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RELAXATION BEHAVIOR OF ULTRADRAWN POLY(ETHYLENE) FILM BY TEMPERATURE WAVE ANALYSIS

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Abstract

A new sensitive thermal analysis for the observation of re-orientation behavior in the melting region of the ultradrawn poly(ethylene) film was proposed by the simultaneous measurement of thermal diffusivity and birefringence under optical microscope in a constant heating rate. Thermal diffusivity was obtained by the phase delay of temperature wave passed through the thickness direction of the specimen. The results correspond with each other over wide temperature range including melting temperature. It was concluded that the thermal diffusivity measurement was more sensitive not only to detect the molecular relaxation in a continuous heating run, but also to find out the delicate variation of chain direction.

Keywords: birefringence, re-orientation, temperature wave, thermal diffusivity, ultradrawn poly(ethylene)

Introduction

The anisotropy of drawn polymers exhibit strong relationship not only with mechanical properties [1, 2] but also with thermal properties. For example, the increase of apparent melting temperature of ultradrawn poly(ethylene) is called super-heating [3]. It is also well known that the thermal conduction is sensitive to the anisotropy of molecular orientation in uniaxially drawn polymer [4], such as thermal conductivity along the drawn direction to be higher than that in the perpendicular direction, because heat transfer in insulator is explained by lattice vibration and the conveyance along the covalent bonds in main chains are predominantly stronger than that of interchain van der Waals forces.

The main chain anisotropy of polymer is usually measured by wide-angle X-ray diffraction, small angle light scattering, and retardation by Berek compensator in optical microscope. However, these techniques are sometimes insufficient to estimate

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the small variation of anisotropy in the relaxation process in heating, which is considered as non-equilibrium state.

Thermal diffusivity and thermal conductivity are the physical properties of heat transport phenomena, the former is defined as a transport coefficient of temperature and the latter is that of heat energy. Thermal conductivity λ is related to thermal diffusivity α according to the formula: $\lambda=\alpha C$, where C is the specific heat per unit volume. From the stand point of measurement technique, it is classified into two categories: one is non-steady state method which directly determines thermal diffusivity and the other is steady-state method which directly determines thermal conductivity.

In temperature wave analysis (TWA) [5], which belongs to the non-steady state method for determining thermal diffusivity, temperature wave is input on the front surface of the film specimen and the phase delay propagating in the thickness direction is precisely measured on the rear surface. The characteristics of TWA are summarized in the following: (1) a small temperature distribution resulting from a small amount of specimen, (2) a wide frequency range of temperature wave, (3) a continuous measurement under heating or cooling run, (4) specimen is fixed tightly by backing material in phase transition or molten state, and (5) a simultaneous measurement of birefringence under optical microscope.

In this study thermal diffusivity in the thickness direction of ultradrawn high molecular mass poly(ethylene) was measured in a constant heating rate. The heating was performed from room temperature to above the melting temperature under an optical microscope to measure the birefringence of the specimen. We propose a new thermal analysis that is sensitive to the re-orientation of molecules in the phase transition region.

Experimental

Materials

A linear poly(ethylene) with the viscosity-average molecular mass of 5×10^6 (Himont Co. Ltd., UHMW1900) was used as starting material. The hot decalin solution was prepared at 135°C containing 0.4 g/100 mL of poly(ethylene) and then it was quenched to ice temperature by pouring into an aluminum tray. The obtained gel was kept a few days to evaporate the solvent. Furthermore, the resulting gel film was vacuum-dried for 1 day to remove the residual trace of decalin. The dry gel film was cut into strip shape, which was clamped in a manual stretching device. The specimens were held in an oven at 135°C and elongated manually up to the desired ratio. The detailed procedure was described in the previous report [6–10].

Method

Density of film was measured at 28°C by a pycnometer with the mixed solvent of chlorobenzene and toluene as the medium. The crystallinity of drawn specimen was calculated on the assumption that crystal and amorphous densities are 1.000 and 0.852 g cm^{-3}, respectively. Birefringence measurements were made by a Berek compensator (Nihon

Chikagakusha Co.) inserted in optical microscope (Nikon) with crossed polarized. Optical micrographs were also taken with crossed polarized and with 530 nm filter.

