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Relation between molecular structure and flow instability for ethylene/ α -olefin copolymers

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Abstract

Surface instabilities in a capillary extrusion have been studied for various ethylene/ α -olefin copolymers. It is found that the onset stress of shark-skin failure for ethylene/1-hexene copolymer (EHR) decreases rapidly with increasing 1-hexene content, whereas that of ethylene/propylene copolymer (EPR) is independent of propylene content in the experimental region. Consequently, EHR with high 1-hexene content exhibits shark-skin at low stress level compared to EPR. Lower rubbery plateau modulus, leading to higher Deborah number at the same stress level, is attributed to the lower onset stress. Further, the low entanglement density will cause cracks at lower stress level like glassy polymers, which is also responsible for the low onset stress for shark-skin. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyolefins; Extrusion; Rheology

1. Introduction

Recent development of metallocene catalyst technology makes it possible to produce a tailored ethylene/ α -olefin copolymer at a commercial scale. As a result, there is a growing great interest in the relation between molecular structure and various kinds of properties, such as thermal, rheological, and mechanical properties [1–6], which gives us information on ‘molecular design’. To the best of our knowledge, however, the effect of molecular structure, especially the species and content of α -olefin unit in copolymers, on flow instabilities has not been clarified yet, although it is very important from the industrial point of view. Further, since metallocene polymers have a narrow molecular weight distribution compared to a conventional polyolefin by Ziegler–Natta catalyst, flow instabilities often take place early, and limit the production speed.

It has been generally accepted that flow instabilities can be roughly classified as follows [7]: (1) surface instabilities occurred at the die exit, such as shark-skin and slip-stick, and (2) gross volumetric melt fracture due to the instability in the entrance of die, which is associated with long time

relaxation mechanism, i.e. melt elasticity [8–10]. In the case of ethylene/ α -olefin copolymers with narrow molecular weight distribution, the former one, surface instabilities at the die exit, are more apt to be the course of the problem. Although the mechanism of surface instabilities has been studied for a long time based on the experimental results, as is well known, controversies still continue to be discussed.

Cogswell [11] proposed that the origin of shark-skin is the crack created by the high level of tensile stress applied in the vicinity of the die exit, which has been elucidated by optical and microscopic methods [12–16] and numerical modeling [17,18]. Further, it was also supported from experimental results that rheological properties under elongational flow, such as melt strength and strain hardening behavior, affect the onset of shark-skin [15,19]. Finally, Gogos et al. [16] proposed possible methods to mitigate the shark-skin failure based on this mechanism. Another well-known mechanism leading to the shark-skin is the slippage, i.e. adhesive failure, between a polymer melt and the die wall [20–23]. Since it is generally accepted that a high viscous polymer melt can slip on the wall [24], the slippage may be the origin of surface instability, especially slip-stick failure, in some cases. Furthermore, Brochard and de Gennes [25] proposed the molecular theory, in which disentanglement between bulk polymer chains and the polymer chains adhered on the wall, i.e. cohesive failure, is the origin of surface instability.

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The role of entanglement couplings, which dominate rheological properties of polymer melts, however, has not been discussed to a great degree [14,26], besides the theory proposed by Brochard and de Gennes [25] and some experimental studies [27,28] based on their theory.

In this study, we have investigated the flow instability for ethylene/propylene copolymers (EPR) and ethylene/1-hexene copolymers (EHR) with various amounts of α -olefin unit, and explored and discussed the critical stress for the onset of shark-skin. Further, molecular characteristics of the copolymers, such as average molecular weight between entanglement couplings, have been also clarified. The obtained result will give us a clue to point out to the mechanism of shark-skin from a viewpoint of molecular dynamics.

2. Experimental

2.1. Materials and blend preparation

The EPR and EHR employed were synthesized by a metallocene catalyst. The details in the molecular characteristics and polymerization methods were described in Ref. [6]. Table 1 summarized the molecular weight, which were determined from combination measurements of intrinsic viscosity (VISCOTEK, Differential Viscometer Model 100) and gel permeation chromatography (Waters, 150-C) in *ortho*-dichlorobenzene at 135 °C, and α -olefin content determined from ^{13}C nuclear magnetic resonance. The nomenclature of the samples used is as follows: e.g. EPR37 is an EPR whose propylene content is ca. 37 mol%. All copolymers except EHR18 are fully amorphous at room temperature because of less ethylene sequence. Further, it was found from a differential scanning calorimetry measurement that the melting point of EHR18 is around 36 °C.

