



Rheological characterization on thermal degradation of ethylene-tetrafluoroethylene copolymer



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ABSTRACT

Oscillatory shear modulus in the molten state is evaluated carefully considering the rheological change during the measurement at high temperature for ethylene-tetrafluoroethylene copolymer (ETFE). The results provide the information on the molecular weight distribution as well as the degradation behaviors, which is affected by the environmental condition, *i.e.*, the existence of oxygen. Even under a nitrogen atmosphere, ETFE is thermally unstable in the molten state; ETFE shows random chain scission reaction without crosslinking. The steady-state shear compliance J_e^0 , which depends on the molecular weight distribution greatly, is not changed during the chain scission. It suggests that the chain scission occurs with keeping the molecular weight distribution. Considering the classical theory on the random scission reaction, the experimental result indicates that M_w/M_n of the initial ETFE sample, prior to the exposure to thermal history, is close to 2. In contrast, under air condition, ETFE shows crosslinking reaction even in the cone-and-plate rheometer. The degree of crosslinking is quantitatively estimated by the plateau modulus $G'_{plateau}$ in the low frequency region. The result suggests that the crosslinking occurs as a first order reaction.

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1. Introduction

The alternative copolymer of ethylene and tetrafluoroethylene (ETFE) is one of the most important melt-processable fluoropolymers. Because of its excellent chemical and thermal stability, electrical properties and surface properties, ETFE is used in various industrial applications such as lining of a chemical plant, highly durable sheath for electrical wire, photovoltaic module, and release film for semiconductor encapsulation process [1–4].

The structure and properties in the solid state for ETFE were studied intensively by Tanigami et al. [5,6], Arai et al. [4,7,8], and Funaki et al. [9,10]. They revealed the crystalline structure and the phase transition in detail as well as the relation with its mechanical properties.

Chen et al. [11] investigated the capillary extrusion properties as compared with those of polyethylene and perfluorinated polymers. They reported that polymers having a large amount of fluorine content tend to exhibit the flow instability even at low shear stress. Furthermore, the swell ratio decreases and the flow activation energy increases with increasing the fluorine content.

The rheological measurements in the molten state are, however, not so easy for ETFE, because ETFE shows the complex

melting behavior which is affected by applied thermal history [12]. The high melting point is another problem because samples show rheological change during measurements due to thermal degradation. However, the rheological properties are significantly important to understand not only processability but also molecular characterization, since the excellent anti-solvent property of ETFE makes it difficult to evaluate its solution properties. Consequently, even the exact information on the molecular weight and its distribution is barely obtained by a conventional method like size-exclusion chromatography.

Tuminelo et al. developed the characterization technique of molecular weight distributions by rheological properties for insoluble fluoropolymers including ETFE [13–15]. They found that the ratio of weight-average molecular weight M_w to number-average molecular weight M_n , *i.e.*, M_w/M_n , of ETFE is approximately 2.8. On the contrary, Chen et al. also evaluated the polydispersity from the viscoelastic properties using a similar method and concluded that a commercially available ETFE has a significantly broad molecular weight distribution ($M_w/M_n > 10$). They concluded that the broad molecular weight distribution is responsible for good processability at melt processing [16]. Chu et al. developed a specific method employing a laser light scattering (LLS) technique to evaluate the molecular weight and its distribution for ETFE at *ca.* 250 °C. They found that ETFE shows significantly narrow molecular weight distribution, *e.g.*, $M_w/M_n = \sim 1.4$ and $M_z/M_w = 1.4–1.8$ [17–20].

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The discrepancy on the molecular weight distribution of ETFE is a serious problem for the molecular design, and thus required to be solved. In this research, oscillatory shear modulus in the molten state is evaluated carefully considering the rheological change during the measurement at high temperature. The results provide the basic molecular characterization as well as the degradation behaviors of ETFE, which is affected by the environmental condition, *i.e.*, the existence of oxygen.

2. Experimental

2.1. Material

The polymer used in this study was a commercially available terpolymer comprising of ethylene, tetrafluoroethylene and 3,3,4,4,5,5,6,6,6-nonafluorohexene (CH₂CHC₄F₉; NFH), that was synthesized by a solution polymerization method using fluorinated hydrocarbon as a solvent [21]. The molar fraction in the polymer is ethylene/tetrafluoroethylene/NFH = 44.6/54.5/0.9 mol%, which was analyzed by the molten-state ¹⁹F nuclear magnetic resonance measurement and fluorine ultimate element analysis [22].

The melt flow rate is 11.8 [g/10 min] according to ASTM D3159 (297 °C, 49 N). It is found from the differential scanning calorimetric measurement that the melting point is 258.7 °C and the crystallization temperature is 238.7 °C at a scanning rate of 10 °C/min. The sample was melt-extruded to pellet form and molded into a flat sheet with *ca.* 500 μm thickness by a compression-molding machine at 280 °C. The sample sheets were kept under vacuum condition at room temperature in 16 h prior to the rheological measurements.

