General paper

UNIAXIAL ELONGATIONAL VISCOSITY OF POLY(STYRENE-BLOCK-BUTADIENE-BLOCK-STYRENE) MELTS

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Abstract: Experimental studies about the effect of block copolymerized structures on the uniaxial elongational viscosity were performed. Two poly(styrene-*block*-butadiene-*block*-styrene) (SBS, S/B weight ratio = 4/6) samples with linear and star (4 arms) structures were used for the elongational viscosity measurement at constant strain rates. The block copolymer samples exhibited the strain-softening elongational viscosity. This property was in contrast to the strain-hardening elongational viscosity which is observed for homopolymer melts. The cause of the strain-softening property was analyzed from the structural change by small angle X-ray (SAX) and transmission electron microscope (TEM). The lamellar structures were more oriented and became longer along the elongational direction by the elongation, while the lamellar thickness remained almost constant. The observation indicates that the lamellar structures, instead of the SBS molecules, were oriented and stretched. The rheological discussion on the strain-softening elongational viscosity was also carried out by the BKZ model. The damping functions of the block copolymers from step-shear relaxation experiments showed larger decrease than that of the Doi-Edwards prediction. The structural change observation and the BKZ analysis suggested that the largely decreased damping functions are due to the lamellar orientation and cause the strain-softening elongational property.

Key words: Block copolymer, SBS, Uniaxial elongational viscosity, Strain-softening, Damping function

1. INTRODUCTION

Studies on the uniaxial elongational viscosity have become active since Meissner developed an uniaxial elongational rheometer[1]. We also developed our home-made elongational rheometer by modifying Meissner-type design in late 1970s[2]. The elongational viscosity of homopolymer melts as a function of time at larger constant strain rates deviates, under large strain, from strain rate independent linear elongational viscosity and show large increase. This has been called the strain-hardening property. The strain-hardening property has been one of interesting research subjects in the elongational viscosity of homopolymer melts. Extensive former studies have shown that the strain-hardening property in homopolymer melts is enhanced by wide molecular weight distribution (MWD) and long chain branching[2-6]. The strain-hardening property is strongly correlated with the existence of very long relaxation time[2-6]. This view is supported by both experiments and constitutive analysis for various homopolymer melts[2-6]. On the other hand, the qualitative relationship between the strain-hardening elongational property and the blow molding processability has been experimentally demonstrated[7]. Thus, the uniaxial elongational viscosity has received a considerable attention as an indicator for the processability under blow molding.

For long years, various kinds of copolymers have been used for the polymer processing which involves elongational deformation. However, little is known for the effect of copolymerized structures on the elongational viscosity. Various copolymerized structures, i.e., block, graft, or random copolymerized structure, have important effects on melt rheology. In homopolymer melts, the strain-hardening property is understandable using relaxation time. However, long time relaxation did not always cause strain-hardening property in some

heterogeneous systems[8]. Thus, a new systematic view about the relationship between various polymer structures and strain-hardening properties has been awaited. Our current research aim is to establish a systematic view of the relationship between various polymer structures and strain-hardening properties. We have already reported the influence of graft copolymerized structure on the elongational viscosity[9]. We have also studied how ionic interaction affects the strain-hardening elongational properties by using partially ionized random copolymers [10, 11].

In this paper, we study the effect of ABA type triblock copolymerized structures on the strain-hardening property from structural change and rheological interpretation. Block copolymers have been utilized as compatibilizer in polymer blends. In recent years, the elongational viscosities of polymer blends containing a block copolymer have been investigated without studying the viscosity of the block copolymer itself[12]. Studies on the elongational viscosities of block copolymers are very useful also for understanding the elongational viscosity of these polymer blends.

2. EXPERIMENTAL

The investigation was carried out by using a linear and a star shaped (4 arms) poly(styrene-*block*-butadiene-*block*-styrene). These are designated as SBS(L) and SBS(S), respectively. Number and weight averaged molecular weights (M_n , M_w) for SBS(L) and SBS(S) are $M_n=60000$, $M_w=80000$ and $M_n=117000$, $M_w=148000$, respectively. The weight ratio of S to B is 4 to 6 for both SBS(L) and SBS(S). Measurements of dynamic shear viscosity were performed using a rotational rheometer (RDA II, Rheometrics) to estimate the transition temperature of the block copolymers.