An Instron capillary rheometer was used for the evaluation of flow instabilities in a capillary extrusion. The extrusion was carried out at 70 and 160 °C. A tungsten carbide die of $L/D = 33.2$, $D = 1.535$ mm, and entrance angle = 90° was employed. The Bagley and Rabinowitsch corrections were not carried out, since L/D is large enough to neglect the end effect. Further, in order to eliminate polymer materials in the capillary, we washed the die prior to each measurement by xylene.

Oscillatory shear moduli, such as shear storage modulus G' and loss modulus G'' , were measured at various temperatures using a parallel-plate rheometer (Rheometrics, RMS-800). The time–temperature superposition was applied to frequency dependence of oscillatory modulus at different temperatures.

3. Results

3.1. Linear viscoelastic properties

Fig. 1 exemplifies the master curves of oscillatory shear moduli for EPR67 at 25 °C. The curves show the terminal and rubbery plateau zones in the reduced angular frequency ωa_T range. The value of rubbery plateau modulus G_N^0 can be determined by [29]

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^a G'' d \ln \omega \quad (1)$$

where a is the upper limit before the transition zone is entered.

In general, the parameter can be obtained by the integration of G'' over $\ln \omega$ encompassing the maximum of G'' . In this study, the G'' versus $\ln \omega$ curve was numerically integrated from $\ln \omega = -\infty$ to the maximum of G'' , and the result was doubled. Table 2 shows G_N^0 for the samples employed, in which some results were shown in the previous paper with the master curves [6]. Because of crystallization, master curves do not cover enough frequency scale to evaluate G_N^0 for EHR18. As seen in the table, G_N^0 decreases with increasing α -olefin content. Further, EHR exhibits a significantly lower G_N^0 than the EPR having the same α -olefin content in mole percent. As a result, G_N^0 of EPR37 is three times as much as that of EHR51. Some authors [6] made it clear that the rubbery plateau modulus G_N^0 of ethylene/ α -olefin copolymers is simply expressed by the following equation based on the theory proposed by Graessley and Edwards [30]

$$G_N^0 = K(m_0/14)^{-2.3} \quad (2)$$

$$m_0 = 14(1 - x) + kx \quad (3)$$

where K is G_N^0 for linear polyethylene, m_0 the average molecular weight per main chain bond, x the mole fraction of comonomer and k the half of the molecular weight of α -olefin unit.

It seemed that the results in Table 2 also agree with the above equations.

3.2. Capillary extrusion

Fig. 2 shows apparent wall shear stress σ plotted against apparent wall shear rate $\dot{\gamma}$ at 70 and 160 °C. The solid line represents the values calculated from linear viscoelastic behavior by the Cox–Merz empirical rule [31]. Further, the arrow indicates the point which shark-skin takes place. It is found that the predicted lines agree with experimental data even though shark-skin takes place, indicating that slip velocity, if present, is negligible. Moreover, there is no sharp change in the slope of flow curves in this experiment. As seen in the figure, the slope of shear stress decreases with increasing 1-hexene content for EHRs, whereas EPR67 has a similar slope as EPR37. Further, the copolymer with high

Table 1
Characteristics of polymers

Sample	α -Olefin		Molecular weight	
	Species	Content (mol%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$
EPR37	Propylene	37.2	7.0	10
EPR67	Propylene	66.7	9.0	14
EHR18	1-Hexene	18.2	13	23
EHR33	1-Hexene	32.5	13	23
EHR40	1-Hexene	39.8	15	25
EHR51	1-Hexene	50.5	14	23

α -olefin content shows a larger shift factor irrespective of α -olefin species. Moreover, it is found that the critical shear stress for the onset of shark-skin, σ_c , at 160 °C is higher than that at 70 °C for all samples, which corresponds with the results of previous studies [11,14,15,17–19,27].