2.2. Measurements

The frequency dependence of the oscillatory shear modulus was measured by a cone-and-plate rheometer (Anton Paar, MCR301) at 300 °C under a nitrogen atmosphere. The diameter of the cone and plate is 25 mm and the cone angle is 2°. The preheating time before the measurement was 5 min. In order to clarify the thermal stability, the measurements were performed without changing the sample. The angular frequency decreases from 314 s⁻¹ to 0.132 s⁻¹, and then increases from 0.132 s⁻¹ to 314 s⁻¹. The same procedure was applied to the sample for 10 cycles. The duration of the measurement for one cycle is approximately 20 min.

A similar measurement was also performed under air atmosphere. The measurements were carried out from 314 s⁻¹ to 0.0188 s⁻¹, and then increases from 0.0188 s⁻¹ to 314 s⁻¹ for 5 cycles.

3. Results and discussion

3.1. Rheological change under nitrogen

The frequency dependence of oscillatory shear modulus under a nitrogen atmosphere at 300 °C is shown in Fig. 1. It is found that the storage modulus G' and loss modulus G'' are proportional to ω^2 and ω , respectively in the low frequency region, demonstrating that the rheological terminal zone is observed. Therefore, the rheological parameters in the terminal zone, such as zero-shear viscosity η_0 , steady-state shear compliance J_e^0 , and weight-average relaxation time τ_w , can be obtained from the following equations.

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G'}{\omega} \quad (1)$$

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{G''^2} \quad (2)$$

$$\tau_w = \eta_0 J_e^0 \quad (3)$$

It is well known that η_0 of a linear polymer is determined by the weight-average molecular weight M_w as follows:

$$\eta_0 \propto M_w^{3.4} (M_w > 2M_e) \quad (4)$$

where M_e is the average molecular weight between entanglement couplings.

As seen in Fig. 1(b), η_0 and thus M_w decrease with the residence time t in the rheometer by chain scission reaction, although the rheological change is not so obvious compared with polyethylene [23–25] owing to the high intrinsic bond dissociation energy of ETFE [26]. Here, the normalized M_w , *i.e.*, $M_w(t)/M_w(0)$, calculated from Eq. (5) assuming $M_w \gg M_e$ without generation of long-chain branches, is plotted as a function of the residence time t in the rheometer.

$$\frac{M_w(t)}{M_w(0)} = \left[\frac{\eta_0(t)}{\eta_0(0)} \right]^{1/3.4} \quad (5)$$

As shown in Fig. 2, the normalized M_w of ETFE in an inert gas decreases monotonically, demonstrating that chain scission occurs.

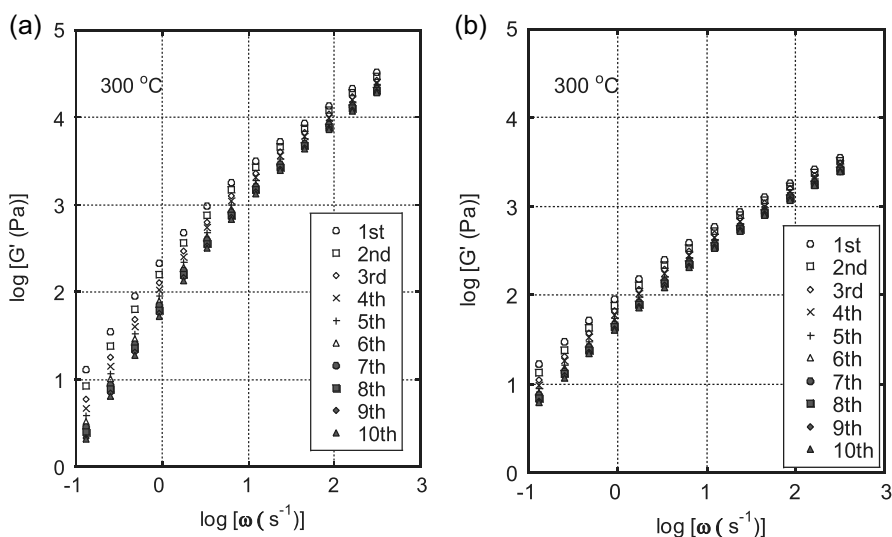


Fig. 1. Frequency dependence of (a) shear storage modulus G' and (b) loss modulus G'' for ETFE at 300 °C under a nitrogen atmosphere. The measurements were performed from 314 s⁻¹ to 0.132 s⁻¹, and then increases from 0.132 s⁻¹ to 314 s⁻¹, which was applied to the same sample for 10 cycles.

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