The uniaxial elongational viscosity at various constant

strain rates was measured using a Meissner-type elongational rheometer (Melten Rheometer, Toyo Seiki Seisaku-Sho, Ltd.) with rod-like samples. The rod-like samples were prepared through extrusion by using a single screw extruder (Labo Plastomil, Toyo Seiki Seisaku-Sho, Ltd.) with and without using a table conveyor. The detailed procedure to evaluate the elongational viscosity under actual strain rates was described in a previous paper[2]. Phase structures of the block copolymers before and after the elongation were observed by small angle X-ray scattering (SAX) (RINT 2500, Rigaku International Co., Ltd.) and transmission electron microscope (JEOL 2000FX).

Measurements of step-shear relaxation modulus[13] were performed using a rotational rheometer (RDA II, Rheometrics) to characterize the damping functions of SBS(L) and SBS(S). A linear polystyrene (PS(L), $M_n=110000$, $M_w=240000$) and a star (4arms) polystyrene (PS(S), $M_n=150000$, $M_w=200000$) were also used as references for the measurement of step-shear relaxation modulus. All samples were used after drying under an vacuum oven at 80°C for a day.

3. RESULTS AND DISCUSSION

3.1. The Influence of Preparation Conditions

Most homopolymers can eliminate a memory of slightly different preparation conditions of rod-like samples by immersing samples about 15 minutes in heated silicone oil before the elongational measurements. Thus, it is known that the preparation conditions have no effect on the elongational viscosity of homopolymer melts by immersing samples in heated silicone oil for enough time. Heterogeneous polymers might keep a memory of preparation conditions because of phase separated structures[14], even after immersing samples in heated silicone oil. First of all, we checked the influence of preparation conditions of rod-like samples on lamellar-like structures of SBS(L) sample and the elongational viscosity.

Figure 1 shows the schematic diagrams for three conditions of rod-like sample preparation by using a single screw extruder having a die hole of 5 mm diameter. Condition (a) was 70rpm of screw speed with using a conveyor which moves at a very low constant speed (about 20cm/min.). The conveyor slightly stretched a molten sample. Conditions (b) and (c) were 5 and 150 rpm of screw speed without using a conveyor. Each rod-like sample was cut and taken from the die immediately before it was elongated by its weight. All rod-like samples were prepared at 185°C of barrel setting temperatures and their diameters were about 5mm. Rod-like samples were immersed in silicone oil at 140°C for 15 minutes and were rapidly cooled into ice/water solution. Three kinds of samples had almost no shrinkage by immersion in silicone oil. Cooled samples were used for SAX measurements.

Figure 2 gives SAX results of three kinds of samples at three different setting conditions which are illustrated in each figure. It shows that using higher screw speed or using a conveyor makes the lamellar-like structure more oriented along the elongational direction. This orientation is explained by shear deformation in a die of the single screw extruder or slight elongation with a conveyor.

Fig.1. Schematic diagrams for three conditions of rod-like sample preparation by using a single screw extruder: (a) 70 rpm of screw speed with a conveyor (a very slow constant conveying speed); (b) 5 rpm of screw speed without a conveyor; (c) 150 rpm of screw speed without a conveyor.

Fig.2. Small angle X-ray (SAX) measurements of SBS(L) samples (before elongation) at three different setting conditions which are illustrated in each figure. The dotted line is for SBS(L) prepared at condition (a) in Fig.1. The solid line is for SBS(L) prepared at condition (b) in Fig.1. The dash-dotted line is for SBS(L) prepared at condition (c) in Fig.1.

3.2. The Uniaxial Elongational Viscosity

Figure 3 shows the elongational viscosities of SBS(L) prepared at the three conditions at 140°C. The lamellar-like structures at three preparation conditions were different from one another. Within these preparation conditions, however, the elongational viscosities for SBS(L) were hardly influenced. The strain-softening properties were observed for all samples.

