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Article

Effect of Flexible Fibers on Rheological Properties of Poly(Lactic Acid) Composites under Elongational Flow

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Rheological properties of polymer composites with flexible fine fibers are studied employing poly(lactic acid) PLA containing a small amount of polymeric fibers of poly(tetrafluoroethylene) PTFE, poly(butylene terephthalate) PBT, and poly(4-methyl-1-pentene) PMP. Both PBT and PMP fibers are prepared by hot-stretching of the blends with PLA, whereas PTFE fibers are obtained by simple mixing of PLA and PTFE powder at the temperature between Tm's of both polymers. The polymer composites with PTFE and PBT fibers whose diameters are smaller than 1 μm show marked strain-hardening behavior in elongational viscosity, *i.e.*, rapid increase in the transient elongational viscosity with time or strain. On the contrary, the composite with PMP fibers with a diameter of *ca*. 2 μm shows no strain-hardening, although the elongational viscosity is enhanced in the measured strain/time range irrespective of the strain rate.
Key Words: Elongational viscosity / Fiber dispersion system / Flexible fibers / Poly(lactic acid)

1. INTRODUCTION

Enhancement of strain-hardening behavior in elongational viscosity is desired for various types of linear polymers to widen processing methods and thus applications. In general, strain-hardening behavior is observed for a polymer melt with long-chain branches[1-6] because of the marked chain stretching between branch points as pointed by advanced molecular models.[7-9] However, it is not easy to incorporate long-chain branches in commercial polymers in the industrial scale. Therefore, a new method is required to provide the strain-hardening behavior. Meanwhile, it was found that addition of a small amount of a weak gel whose chain segment is miscible with a matrix polymer gives marked strain-hardening in elongational viscosity presumably due to chain stretching of the weak gel, whereas the viscous properties under shear are hardly affected.[10-12]

Addition of a linear polymer with high molecular weight also enhances the strain-hardening behavior.[13,14] In particular, interesting results have been reported recently on the blends of low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), in which LLDPE shows higher shear viscosity than LDPE.[14] Although the addition of LLDPE decreases the content of long-chain branches in a system, the chain-stretching becomes pronounced. This phenomenon is attributed to prolonged relaxation time of linear molecules surrounding a branch molecule. As a result, both dynamic tube dilation and constraint release of the branch molecule hardly occur.[6,14]

Recently, mixing with nanofibers is also believed to provide the strain-hardening in elongational viscosity. One of the most famous systems is the blend with nanofibers of poly(tetrafluoroethylene) PTFE.[15,16] In this technique, PTFE particles are turned into fibrous shape in the molten polymer by fragmentation of PTFE agglomerates under shear force.[17] Moreover, fine fibers of poly(butylene terephthalate) PBT, prepared by melt stretching in the matrix polymer of poly(lactic acid) PLA or polypropylene PP, gives the strain-hardening behavior in elongational viscosity.[18,19]

Historically, rheological properties of composites with flexible fibers were originally studied employing a pulp dispersion system. Based on the model proposed by Arlov et al.,[20] in which the role of flexibility of pulp was discussed, Forgacs and Mason predicted the critical stress σ_{crit} to bend a fiber.[21]

$$\sigma_{crit} \equiv \left(\dot{\gamma}\eta_m\right)_{crit} \cong \frac{E_Y\left(\ln\left(2p\right)-1.75\right)}{p^4} \tag{1}$$

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where E_Y is the Young's modulus and p is the aspect ratio.

Recently, Switzer et al. defined the dimensionless bending stiffness.[22)]

$$S^{eff} = \frac{E_Y \pi}{64 \eta_m \dot{\gamma} p^4} \quad (2)$$

When a fiber behaves a completely flexible thread, S^{eff} is zero. On the contrary, S^{eff} becomes infinity when a fiber is considered as a rigid body under flow. Flexible fibers form network structure beyond the critical content, which will deform to the flow direction with keeping interparticle interaction. On the contrary, rigid fibers tend to orient to the flow direction, leading to weak interparticle interaction at the steady-state.

