Anomalous temperature dependence in the elongational viscosity of ethylene-based graft copolymer melts

Tatsuhiro Takahashi, Yasuyuki Takagi, Keiji Minagawa, Kenji Iwakura and Kiyohito Koyama*
Department of Materials Science and Engineering, Yamagata University, Yonezawa, 992 Japan

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The ethylene-based graft-copolymerized structure exhibited an increase in non-linearity in the elongational viscosity with temperature. This behaviour has not been observed in homogeneous polymer melts. Possible sources of the positive increase in non-linearity with temperature are indicated.

(Keywords: graft-copolymerized structure; elongational viscosity; temperature dependence)

Uniaxial elongational rheology plays an important role in the understanding of viscoelastic properties in polymer processing such as blow moulding, film moulding and melt spinning. Elongational viscosity at constant strain rate increases as a function of time in two steps. The first step is a gradual increase in viscosity in the so-called linear region. This is followed by a rapid increase in viscosity in the non-linear region. The extent of the rapid increase in viscosity is defined as the non-linearity. The effects of molecular parameters, such as molecular weight, molecular weight distribution (*MWD*) and long chain branching, on the non-linearity have been studied in the last 20 years. It has been shown that high molecular weight, broad *MWD* and long chain branching enhance non-linearity[1-3]. On the other hand, copolymerization has been used to modify the mechanical properties of polymers in the solid state. It is of interest to characterize how a graft-copolymerized structure influences the non-linearity of elongational viscosity in the molten state.

In this communication, we report the primary results to clarify the effect of graft-copolymerized structure on the non-linearity of elongational viscosity. The uniaxial elongational viscosity measurements were carried out at constant strain rate as a function of time. The dynamic shear viscosities were also measured. We have compared the experimental elongational viscosity with the elongational property predicted from dynamic shear viscosity. The effect of graft-copolymerized structure on the temperature dependence of non-linearity was also examined. Few studies of the effect of copolymerized structure on elongational viscosity have been published to date, though copolymers have been used for film moulding. Recent research on elongational viscosity has been focused on polymer blends and alloys[4]. Experimental results about the effect of copolymerized structure on elongational viscosity have not been reported.

The investigation was performed on low density polyethylene (LDPE; $M_n = 16\,100$ and $M_w = 216\,000$) and LDPE graft-copolymerized with polystyrene (LDPE-*g*-PS). LDPE-*g*-PS was prepared[5] by the melt reaction of PS onto LDPE. The weight ratios of LDPE to PS in LDPE-*g*-PS were 1:1 and 1:0.4, respectively. Details of the method of preparation and sample characteristics have been given in an earlier paper[5]. Oscillatory shear experiments were carried out using a rotational rheometer (Rheometrics mechanical spectrometer RMS800) at 140, 170 and 200°C. The elongational viscosity was measured using a Meissner-type rheometer with rod-like samples at the three different temperatures. The reliability of the experimental apparatus and the method of preparing the rod-like samples have been given in a previous paper[1].

LDPE showed typical elongational viscosity as a function of time; it showed a gradual increase in viscosity followed by rapid increase in viscosity after the Hencky strain was >1. This behaviour was observed to be almost independent of temperature. The elongational viscosity of LDPE obtained was consistent with that from an earlier study[2]. *Figures 1* and *2* show the elongational viscosity of LDPE-*g*-PS (1:0.4) and (1:1), respectively. The linear elongational viscosity became larger than that of LDPE as the PS content increased. The solid curves in *Figures 1* and *2* were calculated from dynamic shear viscosity using an approximation equation[6]. The experimental elongational viscosity almost agreed with that predicted from dynamic shear viscosity.

On the other hand, a study of the morphology by transmission electron microscopy (TEM) suggested that graft copolymerization yields PS particles of $\sim 0.5\ \mu m$ in the LDPE domain. The dynamic shear viscosity was measured for the ordered morphological structure, since the applied strain was in the linear region. The good agreement between the experimental elongational viscosity and that predicted implies that the ordered morphological structure was in the linear elongational region.

Figure 1 suggests that the elongational viscosity of LDPE-*g*-PS (1:0.4) does not show a rapid increase after the Hencky strain exceeds unity at 140°C. It is interesting

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*To whom correspondence should be addressed

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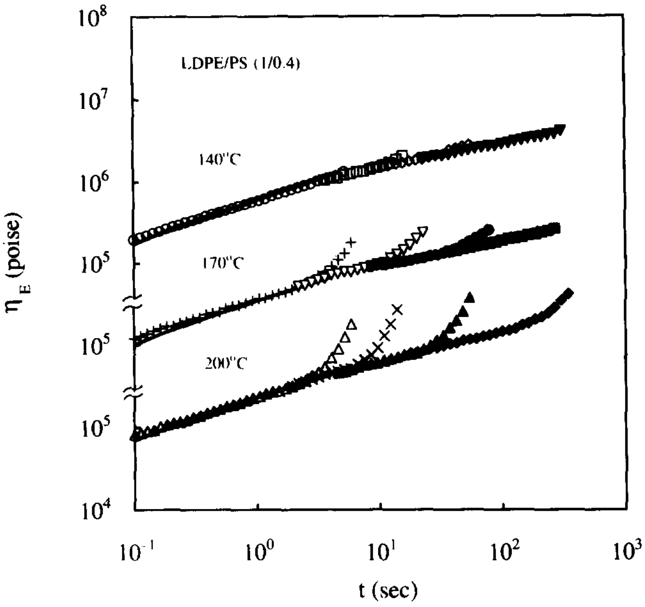

