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Thermal analysis of shear induced crystallization by the shear flow thermal rheometer: isothermal crystallization of polypropylene

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Abstract

In situ differential thermal analysis during steady shear induced crystallization of polypropylene were performed by the shear flow thermal rheometer. Time development of crystallinity was obtained and analyzed by the Avrami equation; $X_c(t) = 1 - \exp\{-k(t-t_0)^n\}$, where X_c is relative crystallinity, k the kinetic constant, t_0 the induction time and n the Avrami exponent. With an increase of shear rate, k decreases slightly and t_0 decreases drastically. The increase of n was also observed but the magnitude of the change was insignificant. The observed value of n suggested the spherulite growth and inhomogeneous nucleation of the crystal even under shear. Against the crystallization temperature, the parameters behaved similar to those under quiescent conditions except that t_0 increases extremely with the increase in t_0. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Shear induced crystallization; Polypropylene; Shear flow thermal rheometer

1. Introduction

Shear induced crystallization of semi-crystalline polymers is one of weighty problems. The importance has been much raised recently by computer aided engineering (CAE) for plastic molding. For example, Ito et al. [1–4] developed a CAE code for injection molding of semi-crystalline polymers. They described the crystallization behavior by an Avrami type equation [5–7], and adopted the effect of flow by modified Hoffman type theory [8,9]. Since any experimental methods to measure crystallization kinetics under steady shear flow have not been established, material parameters in the code were unavoidably obtained by experimental data under quiescent state mainly. Though this study has succeeded to improve accuracy, apparently it is indispensable to have the data under flow because the crystallization is strongly affected by the flow.

Only a few studies, however, have shown time development of crystallinity under steady shear and there still have been open problems. Fritzshe and Price [10] developed a concentric cylinder dilatometer which can measure specific volume change under shear flow. They studied crystallization kinetics of polyethylene oxide and analyzed it based on the Avrami equation

$$X_c(t) = 1 - \exp(-kt^n), \tag{1}$$

where X_c is relative crystallinity, k a kinetic parameter and n the Avrami exponent. They reported that n is increased by increase of shear rate, and it becomes around 10. Sherwood et al. [11] investigated crystallization of poly(ϵ-caprolactone) by the same apparatus and similarly reported n up to 7. They considered that this anomalous value is due to collapsed crystals, which accelerates apparent nucleation rate. Recently Tribout et al. [12] measured crystallinity of ethylene–propylene copolymer by transmitted light intensity using a parallel plate shear generator. The measured value of n was over 12 at the maximum.

The anomalous Avrami exponent is inconsistent with the direct observations. Tribout et al. [12] also observed the growth mode of the crystal and to obtain the induction time directly by an optical microscope and fiber pull-out cell. Inconsistently with the anomalous Avrami exponent, the observed growth mode was essentially spherulite which gives $n = 3$ or $n = 4$ according to the theory, and the collapse of the spherulite was not observed. For polypropylene similar results have been reported [13,14].

In the present paper, using the shear flow thermal rheometer (SFTR) [15], we show isothermal crystallization kinetics of polypropylene under steady shear obtained by

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Abbreviations: SFTR: shear flow thermal rheometer; DTA: differential thermal analysis; DSC: differential scanning calorimetry; CAE: computer aided engineering.

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Nomenclature

$X_c(t)$	Relative crystallinity
n	Avrami exponent
k	Kinetic parameter in the Avrami equation
t_0	Induction time
$\dot{\gamma}$	Shear rate
T_c	Crystallization temperature
ΔT	Differential temperature

thermal measurement which has never been reported. From the data, shear rate and crystallization temperature dependence of the Avrami parameters shall be discussed.

2. Experimental

2.1. Apparatus

A detailed description and test of SFTR have been published [15] thus here we shall mention it briefly. SFTR is based on a shear flow rheometer of model ARES purchased from Rheometrics Co. improved by a pair of thermocouple for differential thermal analysis (DTA). The thermocouple was K-type Sheath from THERMOCOAX Co., and located into the sample and onto an aluminum plate of the rheometer as the reference. To prevent the heat transfer, polyetheretherketon films of 1 mm thickness were put on between the aluminum plates and the sample by an epoxy type adhesive. The aluminum plates were parallel discotic plates with 25 mm diameter, and gap between the upper and the lower plates was 2 mm.