Meyer and Wahren proposed the simple fiber network theory, in which frictional force between fibers provides the elasticity.[23)] Bennington et al. experimentally revealed that the yield stress to flow is proportional to ϕ^β (ϕ is the volume fraction), where the exponent β is in the range between 2.5 and 3.5.[24,25)] Moreover, they pointed that yield stress σ_Y of a pulp dispersion is given by the following relation.

$$\sigma_Y = k E_Y p^2 \phi^3 \quad (3)$$

where k is a constant.

Onogi et al. confirmed the equation and clarified that the yield stress has a close relation with a plateau modulus.[26)] Similarly, Damani et al. proposed the following relation of a plateau modulus,[27)] which was confirmed by Tatsumi et al. using an aqueous dispersion with cellulose fibers.[28)]

$$G = A\phi^a \quad (4)$$

where a is a constant between 2.2-2.7.

Rheological properties of a system with other flexible fibers have been also studied recently because of the rapid increase in the attention to nanofibers. According to the studies, it is believed that flocculation of fibers plays an important role in the rheological properties.[29-32)] Soszynski et al.[29)] found that flocs formation of nylon fibers occurs due to mechanical contacts and coherence of the fibers due to interlocking by the elastic bending of the fibers, which is called "elastic fiber interlocking". Keshtkar et al. demonstrated that the steady-state values as well as the maximum values at overshooting for both shear stress and normal stress difference increase with flexibility of fibers, because of frequent contacts between fibers.[32)]

It has been also demonstrated that the rheological properties of fiber dispersion systems are strongly affected by the flow type. While a small amount of rigid fibers hardly affect shear viscosity, its contribution to elongational stress cannot be ignored.[33)] The marked enhancement of elongational stress, but without strain-hardening, was clearly demonstrated by Mewis and Metzner using composites containing fine glass fibers with large aspect ratio.[34)]

In this study, three types of fine flexible fibers are dispersed in the molten PLA to enhance the melt elasticity. As well nown, PLA, as a biomass-based plastic, is a great candidate to replace from conventional plastics obtained from fossil resources. Although it has various attractive properties such as marked rigidity, high melting point, and biodegradability, processability at some processing operations needs to be improved because of the poor melt elasticity. This is attributed to the linear structure with narrow distribution of molecular weight as similar to another biomass-based polyester.[12] Therefore, the effect of the species of fibers on the rheological properties, especially elongational viscosity, is investigated in detail employing PLA composites.

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

A matrix polymer used was PLA (Mitsui Chemicals, LACEA H-440). The molecular weights were Mn = 1.5 x 10^5 and Mw = 2.5 x 10^5. The optical purity of L-lactic acid is approximately 96 % and the melting point is 152 ºC. Moreover, PBT and poly(4-methyl-1-pentene) PMP were employed for fibers. Besides them, acrylate-modified PTFE (Mitsubishi Rayon, Metablen A3000) was also employed. Melting points of PBT, PMP, and PTFE are 225, 240, and 340 ºC, respectively.

The fiber formation of PBT and the blend preparation method with PLA were mentioned in our previous paper.[18)] The same method was employed to prepare the blend with fibrous PMP. The blend samples were extruded and melt-stretched at 250 ºC by a capillary rheometer (Yasuda Seiki Seisakusho, 140-SAS-2002) equipped with a circular die having the following dimensions; 20 mm in length, 1.0 mm in diameter, and the entrance angle of 180º. The applied shear rate at melt-stretching was 70 s^{-1} and the sample was cooled down in the air gap. The draw ratio was 5, which was the highest one to stretch the extruded strand without any instability. In other words, the diameter of the fibers was controlled to be the smallest value for the blend system.

