly changed by the present heat-treatment conditions. That was also the case with AS and blend samples.

ity of PMMA and AS are quite similar to each other under the measurement condition. As the strain rate increased, the stronger strain-hardening property was observed. Figures 8, 9, and 10 represent the elongational viscosity of miscible PMMA/AS blends at various ratios under 145°C.

PMMA : AS = 9 : 1   30 μm

PMMA : AS = 8 : 2   30 μm

PMMA : AS = 7 : 3   42 μm

Figure 4 Optical micrographs of PMMA/AS blends at blend weight ratios of 9/1, 8/2, and 7/3 in the immiscible stage.

The elongational viscosity of PMMA samples from the three ways were almost identical to one another. The influences of THF solvent and the square bar sample shape were judged to be negligible.

Figure 7 shows the elongational viscosity for PMMA and AS at 145°C. The elongational viscos-

PMMA : AS = 6 : 4   75μm

PMMA : AS = 5 : 5   42 μm

PMMA : AS = 4 : 6   42 μm

Figure 5 Optical micrographs of PMMA/AS blends at blend weight ratios of 6/4, 5/5, and 4/6 in the immiscible stage.

PMMA : AS = 3 : 7 ⟷ 30 μm

PMMA : AS = 2 : 8 ⟷ 30 μm

PMMA : AS = 1 : 9 ⟷ 30 μm

Figure 6 Optical micrographs of PMMA/AS blends at blend weight ratios of 3/7, 2/8, and 1/9 in the immiscible stage.

Figures 11, 12, and 13 give the elongational viscosity of immiscible PMMA/AS blends at various ratios under 145°C. Elongational viscosity was divided into two regions, a strain rate-independent linear elongational region and a strain rate-dependent nonlinear elongational region. The

strain rate-independent linear elongational viscosity was quite similar between PMMA and AS. The linear elongational viscosity was hardly affected by blend ratios and whether it was miscible or immiscible under the measurement condition.

It is interesting and quite important to compare the strain rate-dependent elongational viscosity, i.e., the strain-hardening property. The strain-hardening properties were observed for all samples. To compare the strain-hardening properties among samples, we use the following strain-hardening parameter (λn), which is the ratio of the strain rate-dependent nonlinear elongational viscosity ($\eta_{nonlinear}$) to the strain rate-independent linear elongational viscosity (η_{linear}) at the same time[23]:

$$\lambda n = \eta_{nonlinear}/\eta_{linear} \qquad (1)$$

The strain-hardening parameters of many homopolymers are generally written as:

$$\lambda n = \exp(k\gamma^*) \qquad (2)$$

where k is a constant showing the intensity of strain-hardening property and γ^* is the effective strain described by:

$$\begin{aligned} \gamma^* &= \gamma - \gamma_c \quad \gamma > \gamma_c \\ \gamma^* &= 0 \qquad\quad \gamma < \gamma_c \end{aligned} \qquad (3)$$

Figure 7 Elongational viscosity of PMMA—at constant strain rates: (○) 0.571; (□) 0.28; (△) 0.113; (◇) 0.00762, and AS—at constant strain rates: (○) 0.563; (□) 0.264; (△) 0.109; (◇) 0.0076 at 145°C.

Figure 8 Elongational viscosity of miscible PMMA/AS blends—9/1 at constant strain rates: (○) 0.581; (□) 0.286; (△) 0.116; (◇) 0.0079, 8/2 at constant strain rates: (○) 0.592; (□) 0.274; (△) 0.108; (◇) 0.0077, and 7/3 at constant strain rates: (○) 0.518; (□) 0.279; (△) 0.116; (◇) 0.00768 at 145°C.

where γ_c is the critical strain where the strain-hardening property starts to appear.