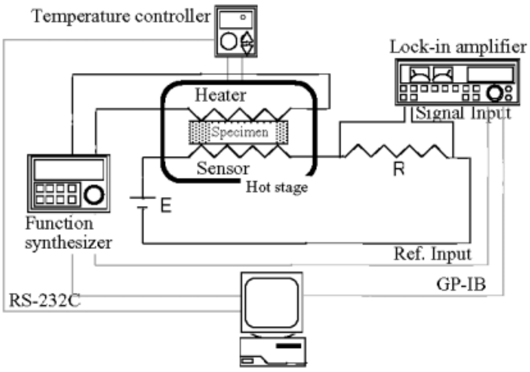

Fig. 1 Measurement apparatus of temperature wave analysis

The measuring system of TWA consists of a function synthesizer (NF Electronic Instruments, NF1946), a digital lock-in amplifier (NF LI5640), a power source of bias current for sensor, a temperature controller (ULVAC HPC7000), a sample holder on hot stage, and a personal computer (Fig. 1). The sinusoidal wave with a frequency of 0.1 Hz~100 kHz is applicable as the inputting temperature wave.

The frequency range for the measurement is chosen by considering the thermal diffusion length $\mu=1/k$, where k is defined as $(\omega/2\alpha)^{1/2}$. The amplitude of generated temperature wave is selected less than 0.1 K on the front surface, and at that time less than 10 mK on the rear surface. A rate of heating or cooling is 0.2 K min^{-1} for minimizing the temperature distribution in the specimen. The Fourier spectrum of temperature wave at rear surface was also observed by a fast Fourier transform (FFT) analyzer.

Basically a gold thin resistor controlled at about 50 Ω with rectangular area of 1×4 mm was sputtered on the surface of the flat glass plate of pyrex 7740 as backing substrate. The specimen was inserted between a pair of glass plates one as a heater and the other as a sensor. The specimen was fixed in the drawn direction to avoid shrinkage as described in Fig. 2.

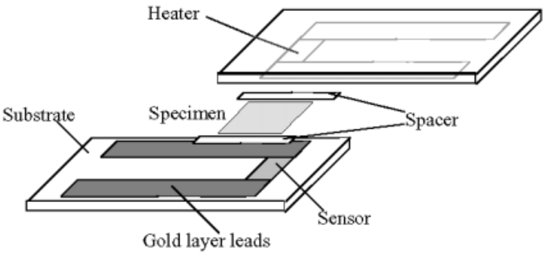

Fig. 2 Schematic diagram of measurement cell

Assuming the one-dimensional heat flux, temperature wave generated on the front surface (x=0) by a.c. Joule heating propagates in the thickness direction and is detected by the sensor attached on the rear surface (x=d), on which the amplitude decay and the phase delay can be observed. The one-dimensional diffusion equation leads to the solution of temperature oscillation at x=d as follows;

$$T(d,t)=\frac{\{j_0\exp(i\omega t)/(1+i)\}\exp\{-(1+i)kd\}}{[(\lambda k+\lambda_s k_s)^2-(\lambda k-\lambda_s k_s)^2\exp\{-2(1+i)kd\}]/2\lambda k} \qquad k=\sqrt{\frac{\omega}{2\alpha}} \tag{1}$$

where T is a.c. temperature, t is time, j_0 is heat flux on the heater, λ is thermal conductivity, α is thermal diffusivity and ω is angular frequency. Subscript s means the property of backing substrates and the other means the specimen. If the conditions of (i) kd>>1 or (ii) $\lambda k\approx\lambda_s k_s$ are satisfied, Eq. (1) becomes to a simple form of

$$T(d,t)=\frac{\sqrt{2}j_0\lambda k\exp(-kd)}{(\lambda k+\lambda_s k_s)^2}\exp\left\{i\left(\omega t-kd-\frac{\pi}{4}\right)\right\} \tag{2}$$

To note the phase term in Eq. (2), we can get more simple equation as follows.

$$\Delta\theta=-\sqrt{\frac{\omega}{2\alpha}}d-\frac{\pi}{4} \tag{3}$$

When the thickness d has been already known, thermal diffusivity is calculated from the slope of the linear relationship between $\Delta\theta$ and $\omega^{1/2}$ in Eq. (3).

By the way, we can rewrite Eq. (3) as follows if the intercept of this straight line equals to $-\pi/4$,

$$\alpha=\frac{\omega d^2}{2\left(\Delta\theta+\frac{\pi}{4}\right)^2} \tag{4}$$

By using Eq. (4) thermal diffusivity is determined as a function of temperature under constant heating rate at a fixed frequency which is suitable for the measurement. In the polymer film the variation of sample thickness is considered less than 1% in whole temperature range.

