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Control of nonlinear viscoelasticity for polymer melts

Kiyohito Koyama*
Department of polymer Science and Engineering, Yamagata University, Yonezawa 992-8510, Japan
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1. Introduction

Numerous efforts have been made on the study of the shear and elongational properties of polymer melts. The characteristics are used to describe the physical properties of a polymeric material so that we know what to expect when the polymer is processed by injection molding, film (or sheet) extruding, fiber-spinning apparatus. The two basic flows are used to characterize polymers: shear and shear-free flows. Usually polymer processings are a combination of these flows or sometimes are dominated by one or the other. The shear flow properties can be reported in many cases by manufactures and fabricators. Only this characteristic is sometimes insufficient for the processings to provide a complete picture of the relationship between the processability and the flow behavior when underwent free-surface processes in which the shape and thickness of the extrudate are determined by the rheological properties of the melt, the die dimensions etc. Therefore, we have focused attention on the melt rheology control and its processability. In this paper the methodology of control of elongational flow is discussed.

2. Spiky bimodality

We carried out research for the role of a small amount of long relaxation time mode on the strain hardening by theoretical and experimental methods (Minegishi *et al.*, 2001; Sugimoto *et al.*, 2001). It is possible to introduce the spiky high-molecular-weight components via blending or polymerizing process. In miscible blends it is important that the concentration of the spiky high-molecular-weight component reaches and exceeds the critical concentration for entanglement for the spiky chains. Fig. 1 shows uniaxial elongational viscosity of polystyrene (PS) blended with ultra-high molecular weight (uhmw) PS. The weight-average molecular weight (Mw) of matrix and uhmw-PS is 220 K and 2,880 K, respectively. In Fig. 1, the strain hardening was apparently enhanced at 2 wt% of uhmw component. The number of entanglement of uhmw-chain is 3.6 in the blend. By contrast, such enhancement of the strain hardening was not observed for immiscible blend of styrene-acrylonitrile-copolymer with uhmw-PS.

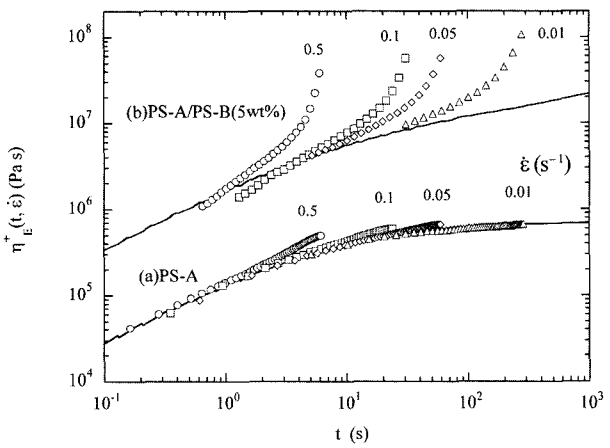

Fig. 1. Variation of uniaxial elongational viscosities with time at constant strain rates (160°C). Mw of PS-A and PS-B is 2.2×10^5 and 6.8×10^6, respectively. The solid lines represent linear viscoelastic function predicted from the shear viscosity.

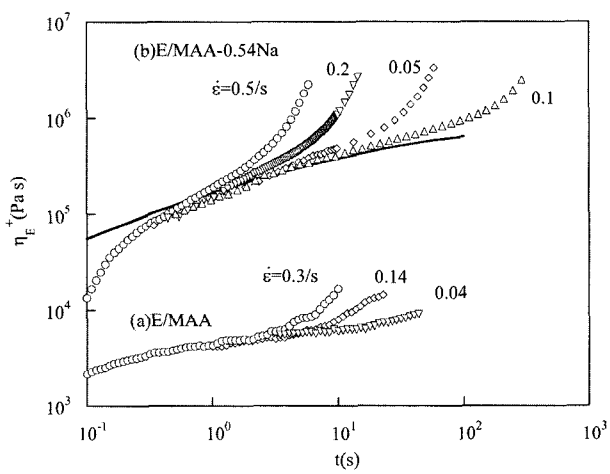

Fig. 2. Variation of transient elongational viscosities with time at constant strain rates (140°C) of (a) E/MMA and (b) E/MMA-0.54Na. The solid lines represent linear viscoelastic function predicted from the shear viscosity.