The influences of blend ratios on the strain-hardening parameter and the critical strain were analyzed in a series of miscible blends and immiscible blends, respectively. Figure 14 shows the strain-hardening parameter, λn, as a function of the Hencky strain for PMMA, AS, and various miscible blends around the strain rate of 0.25. The strain-hardening parameters of all miscible samples were relatively close to one another. The critical strain, γ_c, of all miscible samples was almost similar, and was around 0.55. This value was quite similar to that of linear homopolymers from a former study.[9] The critical strain was not affected by miscible blends. The strain-hardening parameters and the critical strains were also obtained for immiscible blends in the same way. The strain-hardening parameters and the critical strains of all immiscible samples were close to one another. The critical strain of all immiscible samples was similar, and was around 0.55.

The effect of miscibility was analyzed in terms of the intensity of the strain-hardening property. The intensity of the strain-hardening property, k, was calculated from the slope of the relationship between the Hencky strain and the strain-hardening parameter. Figure 15 exhibits the comparison of the intensity of strain-hardening property, k, for a series of miscible and immiscible blends. The intensity of PMMA was the same as that of AS. For immiscible blends, the intensities were almost constant with those of PMMA and AS. For miscible blends, Figure 15 shows the tendency that the intensities of miscible blends are almost similar to or very slightly stronger than those of immiscible blends.

Immiscible Blends

The cause of the similarity of the intensities of the strain-hardening properties among miscible and immiscible samples is discussed. Table I suggests that there is a difference on molecular weight between PMMA and AS. However, the polydisper-

Figure 9 Elongational viscosity of miscible PMMA/AS blends 6/4 at constant strain rates: (○) 0.552; (□) 0.250; (△) 0.118; (◇) 0.00742, 5/5 at constant strain rates: (○) 0.552; (□) 0.25; (△) 0.118; (◇) 0.00742, and 4/6 at constant strain rates: (○) 0.532; (□) 0.281; (△) 0.109; (◇) 0.008 at 145°C.

Figure 10 Elongational viscosity of miscible PMMA/AS blends—3/7 at constant strain rates: (○) 0.563; (□) 0.278; (△) 0.115; (◇) 0.0079, 2/8 at constant strain rates: (○) 0.601; (□) 0.266; (△) 0.119; (◇) 0.0079, and 1/9 at constant strain rates: (○) 0.552; (□) 0.280; (△) 0.115; (◇) 0.00774 at 145°C.

sity was almost constant among all samples. In addition, the elongational viscosity of PMMA is quite similar to that of AS under the measurement condition. These results suggest that relaxation is similar between PMMA and AS.

In immiscible blends having an island–sea-type structure, such as ABS polymers, we have found that the intensity of the strain-hardening property was strongly correlated with the degree of domain deformation.[12] If the island domain was elongated in the same way as the sample was stretched, the intensity of the sample was similar to that of matrix. As the degree of domain deformation was reduced, the intensity became smaller and even negative. The intensity of the sample did not exceed that of matrix polymer. Our ABS study also suggests that the enhanced interaction between domain and matrix with a higher degree of grafting makes the stain rate-independent linear elongational viscosity larger, while it has little effect on the intensity of the strain-hardening property.[12] In immiscible blends of PMMA/AS having an island–sea-type

two-phase structure, both phases were considered to be equally stretched, because the elongational viscosity of PMMA and AS was quite similar to each other. This seems to explain the fact that the immiscible blends having an island–sea-type phase structure showed the same intensity as PMMA or AS. In an immiscible interpenetrated cocontinuous two-phase structure, both phases should be stretched at the same time, resulting in the same elongational viscosity as PMMA or PS. Thus, the intensity of various immiscible blends was almost constant in all blend ratios.

The above interpretation suggested that the strain-hardening property is not influenced by the size and type of phase-separated structure for immiscible blends. To reconfirm this statement, we have prepared immiscible blends with a different size of phase-separated structure at the same composition in two ways without using THF solvent. One way is the hot press of the mixture of PMMA and AS pellets (about 3–5 mm particles). The other way is the hot press of the mixture of powdered PMMA and AS (about 0.5–1 mm parti-

Figure 11 Elongational viscosity of immiscible PMMA/AS blends—9/1 at constant strain rates: (○) 0.559; (□) 0.273; (△) 0.112; (◇) 0.00745, 8/2 at constant strain rates: (○) 0.571; (□) 0.276; (△) 0.110; (◇) 0.00778, and 7/3 at constant strain rates: (○) 0.562; (□) 0.278; (△) 0.118; (◇) 0.00756 at 145°C.

