



Flow property at capillary extrusion for ethylene–tetrafluoroethylene copolymer



Seigo Kotera^{a,b}, Masayuki Yamaguchi^{a,*}

^a School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi 923-1292, Ishikawa, Japan

^b Asahi Glass Co., Ltd., 1150 Hazawa-cho, Kanagawa-ku, Yokohama 221-0863, Japan

ARTICLE INFO

Article history:

Received 3 March 2015

Received in revised form 16 April 2015

Accepted 2 May 2015

Available online 22 May 2015

Keywords:

Ethylene–tetrafluoroethylene copolymer

Rheological properties

Extrusion

Melt fracture

ABSTRACT

The capillary extrusion property of ethylene–tetrafluoroethylene copolymer (ETFE) is evaluated. It is found that ETFE shows several types of flow instabilities. The shark-skin failure is observed over the first critical shear stress 7.9×10^4 Pa. Then, the slip-stick instability is detected at 1.8×10^5 Pa, which corresponds to the critical stress of the slippage at the die wall, evaluated by the Mooney method. Moreover, gross wavy melt fracture appears at high out-put rate condition. It is interesting to note that quasi-stable flow region; so-called “super-extrusion”, is observed between slip-stick and wavy melt fracture regions. Because of the steady slippage, ETFE can be extruded at a high out-put rate condition without surface roughness and distortion of extrudates.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

It has been well known that flow instability at capillary extrusion is roughly classified into two categories; surface instability known as shark-skin failure and gross, volumetric, and wavy melt fracture [1–4]. Meller et al. summarized that the shark-skin failure occurs beyond the critical shear stress at the die exit and the wavy melt fracture takes place beyond the critical elongational stress at the die entry [5]. Therefore, the rheological properties, especially strain-hardening behavior in elongational viscosity, affect the type of flow instability. For example, linear low-density polyethylene (LLDPE) having no strain-hardening shows the shark-skin failure at low shear rate, whereas low-density polyethylene with long-chain branches (LDPE), that is known to show marked strain-hardening in elongational viscosity, exhibits the wavy melt fracture prior to shark-skin. Moreover, there are at least two origins of the shark-skin failure [2–4,6]; one is the cohesive rupture by the sudden deformation of the surface area after passing the die exit, and the other is the irregular slippage. The critical stresses of both mechanisms were discussed by Allal et al., which were summarized in the following relations [7,8],

$$\sigma_c = \frac{1}{2} G_N^0 \frac{N_e}{\sqrt{N_0}} \quad (1)$$

$$\sigma_s = \frac{9}{4\pi} G_N^0 C_{ad} \frac{N_e}{\sqrt{N_0}} \quad (2)$$

where G_N^0 is the rubbery plateau modulus, N_e is the number of monomers between entanglements and N_0 is that of monomers per chain, and C_{ad} is the factor expressing the fraction of a polymer adsorbed on the wall surface.

Since the average molecular weight between entanglement couplings M_e is inversely proportional to G_N^0 , a polymer having high M_e tends to show shark-skin failure at low shear stress [9]. Furthermore, it has been clarified that the narrow distribution of molecular weight also leads to the flow instability at low shear stress, which was theoretically derived using the concept of Deborah number [9].

Besides the control of molecular weight distribution, the flow instability is avoided by the addition of various types of processing aids. It is well known that some fluoropolymers such as vinylidene fluoride and hexafluoropropylene copolymer are employed as the processing aid to minimize the shark-skin failure [3]. In particular, they are frequently used for LLDPE. The addition lowers the extrusion stress by steady slippage at the die wall and thus the shark-skin failure does not occur even at high out-put rate condition.

When a fluoropolymer itself is processed at extrusion, the flow instability should be also considered seriously, because it decides the production speed. However, there have been only a couple of reports on the flow instability of fluoropolymers. Hatzikiriakos

* Corresponding author. Tel.: +81 761 51 1621; fax: +81 761 51 1621.
E-mail address: m.yama@jaist.ac.jp (M. Yamaguchi).

et al. reported that typical perfluoropolymers such as poly (tetrafluoroethylene-co-perfluoroalkylvinylether) (PFA) and poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP) show a relatively low critical onset shear stress of shark-skin failure by the capillary extrusion [3]. They also revealed that the addition of specific fillers, e.g., Boron nitride, can increase the critical shear stress, leading to high out-put rate operation. According to them, Boron nitride plays a role on the internal lubricant to stabilize the streamlines at the die entrance. Rosenbaum, one of their colleagues, studied instable phenomena of FEP at capillary flow and summarized the types of flow instabilities [10]. According to him, “super-extrusion region” is observed between slip-stick and wavy melt fracture regions in the case of FEP. The effect of fluorine content in fluoropolymers on the capillary extrusion properties was investigated by Chen et al., as compared with polyethylene and perfluorinated polymers [11]. They reported that perfluorinated polymers tend to exhibit the flow instability even at a low shear stress and a partially fluorinated polymer like ethylene-tetrafluoroethylene (ETFE) copolymer shows different flow instability that depends on the fluorine content.

