

Polymer Materials Design for Good Processability of Polymer Processing

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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 in terms of relaxation time control of the polymer melts.

2. Bimodal blends

We carried out research for the role of a small amount of very long chain on the strain hardening by theoretical and experimental methods¹²⁾. 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

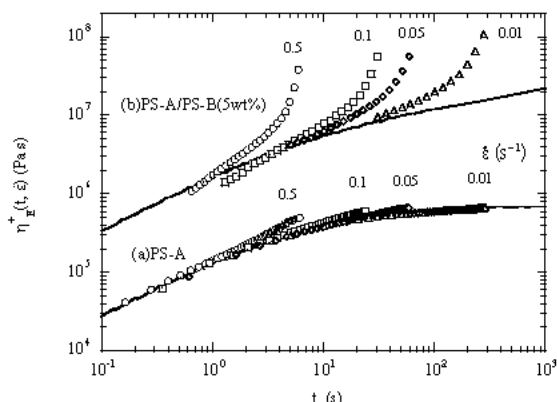


Fig. 1 Variation of uniaxial elongational viscosities with time at constant strain rates (160_C). Mw of PS-A and PS-B is 2.2×10^5 and 6.8×10^6 , respectively. The solid lines represent linear viscoelastic function predicted from the shear viscosity.

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 220K and 2,880K, respectively. In Fig.1, the strain hardening was apparently enhanced at 2wt% 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.

3. Long-chain branching

One option to improve the processability of polymers is to introduce a small amount of long-chain branches³⁾. 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 copolymer⁴⁾. The content of the diene was kept very low. This is practically important since a usage of the diene 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

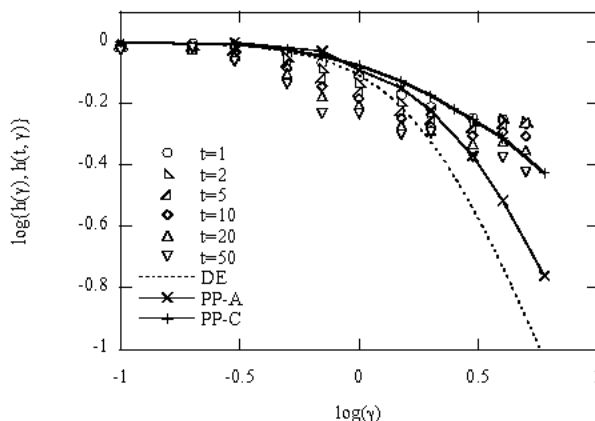


Fig. 2 Damping function $h(\gamma)$ for PP-A and PP-C, and time-dependent damping function $h(t, \gamma)$ for PP-B at various shear strains at 180°C. The dashed line, DE, is the damping function predicted by the Doi and Edwards theory

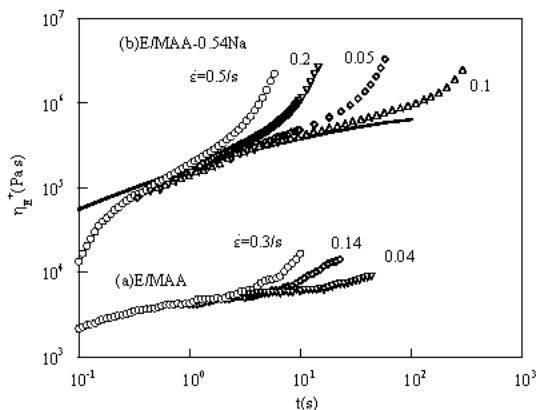


Fig. 3 Fig. 2 Variation of transient elongational viscosities with time at constant strain rates (140_C) of (a)E/MMA and (b)E/MMA-0.54Na. The solid lines represent linear viscoelastic function predicted from the shear viscosity.

dependence as shown in Fig. 2. In order to discuss a relationship between the chain structure and rheological properties, the large amplitude oscillatory experiment was conducted under nonlinear strain region. The results showed different stress curves at large strain (nonlinear region). The LAOS experiments provided some interesting results from stress intensity and phase angle. The results implied that modified PPs the nonlinear structure such as branching plays a role as a resistance or an obstacle for the alignment of polymer chains to the flow direction.