Moreover, PTFE was mixed with PLA at 180 ºC, lower than Tm of PTFE, using an internal batch-type mixer (Toyoseiki, Labo-plastmil) for 3 min at the blade rotation speed of 40 rpm. The peculiar fiber formation mechanism of PTFE during mixing was described in our previous paper.[17)]

The fiber contents in each blend system were 1 and 5 wt%.

The blend samples were compressed into flat sheets by a laboratory compression-molding machine at 180 ºC under 10 MPa for 3 min. Furthermore, flat sheets of pure PTFE, PBT, and PMP were also prepared by the compression-molding at 250 ºC under 10 MPa for 3 min to evaluate the modulus of the fibers. Because the cohesive force between neighbor crystalline chains is not strong for PTFE, they are reorganized by the exposure to a low level of shear force even in the solid state.[16] As a result, a PTFE flat sheet with smooth surface can be prepared even below Tm.

2.2 Measurements

The temperature dependence of tensile storage modulus in the solid state was measured at 10 Hz using rectangular films at the heating rate of 2 ºC/min. The steady-state shear viscosity of PLA, PBT and PMP was measured at 250 ºC by the capillary rheometer using the same die employed for melt-stretching.

The shape of fibers was checked by a scanning electron microscope (SEM) (Hitachi, S4100). For the purpose, PLA fraction was removed out by chloroform as mentioned in our previous paper.[18] Prior to the observation, the samples were coated by Pt-Pd. The number average diameter was calculated using more than 100 fibers.

The frequency dependence of oscillatory shear moduli was evaluated at 180 ºC by a cone-and-plate rheometer (UBM, MR-500). The shear stress and primary normal stress difference were also measured at 180 ºC as a function of shear rate.

The drawdown force, defined as the force required for the uniaxial extension of a polymer melt, was evaluated at 180 ºC by the capillary rheometer equipped with a capillary die having the following dimension: 8 mm in length, 2.095 mm in diameter, and an entrance angle of 90°. An extruded strand was vertically pulled through a tension detector (Nidec-Shimpo, tension-meter PLS) at a constant draw ratio of 7.

The transient curves of uniaxial elongational viscosity were measured by a rotational rheometer (TA Instruments, AR 2000ex) equipped with a universal testing platform and a CCD camera.

3. Results and DISCUSSION

3.1 Characteristics of Raw Materials

Figure 1 shows the temperature dependence of the dynamic tensile moduli for the materials employed as fibers. As seen in the figure, all three polymers such as PBT, PMP, and PTFE exhibit almost the same tensile storage modulus, i.e., approximately 0.2 GPa, at the temperature of the rheological measurements, 180 ºC. The modulus of PTFE is almost a constant in the temperature range due to the high melting point. PMP shows marked α dispersion ascribed to the motions outside the lattice such as sliding of the lamellae with respect to each other with a frictional resistance.[35]

Figure 2 compares the shear viscosity at the mixing temperature with PLA. Neither Bagley nor Rabinowitsch corrections are carried out. Since the melting point of PTFE is greatly higher than the mixing temperature, it is not shown in the figure.

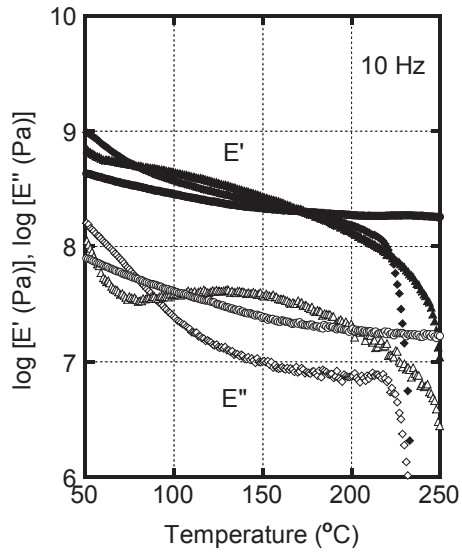

Fig. 1. Temperature dependence of (closed symbols) tensile storage modulus E' and (open symbols) loss modulus E" at 10 Hz for (circles) PTFE, (diamonds) PBT, and (triangles) PMP.