For comparison, we also performed thermal measurement under quiescent state by a differential scanning calorimetry (DSC) purchased from Perkin–Elmer Co. type DSC-7.

2.2. Sample

Material was isotactic-polypropylene kindly supplied by Mitsuichemical Co. (Code JHH-G). Weight average molecular weight, number average molecular weight, tacticity and equilibrium melting point were 180,000, 28,000, 0.91 and 180°C, respectively. For SFTR measurement, the sample was processed from pellet by a hot press machine into a discotic shape with diameter of 25 mm and thickness of 2 mm. To eliminate thermal histolysis, the sample was kept at 185°C for 20 min before the measurement. During the measurement, to avoid the oxidation, the sample was in nitrogen atmosphere. For DSC measurement, 8 mg of the sample was melted at 185°C for 10 min before the measurement.

2.3. Data acquisition

Effect of shear rate $\dot{\gamma}$ was investigated for a fixed crystallization temperature $T_c = 142.5°\mathrm{C}$ with $0.05\ \mathrm{s}^{-1} \le \dot{\gamma} \le 1.0\ \mathrm{s}^{-1}$. To examine effect of T_c, T_c was varied from 138.0 to 148.0°C with fixed $\dot{\gamma}$ of $0.2\ \mathrm{s}^{-1}$.

DSC measurement was performed for quiescent state of T_c from 125 to 137°C. Note that crystallization behavior virtually did not occurred at the higher temperatures under the quiescent state.

2.4. Data analysis

Relative crystallinity based on the thermal measurement, $X_c(t)$, was calculated from the differential temperature $\Delta T(t)$ by

$$X_c(t) = \frac{\int_{t_0}^{t_f} \Delta T('t)\, \mathrm{d}t'}{\int_{t_0}^{t_f} \Delta T('t)\, \mathrm{d}t'} \tag{2}$$

where t_0 and t_f are starting and finishing time of the crystallization peak. Note that in the previous study [15] we have shown that under steady shear flow and isothermal conditions, crystallinity obtained by the thermal basis (Eq. (2)) is sensitive than that obtained by the mechanical basis so that in the present study we shall concentrate the thermal basis ones. Introducing induction time t_0, $X_c(t)$ was analyzed accordingly to the following Avrami type equation:

$$X_c(t) = 1 - \exp\{-k(t-t_0)^n\}. \tag{3}$$

because t_0 could affect the value of n. Parameters in the equation were optimized by Levenberg–Marquardt non-linear fitting method [16]. Because of the non-linearity of Eq. (3), it might be possible that the chi-square minimization during the fitting iteration does not work successfully. To eliminate this, we confirmed that the best fit parameters are independent of the initial values varied within the reasonable range.

3. Results and discussion

3.1. Differential temperature and shear viscosity

Figs. 1 and 2 show time development of differential temperature and shear viscosity simultaneously measured by SFTR for various T_c (Fig. 1) and $\dot{\gamma}$ (Fig. 2). Viscosity increase and peak of the differential temperature induced by the crystallization are observed. Kamoto et al. [17] investigated crystallization of polyethyleneterephthalate under steady shear flow by a rotaviscometer and measured induction time of the viscosity increase. They reported that the induction time of the viscosity increase is reduced by increase of $\dot{\gamma}$. Though their experiment was under non-isothermal condition while ours was under isothermal one, our result is consistent with it. Induction time for the peak of the differential temperature shows similar behavior.

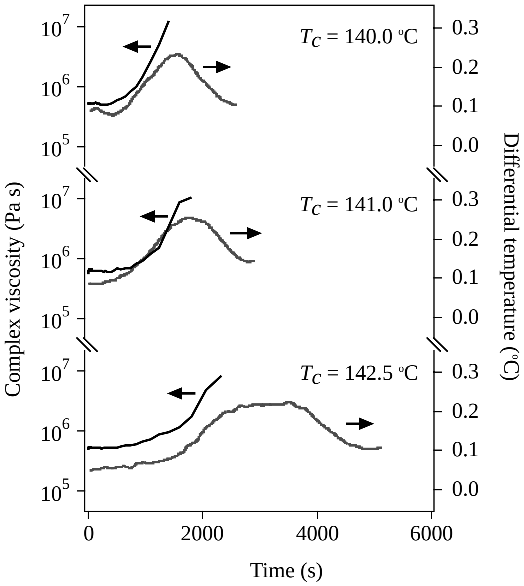

Fig. 1. Time development of differential temperature and shear viscosity for $\dot{\gamma} = 0.2\ \mathrm{s}^{-1}$ with various T_c.