Fig. 3 shows extrudates of EHR18 obtained at 70 °C. As seen in the figure, smooth, gloss surface is observed at $6.81 \times 10^{-1} \text{ s}^{-1}$ (Fig. 3(a)) and shark-skin is detected by naked eyes at 1.36 s^{-1} (Fig. 3(b)). Thus, the onset stress is between $9.7 \times 10^4 \text{ Pa}$ at $\dot{\gamma} = 6.81 \times 10^{-1} \text{ s}^{-1}$ and $1.41 \times 10^5 \text{ Pa}$ at 1.36 s^{-1} . Increasing shear rate, the periodic distortion with small amplitude appears markedly as shown in Fig. 3(c) and (d). After showing pine cone shape (Fig. 3(d) and (e)), gross, chaotic, and volumetric melt fracture takes place at higher shear rate (Fig. 3(g)). As shown in the figure, it is difficult to differentiate between the region of shark-skin and that of gross melt fracture. All EHRs exhibit similar behavior as EHR18 irrespective of extrusion temperature.

Fig. 4 shows extrudates of EPR37 at 70 °C. Shark-skin starts appearing at 2.04 s^{-1} and $1.54 \times 10^5 \text{ Pa}$, suggesting that the onset stress of EPR 37 is at the same level as that of EHR18. The amplitude of the periodic distortion increases with shear rate, and screw-type distortion appears as shown in Fig. 4(d). Further, the screw-type distortion and smooth surface appear alternatively at $3.41 \times 10 \text{ s}^{-1}$ (Fig. 4(e)). Then, smooth surface appears again at relatively higher

Table 2

Rubbery plateau modulus G_N^0 , entanglement density ν_e , and number of entanglement couplings per chain M_w/M_e

Sample	G_N^0 , exp. (MPa)	ν_e , calc. (mol/m ³)	M_w/M_e , calc.
EPR37	1.06	315	53.8
EPR67	0.88	240	56.9
EHR18	–	229	89.1
EHR33	0.42	148	58.1
EHR40	0.44	121	50.9
EHR51	0.31	93.6	37.1

shear rate (Fig. 4(f)), which is observed also for EPR67 at 70 °C but not at 160 °C. After smooth surface, the region of gross melt fracture takes place at higher shear rate, as shown in Fig. 4(g). Because of the existence of smooth surface region at relatively high shear rate, the critical shear stress for the onset of gross melt fracture is also identified at 70 °C; $4.45 \times 10^5 \text{ Pa}$ for EPR37 and $4.04 \times 10^5 \text{ Pa}$ for EPR67. At 160 °C, however, smooth surface does not appear at higher shear rate after shark-skin failure. Therefore, it is impossible to evaluate the onset stress for gross melt fracture.

Fig. 5 shows the relation between the onset stress of shark-skin σ_c at 160 °C and α -olefin content in the copolymers. It is found that the onset stresses of EPRs and EHR18 are similar to that for metallocene HDPE reported by Vega et al. [32]. Furthermore, σ_c decreases rapidly with 1-hexene content in EHR, whereas both EPRs show similar level. The figure demonstrates that EHR with high 1-hexene content exhibits the shark-skin failure at lower level of the wall stress.

4. Discussion

We ascribe the difference in σ_c between EPR and EHR to the difference in the density of entanglement couplings ν_e , because G_N^0 , which is proportional to ν_e (Eq. (4)), is significantly dependent on the species and content of α -olefin unit in the copolymer:

$$\nu_e = \frac{\rho}{M_e} = \frac{G_N^0}{RT} \quad (4)$$

where M_e is the average molecular weight between entanglement coupling points.

As shown in Table 2, EPR has a high G_N^0 , even though propylene content is high. On the other hand, G_N^0 of EHR falls off sharply with 1-hexene content [6]. This result demonstrates that EHR with high 1-hexene content exhibits a quite low G_N^0 , i.e. low density of entanglement couplings. According to El Kissi and Piau [14], the onset stress slightly decreases with the number of entanglement couplings per chain, which has been supported by the experiments employing various samples with different molecular weights [26]. Table 2 also shows the values of ν_e at 160 °C and M_w/M_e calculated by Eqs. (2) and (4) in order to

