Note

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Morphological Study on Polytetrafluoroethylene During the Crystallization Process at a Constant Cooling Rate from the Melt

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Abstract : Polytetrafluoroethylene (PTFE) was slowly crystallized from the melt and quenched into ice water just when the sample reached a prescribed temperature (T_p) to terminate the excess crystallization. The T_p -dependence of the surface morphology of PTFE was examined in a scanning electron microscope to find that thin bands ca. 120 nm wide appeared in the early stage of the crystallization and grew up with decreasing T_p finally to merge each other. The in situ observation by polarized light microscopy suggested that PTFE molecules lay parallel to the substrate.

1. Introduction

Several studies have been reported [1-7] for the external surface structure of polytetrafluoroethylene (PTFE) as well as the fractured internal surface since morphological structure on the fractured surface of the melt-crystallized PTFE was observed by electron microscopy to show that the fractured surface was covered with thick bands with fine longitudinal striations [8]. We reported the developing process of the bands observed on the fractured surface during slow-cooling of the sample, being correlated with the sheaf-like bands on the external surface [9]. From the viewpoint of practical use of the polymer, it seems to be important to study the structural development during the crystallization processes at slow-cooling rates or the non-isothermal crystallization processes.

In this study, an apparatus is designed to quench the sample to 0 °C (ice water) from the prescribed final crystallization temperature (T_p), to which the sample was cooled slowly from the melt. The T_p -dependence of the morphology on the external surface of the melt-crystallized PTFE was examined by scanning electron microscopy (SEM) as well as light microscopy (LM).

2. Experimental

The original sample was supplied by DuPont Company

Fig. 1 A scheme of an apparatus which quenches the slow-cooled sample at T_p .

as an aqueous dispersion (TE-30J). An aluminum substrate was immersed in the PTFE dispersion at room temperature and then withdrawn vertically to form the thin layer of PTFE on the substrate. After drying at 110 °C, the layers or films of PTFE were so thin (thinner than 20 μm) that the heat transfer factor in the film was considered to be negligible. The sample was placed in an electric oven as shown in Fig. 1 to be held at 380 °C for 60 min and then cooled down at a rate of 0.5 °C/min to a prescribed temperature (T_p) between 250 and 380 °C (the melting point is 327 °C). The sample was dropped into ice water to terminate the crystallization just when the temperature became T_p . This method followed the ultra-quenching technique developed by Jones et al [10]. The samples were dried in air at room

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Fig. 2 A DSC thermogram of PTFE during cooling process from 380 °C at 20 °C/min.

temperature before the following experiments.

The external surface of the film was observed in a scanning electron microscope (SEM, JSM-5200LV) at an accelerating voltage of 15 kV and at a viewing angle of 30° after being coated with Au.

The thermal property of the sample was analyzed using a differential scanning calorimeter (DSC, Seiko, S-220) at a scanning rate of 20 °C/min (or -20 °C/min).

One drop of the PTFE dispersion was applied onto a glass plate at room temperature only for light microscopic (LM) observation. After being dried, the sample was heated to 380 °C and kept for 60 min in a hot stage (Linkam, TM-600PM). The polarized light micrographs of the sample were taken at different temperatures during the cooling process at a rate of 0.1 °C/min from 380 to 200 °C by Nikon Optiphot-Pol with a color sensitive plate (retardation: $R=530$ nm)

3. Results and Discussion

A DSC thermogram on cooling (20 °C/min) of PTFE as-dried from the original dispersion is shown in Fig. 2, which shows that the crystallization starts around 330 °C and a single exothermic peak is observed at 313 °C.

The degree of crystallinity of the PTFE thin film peeled from the aluminum substrate was estimated from the heat of fusion assuming that the heat of fusion of the PTFE crystal is 14.6 cal/g [11,12]. The T_p -dependence of the degree of crystallinity for the slow-cooled PTFE from the melt is shown in Fig. 3, which apparently indicates development of the crystallinity of PTFE from 30

Fig. 3 The T_p -dependence of the degree of crystallinity of PTFE slow-cooled and quenched into ice water from the melt.

to 85% with decreasing T_p especially between 320 and 300 °C.

A series of SEM photographs for the external surface of the slow-cooled PTFE with different T_p are shown in Figs. 4(a)-(f). Any characteristic crystallization feature is not observed on the smooth surface of the quenched film from 330 °C as shown in Fig. 4(a), while a band appears when the sample is quenched from 315 °C (note a white striation pointed by an arrow in Fig. 4(b), which corresponds to the protruded region caused by the sheaf-like band formation). The number and size of the band increase with decreasing T_p as shown in Figs. 4(c)-(f).

In situ observation on PTFE during the cooling process from 380 °C was also performed by polarized light microscopy. The results are shown in Figs. 5(a)-(d). Any characteristic fine structure is not observed in Fig. 5(a), taken at 380 °C. The optically anisotropic or birefringent regions are observed in Fig. 5(b), which suggests that crystallization starts even at 330 °C nevertheless any band was not observed by SEM on the external surface for the quenched film from 330 °C (T_p). It is shown from Figs. 5(c)-(d) that the number and size of crystalline regions of PTFE increase during the cooling process. Such birefringent feature in the crystalline region suggests that PTFE molecules lie parallel to the substrate surface because the refractive indices in the directions along the a- and b-axes are considered to be almost the same in the high-temperature pseudohexagonal phase (phase I) [13,14] and the refractive index in the direction along the c-axis (chain axis) is greater than

Fig. 4 SEM photographs of the external surfaces of PTFE which were slow-cooled from the melt and quenched into ice water form a variety of T_p ; (a)330 °C, (b)315 °C, (c)312 °C, (d)310 °C, (e)304 °C, and (f)280 °C.

Fig. 5 In-situ-observed polarized LM-photographs during the cooling process from 380 °C. The observed temperatures are (a)380 °C, (b)330 °C, (c)320 °C, and (d)280 °C.

the others. This is consistent with the report [7] suggesting that the higher refractive index is in the direction perpendicular to the long axis of the band.

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