Results and discussion

Figure 3 shows a relationship between phase delay $\Delta\theta$ and angular frequency $\omega^{1/2}$ of uniaxially drawn poly(ethylene) film with drawn ratio of 100, measured at 28°C. As predicted by Eq. (3), a linear relationship is observed between $\Delta\theta$ and $\omega^{1/2}$ in the condition kd>1 with the extrapolated intercept of $-\pi/4$. The responsibility and S/N ratio of the sensor was good enough to detect a small temperature variation up to 14.4 kHz, which corresponds to kd=4. In this way, when the thermal property of backing mate-

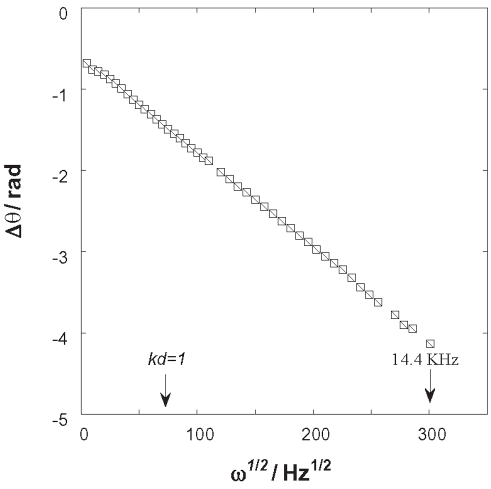

Fig. 3 Phase delay $\Delta\theta$ *vs*. square root of angular frequency $\omega^{1/2}$ of temperature wave measured at 28 °C in the ultradrawn poly(ethylene) film with the drawn ratio of 100. The film thickness is 6μm

rial is similar to that of the specimen, the approximation from Eq. (2) to Eq. (3) is allowed in the wide frequency range.

Thermal diffusivity is directly calculated from the slopes of the straight line determined by curve fitting of the measurement results. Thermal diffusivity of specimen with various drawn ratio of 1, 20, 50 and 100 were summarized in Table 1 with birefringence Δn at 28°C which is calculated from retardation R and thickness d. With increasing the drawn ratio, the thermal diffusivity (α) decreases but the density (ρ) and birefringence (Δn) increases. Table 1 also shows the variation in density, crystallinity, and thickness with drawn ratio. These results clearly indicate that the increasing of crystallinity with the drawn ratio is obviously due to the crystallization introduced by orientation.

Table 1 Thermal diffusivity and birefringence of ultradrawn poly(ethylene) with draw ratio, density and crystallinity

Drawn ratio	Thickness/ μm	Density/ g cm^{-3}	Crystallinity/ %	Birefringence	Thermal diffusivity/ mm^2 s^{-1}
1	50	0.974	84.8		0.50
20	27	0.976	85.9	52	0.19
50	20	0.985	90.8	55	0.15
100	6	0.988	92.8	58	0.12

Figure 4 illustrates the plots of the thermal diffusivity α and the birefringence Δn *vs*. the drawn ratio at room temperature. The birefringence increases with increasing

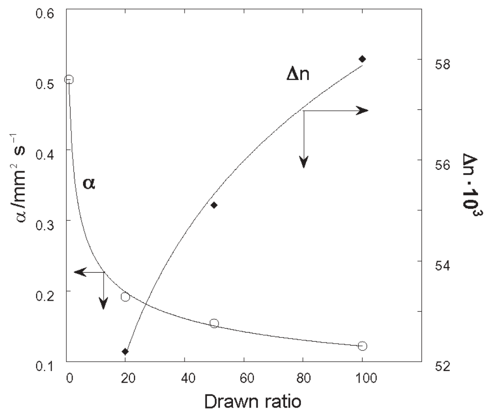

Fig. 4 Thermal diffusivity α and birefringence Δ*n* of ultradrawn poly(ethylene) film measured at 28°C as a function of drawn ratio

the drawn ratio as same as reported in the previous study [11]. On the other hand the thermal diffusivity in the thickness direction decreases with increasing the drawn ratio. The gelation/crystallization film was widely studied by small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) [8, 9, 12]. It is well known that in the dried gel film the composed of crystal lamella are highly oriented with their large flat faces parallel to the film surface. Within the lamellar crystals, the *c*-axis are oriented perpendicular to the large flat faces. In the highly drawn film the molecular chain axis is mainly aligned in the stretching direction [12].

