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Influence of glass beads on the elongational viscosity of polyethylene with anomalous strain rate dependence of the strain-hardening

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The elongational viscosity of HDPE and the same polymer filled with glass beads was measured. The strain-hardening of neat HDPE showed anomalous strain rate dependence; the behaviour became weaker as the strain rate increased. The strain-hardening of the HDPE filled with glass beads weakened with increasing bead contents. Suppression of the strain-hardening by the beads is stronger at high strain rate, where the strain-hardening of neat HDPE is weak. Especially, the strain-hardening did not appear if the bead contents and the strain rate are sufficiently high. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Since the elongational flow is dominant in various polymer processings such as blow moulding, film moulding and melt spinning, the elongational properties of polymer melts play an important role in understanding the processability of polymers. For example, polymers whose elongational viscosity shows strong strain-hardening have a good processability in the blow moulding.

For the last two decades, uniaxial elongational viscosities have been investigated for various homogeneous polymers such as polystyrene (PS)[1,2], polypropylene (PP)[3,4], polybutene-1[5] and polyethylenes (high density polyethylene (HDPE)[6–8], linear low density polyethylene (LLDPE)[9,10] and low density polyethylene (LDPE)[11–13]). In these polymers, the increase of the viscosity with time can be divided into two stages. In the first stage, which appears at small strain, the viscosity is independent of strain rate and increases slowly with time, until a critical time is reached. The viscosity at various strain rates is shown as a common curve. In the second stage, which appears at large strain, the viscosity depends on the strain rate. Beyond the critical time, the viscosity curves deviate from the first stage and rapidly increase. This increased behaviour is called the strain-hardening phenomenon. In this paper, these stages are designated as strain rate independent region and strain-hardening region, respectively. A number of experimental studies[1–13] on the elongational flow of homogeneous polymer melts have been made to clarify the effects of molecular parameters such as molecular weight, molecular weight distribution and long-chain branching. These studies have shown that the strain-hardening phenomenon of homogeneous polymers is closely related with the long-time relaxation which is caused by the existence of the long-chain branching or a small amount of extremely high molecular weight chains.

In most homogeneous melts, the strain-hardening phenomenon is more remarkable at higher strain rate than at lower strain rate. However, we[14] found that the viscosity curves for a certain blow grade HDPE show stronger strain-hardening at lower strain rate. This anomalous strain rate dependence is contrary to the standard belief. In blow moulding, high molecular weight HDPE and composites of it with inorganic fillers have been employed for many years. Therefore, the elongational viscosity for the composite whose base polymer shows the anomaly must also be examined.

In the previous papers, we have measured the elongational viscosity of polystyrene/potassium titanate whisker composite melts[15,16]. From those results, it has turned out that, with increasing whisker content, the viscosity in the strain rate independent region increases but the strain-hardening is suppressed.

In this paper, we examine the effects of spherical glass filler on the strain-hardening of high molecular weight HDPE which has the anomalous strain rate dependence. We also study whether Trouton law[17] can be applied to the reinforced polymer.

Experimental

The polymer employed in this study was a high molecular weight HDPE with a broad and bimodal molecular weight distribution. The weight-average molecular weight (M_w) is 2.5×10^5, and the molecular weight distribution (M_w/M_n) is 32. The spherical-shaped fillers used in this study were untreated glass beads. Specific gravity of the beads is 2.6, and the average diameter is 18 μm. Composite samples with various volume fractions of the beads were prepared. The HDPE and the glass beads were mixed by using a twin-screw extruder and were subsequently pelletized. The pellets were used for the dynamic viscoelasticity measurement. Rod-shaped composite samples for the elongational viscosity measurement were prepared by using the pellets and a

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single screw extruder. Rod-shaped samples of neat HDPE (0 vol% glass beads) were also prepared in the same way. These samples had uniform diameter of about 3 mm, and a length of about 40 cm. The contents of the glass beads are 5, 10 and 20 vol%. These are designated as PEG-5, PEG-10 and PEG-20 respectively.

Experiments under oscillatory shear were conducted by using a rotational rheometer (Rheometrics System-4) at 160°C. The test fixtures were parallel discs with a diameter of 25 mm.