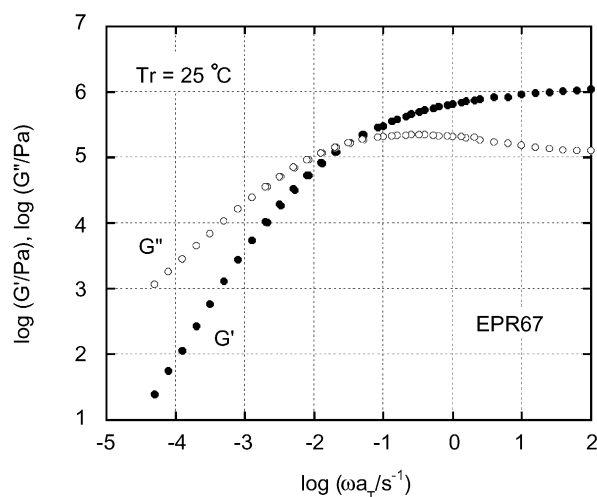


Fig. 1. Master curves of oscillatory shear moduli at 25 °C for EPR67.

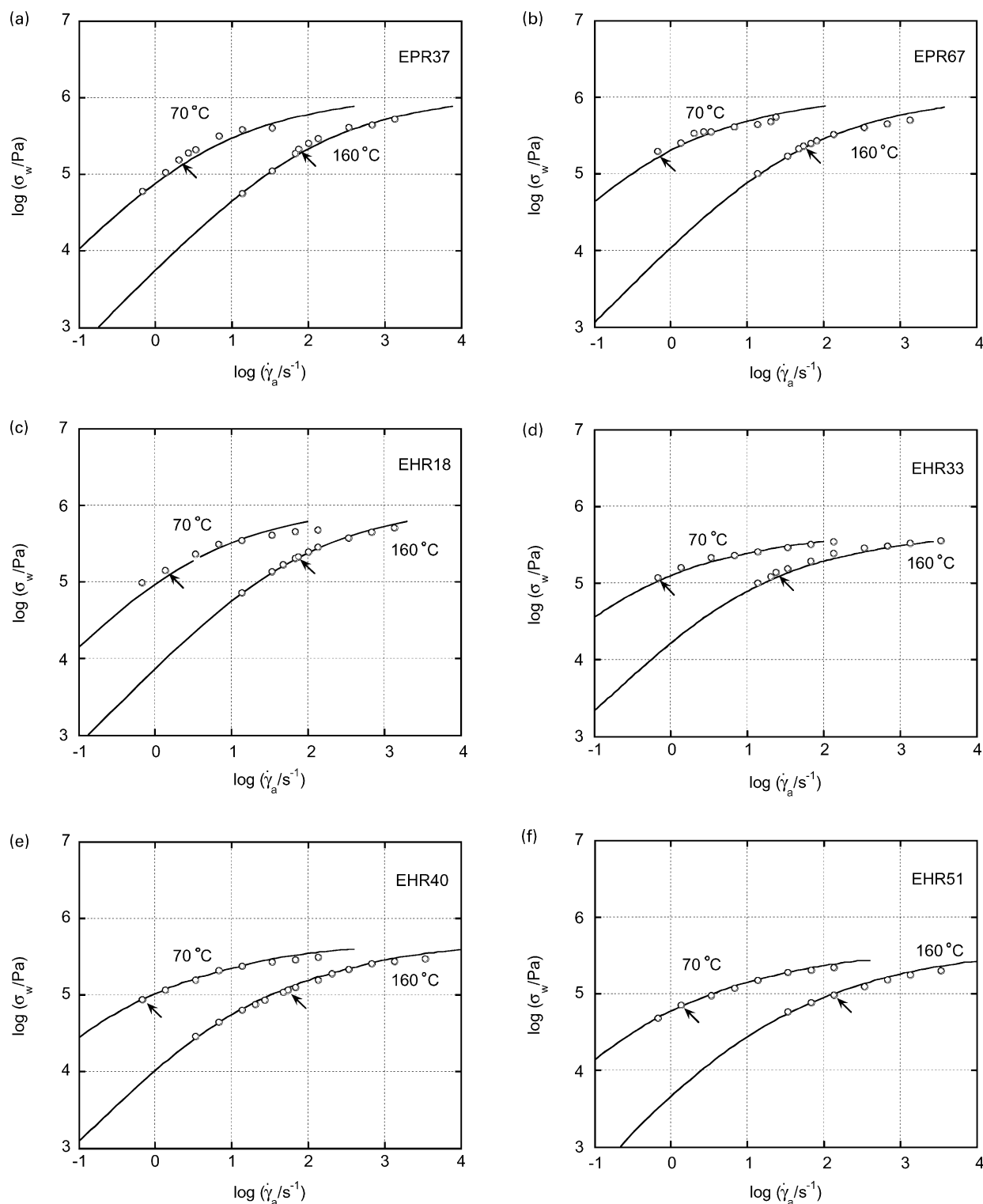


Fig. 2. Flow curves at 70 and 160 °C for (a) EPR37, (b) EPR67, (c) EHR18, (d) EHR33, (e) EHR40, and (f) EHR51. The arrows indicate the point which shark-skin start appearing, and the solid lines are the calculated shear stress from oscillatory shear modulus.

avoid an experimental error. As seen in the table, however, the number of entanglement points per chain seems to have no/less relation with the onset stress.

In Fig. 6, the experimental onset stress σ_c , which is shown in Fig. 5, is plotted against ν_e . As seen in the figure,

σ_c increases with ν_e , irrespective of the species of α -olefin unit in the copolymers, suggesting that the entanglement density is related to the onset stress of shark-skin. This result demonstrates that a polymer having a low ν_e , i.e. low G_N^0 , shows shark-skin failure at low stress levels. Let us consider

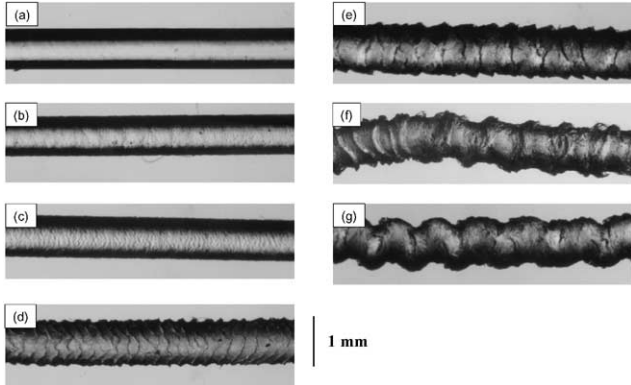