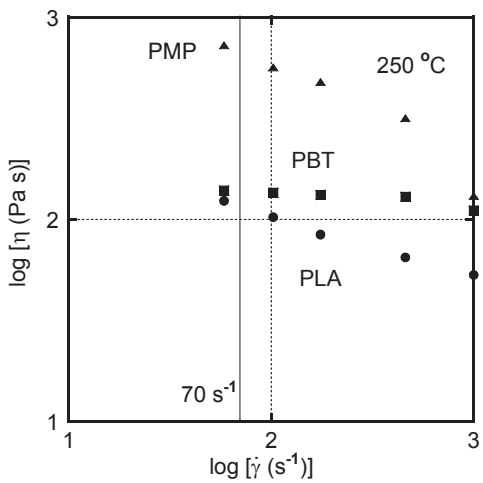

Fig. 2. Shear viscosity 7 as a function of shear rate $\dot{\gamma}$ at 250 ºC for (circles) PLA, (diamonds) PBT, and (triangles) PMP.

As seen in the figure, shear viscosities of both PBT and PMP at 250 ºC are higher than that of PLA in the intense fashion of PMP. Considering that the shear rate in the capillary die at the melt stretching process was calculated to be 70 s^{-1}, PBT shows similar shear viscosity to PLA. On the contrary, PMP has significantly higher shear viscosity, which prohibits the deformation of PMP phase in the shear flow as originally suggested by Grace.[36] The viscosity difference results in the large diameter of PMP fibers.

3.2 Characteristics of Fibers

Figure 3 exemplifies the SEM picture of PMP fibers after removal of PLA by chloroform. Prior to SEM observation, the attenuated total reflectance of infra-red spectroscopy and thermal analysis by a differential scanning calorimeter are carried out employing the insoluble parts, and it is confirmed that PLA is fully extracted. The result demonstrates that the fibers are not covered by PLA chains. This is reasonable because the interfacial tension is 0.4 mN/m even between PLA and PBT,[18] suggesting that interfacial thickness in the molten state is much smaller than the radius of gyration of a molecule. Moreover, the specific interaction between PLA chains and the fibers cannot be detected by the characterization performed in this study.

The diameter of the fibers is in the range between 0.5 μm and 7.0 μm, and the number average value is 2.2 μm. This fiber formation is attributed to the large value of the critical Capillary number as discussed in the previous work.[18] Moreover, the diameter of the PMP fibers is larger than that of the PBT fibers (average value is 600 nm). This is attributed to the large interfacial tension as well as the high shear viscosity at the melt-stretching process. As mentioned in the experimental part, they are the finest fibers for each blend system at the present experimental condition. In the case of PTFE fibers, the average diameter (200 nm) is the same as that of the primary particles after polymerization. Furthermore, the diameter of PTFE fibers cannot be controlled by the stretching condition owing to the peculiar fiber formation process.[17]

Since the aspect ratio of all fibers is much larger than 100, the dimensionless bending parameter S^{eff} defined by eq. 2 is lower than 10^{-5} (assuming that the stress is 10 kPa s), indicating that all fibers are significantly flexible following the definition by Switzer et al.[22]

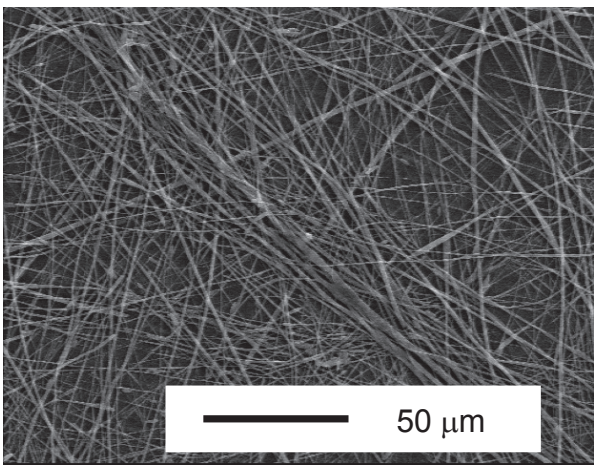

Fig. 3. SEM pictures of PMP fibers extracted from drawn PLA/PMP (80/20) by chloroform.