Uniaxial elongational viscosity measurements were performed by using a Meissner-type elongational rheometer. The apparatus was the same as those reported in our previous study[3]. A rod-shaped sample was held in a bath filled with silicon oil KF50-100cs (Shinetu Chemical Company, Japan) and was melted at 160°C. The sample was relaxed completely before elongation. Then the molten sample was elongated at a constant strain rate. By monitoring the sample diameter during elongation by CCD camera (PHOTRON Co. Ltd., CCD video camera module), slippage between the sample and the rotating clamps was corrected. The setting strain rates used were in the range 0.005–0.5 s^{-1}.

Results and discussion

The storage modulus G' and loss modulus G'' were obtained as a function of angular frequency ω. The resulting G' and G'' increased with glass bead contents at both low and high frequencies. Generally, a second plateau at low frequencies appears in the G' and G'' curves of high-filled samples. However, the second plateau did not appear in our samples within the range studied.

The elongational viscosity as a function of time was obtained. By observing time dependence of the sample diameter during elongation, it was confirmed that the uniform elongational deformation was achieved in the composite melts as well as homogeneous polymer melts. *Figures 1* and *2* show the time variation of the elongational viscosity for HDPE, PEG-5, PEG-10 and PEG-20 at 160°C. In the case of homogeneous polymers, it is well known that the elongational viscosity $\eta_E^+(t)$ in the strain rate independent region is very close to three times the shear viscosity $\eta^+(t)$ (Trouton law);

$$\eta_E^+(t) = 3\eta^+(t) \qquad (1)$$

To see whether this relation also holds in our composite samples, we have used the following approximate equation proposed by Osaki *et al.*[18] which enables us to estimate the shear viscosity $\eta^+(t)$ from $G'(\omega)$ and $G''(\omega)$.

$$\eta^+(t) \simeq t[G''(\omega) + 1.12G'(0.5\omega) - 0.200G'(\omega)]_{\omega=1/t} \qquad (2)$$

Solid lines in *Figures 1* and *2* are $\eta_E^+(t)$ calculated by equations (1) and (2). It can be seen that the Trouton law holds for the composite systems as well as for neat HDPE.

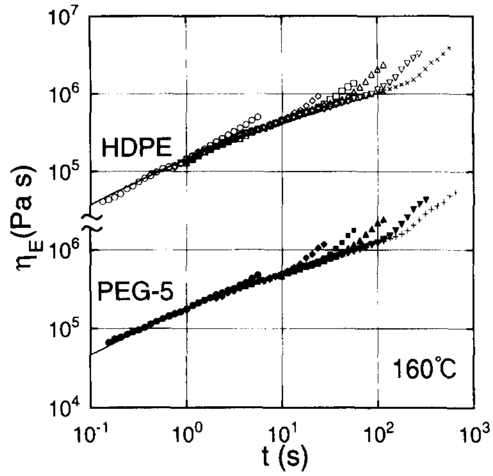

Figure 1 Uniaxial elongational viscosity as a function of time for PE and PEG-5 at various strain rates: (○) 0.40 s^{-1}; (◇) 0.077 s^{-1}; (□) 0.035 s^{-1}; (△) 0.018 s^{-1}; (▽) 0.0072 s^{-1}; (×) 0.0035 s^{-1}; (●) 0.31 s^{-1}; (◆) 0.078 s^{-1}; (■) 0.037 s^{-1}; (▲) 0.018 s^{-1}; (▼) 0.0073 s^{-1}; (+) 0.0037 s^{-1}. Solid lines are $3\eta^+(t)$ calculated from G' and G'' using equation (2)

