Elongational Viscosity for Miscible and Immiscible Polymer Blends. II. Blends with a Small Amount of UHMW Polymer

TATSUHIRO TAKAHASHI, JUN-ICHI TAKIMOTO, KIYOHITO KOYAMA

Department of Materials Science and Engineering, Yamagata University, Yonezawa 992-8510, Japan

ABSTRACT: The effect of miscibility on elongational viscosity of polymer blends was investigated in homogeneous, miscible, and immiscible states by the blend of 1.5 wt % of ultrahigh-molecular-weight (UHMW) polymer. The matrix polymer was either poly-(methyl methacrylate) (PMMA), or poly(acrylonitrile-*co*-styrene) (AS) that has a comparable elongational viscosity value. The homogeneous blend consisted of 98.5 wt % of PMMA and 1.5 wt % of UHMW–PMMA. The miscible blend was composed of AS and UHMW–PMMA at the same ratio. The immiscible blend was a combination of AS and UHMW–polystyrene (PS) at the same ratio. The strain-hardening behavior of the different blends were compared with that of pure PMMA. It was demonstrated that 1.5 wt % of UHMW induces a strong strain-hardening property in the homogeneous and miscible blends but was hardly changed in the immiscible blend. The optical microscope observation of the immiscible blend suggested that the UHMW domains were stretched, but that the degree of domain deformation was less than a given elongational strain. It was concluded that the strain-hardening property is strongly affected by the miscibility of UHMW chain and matrix. The strong strain-hardening property is caused by the deformation of the UHMW polymer. UHMW chains are stretched when they are entangled with surrounding polymers. However, UHMW chains in an immiscible state are not so deformed because of viscosity difference and no entanglements between domain and matrix. A smaller degree of UHMW chain deformation in immiscible state results in weaker strain-hardening property. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 961–969, 1999

Key words: elongational viscosity; polymer blends; homogeneous; miscible; immiscible; UHMW; strain-hardening

INTRODUCTION

Polymer blends have been used to control melt rheology and to improve processability.[1] It has been accepted that elongational rheology acts as an excellent indicator for processability, including elongational flow, such as film blowing, blow molding, and melt spinning.[2–8] With this back-ground, a number of studies on elongational rheology of polymer blends have been published.[9–25]

Most of the blend studies provide elongational viscosity by changing the blend ratio of two components from 90 : 10 to 10 : 90. Valenza et al. reported the polymer blends of high-density polyethylene (HDPE) and low-density polyethylene (LDPE).[10] Schlund and Utracki gave two series of polymer blends of linear low-density polyethylene (LLDPE) and LDPE.[12] Mantia et al. presented three series of polymer blends of LDPE and LLDPE.[14] Utracki and Sammut showed the polymer blends of polystyrene (PS) and polyethylene (PE).[13] Tanaka et al. reported the polymer

blends of LDPE/HDPE.[15] The strain-hardening properties of these polymer blends were between those of two components, whether they were either miscible or immiscible. To make PE-based miscible and immiscible blends, different combinations of polymers were required. Thus, it was difficult to discuss the effect of miscibility on the strain-hardening property.

In another series of studies, the effect of phase structure in an immiscible blend was reported by using a compatibilizer at the same blend composition. Utracki and Sammut mentioned the effect of styrene–ethylene butylene block copolymer (SEB).[13] Hattori et al. discussed the influence of styrene–ethylene propylene block copolymer (SEP).[17] Tanaka et al. reported the effect of styrene–butadiene–styrene block copolymer (SBS).[16] These studies teach that the strain-hardening property was reduced by the addition of a compatibilizer. A compatibilizer should be located not only at the interface but also in the dispersed phase and in the matrix. The weaker strain-hardening property by the addition of a compatibilizer now become understandable since block copolymers show a strain-softening property.[24,25]

Schlund and Utracki pointed out the important phenomenon that the increased molding time induces a stronger strain-hardening property in LLDPE.[11] It was interpreted that the entanglement increases with time. The origin of the phenomenon is rooted in the fact that some of the PEs themselves are not homogeneous because of using no single phase catalyst or two-step polymerization. This complexity also caused the difficulty to study the effect of miscibility on the strain-hardening property when using a series of PEs.