*Corresponding author: koyama@yz.yamagata-u.ac.jp

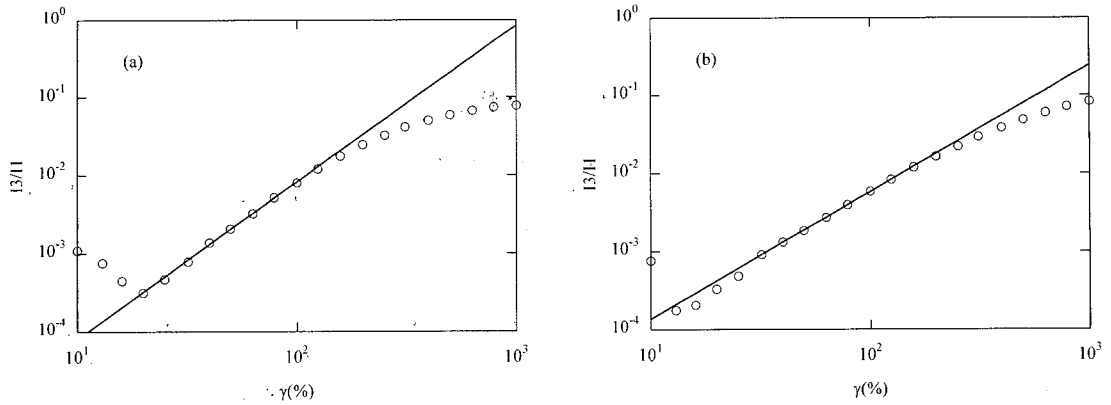

Fig. 3. Relative third harmonic intensity I_3/I_1 as a function of strain amplitude from 10 to 1000% measured at 1 rad/s for (a) PP-B and (b) PP-C.

3. Ionic interaction

Ionomers have hydrophobic polymer structure with ionic groups randomly located along the hydrocarbon backbone. Fig. 2 shows the elongational viscosity of ethylene-co-methacrilic-acid copolymer (EMMA) partially neutralized by sodium. The samples were kindly supplied by Mitsui-DuPont Polychemicals Co. EMMA ionomer showed outstanding strain hardening behavior (Takahashi *et al.*, 1994). This is generally attributed to the formation of ionic clusters within a polymer matrix which act as temporary physical crosslinks and efficiently retard the motion of matrix chains (Longworthand and Morawetz, 1958). It may be, however, difficult to process the ionomers due to the high viscosity in some cases. The incorporation of low molecular weight acid reduced the viscosity by a local environmental change in ionic aggregates and plasticizing effect (Nishioka *et al.*, 2004).

4. Long-chain branching

One option to improve the processability of polymers is to introduce a small amount of long-chain branches (Sugimoto *et al.*, 2001). A typical example may be polypropylene, in which the strain hardening is usually unexpected. The polypropylene we used for the study of the effect of the long-chain branches is propylene and nonconjugate diene copolymer (Paavola *et al.*, 2004). The content of the diene was kept very low. This is practically important since an usage of the dine often gives rise to bad odor. The propylene-diene copolymer shows strong elastic response in shear flow and the distinct strain hardening in elongational flow, resulting from a small amount of long-chain branches. These behaviors are very similar to those of modified PP by electron beam irradiation (Kurzbeck *et al.*, 1999). Here, in order to discuss a relationship between the chain structure and rheological properties further, the large amplitude oscillatory experiment was conducted under nonlinear strain region (Hyun *et al.*, 2002; Hyun *et al.*, 2003). It is possible to quantify the nonlinearity by the ratio of third harmonic I_3 to the fundamental frequency intensity I_1. The corresponding result from Fourier transformation analysis is shown in Fig. 3. The slope in the figure reflects the structural difference. By selecting the linear portion of the strain amplitude data, the slopes were found to be 2.0 and 1.7 respectively. The value of the linear PP was 1.5. Here note that the difference is not trivial, which implies that these materials have different microstructures even though the two samples showed similar shear and elongational behavior.