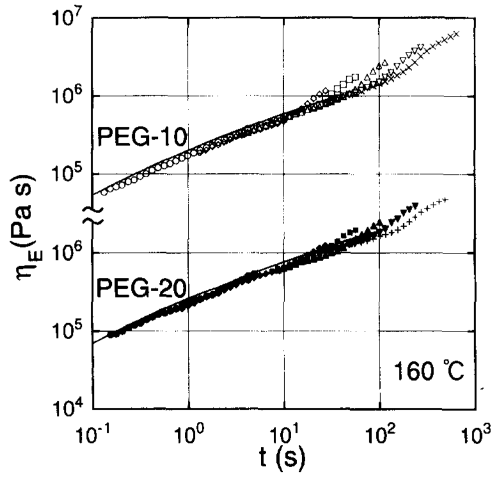

Figure 2 Uniaxial elongational viscosity as a function of time for PEG-10 and PEG-20 at various strain rates: (○) 0.32 s^{-1}; (◇) 0.077 s^{-1}; (□) 0.038 s^{-1}; (△) 0.018 s^{-1}; (▽) 0.0071 s^{-1}; (×) 0.0037 s^{-1}; (●) 0.37 s^{-1}; (◆) 0.075 s^{-1}; (■) 0.036 s^{-1}; (▲) 0.018 s^{-1}; (▼) 0.0072 s^{-1}; (+) 0.0037 s^{-1}. Solid lines are $3\eta^+(t)$ calculated from G' and G'' using equation (2)

The strain-hardening of our HDPE has the anomalous strain rate dependency; it is more remarkable at lower strain rate. HDPE with high molecular weight and broad molecular weight distribution tends to possess the anomaly in consideration for results obtained by Shinohara[6]. Strain rate dependence of the strain-hardening for our composite systems is similar to that for the neat HDPE. These strain rate dependences are analysed more quantitatively as follows. We define strain-hardening parameter (η_n) as the ratio of the viscosity value $[\eta_E^+(t,\dot{\varepsilon})]$ in the strain-hardening region to the viscosity value $[\eta_E^+(t)]$ in the strain rate independent region at the same time.

$$\eta_n = \eta_E^+(t,\dot{\varepsilon})/\eta_E^+(t) \qquad (3)$$

A plot of log η_n against Hencky strain ε for homogeneous polymer melts has a linear relation in many cases[3,5,8,13]. Strain-hardening intensity α is defined as the slope of this plot. Then, η_n can also be written as

$$\eta_n = \exp(\alpha\varepsilon^*) \qquad (4)$$

where ε^* is effective strain given by

$$\varepsilon^* = \varepsilon - \varepsilon_c, \quad \varepsilon > \varepsilon_c$$

$$\varepsilon^* = 0, \quad \varepsilon < \varepsilon_c$$

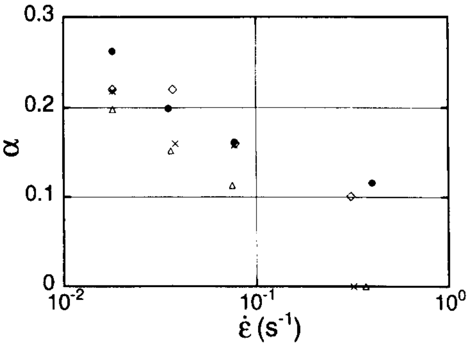

Figure 3 Strain-hardening intensity with strain rates: (●) HDPE; (◇) PEG-5; (×) PEG-10; (△) PEG-20

ε_c is the critical strain at which the strain-hardening phenomenon begins to appear. In a previous paper[16], we have reported that equation (4) also holds for polymers reinforced with fibre-shaped fillers. Equation (4) is also found to hold in the present case of HDPE reinforced with spherical fillers. The α is obtained by least square fit, and the result is shown in *Figure 3*. The α can be obtained only for the higher strain rate than $10^{-2}\,s^{-1}$. The α of neat HDPE decrease as the strain rate increases. As the bead content increases, α decreases at all strain rates. The suppression of α by the beads is more remarkable at higher strain rate. In the case of PEG-10 and PEG-20, no strain-hardening appears at sufficiently high strain rate. The strain-hardening phenomenon appears at large strain, and is generally believed to be caused by elastic behaviour of elongated polymer chains. The glass beads suppress the large deformation of matrix polymer chains around them. This may be one of the causes of the suppression of the strain-hardening by the beads.

In the blow moulding, it is important for the parison to be able to resist the draw-down. Since the draw-down occurs slowly, it can be expected that resin with the strong strain-hardening at low strain rate has a good processibility. The present composite systems show the strong strain-hardening at low strain rate and they are expected to show enough resistance to the draw-down.

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