An unique characteristic of the elongational viscosity is that the strain-hardening property is enhanced by a small amount of UHMW polymer.[5] This has been accepted by constitutive analysis and experimental studies.[2–7] Munstedt reported the evidence of a dramatic strain-hardening increase by a higher molecular weight segment.[6,7] These studies allow us to get an idea of the effect of miscibility on the strain-hardening property by using a small amount of UHMW polymer. In this study, we compared the strain-hardening properties of the three types of polymer blends (i.e., homogeneous, miscible, and immiscible) by incorporation of a small amount of UHMW polymer. Samples of PMMA, AS, and PS, rather than PEs,

Table I   Molecular Characteristics

Sample	M_n	M_w	M_z
PMMA	76,200	146,000	254,000
AS	142,000	259,000	406,000
UHMW–PMMA	1,450,000	1,500,000	—
UHMW–PS	2,900,000	3,000,000	—

were used through the solution blend method to overcome the difficulty mentioned earlier.

EXPERIMENTAL

Preparation of Samples

Rodlike samples, which are prepared with a single extruder through a slow extrusion, have been generally used for elongational measurement. A twin-screw extruder has been used for making polymer blends. However, it was reported by Dumoulin et al. that incorporation of the UHMW polymer into the matrix polymer to make a homogeneous phase with melt compounding had failed.[9] Thus, a different sample preparation method, in the following three steps, was tried: solution blend, cast film, and hot press.

Poly(methyl methacrylate) (PMMA) and poly(acrylonitrile-*co*-styrene) (AS, 30 wt % of AN) from Asahi Chemical Industry Co., Ltd. were used. UHMW–PMMA and UHMW–PS (GL Sciences Inc., Tokyo, Japan) were purchased and used as the UHMW segment. Table I summarizes the molecular characteristics of PMMA, AS, UHMW–PMMA, and UHMW–PS. The blend weight ratio of medium molecular weight to UHMW polymer is either 98.5 : 1.5 or 99.9 : 0.1. The homogeneous blend consisted of PMMA and UHMW–PMMA. The miscible blend was composed of AS and UHMW–PMMA. The immiscible blend was a combination of AS and UHMW–PS. Four samples, PMMA, AS, UHMW–PMMA, and UHMW–PS, as received, were dried in a vacuum oven at 80°C overnight. The dried samples were blended at certain 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 2 days.

The blend solutions were poured into several pans and 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 (150 × 150 mm, 2 mm thickness) was made by the hot press method at 140°C for 15 min using a stack of cast films. Samples for elongational measurement were made by cutting the transparent plate into bars (2 × 3 mm of the cross section, 150 mm long). In a previous report, an illustrated preparation method was presented.[26]

Optical Microscope Observation

Optical microscope observation was carried out for all samples using the 2-mm-thick bars. For immiscible blends only, optical microscope photographs before and after elongation are shown.

Elongational Measurement

Measurements of uniaxial elongational viscosity at constant strain rates were carried out using our homemade elongational rheometer at 145°C. A detailed description and a discussion of the reliability of the elongational rheometer were given in previous articles.[2,3] Bar samples were pretreated in a vacuum oven at 80°C for 1 day just before measurement. No void generation of samples in the heated silicone oil was checked with eyes. Since bar samples shrank slightly in the heated silicone oil, 10 min of equilibration time was allowed before measurement. The force was very high and was out of the measurement range at the strain rate of 0.5 s^{-1}. The strain rates in this study were around 0.25, 0.1, 0.05, and 0.005 s^{-1}. The actual strain rates were calculated from measuring the actual width, which is obtained from recording the width change of bar by a video. The homogeneity of the bar deformation was checked visually. Dynamic shear measurements (Rheometrics, ARES) were also carried out to obtain complex viscosity for PMMA and AS at 145°C. Disklike samples were made and dried under vacuum oven at 80°C for 1 day before measurements.

RESULTS AND DISCUSSION

Optical Microscope Observation

Optical microscope observation suggested the complete transparency of the homogeneous blends and miscible blends at a 98.5 : 1.5 blend ratio. Nothing was observed for these two blends up to the magnification of 400. We attempted to

Figure 1 Elongational viscosity of PMMA at constant strain rates (s^{-1}): (○) 0.271, (□) 0.113, (△) 0.0588, and (◇) 0.00602 at 145°C.

get phase separation of the miscible blend by keeping it at a higher temperature using a lower critical solution temperature (LCST) diagram. However, it did not clearly show a cloud point or a phase separation up to 220°C when immersing into the silicone oil for 30 min. Thus, the immiscible blend was prepared through the combination of AS and UHMW–PS. Finally, the immiscible blend was observed and showed dispersed particles having diameters from 10 to 100 μm.