3.3 Rheological Properties of Blend

Figure 4 shows the oscillatory shear moduli for PLA and the blends with fibers at 180 ºC. Since the melting points of all fibers are higher than 180 ºC, they exist in the solid state. As increasing the fiber content, both moduli increase especially

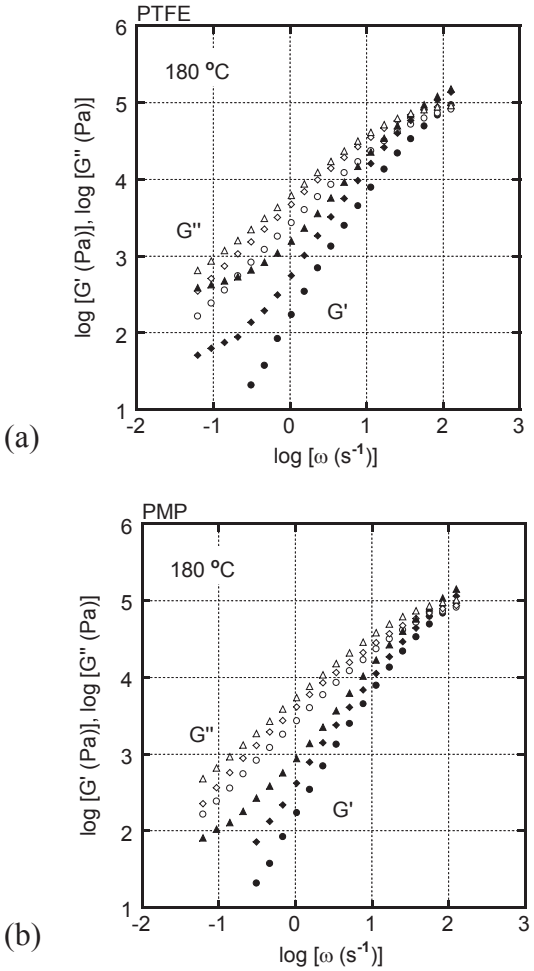

Fig. 4. Frequency dependence of (closed symbols) shear storage modulus G' and (open symbols) loss modulus G'' at 180 ºC for (a) PLA/PTFE blends (circles) PLA, (diamonds) PLA/PTFE (99/1) and (triangles) PLA/PTFE (95/5); and (b) PLA/PMP blends (circles) PLA, (diamonds) PLA/PMP (99/1), and (triangles) PLA/PMP (95/5).

in the low frequency region because of the interparticle interaction. The enhancement is more obvious in the blends with PTFE. Although the data of PLA/PBT blends are not shown here (see Fig. 4 in the previous paper[18]), both moduli are located between PLA/PTFE and PLA/PMP. The results indicate that the interparticle interaction is pronounced for fine fibers, although detailed discussion should be carried out using the fibers prepared from the same polymer species, having various diameters.

Figure 5 shows the shear stress and primary normal stress difference for the PLA and the blends with PTFE or PMP at 180 ºC. In this experiment, both stress levels become almost constant in a short time, which are recognized as the steady-state values. As similar to the oscillatory shear modulus in Fig. 4, the data of PLA/PBT are located between PLA/PTFE and PLA/PMP.[18] Therefore, it is suggested that the normal stress is pronounced for the system with finer fibers. On the other hand, it has a negligible effect on the shear stress even by PTFE fibers. The enhanced elastic nature, especially for blends with finer fibers, is also confirmed by the drawdown force as summarized in Table I. However, the flocculation, which is greatly affected by the flow history, should be considered seriously for quantitative discussion as preliminary indicated for the blend of PP and PTFE fibers.[16]