Figure 1 Uniaxial elongational viscosity for LDPE-*g*-PS (1:0.4) at 140, 170 and 200°C at various constant strain rates (s^{-1}): (○) 0.30; (□) 0.15; (◇) 0.042; (▼) 0.0045; (+) 0.38; (▽) 0.11; (●) 0.034; (■) 0.0034; (△) 0.40; (×) 0.16; (▲) 0.033; (◆) 0.0033

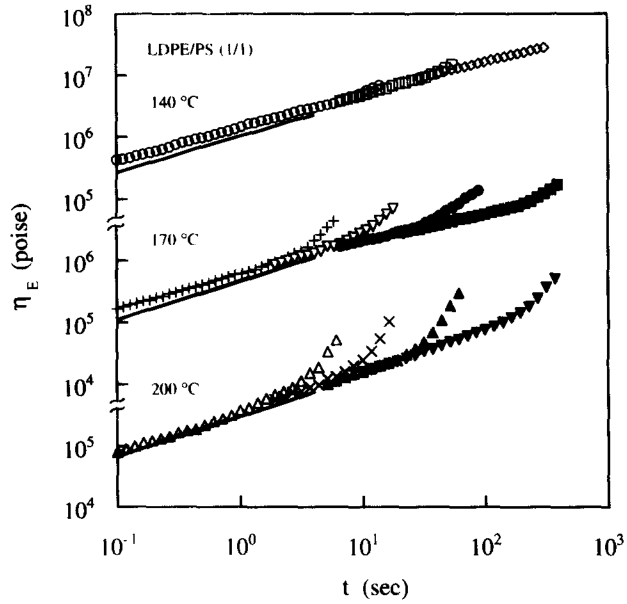

Figure 2 Uniaxial elongational viscosity for LDPE-*g*-PS (1:1) at 140, 170 and 200°C at various constant strain rates (s^{-1}): (○) 0.10; (□) 0.034; (◇) 0.0031; (+) 0.40; (▽) 0.11; (●) 0.031; (■) 0.0033; (△) 0.38; (×) 0.12; (▲) 0.031; (▼) 0.0032

that almost no rapid increase was seen at 140°C in spite of the long chain branching of PE and PS. According to TEM observation, the presence of the dispersed particles was regarded as the cause of the lack of rapid increase in viscosity. *Figure 2* also confirms almost no non-linearity in the LDPE-*g*-PS (1:1) system at 140°C. The lack of a rapid increase in viscosity is similar to the behaviour shown by acrylonitrile–styrene–butadiene (ABS) resin. ABS with >30% crosslinked butadiene particles[7] also showed yielding in stress growth in the molten state. This behaviour can be common in polymer melts with dispersed particles.

Let us discuss the origin of the small non-linearity in the polymer systems containing particles. The dynamic shear measurement revealed that LDPE-*g*-PS exhibited higher storage and loss moduli in the lower frequency region compared with LDPE. In other words, LDPE-*g*-PS gave a longer time relaxation modulus than LDPE. However, the small non-linearity in the elongational viscosity conflicts with longer time relaxation. According to the BKZ model[8], a large damping function should be the cause of small non-linearity for systems including dispersed particles. The damping functions of systems containing small particles will be reported elsewhere.

As the temperature was increased, a rapid increase in viscosity occurred after the Hencky strain was >1 (*Figures 1* and *2*). Large non-linearity is consistent with the existence of longer relaxation modes from dynamic shear measurements. In heterogeneous systems, the degree of deformation of particles and interfacial properties are important together with the existence of particles for melt rheology[4]. The degree of non-linearity of PS decreases with increasing temperature[3,9]. This tendency is hardly affected by the *MWD*[3,9]. Thus, the temperature-dependent non-linearity of PS was not considered as the main cause of the positive increase in non-linearity with temperature. We observed the shape of particles after elongational testing at both 140°C and 200°C. We rapidly cooled elongated samples with a Hencky strain of 3 in dry ice/ethanol solution, immediately after the tests (strain rate 0.2 s^{-1}). TEM observation in cross-sections of elongated samples showed that there is almost no change in the samples before and after the tests at these temperatures.

LDPE-*g*-PS has different glass transition temperatures (T_g) for the main chains and branches; 140°C is close to the T_g of PS and chain motions of LDPE are restricted by PS. As temperature increases, the viscosity of PS decreases more rapidly than that of LDPE. LDPE segments move more easily because of the low viscosity of PS at 200°C. Thus, TEM observation allows us to speculate that the large chain mobility of the graft copolymer at higher temperature caused the large non-linearity. The detailed analysis of chain motion in graft copolymers will be the subject of a further study. The effect of other copolymerized structures, random and block copolymerized structures, on the elongational viscosity are under investigation.

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