Strain-Rate-Independent Linear Elongational Viscosity

The preparation method of the sample bar was a new way for the elongational viscosity study. The influences of heat history, residual THF, and sample shape were carefully checked and were reported in a previous article.[26] The influences of heat history, THF solvent, and the square bar sample shape were judged to be negligible on the elongational viscosity results.

The viscosity increases with the following two steps: a gradual increase (strain-rate-independent linear elongational viscosity) and a rapid increase (strain-rate-dependent nonlinear elongational viscosity). Here, the elongational viscosity growth $\eta^+(t)$ is defined as the viscosity increase, including two steps. Figures 1 and 2 represent the elongational viscosity growth for PMMA and AS at 145°C. The elongational viscosity growth of PMMA and AS are quite similar to each other under the tested conditions. The higher the strain rate, the stronger the strain-hardening property is. Figures 3–5 show the elon-

Figure 2 Elongational viscosity of AS at constant strain rates (s^{-1}): (○) 0.266, (□) 0.109, (△) 0.0521, and (◇) 0.00534 at 145°C.

Figure 4 Elongational viscosity of miscible AS : UHMW–PMMA blends of a 98.5 : 1.5 ratio at constant strain rates (s^{-1}): (○) 0.254, (□) 0.113, (△) 0.0567, and (◇) 0.00506) at 145°C.

gational viscosity growth for homogeneous, miscible, and immiscible blends at the blend ratio of 98.5 : 1.5. The strain-rate-independent linear elongational viscosity was quite similar between PMMA and AS under the measurement region. It was also found that the strain-rate-independent linear elongational viscosity was similar among the following five samples: PMMA, AS, homogeneous, miscible, and immiscible blends. The linear elongational viscosity was hardly affected by a small amount of UHMW polymer, whether it was homogeneous, miscible, or immiscible under the measurement condition.

The UHMW polymer in three blend stages causes a very long relaxation time, which appears in a much longer time region than the measurement range. Thus, in the measurement region, the effect did not appear. A similar result was reported in a previous report.[9] Dumoulin et al.[9] studied polymer blends of medium-density polyethylene (MDPE) and UHMW–PE at the blend ratio of 98 : 2. Optical observation showed that UHMW–PE was dispersed as particles with 10–50 μm diameter. The strain-rate-independent linear elongational viscosity of the blend of MDPE : UHMW–PE of 98 : 2 agreed well with that of pure MDPE.

Figure 3 Elongational viscosity of homogeneous PMMA : UHMW–PMMA blends of a 98.5 : 1.5 ratio at constant strain rates (s^{-1}): (○) 0.262, (□) 0.117, (△) 0.0515, and (◇) 0.00596 at 145°C.

Figure 5 Elongational viscosity of immiscible AS : UHMW–PS blends of a 98.5 : 1.5 ratio at constant strain rates (s^{-1}): (○) 0.255, (□) 0.117, (△) 0.0513, and (◇) 0.00486 at 145°C.

Figure 6 The strain-hardening viscosity ratio, SH, as a function of Hencky strain at 145°C around the strain rate of 0.1 (s^{-1}) for various polymer systems: (○) PMMA, (□) AS, (●) homogeneous PMMA : UHMW–PMMA blends of a 98.5 : 1.5 ratio, (■) miscible AS : UHMW–PMMA blends of a 98.5 : 1.5 ratio, (▲) and immiscible AS: UHMW–PS blends of a 98.5 : 1.5 ratio.

Strain-Rate-Dependent Nonlinear Elongational Viscosity

The strain-hardening properties were observed for all samples. To compare the strain-hardening properties among samples, we use the term of strain-hardening viscosity ratio (SH), which is the ratio of the strain-rate-dependent nonlinear elongational viscosity ($\eta_{\mathrm{nonlinear}}$) to the strain-rate-independent linear elongational viscosity (η_{linear}) at the same time.[1,4] We also use the critical strain ε_c, where the strain-hardening property starts to appear.[4] So when SH is greater than 1, it means that the viscosity growth is strain-rate-dependent.