Figure 12 Elongational viscosity of immiscible PMMA/AS blends—6/4 at constant strain rates: (○) 0.591; (□) 0.272; (△) 0.108; (◇) 0.00781, 5/5 at constant strain rates: (○) 0.581; (□) 0.271; (△) 0.115; (◇) 0.00749, and 4/6 at constant strain rates: (○) 0.533; (□) 0.280; (△) 0.111; (◇) 0.00794) at 145°C.

Figure 13 Elongational viscosity of immiscible PMMA/AS blends—3/7 at constant strain rates: (○) 0.563; (□) 0.267; (△) 0.114; (◇) 0.00779, 2/8 at constant strain rates: (○) 0.579; (□) 0.291; (△) 0.107; (◇) 0.00766, and 1/9 at constant strain rates: (○) 0.549; (□) 0.275; (△) 0.116; (◇) 0.00756 at 145°C.

cles). If the blend composition was the same, the elongational viscosity of immiscible blends did not depend on the preparation. In the present study, the elongational viscosity of PMMA was similar to that of AS. The two phases were elongated equally during elongation. The interfacial area between PMMA and AS should be different by using different preparation methods; however, the interfacial interaction does not affect the strain-hardening property. Thus, the size and shape of phase-separated structure did not affect the strain-hardening property of the tested immiscible blends.

It has been reported that immiscible blends become miscible by flow at a slightly higher temperature than cloud point in LCST diagram.[6] Former studies suggested that the cloud points became higher by flow.[6] It was confirmed that the phase structure was not changed by microscope observation after keeping immiscible samples at 145°C for 30 min (which is the elongation time) without deformation. This seems to have the possibility that immiscible samples became miscible by large elongational deformation. In the present experiments,

however, it was hard to see the evidence of flow-induced miscibility change by eye observation, because the initial sample is 2 mm of thickness and the samples became very thin when stretched.

Figure 14 The strain-hardening parameter as a function of the Hencky strain for miscible PMMA/AS blends at various blend weight ratios: (○) 9/1; (●) 8/2; (□) 7/3; (■) 6/4; (◇) 5/5; (◆) 4/6; (△) 3/7; (▲) 2/8; (×) 1/9.

Figure 15 The intensity of the strain-hardening property as a function of various blends weight ratio of PMMA/AS in the miscible (○) and immiscible (△) stage.

Miscible Blends

For miscible blends, it was reported that relaxation behavior of miscible blends is close to that of a blend consisting of homologous polymers.[4] By blending of homologous polymers, the relaxation, at least, becomes longer because the increase was generally seen in the polydispersity of molecular weight. The tested PMMA and AS have a similar relaxation time from the similarity of elongational viscosity, and the polydispersity was not changed. Thus, the relaxation time is regarded to be the same in the miscible blends system. This caused little influence of the miscibility and blend ratios on the intensity of the strain-hardening parameters in the blend samples.

CONCLUSION

The present study provided the following new findings:

1. A method to prepare miscible and immiscible blend samples at the same composition for elongational viscosity was established. The method included three steps, solvent blend, cast film, and hot press. The effect of residual solvent, heat history, and square bar shape was negligible.
2. The effects of miscibility and blend ratios on the strain-hardening property of elongational viscosity were studied with miscible and immiscible blend samples at the same composition using PMMA and AS. Miscibility and blend ratios did not affect the stain-hardening parameters, the critical strain, and the intensity of the strain-hardening property.
3. It was concluded that little influence of miscibility and blend ratios was caused by the similarity of the polydispersity of molecular characteristics and the relaxation among all samples.

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