3.2. Time development of relative crystallinity

Figs. 3 and 4 show time development of relative crystallinity, $X_c(t)$, obtained from DTA data. Fig. 5 is obtained by DSC under quiescent state for comparison. The Avrami equation (Eq. (3)) is in good agreement with the experimental results even under the shear flow. It should be noted that the experimental data also can be well described by Eq. (1) with anomalous values of the Avrami exponent n. For example, it is 19.4 at $T_c = 148°\mathrm{C}$ and $\dot{\gamma} = 0.2\ \mathrm{s}^{-1}$ for Eq. (1), while it is 3.11 at the same condition for Eq. (3). Phenomenologically, both the equations could be applicable to describe the crystallization kinetics. However, because the Avrami exponent is strongly related to the crystal growth mode, above two results give completely different information about the crystal morphology. We adopt Eq. (3) based on the results in the other studies [12,14] where the spherulite growth is directly observed. This point shall be discussed later.

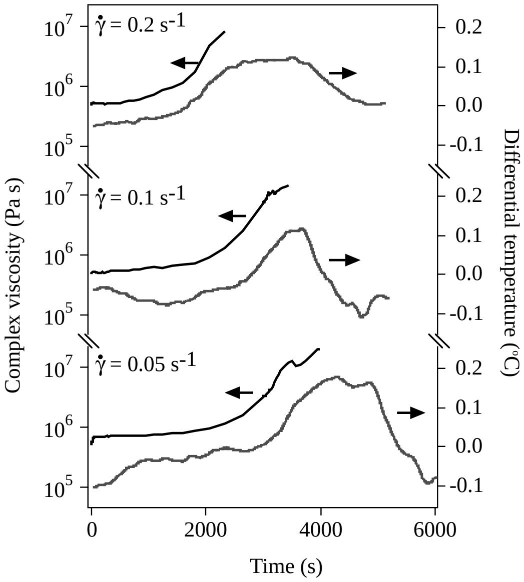

Fig. 2. Time development of differential temperature and shear viscosity for $T_c = 142.5°\mathrm{C}$ with various $\dot{\gamma}$.

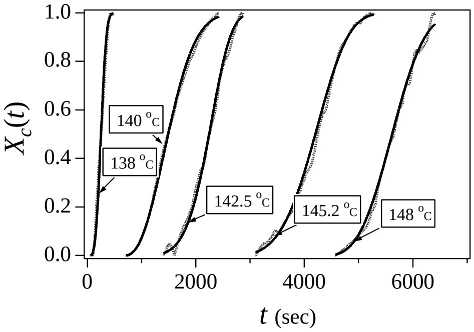

Fig. 3. Relative crystallinity ($X_c(t)$) calculated from DTA data obtained by SFTR for $\dot{\gamma} = 0.2\ \mathrm{s}^{-1}$ with various T_c indicated on each line. Dotted lines are experimental data and solid lines are drawn according to Eq. (3) with optimized parameters.

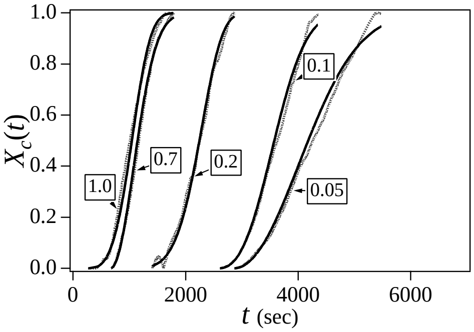

Fig. 4. Similar to Fig. 3 for $T_c = 142.5°\mathrm{C}$ with various $\dot{\gamma}$ indicated on each line.