Figure 6 represents the strain-hardening viscosity ratio, SH, as a function of Hencky strain for PMMA, AS, homogeneous, miscible, and immiscible blends around the strain rate of 0.1 s^{-1}. The strain-hardening viscosity ratios of PMMA, AS, and immiscible blend are quite similar to one another. The strain-hardening viscosity ratios of homogeneous and miscible blends were much larger than those of matrix polymers. The strain-hardening viscosity ratio of miscible blend was similar to or slightly smaller than that of homogeneous blend. It was also the case with the strain-hardening viscosity ratio at other strain rate conditions. The critical strains ε_c of all samples were almost similar and was around 0.55. This value was quite similar to that of linear homopolymers from former studies.[20]

First, let us discuss why immiscible blends show a weaker strain-hardening property than homogeneous or miscible blends. In the case of homogeneous polymers, it is known that the correlation between longer time relaxation and stronger strain-hardening exists from prediction and experiments. However, in the case of heterogeneous systems, from some experimental evidence[23–25,27,28] it has been pointed out that there is no correlation between the two terms. The main reason for no correlation comes from that actual matrix flow was strongly affected by the type of heterogeneous phase and the degree of domain deformation. In particle-dispersed immiscible blends, the strain-hardening property needs to be discussed from various factors, such as agglomerization, particle size, particle deformation, interfacial interaction, and particle content. It is important to observe whether dispersed UHMW–PS particles were deformed or not. Figure 7 shows the optical microscope photographs of the immiscible blend at the blend ratio of 98.5 : 1.5 before and after elongation. Figure 7 suggests that UHMW–PS particles were dispersed well and were deformed by the elongation. However, the received strain in particles was found to be about half of the given strain from aspect ratio of stretched particles. It was thought that the UHMW–PS particles did not deform in a similar degree to the matrix because of very high viscosity and increased interfacial tension. The strong strain-hardening property in miscible blend is caused by the deformation of UHMW polymers, which are entangled with surrounding polymers. Smaller deformation of UHMW–PS particles means that the UHMW chains in the immiscible blend are not stretched compared with those in miscible blend, resulting in a smaller strain-hardening property.

This interpretation was also supported by a previous study of acrylonitrile–butadiene–styrene (ABS) polymers.[23] The effect of the degree of dispersed particle deformation on the strain-hardening property in ABS was reported.[23] Through a number of research activities on ABS polymers,[18–23] the strain-hardening property of ABS did not exceed that of matrix AS. ABS, including soft butadiene, which was deformed during elongation, showed a similar strain-hardening property to the matrix AS. The reason would come from the observation result that butadiene particles were not deformed in the similar degree to the given elongational strain.

Figure 8 Complex shear viscosity for PMMA (solid line) and AS (dotted line) at 145°C from dynamic shear measurement, and shear viscosity calculated from linear elongational viscosity for PMMA ($\square$) and AS ($\bigcirc$).

Secondly, let us discuss why the strain-hardening property of miscible blend was similar to or slightly smaller than that of the homogeneous blend. Here, the relaxation time difference between matrix PMMA and AS was checked using dynamic shear measurement. Figure 8 represents complex shear viscosity for PMMA and AS at 145°C. Figure 8 also suggests that the complex shear viscosity of PMMA was very consistent with the values that are calculated from the strain-rate-independent linear elongational viscosity of PMMA. This is also the case with AS. The complex shear viscosity between PMMA and AS resembles each other in the frequency region from 0.01 to 10. However, the very low frequency region of Figure 8 suggests that the AS matrix has a longer relaxation time than PMMA.

From the constitutive equation prediction for homogeneous blends, the relaxation time difference between matrix polymer and UHMW polymer determines the intensity of the strain-hardening property.[5] The larger the difference, the stronger the intensity of the strain-hardening property. A miscible blend can be much closer to a homogeneous blend than an immiscible blend, and the above concept was applied to miscible blends. The relaxation time difference between

Figure 7 Optical microscope photographs of immiscible AS : UHMW–PS blends of a 98.5 : 1.5 ratio at the strain rate of 0.1 under 145°C under three elongational

stages: (top) before elongation, (middle) after elongation at a Hencky strain of 2.0, and (bottom) after elongation at a Hencky strain of 2.3. The samples were elongated in the horizontal direction.

Figure 9 Elongational viscosity of homogeneous PMMA : UHMW–PMMA blends of a 99.9 : 0.1 ratio at constant strain rates (s^{-1}): (○) 0.274, (□) 0.103, (△) 0.0550, and (◇) 0.00582 at 145°C.

AS and UHMW–PMMA was smaller than that between PMMA and UHMW–PMMA, resulting in that the strain-hardening property for the miscible blend is slightly smaller than that for homogeneous blend.