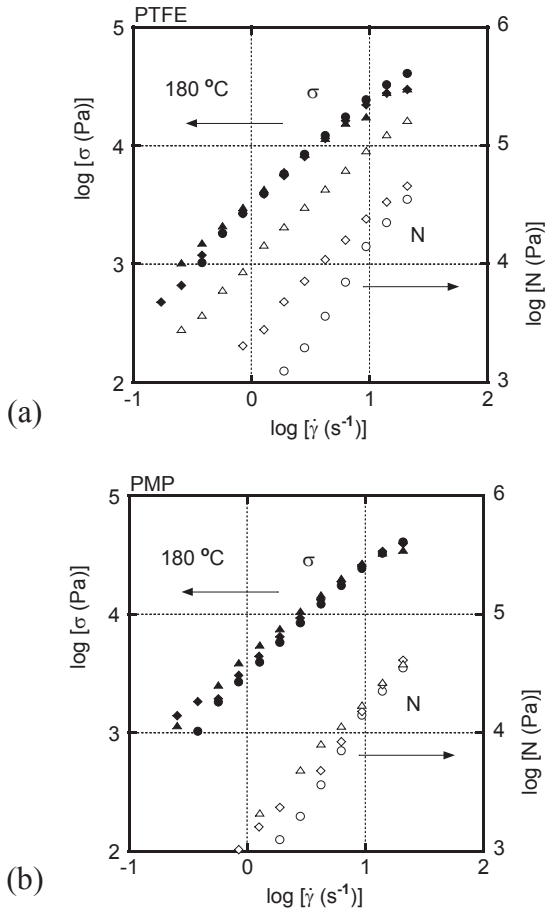

Fig. 5. Shear rate dependence of (closed symbols) shear stress σ and (open symbols) normal stress difference N at 180 ºC for (a) PLA/PTFE blends (circles) PLA, (diamonds) PLA/PTFE (99/1) and (triangles) PLA/PTFE (95/5); and (b) PLA/PMP blends (circles) PLA, (diamonds) PLA/PMP (99/1), and (triangles) PLA/PMP (95/5).

Figure 6 shows the growth curves of uniaxial elongational viscosity. The solid line in the figure, $3\eta^{+}(t)|_{\dot{\gamma}\to 0} = \eta_E^{+}(t)|_{\dot{\varepsilon}\to 0}$, represents the elongational viscosity in the linear region calculated from the oscillatory shear modulus in Fig. 3 by the following relation.

$$\eta_E^{+}(t)\Big|_{\dot{\varepsilon}\to 0} = 3\sum_{i=1}^{N}\tau_i\left(1-e^{-t/\tau_i}\right)H(\tau_i) \qquad (5)$$

where $\dot{\varepsilon}$ is the elongational strain rate and $H(\tau)$ is the relaxation spectra.

The elongational viscosities of pure PLA are independent of the strain rate and correspond with the predicted values by eq.5.[18] On the contrary, the blend with 1 wt% of PTFE fibers shows marked strain-hardening as similar to the blend with PBT fibers,[18] which is considerably important for polymer processing because it prevents localized deformation at foaming, blow-molding, and thermoforming. Furthermore, the reduction of neck-in is also expected.

The experimental results roughly correspond with the drawdown force. Moreover, the figures demonstrate that the elongational viscosity of the composites with flexible fibers has the following two aspects; (1) the strain-hardening behavior is detected when the fiber is fine; and (2) elongational viscosity prior to strain-hardening is enhanced irrespective of the strain rate.

In the case of the former one, stretching and orientation of the fibers may affect the strain-hardening to some degree. However, they will not be a dominant mechanism considering

Table I Drawdown Force of Various Composites with Fibers

Polymer	Content (wt%)	Drawdown Force (mN)
—	0	15 - 20
PTFE	1	55 - 65
	5	220 - 475
PBT	1	50 - 60
	5	160 - 195
PMP	1	30 - 35
	5	45 - 55

the diameter of fibers (they are too large to show marked Brownian motion). Considering the studies on pulp-dispersion systems, the strain-hardening could be attributed to the frictional force between fibers and bending force. They will become less important for fibers with large diameter due to the lack of flexibility, although the dimensionless bending parameter of all fibers employed is lower than 10^{-5}. The experimental results indicate that more appropriate parameter to express the flexibility is required.