Fig. 3. Extrudates of EHR18 at 70 °C. Shear rates are (a) 1.36 s^{-1} , (b) 2.72 s^{-1} , (c) 6.81 s^{-1} , (d) $1.36 \times 10^1 \text{ s}^{-1}$, (e) $3.41 \times 10^1 \text{ s}^{-1}$, (f) $6.81 \times 10^1 \text{ s}^{-1}$, and (g) $1.36 \times 10^2 \text{ s}^{-1}$.

the effect of G_N^0 on the rheological properties under steady-state shear flow.

As is well known, the generalized Newtonian fluid (GNF) representation of the wall shear stress $\sigma(\dot{\gamma})$ is given by

$$\sigma(\dot{\gamma}) = \eta(\dot{\gamma})\dot{\gamma} \quad (5)$$

According to the Carreau GNF equation [33], shear viscosity in the non-Newtonian region $\eta(\dot{\gamma})$ is expressed by

$$\eta(\dot{\gamma}) = \eta_0 \left[1 + (\tau_w \dot{\gamma})^2 \right]^{(n-1)/2} \quad (6)$$

where η_0 is the zero-shear viscosity, n (< 1) the constant which is the function of molecular weight distribution, and τ_w is the weight-average relaxation time given by Eq. (7):

$$\tau_w \equiv \frac{\int \tau^2 H(\tau) d \ln \tau}{\int \tau H(\tau) d \ln \tau} = \eta_0 J_e^0 \quad (7)$$

where $H(\tau)$ is the relaxation spectrum and J_e^0 is the steady-state shear compliance.