The results in Fig. 4 mean that α is affected by the main chain direction, which indicates higher thermal diffusivity than that of van der Waals direction. The thermal diffusivity of 100 times drawn film is 0.12 mm^2 s^{-1}, much smaller than the value of non-stretched crystalline polymer film (0.5 mm^2 s^{-1}), almost the same as the value of amorphous polymer (for example α=0.11 mm ^{2} s^{-1} for polystyrene, injection grade) and a little bit higher than the isotropic liquid (0.06~0.08 mm^2 s^{-1}). It is known that near complete chain alignment along the drawn direction is already achieved at relatively low drawn ratios of 15–20, but at high drawn ratio above 100, in addition to the near perfect *c*-axis orientation, the orientations of *b*-axis (in the plane of the film) and *a*-axis (perpendicular to film) are observed [13, 14]. The detail of correlation of thermal diffusivity and the crystallographic structure is beyond the scope of this study and will be published in future, but qualitatively the decrease of thermal diffusivity with high drawn ratio suggests the near perfect *c*-axis orientation in the direction of draw. It also means that thermal diffusivity is much more influenced by the orientation in draw direction than the small increase of crystallinity.

On the basis of these results, a new thermal analysis TWA, in which α is obtained as a function of temperature can be proposed for the analysis on the re-orientation behavior at high temperature.

Figure 5 shows the results on simultaneous measurements of α and Δ*n* in a heating run of constant rate 0.2°C min^{-1} with temperature wave frequency of 80 Hz in the vicinity of melting temperature.

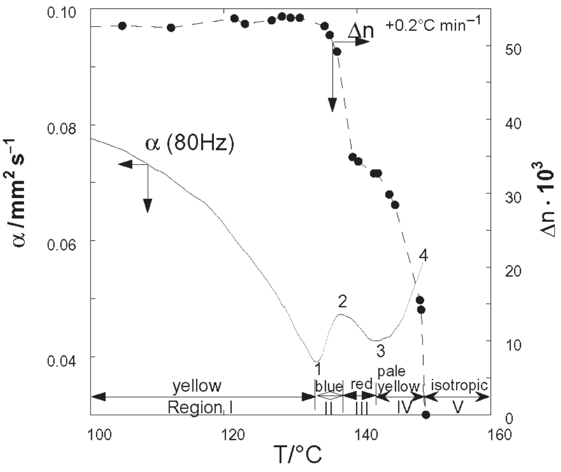

Fig. 5 Simultaneous measurements of thermal diffusivity α and birefringence Δ*n* of ultradrawn poly(ethylene) film with a drawn ratio of 20. The heating rate is 0.2°C min^{-1} and the frequency of temperature wave is 80 Hz

The color changes under crossed polarized optical microscope are clearly divided into 5 regions at the critical temperatures (1, 2, 3 and 4) indicated in Fig. 5. With increasing temperature Δ*n* is kept almost constant but α decreases up to 135°C. In this lower temperature region (Region I) the fibril morphology is colored yellow. It means that the main chain is aligned in the machine direction. From 135 to 139°C α and Δ*n* both inversely change, α rapidly increases but Δ*n* decreases, the color changes from yellow to blue (Region II). At 139°C α shows a maximum and then begins to decrease again up to 143°C, on the other hand Δ*n* only slows down the decreasing rate. In this region the fibril structure is still remained and observed as red (Region III). Above 143°C the color changes to pale yellow and it gradually fades with increasing temperature (Region IV). At 150°C the color is almost faded and Δ*n* becomes zero and then the thin gold sensor was almost broken by the drastic shrinkage of the fibrils.

The color change from yellow to blue (from Region I to Region II) means that the major molecular chain axis has become aligned to the perpendicular direction to the stretching direction. It corresponds to the re-orientation and/or re-crystallization of some molecules from the near perfect extended chain to the folded lamellar crystal. In Region III the color changes from blue to red, it corresponds to the decrease of α due to the partially melting of lamellar crystal. From Region III to Region IV, the red color fades into pale yellow and the fibril structure becomes indistinct with increasing temperature. It corresponds to the dispersed re-orientation of residual extended chain.