Fig.3. Uniaxial elongational viscosity of SBS(L) at three different preparation conditions: (top) condition (a); (middle) condition (b); (bottom) condition (c). Uniaxial elongational measurements were conducted at 140°C under different constant strain rates (s^{-1}): (●)0.35; (■)0.032; (▲)0.0027; (○)0.38; (□)0.031; (△)0.0041; (▽)0.31; (◇)0.032; (×)0.0027.

The elongational viscosities of SBS(L) and SBS(S) were measured at different temperatures. It is important to clarify whether the SBS block copolymers have single- or two-phase structure at measurement temperatures, since these SBS samples have UCST (upper critical solution temperature) phase diagram. Rheological and SAX analysis are well-known techniques to determine their transition temperatures between single- and two-phase structures. Here, rheological measurement was carried out to estimate them[15]. Dynamic shear viscosity of SBS (L) and SBS (S) samples under 220°C increased as decreasing frequency down to $0.1 s^{-1}$. This dynamic shear behavior indicates that their transition temperatures are substantially higher than 220°C. Thermal gravimetric analysis (TGA) shows that both samples are stable only below 220°C. Thus, it is difficult to determine their precise transition temperatures due to their thermal instability. All of our measurements were performed below 220°C where both samples have two-phase structure.

Figure 4 shows the elongational viscosities of SBS (L) at 140, 160, and 180°C. Note that the strain-softening properties were observed for the elongational viscosities at all the strain rates studied (0.005 to $0.5 s^{-1}$). The

Fig.4. Uniaxial elongational viscosity for linear SBS (L) melt at 140, 160, and 180°C under various constant strain rates (s^{-1}): (○)0.35; (□)0.14; (△)0.033; (◇)0.0027; (●)0.37; (■)0.14; (▲)0.038; (▽)0.33; (◆)0.17; (▼)0.042.

Fig.5. Uniaxial elongational viscosity for star SBS (S) melt at 140, 160, and 180°C under various constant strain rates (s^{-1}): (○)0.36; (□)0.13; (△)0.038; (◇)0.0040; (●)0.35; (■)0.12; (▲)0.032; (◆)0.0035; (▽)0.39; (+)0.13; (▼)0.043; (×)0.0044.

linear elongational viscosity was consistent with that predicted from dynamic shear measurement. This is the first observation of the strain-softening property in the elongational viscosities of polymer melts, which is quite opposite to the strain-hardening property of linear homopolymer melts. The other characteristic is the Hencky strain at which the strain-softening property starts to appear, i.e., the critical strain. The critical strain of SBS (L) was found to be around 0.3, which is slightly

smaller than the usual starting point for linear homopolymers' strain-hardening property[16]. Figure 5 illustrates the elongational viscosities of SBS (S) at 140, 160, and 180°C. The linear elongational viscosity was consistent with that predicted from dynamic shear measurement. The strain-softening properties were also observed for the elongational viscosities at all the strain rates studied (0.005 to 0.5 s^{-1}). The critical strain of SBS (S) was also found to be around 0.3.

3.3. The Observation of Structural Changes

Now let us study the structural change before and

after elongation in order to get insight into the origin of the strain-softening property. In heterogeneous polymer systems, the change of microdomain structure has strong influence on the melt rheology. The sample prepared at the condition (a) in Fig. 1 was used for the observation of structural changes. To study this influence, we rapidly cooled the samples in ice/water solution, immediately after the Hencky strain became 2 at the strain rate of 0.2 s^{-1} . Figures 6 and 7 show SAX before and after elongation (Hencky strain of 2, strain rate of 0.2 s^{-1} at 140°C) for SBS (L) and SBS (S), respectively. Results suggested that the lamellar structures are oriented along the

Fig.6. SAX for lamellar structures of SBS (L) before (upper data in each figure) and after elongation (lower data in each figure) (Hencky strain of 2, strain rate of 0.2 s^{-1}). Top, middle, and bottom figures show SAX data at three different setting conditions, respectively.