The τ_w is replaced by the lower-order, number average

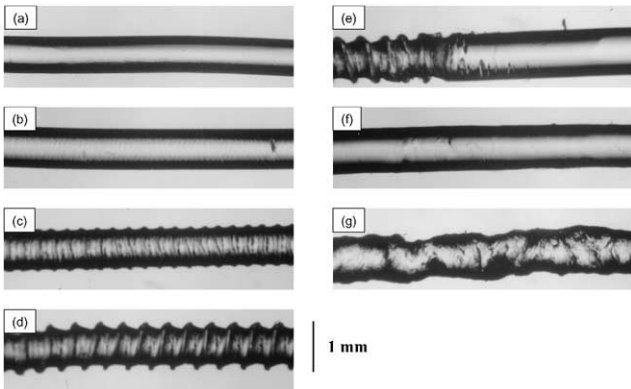


Fig. 4. Extrudates of EPR37 at 70 °C. Shear rates are (a) $6.81 \times 10^{-1} \text{ s}^{-1}$, (b) 1.36 s^{-1} , (c) 3.41 s^{-1} , (d) 6.81 s^{-1} , (e) $1.36 \times 10^1 \text{ s}^{-1}$, (f) $3.41 \times 10^1 \text{ s}^{-1}$, and (g) $6.81 \times 10^1 \text{ s}^{-1}$.

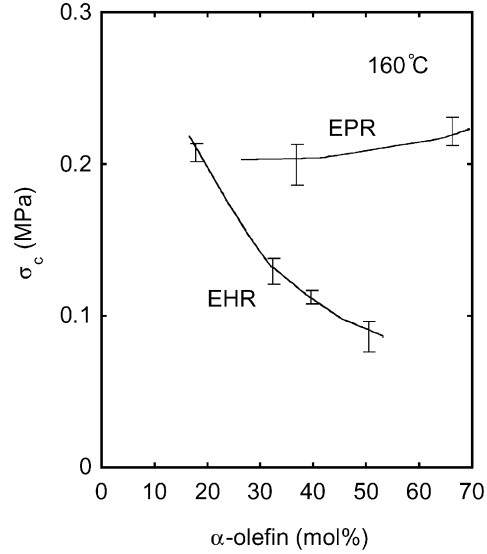


Fig. 5. Relation between onset stress for shark-skin σ_c at 160 °C and the content of α -olefin unit in the copolymers.

relaxation time, τ_n , defined by

$$\tau_n \equiv \frac{\int \tau H(\tau) d \ln \tau}{\int H(\tau) d \ln \tau} = \frac{\eta_0}{G_N^0} \quad (8)$$

Therefore

$$\frac{\tau_w}{\tau_n} = \frac{J_e^0}{J_N^0} = f \quad (9)$$

where f (> 1) the constant which is the function of molecular weight distribution [29], and $J_N^0 = 1/G_N^0$.

Consequently, the wall shear stress $\sigma(\dot{\gamma})$ is represented by

$$\sigma(\dot{\gamma}) = \dot{\gamma} \eta_0 \left[1 + f^2 (\tau_n \dot{\gamma})^2 \right]^{(n-1)/2} \quad (10)$$

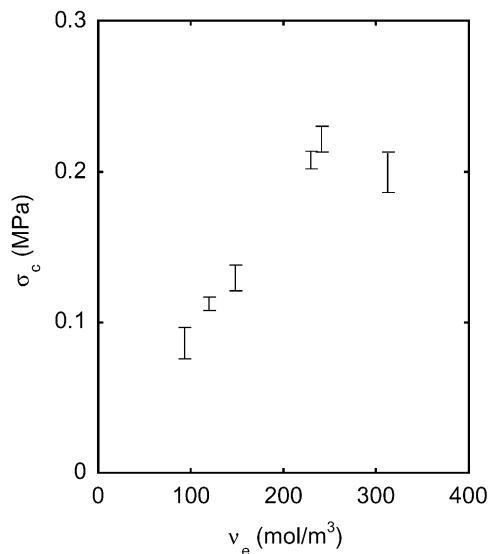


Fig. 6. Relation between ν_e and σ_c at 160 °C.

Further, Eq. (10) can be expressed using Deborah number, $De (= \tau_n \dot{\gamma})$, and G_N^0 as

$$\sigma(\dot{\gamma}) = De G_N^0 [1 + f^2 (De)^2]^{(n-1)/2} \quad (11)$$

Since f is usually considerably larger than 1, i.e. $1 \ll f^2 (De)^2$

$$\sigma(\dot{\gamma}) \cong f^{n-1} (De)^n G_N^0 \quad (12)$$

Eq. (12) demonstrates that a polymer with lower G_N^0 , i.e. lower ν_e , shows a higher De at the same level of the wall stress, which may explain the result of Fig. 6. It is generally accepted that a polymer stores more energy during flow at high De conditions, and thus behaves like a solid material. As a result, slip or crack, which will be the origin of shark-skin failure as mentioned below, takes place for a polymer melt [24]. Further, the equation also explains that a polymer with narrow molecular weight distribution, i.e. having a small f , is easy to exhibit surface instabilities.