Figure 6 shows a differential coefficient $d\alpha/dT$ from Fig. 5 to make clear the complicated change of α. In Region I $d\alpha/dT$ is negative, as explained by the general heat conduction model for insulating solid. At high temperatures as in this study most of phonons are exited and the probability of interaction among the phonons through the Umklapp processes is proportional to the number of phonons. Thus the mean free path of phonon is proportional to T^{-1}, thermal conductivity or thermal diffusivity is

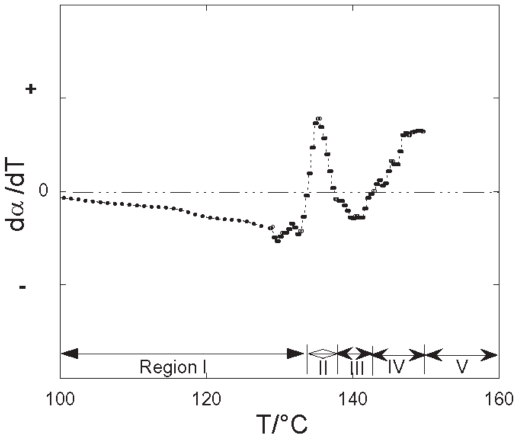

Fig. 6 Differential coefficient of thermal diffusivity dα/dT in the heating run as depicted in Fig. 5

inversely proportional to T. In Region II dα/dT is positive corresponding to the re-orientation and re-crystallization of highly extended molecular chain into the thickness direction. The decrease of α in Region III (dα/dT is negative) is assumed corresponding to the decrease of crystallinity by the partially melting of some parts of crystalline lamellae as shown in the previous study [15]. In Region IV dα/dT is positive but the color fades. It corresponds to the dispersed re-orientation of residual extended chain (fibrils) and the relaxation of molecular anisotropy. Assuming the partially re-orientation process of highly extended molecular chain both by the observation of Δn and color under polarized optical microscope, the complicated temperature dependence of α just below the melting temperature is well explained.

It should be mentioned that TWA method is suited to the measurement of re-orientation process because the specimen can be firmly fixed up to the melting temperature and the measurement is done in one direction.

Conclusions

A new sensitive thermal analysis for the observation of re-orientation in the melting region of the ultradrawn poly(ethylene) film was proposed by the simultaneous measurement of birefringence and thermal diffusivity. Thermal diffusivity was obtained by TWA, in which the decay and the phase delay of temperature wave in the thickness direction of the specimen were analyzed. The results showed the good agreement with each other over wide temperature range including just before and over the melting temperature, but TWA was quantitatively more sensitive to the small change of re-orientation in highly oriented ultradrawn poly(ethylene) film. It was concluded that the thermal diffusivity measurement was sensitive not only to detect the molecular relaxation and the melting temperature, but also to find out the delicate variation of chain direction.

References

1 J. Smook, J. C. Torfs, P. F. van Hulten and A. J. Pennings, Polym. Bull., 2 (1980) 293.
2 P. J. Barham and A. Keller, J. Mater. Sci., 15 (1980) 2229.
3 C. Sawatari and M. Matsuo, Coll. Polym. Sci., 263 (1985) 783.
4 C. L. Choy, Polymer, 18 (1977) 984.
5 T. Hashimoto, Y. Matsui, A. Hagiwara and A. Miyamoto, Thermochim. Acta, 163 (1990) 317.
6 P. Smith, P. J. Lemstra and H. C. Booij, J. Polym. Sci. Polym. Phys. Ed., 19 (1981) 877.
7 P. Smith, P. J. Lemstra, J. P. L. Pijpers and A. M. Kiel, Coll. Polym. Sci., 258 (1981) 1070.
8 M. Matsuo and R. St. J. Manley, Macromolecules, 15 (1982) 985.
9 M. Matsuo and R. St. J. Manley, Macromolecules, 16 (1983) 1500.
10 C. Sawatari and M. Matsuo, Coll. Polym. Sci., 269 (1991) 795.
11 C. Sawatari and M. Matsuo, Polymer, 30 (1989) 1603.
12 M. Matsuo, C. Sawatari and T. Ohhata, Macromolecules, 21 (1988) 1317.
13 P. Smith and P. J. Lemstra, J. Mater. Sci., 15 (1980) 505.
14 P. Smith, P. J. Lemstra, J. P. L. Pijpers and A. M. Kiel, Coll. Polym. Sci., 259 (1981) 1070.
15 T. Hashimoto, J. Morikawa, T. Kurihara and T. Tsuji, Thermochim. Acta, 299 (1997) 95.