4. 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-methacrylic-acid copolymer (EMMA) partially neutralized by sodium. The samples were kindly supplied by Mitsui-DuPont Polychemicals Co. EMMA ionomer showed outstanding strain hardening behavior⁹. This is generally attributed to the formation of ionic clusters within a polymer matrix which act as temporary physical crosslinks and efficiently retard the

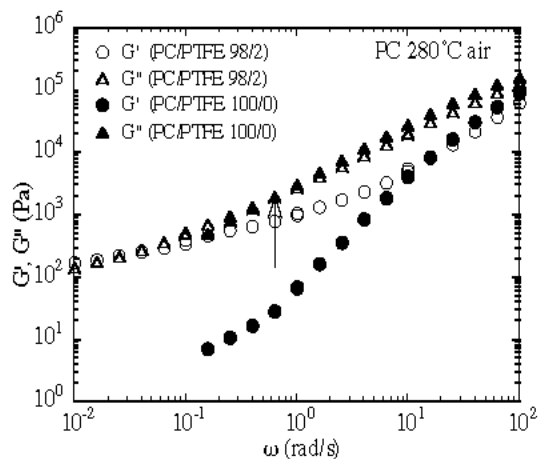


Fig. 4 Storage modulus G' and loss modulus G'' as a function of angular frequencies for PC/PTFE 100/0 and 98/2 at 280 °C.

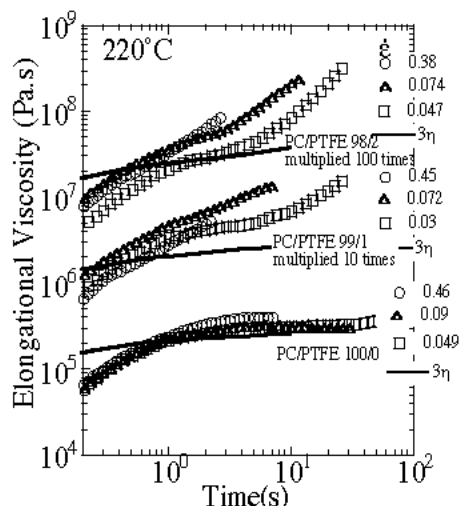


Fig. 5 Uniaxial elongational viscosity of PC/PTFE 100/0, 99/1 and 98/2 under constant strain rates at 200 °C. The values of PC/PTFE 99/1 and 98/2 are multiplied by 10 and 100, respectively.

motion of matrix chains⁹. 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 effect⁸.

5. Fabrication of PTFE

The effect of blending polytetrafluoroethylene (PTFE) on the rheological behavior of thermoplastic polymers was studied^{8,10}. The average diameter of PTFE powder was 470nm, which was prepared by emulsion polymerization. The matrix polymer was polycarbonate (PC). The blend samples were prepared by twin-screw internal mixer (Labo Plastmill). The oscillatory shear experiments of PC/PTFE 98/2 blend is shown in Fig. 4. G' in the low frequencies increased with addition of PTFE, suggesting generation of a long relaxation time component by incorporation of PTFE fiber. The similar behavior has been reported for composite system with fillers such as particles and rigid fibers. A presence of the fillers generally decreases steep deviation of the elongational viscosity from the linear viscoelastic regime, even though the matrix polymer has so-called strong strain hardening in the large strains. Fig. 5 shows the transient elongational flow behavior of the PC/PTFE blend as a function of time. Note that the PC incorporated with a small amount of PTFE clearly indicated the strain hardening, while neat PC hardly showed. From the morphological observation PTFE was obviously fibrillated in PC matrix by kneading with molten PC. The fibrils were oriented and extended to the deformational direction under elongational flow. The contribution of fibrillated PTFE on the elongational stress was estimated by elongational tests of neat fibrillated PTFE films, which was prepared by alkali etching of PC/PTFE blends. These results suggest that the enhancement of the strain hardening of elongational viscosity in the system should be attributed to the generation of restoring force by stretching PTFE fibrils.

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