Hereafter, we will discuss the mechanism of the shark-skin failure from the molecular point of view. When the debonding stress between the wall and a polymer melt is less than the cohesive strength of the polymer melt, the polymer slips on the wall at levels of the wall shear stress higher than the debonding stress. If the slip does not take place constantly, it will lead to surface instabilities such as slip-stick failure. However, in many cases, as pointed out by Venet and Vergnes [18], adhesive failure may not be the main origin of, at least, shark-skin instability. As discussed extensively in recent studies [15,16,18,19], some form of the crack mechanism, originally proposed by Cogswell [11], is becoming to be more accepted as the probable origin of shark-skin instability, although there is still possibility that slip or other mechanism is responsible for shark-skin in some cases. Further, Cogswell [11] also indicated that the discontinuity of velocity at the die exit wall region, leading to elongational wall velocity acceleration and tensile stresses, is responsible for the cracks, which eventually may appear like a ‘peel-off’ failure [16]. The stress at the crack-opening can be discussed referring to the failure mechanism of glassy amorphous polymers [34–37], because of the high Deborah number at the prevailing flow conditions as mentioned above. According to Kausch [35], localized decohesion of molecular coils, which takes place in the region with less degree of entanglement couplings, is the primary step of microvoids leading to a macroscopic crack through crazing. As a result, cracks are easily generated in polymers with less entanglement density. The relationship between entanglement density ν_e and the critical stress for crazing, the precursor of the crack, σ_b , has been studied both theoretically [36,38] and experimentally [38,39]. According to them, σ_b falls off rapidly with increasing ν_e . Turning to Fig. 6, we observe a strikingly similar strong dependence of the onset stress σ_c (at the capillary wall) to ν_e of the samples employed. In examining this similarity, we may conclude that in the case

of the extrusion at higher elastic, i.e. higher Deborah number, conditions, the origin of instability will be the cracking of the ‘elastic’ melt on the surface above ν_e . Further, the propagation of these surface cracks on the extrudate emerging from the capillary, which will also be facilitated by lower ν_e , will be responsible for the shark-skin topography. Moreover, it has been generally accepted that σ_b slightly decreases with increasing temperature [39–41], which corresponds with the onset stress for shark-skin instabilities.

5. Conclusions

Flow instabilities in a capillary extrusion have been investigated employing various ethylene/ α -olefin copolymers with narrow molecular weight distributions. In this study, we focused on the effect of the species and content of α -olefin unit in the copolymers. It was found that the critical stress for the onset of shark-skin failure for EHR decreases monotonically with increasing 1-hexene content, whereas EPR with 67 mol% of propylene exhibits a similar level of the onset stress as EPR with 37 mol% of propylene. As a result, the EHR with high 1-hexene content exhibits shark-skin instabilities even at low shear stress. Further, the onset stress decreases with increasing the average molecular weight between entanglement couplings. Having low rubbery plateau modulus, which leads to high Deborah number at the same stress level, will be one of the reasons for the low level of the onset stress for EHR with high 1-hexene content. Furthermore, the relationship between the onset stress and the entanglement density is well explained following the fracture mechanism of glassy amorphous polymers qualitatively.

Moreover, shark-skin starts appearing at lower stress level when the extruded melt temperature is high, irrespective of the molecular structure, which is also explained by the fracture mechanism of glassy polymers. In the case of EPR at 70 °C, smooth surface appears again at higher stress region than the onset stress of shark-skin failure. On the other hand, smooth surface is observed only in the lower shear rate region for EHR.