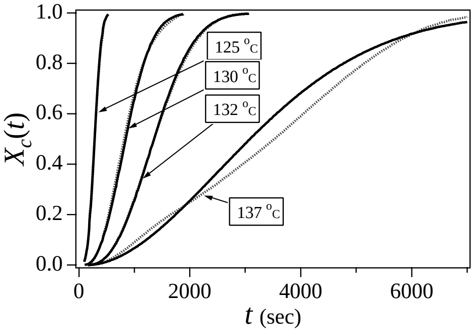

Fig. 5. Relative crystallinity ($X_c(t)$) obtained by DSC under quiescent conditions for various T_c indicated on each line. Meaning of solid and dotted lines are the same with Fig. 3.

3.3. Avrami parameters

Parameters to fit the data are shown in Figs. 6–8 against $\dot{\gamma}$ or T_c, respectively. Fig. 6 and Fig. 8 indicate that the Avrami exponent is slightly affected by shear; n slightly increases with increase of T_c under the flow. Against $\dot{\gamma}$, n tends to increase with increase of $\dot{\gamma}$ (see Fig. 7a). Though the adopted equation is different, this is consistent with the earlier results [10–12]. k slightly decreases with increase of $\dot{\gamma}$ and drastically decreases with increase of T_c. This behavior shall be discussed later relating to the nucleation rate, the growth rate and the shape of the crystal growth. Behavior of t_0 against T_c under shear are reasonable and consistent with those under quiescent state; with increase of T_c, t_0 increases in both Figs. 6 and 8.

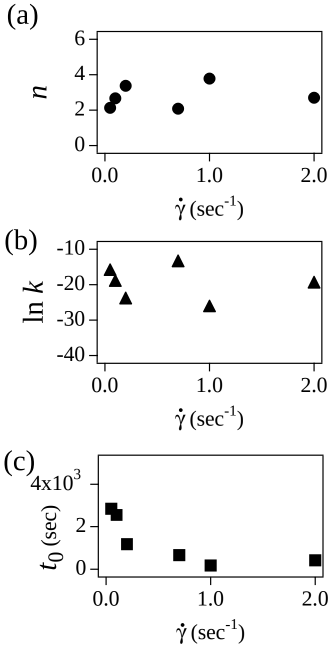

Fig. 7. Shear rate dependence of the parameters in the Avrami equation (Eq. (3)) obtained from Fig. 4 at $T_c = 142.5°C$.

4. Discussion

4.1. Avrami exponent

Though the Avrami exponent n slightly tends to increase with increase of $\dot{\gamma}$ and decrease of T_c, it is reasonably within $2 \le n \le 4$. It seems to be inconsistent with the earlier results [10–12]. We consider that this could be due to the difference of the method of analysis. As we mentioned before, introduction of the induction period into the Avrami equation could reduce the Avrami exponent. Recently, Watanabe et al. [14] performed direct observation of crystallization of polypropylene by coaxial cylinder type flow generator and reported that the spherulite growth was observed and the nucleation rate and the growth rate were almost steady against time. This supports our results where the Avrami exponent corresponding to the spherulite growth is obtained. The slight increase of n suggests that the crystallization mechanism is changed from inhomogeneous nucleation into homogeneous nucleation, i.e. the nucleation rate is an increasing function against time. This behavior has been discussed earlier [10–12]. It has been suggested that

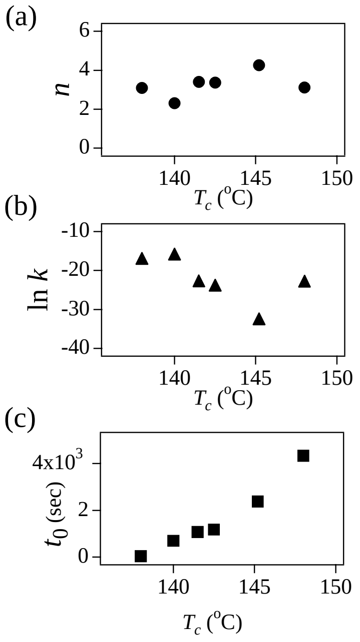

Fig. 6. Crystallization temperature dependence of the parameters in the Avrami equation (Eq. (3)) obtained from Fig. 3 at $\dot{\gamma} = 0.2\ s^{-1}$: (a) Avrami exponent n; (b) kinetic constant k; and (c) induction time t_0.