The poor information on the flow instability for fluoropolymers is a serious problem for the industrial application, because the demand of melt-processable fluoropolymers increases recently due to the excellent electrical properties, surface properties, and chemical and thermal stability. Among them, intense attention has been focused on ETFE, which is often used in the forms of sheet, film, and wires [12,13]. Therefore, it is important to comprehend the processability at extrusion including the flow instabilities. Since it is predicted that G_N^0 of ETFE is much lower than that of polyethylene, the shark-skin failure is expected to occur at a low shear stress and limits the out-put rate. Therefore, the understanding of the flow instability at capillary extrusion is inevitable for the industrial application of ETFE.

2. Experimental

2.1. Material

A commercially available terpolymer comprising of ethylene, tetrafluoroethylene, and 3,3,4,4,5,5,6,6,6-nonafluorohexane ($\text{CH}_2\text{CHC}_4\text{F}_9$; NFH), was employed in this study. The details of the characteristics were mentioned in our previous paper [14]. The melt flow rate is 11.8 [g/10 min] (297 °C, 49 N) and the melting point is 258.7 °C.

2.2. Measurements

Frequency dependence of the oscillatory shear modulus was measured by a cone-and-plate rheometer, (TA instrument, Ares GII) at 260–300 °C. The diameter of the plates is 25 mm. 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 628 to 0.314 s^{-1} .

The steady-state shear viscosity was measured by a capillary rheometer (Toyoseikiseisakusyo, Capirograph 1C) at 300 °C using various types of circular dies shown in Table 1.

The shear rate and shear stress were calculated by the Hagen–Poiseuille law with the Bagley and Weissenberg–Rabinowitsch corrections. The complex shear viscosity was calculated from the oscillatory moduli. The angular frequency ω is converted to the shear rate $\dot{\gamma}$ by applying the following Cox–Merz rule.

$$\eta(\dot{\gamma}) = \eta^*(\omega)|_{\omega \rightarrow \dot{\gamma}} \quad (3)$$

Table 1
Dies used in this research.

Die (no.)	<i>D</i> (mm)	<i>L</i> (mm)	Entrance angle (degree)
1	1	40	180
2	1	20	180
3	1	10	180
4	2	20	90
5	0.8	8	90
6	0.5	5	90

$$\eta^*(\omega) = \frac{\sqrt{G'(\omega)^2 + G''(\omega)^2}}{\omega} \quad (4)$$

The appearance of the extruded strands was observed by an optical microscope to evaluate the flow instability.

3. Results and discussion

Fig. 1 shows the master curves of angular frequency dependence of oscillatory shear modulus at 300 °C. The time-temperature superposition principle seems to be applicable in this temperature range, although thermal degradation occurs slightly at 300 °C [14]. The storage modulus G' and loss modulus G'' are proportional to ω^2 and ω , respectively, in the low frequency region; i.e., the rheological terminal zone is observed.

The flow activation energy, calculated by the Andrade equation, is found to be 89 kJ/mol, which is slightly larger than the value reported previously, 65 kJ/mol [15]. These values are intermediate between the typical values of linear polyethylene (21–30 kJ/mol) and that of polytetrafluoroethylene (PTFE) (75–150 kJ/mol) [16–22]. The modulus of the crossover point, i.e., $G_x = G' = G''$, is 1.2×10^5 Pa and the angular frequency of this point is $1.1 \times 10^3 \text{ s}^{-1}$. According to the empirical relation proposed by Wu [23], the rubbery plateau modulus G_N^0 is given by the following relation.

$$\log\left(\frac{G_N^0}{G_x}\right) = 0.380 + \frac{2.36 \log(M_w/M_n)}{1 + 2.45 \log(M_w/M_n)} \quad (5)$$

Since M_w/M_n of the present sample was found to be 2.0 [14], G_N^0 is calculated to be 7.2×10^5 Pa. The value is significantly lower than that of polyethylene, 2.3×10^6 Pa [24].

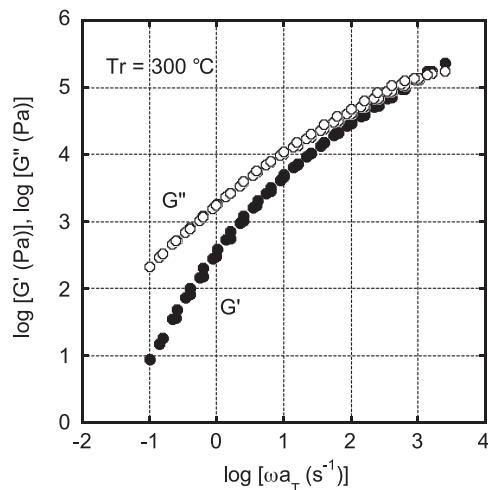


Fig. 1. Master curves of the frequency dependence of the oscillatory shear moduli such as storage modulus G' and loss modulus G'' at 300 °C.

Download English Version:

<https://daneshyari.com/en/article/1313932>

Download Persian Version:

<https://daneshyari.com/article/1313932>

[Daneshyari.com](https://daneshyari.com)