Fig.7. SAX for lamellar structures of SBS (S) before (upper data in each figure) and after elongation (lower data in each figure) (Hencky strain of 2, strain rate of 0.2 s^{-1}). Top, middle, and bottom figures show SAX data at three different setting conditions, respectively.

elongational direction after the test for both samples. The lamellar thickness (S+B phases) and orientation were evaluated for samples before and after elongation by peak angle and intensity. Rod-like samples before and after the elongation were obtained through rapid cooling from heated silicon oil bath into ice/water solution. Sample length did not change while it was kept at room temperature for measurement of SAX. For SBS (L), the lamellar thickness changed from 28.7 to 26.3 nm by elongation. For SBS (S), the lamellar thickness was changed from 26.9 to 24.5 nm. These results suggested that lamellar thickness was hardly changed during elongation. Enhanced orientation of the lamellar structure through elongation was observed as increased peak intensity after elongation for both samples in Figures 6 and 7. Little change of lamellar thickness and more orientation of lamellar structure through elongation were confirmed by TEM.

Here, the origin of the strain-softening properties of SBS melts samples is discussed by comparing with the origin of the strain-hardening properties, i.e., high elasticity, of SBS solid observed at a room temperature. The structural change of SBS under elongation at a room temperature was reported before [17, 18]. The structure of molten SBS(L) after elongation is distinguished from that after elongation at 23°C, which exhibits fragmented PS domains in PB matrix[17, 18]. Hashimoto et al. reported that an enormous increase of interfacial regions by fragmentation induced high elasticity[17, 18]. In solid SBS(L), the interfacial area at large deformation increases by the fragmentation of PS phase because the mobility of SBS molecules is very low. On the other hand, in molten SBS(L), the increase of the interfacial area is prevented by the large mobility of SBS molecules. In molten SBS(L), the amount of interfacial regions seems to be constant during elongation, since the lamellar thickness seems to be almost constant and no fragmentation is observed. In addition, weight averaged molecular weight of a PS block in one part is 16000, which is slightly smaller than M_e (entanglement molecular weight)[19] of PS. Structural change with the constant lamellar thickness during deformation easily occurs. To keep the constant interfacial tension, the lamellar structure needs to be oriented along the elongational direction. This seems to be the major cause for the molten SBS(L) to exhibit lack of elasticity during elongation.

3.4. The Interpretation based on the BKZ Model

It is difficult to explain the strain-softening property of SBS samples by long relaxation time in a similar way to homopolymer systems. A new interpretation needs to be proposed to solve this contradictory. We try to interpret strain-softening properties of SBS(L) and SBS(S) by using two terms, relaxation time and damping parameter. The BKZ constitutive analysis was carried out to understand the strain-softening property from the two terms. In the BKZ model, the elongational viscosity is described by the memory function which is determined by the relaxation spectrum and the damping function which is estimated by step-shear stress relaxation. The followings are the BKZ equations[20] we use here:

$$\sigma(t) = \int_{-\infty}^t \mu(t-t') h(I, II) C^{-1}(t, t') dt' \quad (1)$$

$$\mu(t-t') = \sum_i \frac{G_i}{\tau_i} \exp\left[-\frac{(t-t')}{\tau_i}\right] \quad (2)$$

$$h(I, II) = \frac{\alpha}{(\alpha-3) + \beta I + (1-\beta) II} \quad (3)$$

and

$$C^{-1}(t, t') = \begin{bmatrix} \exp[2\varepsilon(t-t')] & 0 & 0 \\ 0 & \exp[-\varepsilon(t-t')] & 0 \\ 0 & 0 & \exp[-\varepsilon(t-t')] \end{bmatrix} \quad (4)$$

where $\mu(t-t')$ is the time-dependent memory function, $h(I, II)$ is the strain dependent function, i.e., the damping function, $C^{-1}(t, t')$ is the Finger strain tensor.

The BKZ model is based on the separability of the linear stress relaxation modulus $G^*(t)$ and the damping function $h(\gamma)$. Step-shear relaxation modulus $G(t, \gamma)$ of SBS(L) at various strains was measured to examine whether the separability was applicable or not. The separability was applicable to the four samples. Figure 8 shows the damping functions of the four samples. For PS(L) and PS(S), the damping functions are relatively close to the prediction from Doi-Edwards theory[21].