On the other hand, the latter one will be explained by the excess deformation of a matrix polymer located between neighboring fibers as predicted by the slender-body theory.[33)]

$$\eta_E = 3\eta_m + \frac{4}{3}\eta_m \frac{\phi\, p^2}{\ln(\pi/\phi)} \qquad (6)$$

where η_E is the uniaxial elongational viscosity of a suspension and η_m is the shear viscosity of a matrix.

The enhancement of elongational viscosity prior to the strain-hardening is almost similar for all three composites.

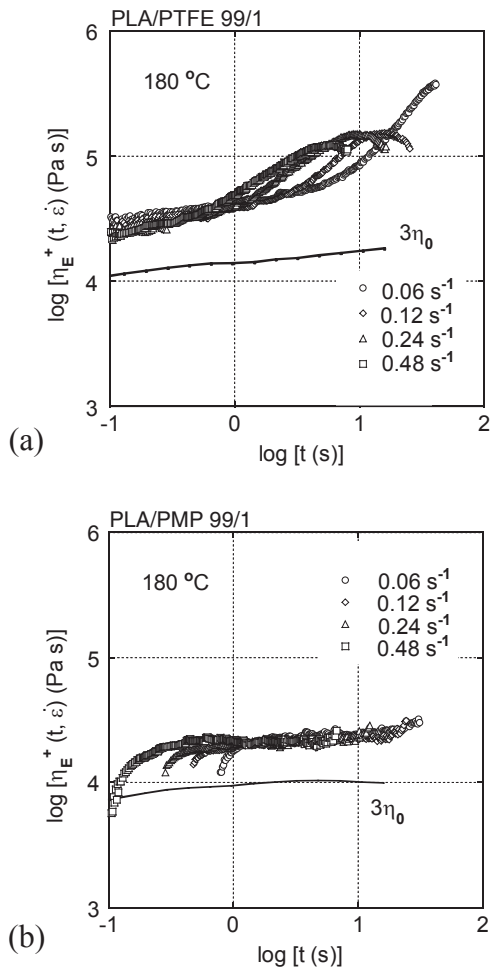

Fig. 6. Growth curves of elongational viscosity at various strain rates at 180 ºC for (a) PLA/PTFE (99/1) and (b) PLA/PMP (99/1).

Although the aspect ratio of the fibers employed cannot be evaluated quantitatively, eq.6 predicts that three species of fibers have a similar value.

4. CONCLUSION

Rheological properties of polymer composites of PLA with flexible polymeric fibers are studied using three types of fibers with various diameters, such as PTFE (200 nm), PBT (600 nm), and PMP (2.2 μm). The composites show enhanced normal stress difference, when the fiber is fine. It is also found that elongational viscosity prior to the strain-hardening is enhanced irrespective of the strain rate for all composites, as similar to composites with rigid fibers. The excess deformation of a matrix between fibers will be responsible for the enhancement. Moreover, a small amount of PTFE and PBT fibers provides the strain-hardening behavior in elongational viscosity, although it is not observed for the composite with PMP fiber whose diameter is around 2.2 μm. As similar to a pulp dispersion system, frictional force between the fibers and/or bending force could be the main origins of the strain-hardening. However, the detailed mechanism with the effect of flocculation is still unknown. Systematic experiments using fibers with various diameters, prepared from the same polymer species, will be required for the further discussion. The present experimental results, at least, demonstrate that the diameter, *i.e.*, flexibility, is the critical factor to decide the strain-hardening behavior, although the stiffness parameter proposed cannot predict the difference in the rheological properties.

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