References

- [1] Carella J, Graessley WW, Fetter LJ. *Macromolecules* 1984;17:2775.
- [2] Vega JF, Santamaria A, Minoz-Escalona A, Lafuente P. *Macromolecules* 1998;31:3639.
- [3] Lohse DJ, Graessley WW. In: Paul DR, Bucknall CB, editors. *Polymer blends*. New York: Wiley-Interscience; 1999. chapter 8.
- [4] Yamaguchi M. *Structure and properties for binary blends of polypropylene and ethylene- α -olefin copolymers*. Dissertation. Kyoto University, Kyoto, Japan. 1999.
- [5] Mäder D, Heineman J, Walter P, Mühlaupt R. *Macromolecules* 2000; 33:1254.
- [6] Miyata H, Yamaguchi M, Akashi M. *Polymer* 2001;42:5763.

- [7] Tordella JP. In: Erich FR, editor. *Rheology*. New York: Academic Press; 1969. p. 57.
- [8] White JL. *Appl Polym Symp* 1973;20:155.
- [9] Yamaguchi M. *J Appl Polym Sci* 2001;82:1277.
- [10] Yamaguchi M, Todd DB, Gogos CG. *Adv Polym Technol*, submitted for publication.
- [11] Cogswell FN. *J Non-Newtonian Fluid Mech* 1977;2:37.
- [12] Sornberger G, Quantic JC, Fajdle B, Vergnes JF, Agassant JF. *J Non-Newtonian Fluid Mech* 1987;23:123.
- [13] Beaufils P, Vergnes B, Agassant JF. *Int Polym Proc* 1989;4:78.
- [14] El Kissi N, Piau JM. In: Piau JM, Agassant JF, editors. *Rheology for polymer melt processing*. New York: Elsevier; 1996.
- [15] Venet C, Vergnes B. *J Rheol* 1997;41:873.
- [16] Gogos CG, Qian B, Todd DB, Veariel TR. *Proceeding of ANTEC 2002*, San Francisco, CA. 2002.
- [17] Tanner RI. *Engineering rheology*. New York: Oxford University Press; 1985.
- [18] Venet C, Vergnes B. *J Non-Newtonian Fluid Mech* 2000;93:117.
- [19] Rutgers R, Mackley M. *J Rheol* 2000;44:1319.
- [20] Blyer LL, Hart AC. *Polym Engng Sci* 1970;10:193.
- [21] Ramamurthy AV. *J Rheol* 1986;30:337.
- [22] Kalika DS, Denn MM. *J Rheol* 1987;31:815.
- [23] Ghanta VG, Riise BL, Denn M. *J Rheol* 1999;43:435.
- [24] Larson RG. *The structure and rheology of complex fluids*, New York: Oxford University Press; 1988.
- [25] Brochard F, de Gennes PG. *Langmuir* 1992;8:3033.
- [26] Vlachopoulos J, Alam M. *Polym Engng Sci* 1972;12:184.
- [27] Wang SQ, Drda PA. *Macromolecules* 1996;29:2627. see also page 4115.
- [28] Hatzikiriakos SG, Kazatchkov IB, Vlassopoulos D. *J Rheol* 1997;41:1299.
- [29] Ferry JD. *Viscoelastic properties of polymers*, 3rd ed. New York: Wiley; 1980.
- [30] Graessley WW, Edwards SF. *Polymer* 1981;22:1329.
- [31] Cox WP, Merz EH. *J Polym Sci* 1958;28:619.
- [32] Vega JF, Minoz-Escalona A, Santamaria A, Munoz ME, Lafuente P. *Macromolecules* 1996;29:960.
- [33] Carreau PJ. PhD Thesis. University of Wisconsin. 1968.
- [34] Kambour RP. *J Polym Sci, Macromol Rev* 1973;7:1.
- [35] Kausch HH. *Polymer fracture*. Berlin: Springer; 1978. chapter 9.
- [36] Kramer EJ, Berger LL. *Adv Polym Sci* 1990;91/92:1.
- [37] Estevez R, Tijssens MGA, Van der Giessen E. *J Mech Phys Solids* 2000;48:2585.
- [38] Wu S. *Polym Engng Sci* 1990;30:753.
- [39] Yamamoto T, Furukawa H. *Polymer* 1995;36:2393.
- [40] Ishikawa M, Ogawa H, Narisawa I. *J Macromol Sci Phys* 1977;15:1791.
- [41] Ishikawa M, Ogawa H. *J Macromol Sci Phys* 1981;19:421.