In contrast to these homopolymers, the damping functions of SBS(L) and SBS(S) show a stronger decrease. The stronger decrease than the prediction of Doi-Edwards theory seems to be associated with the two-phase structure of the block copolymers. The elongational strain into the samples was used for orienting lamellar like structures. This seems to be the major cause for the stronger decrease in the damping functions of the block copolymers.

Let us discuss why the damping function of SBS(S) exhibits stronger decrease than that of SBS(L). The S/B weight ratio of SBS(S) is similar to that of SBS(L). The arm length of SBS(S) is similar to the half of SBS(L). If one arm is pulled out from S domain by large deformation, another arm would be easily pulled out together in SBS(S)[22]. This seems to be one cause for the difference of the damping functions between SBS(S) and SBS(L).

Fig.8. Comparison of damping functions among homopolymers and block copolymers: PS (L) (○); PS(S) (□); SBS(L) (●); SBS(S) (■). The solid line is the prediction from the Doi-Edwards theory. The dotted line is obtained from the equation: $1 / (1 + a\gamma^2)$, by using the parameter "a" of 0.42.

One important factor is the damping function in the BKZ model. For SBS(L), the damping function was fitted with the following Eq.(5) by using the parameter "a" of 0.42:

$$h(\gamma) = 1 / (1 + a \gamma^2) \quad (5)$$

The reciprocal value of "a" is the value for " α " in the Eq.(4). The other important factor, the relaxation spectrum, was calculated from storage modulus G' and loss modulus G'' . The relaxation spectrum of SBS(L) is listed in Table 1. The longest relaxation time is assumed based on the fact that it is much longer than 100s from G' and G'' , since it is difficult to determine the longest value precisely.

By using the result of the damping function ($\alpha=2.4$) and the relaxation spectrum in Table 1, the elongational viscosity of SBS(L) at 140°C was predicted by the BKZ model. Figure 9 shows the comparison of the prediction and the experimental values of the elongational viscosity of SBS(L) at 140°C. Figure 9 suggests that the experimental elongational viscosity of SBS(L) at 140°C is predicted by the BKZ model. The good agreement suggests that the strain-softening property of SBS(L) melt is induced by the strong decrease of the damping function.

Let us examine the small critical strain value of SBS(L) and SBS(S). The critical strain of low density polyethylene (LDPE) is around 0.75, while that of linear homopolymer such as polystyrene (PS) is around 0.5[16]. The damping function of LDPE starts to decrease around shear strain

of two, while that of PS starts to decrease around unity. SBS(L) and SBS(S), on the other hand, shows strong decrease of the damping function which starts at shear strain less than unity. It is supposed that this early start of the decrease of damping functions causes the small critical strain of SBS(L) and SBS(S).

4. CONCLUSION

1. During elongation of SBS(L) and SBS (S) in the molten stage, the lamellar structures are oriented but the lamellar thickness remains almost constant. The number of lamella along the diameter direction decrease, resulting in the strain-softening property. The strain-softening property is hardly influenced by chain structures (linear or 4 arms star) and preparation conditions.

2. The cause of strain-softening property of SBS(L) is discussed by two terms, i.e., relaxation time and damping parameter. The stronger damping of SBS(L) and SBS(S) than that of Doi-Edwards prediction causes the strain-softening elongational viscosity. The small critical strain in the elongational viscosity is also associated with the strong damping.

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Table 1. Relaxation spectrum of SBS (L) at 140°C

Time(s)	Modulus(Pa)	Time(s)	Modulus(Pa)
0.00100	180000	10.0	5750
0.00316	118000	31.6	3020
0.0100	98100	100	1330
0.0316	65600	316	590
0.100	53300	1000	256
0.316	33800	3160	104
1.00	18100	10000	43.0
3.16	11700	31600	15.7
		100000	5.27

Fig.9. The predicted elongational viscosity from BKZ model ($\alpha=2.4$, $\beta=6$) and the experimental elongational viscosity for SBS(L) at 140°C under various constant strain rates (s^{-1}): (○)0.35; (□)0.14; (△)0.032; (◇) 0.0027.