5. Modification of rheology by flow histories

Although most descriptions of rheological properties assume an equilibrium state, any previous thermo-mechanical history affects the material response in actual polymer processings. The effect of thermomechanical history on the

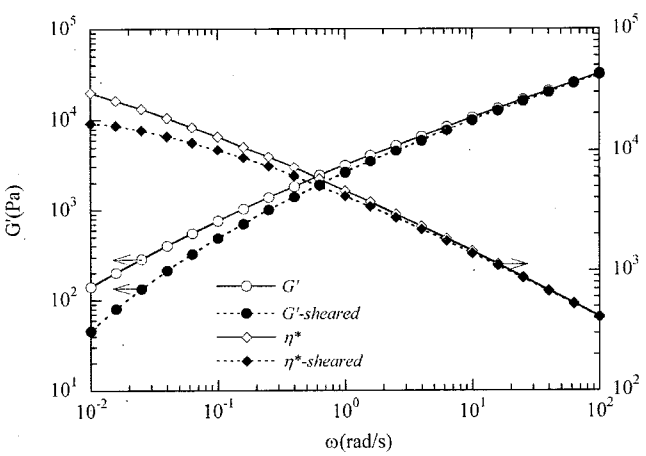

Fig. 4. Effect of shearing in a twin kneader on the elongational viscosity of long-chain branched PP. The viscosities were measured at 180°C.

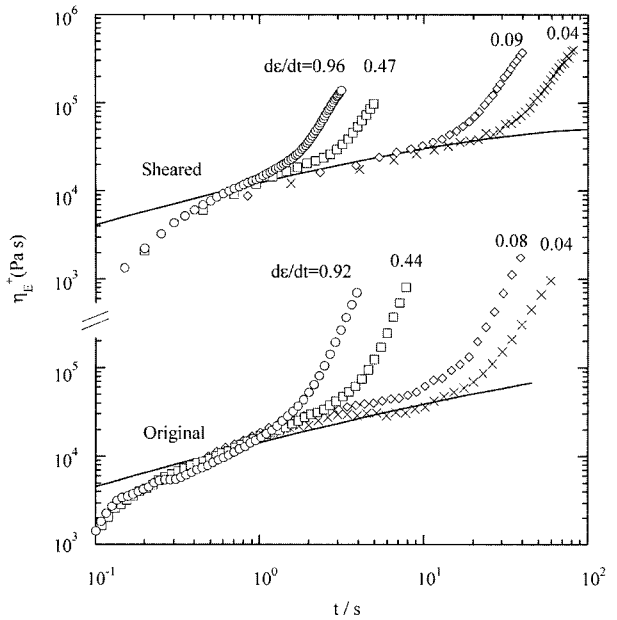

Fig. 5. Effect of shearing in a twin kneader on the linear viscoelasticity of long-chain branched PP. The tests were conducted at a temperature of 180°C and strain of 5%.

rheological properties was studied for long-chain branched PP and the blends with linear PP. For this purpose, the internal mixer and co-rotating twin extruder were used for the sample preparation. The elongational viscosity $\eta_E^+(t, \varepsilon\dot{u})$ of original and sheared samples was measured under transient elongational flow with constant tensile strain rates using a Meissner-type rheometer. Fig. 4 illustrates the effect of shear deformation history on η_E^+ for various strain rates $\varepsilon\dot{u}$ at 180°C. The solid lines in the figure are 3 times viscosities predicted from linear viscoelasticity. For original PP-B η_E^+ shows strong upward deviation from linear viscosities and an increase of the slopes as the growth of viscosity accelerates. As Fig. 4 shows, the strain hardening decreases clearly with a number of extrusions. This effect can be seen in the linear response under shear flow (see Fig. 5). Such effects, which might at first appear to be due to degrading the polymer, are recovered by annealing under quiescent state and dissolution-treatment in a solvent. GPC equipped with light scattering system also proves no change in the molecular weight distribution and the branching degree. Similar change has been reported for LDPE (Rokudai, 1979), while no change appears for linear PP and only marginal change for a bimodal HDPE. The effect of the shearing on the elongational viscosity was confirmed for the various blends of long-chain branched PP with linear one by authors.

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