To get more insight into the difference between homogeneous and miscible blends,[29–31] the structural difference is discussed here. Saito reported the presence of local ordering structures in miscible blends, which are not observed in homogeneous blends.[29,30] The local ordering causes a reduction of the entanglement density. The experimental value for PMMA of entanglement molecular weight between entanglements has been reported to be 9200.[32] It means that the averaged number of entanglement points along the UHMW–PMMA is 163, and it could be even lower due to the local ordering structure. The reduction of the entanglement density for PMMA–AS miscible blends was experimentally suggested by Wu.[31] However, the shear viscosity and the strain-hardening behavior are affected by the following three factors[31]: entanglements, friction constant, and free volume[31] all play a role. It was reported that the zero shear viscosity of miscible blends of PMMA and AS mostly obeys the additive rule by cancelling the above three factors against one another.[31] Under large elongational deformation, it was difficult to analyze the effect of the three factors on the strain-hardening property in the present study and should be investigated in future work.

The Effect of a Trace of UHMW Polymer

The idea that elongational measurements are very sensitive to trace amounts of UHMW polymer has been widely accepted. Thus, it is worthwhile to check whether a trace amount of UHMW polymer can increase the strain-hardening property or not. Since 1.5 wt % of UHMW polymer did not have an influence on the strain-hardening property of immiscible blend, here, only homogeneous and miscible blends at ratio of 99.9 to 0.1 were studied.

Figures 9 and 10 show the elongational viscosity for homogeneous and miscible blends at ratio of 99.9 to 0.1 at 145°C under constant strain rates. Strain-rate-independent linear elongational viscosity of the homogeneous blend was almost consistent with that of miscible blends. To compare the strain-hardening property of homogeneous blend with that of the miscible blend, the strain-hardening viscosity ratio as a function of Hencky strain were plotted for homogeneous and miscible blends. Figure 11 represents the strain-hardening viscosity ratios for the two pure polymers, PMMA and AS, and for the homogeneous and miscible blends. The strain-hardening viscosity ratios and the critical strains were quite similar to one another among the four samples. It means that the elongational measurement was not sensitive to very low concentrations of UHMW–PMMA. Another explanation for the lack of sensitivity is that the relaxation modulus and time of UHMW–PMMA in the tested blends were not large and long enough. The strain-harden-

Figure 10 Elongational viscosity of miscible AS : UHMW–PS blends of 99.9 : 0.1 ratio at constant strain rates (s^{-1}): (○) 0.251, (□) 0.112, (△) 0.0506, and (◇) 0.00496 at 145°C.

Figure 11 The strain-hardening viscosity ratio, SH, as a function of Hencky strain at 145°C around the strain rate of 0.25 (s^{-1}) for various polymer systems: (○) PMMA, (□) AS, (●) homogeneous PMMA : UHMW–PMMA blends of a 99.9 : 0.1 ratio, and (■) miscible AS : UHMW–PMMA blends of a 99.9 : 0.1 ratio.

ing property of immiscible blend at 0.1 wt % of UHMW–PMMA also should show similar intensity to that of the matrix. At a very low content of UHMW polymer, the strain-hardening property was not affected whether it was miscible or immiscible since the effect of the addition of UHMW polymer was negligible.

CONCLUSION

The present study provided the following new findings.

1. The effects of miscibility on the elongational viscosity of polymer blends were investigated through blending with a small amount of UHMW polymer. Three types of blends, homogeneous (PMMA and UHMW–PMMA), miscible (AS and UHMW–PMMA), and immiscible (AS and UHMW–PS) blends were prepared. The matrix polymer was either PMMA or AS, which has comparable elongational viscosity value. For the three types of blends, the effect of addition of UHMW polymer did not affect the strain-rate-independent linear elongational viscosity in the measurement range, when the content of UHMW was up to 1.5 wt %.
2. The strain-hardening property was quite different from miscible to immiscible blends at 1.5 wt % of UHMW polymer. The

deformation of UHMW polymer domain particles in the immiscible blend did not contribute to the increase of strain-hardening property (the intensity of the immiscible blend was similar to that of the matrix polymer.). However, in homogeneous or miscible blends, the deformation of UHMW polymer entangled with surrounding matrix polymer exhibited the drastic increase of the strain-hardening property.

3. The strain-hardening property of miscible blend was slightly smaller than that of the homogeneous blend at 1.5 wt % UHMW content. It was explained by a slightly smaller relaxation time difference of the miscible blend compared with that of the homogeneous blend.
4. The effect of miscibility on the strain-hardening property was not detected when the content of UHMW polymer was 0.1 wt %. It was interpreted by the idea that either the UHMW concentration was too low or the relaxation modulus and time were not large and long enough to exhibit the increase of the intensity.

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