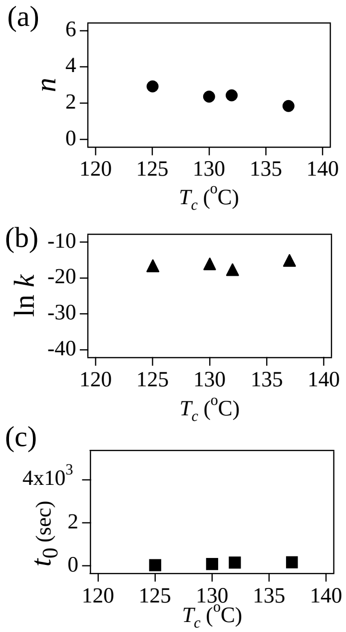

Fig. 8. Crystallization temperature dependence of the parameters in the Avrami equation (Eq. (3)) under quiescent conditions obtained by DSC.

the collapse of spherulite induced by flow occurs and generates small nuclei resultantly. In the direct observations [12–14], however, this kind of behavior has not been observed. Watanabe et al. [14] observed domain structure composed by a lot of small nuclei aligned along the flow direction. Kinetics of this type of structure might explain the increase of n.

4.2. Kinetic parameter

Most simply, the kinetic parameter k is described by the linear growth rate G and the linear nucleation rate N as

$$k = k_f N G^m \tag{4}$$

where k_f is the shape factor and m is dimension of the crystal growth. Behavior of k against $\dot{\gamma}$ and T_c should be explained by this relation. Concerning shear rate, it was [14] reported for polypropylene that (i) the spherulite was observed and its deformation due to the flow is negligible, i.e. m equals to 3, that (ii) N is increased with increase of $\dot{\gamma}$, and that (iii) G is almost independent of $\dot{\gamma}$. In our result (see Fig. 7b) however, k slightly decreases with increase of $\dot{\gamma}$. The reason is unknown. We conjecture that the nucleation kinetics is changed as discussed above and thus Eq. (4) is not available.

The effect of the supercooling is consistent with the earlier discussions based on Hoffman type theories where both G and N are described by convex functions of T_c with a peak in between glass transition temperature and melting temperature. Because k decreases with increase of T_c even under the quiescent condition (see Fig. 8b), our T_c is rather high so that G and N seem to decrease with increase of T_c.

4.3. Induction time

The induction time t_0 is monotonically decreased with increase of $\dot{\gamma}$ and decrease of T_c. This phenomenon could be explained by the ordering of polymer orientation induced by the flow. It has been reported that during the induction period ordering of the molecular orientation preceding the molecular packing occurs. Imai et al. [18–21] observed by small-angle X-ray scattering of polyethyleneterephthalate that orientational fluctuation of polymer segments occurs before the density fluctuation. They concluded that this corresponds to parallel ordering of polymer chains prior to crystallization. This picture is also supported by molecular dynamics simulation [22]. Thus it can be considered that the molecular ordering process in the induction period is accelerated by the flow and it gives rise to the reduction of the induction time. Because degree of the ordering is increased with increase of $\dot{\gamma}$ and decrease of T_c, t_0 is decreased correspondingly.

5. Concluding remarks

Kinetics of shear induced crystallization of polypropylene was obtained from in situ thermal measurement by SFTR. Consistent with the earlier results, time development of the relative crystallinity can be well described by an Avrami type equation. Parameters to achieve the best fit against the experimental data were presented and their behavior against shear rate and crystallization temperature was discussed.

Though this study gives a new insight into the shear induced crystallization of polypropylene, further researches are apparently required. First the competition between the effect of the flow and the effect of the supercooling. As it is hard to perform the measurements at the lower temperature under shear or at the higher temperature under quiescent condition, series of the measurements varying both T_c and $\dot{\gamma}$ are required to discuss the competitive effect. Second is the consistency with the direct observations. Even though we adopted the induction time in the Avrami equation, we found the increase in the Avrami exponent with an increase of shear rate suggesting that the change of nucleation kinetics. Explanation of this phenomenon should be obtained by the complemental study to the direct observations. Third is the applicability of the Avrami equation. Though the experimental data can be well described by the Avrami equations, the behavior of the parameters cannot be fully understood physically. Theoretical study based on the morphological kinetics is necessary. Studies on the above points are being done and the results will be published elsewhere.

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