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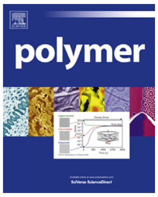

Polymer communication

The characteristic length of cooperative rearranging region for uniaxial drawn poly(ethylene terephthalate) films

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ABSTRACT

Mobile amorphous fraction and crystallinity of uniaxial poly(ethylene terephthalate) (PET) films were quantitated, using temperature modulated differential scanning calorimetry (TMDSC), and differential scanning calorimetry (DSC). Our results show that the crystallinity increases with decreasing drawn temperature and increasing draw ratio. The strain rate also affects the crystallinity. From complex heat capacity measurement, we estimated an average length of Cooperative Rearranging Region (CRR), ξ_α, a characteristic parameter of the dynamic heterogeneity in glass transition. Despite the changes in the drawing or annealing condition, the ξ_α increased linearly with increasing weight fraction of the mobile amorphous phase. Crystal and rigid amorphous PET suppressed the formation of CRR. Finally, we also estimate from extrapolation, $\xi_\alpha = 3.8$ nm, for a perfect amorphous PET.

1. Introduction

1.1. Average size of CRR at the glass transition

Adam and Gibbs introduced the notion of a cooperatively rearranging region (CRR) [1]. In the high temperature region, above the glass transition temperature (T_g), macromolecules can move independently, while the motion of a particular molecule depends to some degree on that of its neighbors. The rearranging movements of some molecules (or monomer units of polymer) are only possible when a certain number of neighbor molecules move simultaneously. The CRR is defined as a subsystem, which can rearrange into another configuration independently, regardless of its environment. According to the method developed by Donth [2,3], the size of CRR is determined by spatial aspect based on statistical independence of thermal fluctuations, which in turn can be calculated from the complex heat capacity measurement using temperature modulated differential scanning calorimetry (TMDSC).

Donth [4–6] reported that macromolecules have a similar characteristic CRR length in the range 1.0–3.5 nm, and the CRR is affected by the individual properties of molecules. With a focus on the crystalline polymeric materials, Saiter et al. determined the CRR length of poly(L-lactide acid) as a function of crystallinity [7,8]. They put forward two types of mobile amorphous phase: amorphous matrix and amorphous fraction trapped in spherulites. The average CRR size of those amorphous phases decreased as the crystallinity increased. In a similar vein, they employed the scheme on the drawn poly(ethylene terephthalate) (PET) film with various draw ratios. The average CRR size decreased with increasing draw ratio. The CRR size dependence on the draw ratio was explained in terms of the concept that the amorphous segments chemically linked to crystalline lamellae enhance a geometrical confinement effect [9,10]. So far, it is believed that the cooperative length depended on crystallinity and was sensitive to a macromolecular orientation. However, X-ray diffraction (XRD) revealed that the orientation of the drawn PET films changes with draw ratio and strain rate [11–19]. Taking into account of these results of XRD, previous report of the CRR should be reconsidered, focusing on the annealed temperature and strain rate. Furthermore, the present study shows a relation between CRR size and the weight fraction of amorphous phase.

2. Experimental section

2.1. Material

Various PET films used in this study were purchased from Toray Industry, Inc. The mass of the repeating unit was 192.2 g mol^{-1}. The weight-averaged molecular weight, M_w, of the sample was 30,000 g mol^{-1} and the molecular weight distribution in terms of

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M_w/M_n was $\sim$2, where M_n was the number-averaged molecular weight. Before drawing or annealing, the sample was completely amorphous, with no detectable crystallinity by XRD. The density of the undrawn sample was 1.25 g cm^{-3} at 85 °C. The details of the samples used in this study are summarized in Table 1. The drawn samples (E–J, Q–Z) were uniaxially drawn using stretching machine at 90, 95 and 100 °C with the strain rate of 300% min^{-1}.

2.2. Differential scanning calorimetry (DSC)

A commercial DSC of the type Q100 from TA Instruments Inc. was used for the TMDSC and DSC measurements. Dry nitrogen gas with a flow rate of 50 mL min^{-1} was purged through the cell. The sample mass was 5 mg. There were no changes in the mass of samples before or after the measurements.

2.3. Crystallinity

A standard DSC measurement was carried out under $q = 10$ °C min^{-1} with the sample mass of 10 mg. The crystallinity of the PET sample, $X_{\text{cryst.}}$, was calculated using standard DSC measurement as follows:

$$X_{\text{cryst.}} = \left(\Delta H_m/\Delta H_{\text{cryst.}}\right) \times 100, \tag{1}$$

where ΔH_m is the observed heat of fusion, and $\Delta H_{\text{cryst.}}$ ($= 140.1$ J g^{-1}) is the heat of fusion for perfect crystallinity PET [20].

2.4. Complex heat capacity

Two types of measurements for TMDSC were applied with the sample mass of 5 mg.

First, the heating process for TMDSC measurements was carried out under an underlying heating rate, q, of 0.5 °C min^{-1}, maximum temperature amplitude, T_a, of 0.5 °C and modulation period, t_p, of 150 s. In this method, the apparent complex heat capacity, C_p^*, is calculated from following equation [9,21]:

$$C_p^* = KA_{\text{HF}}/(A_T\omega), \tag{2}$$

where A_{HF} is the amplitude of the modulated heat flow rate, A_T is the amplitude of temperature modulation with frequency , $\omega = 2\pi t_p^{-1}$, and K is a calibration factor for the specific conditions of the measurement, which is determined as a function of temperature from sapphire calibration [22]. In addition, the real part, C', and the imaginary part, C'', are calculated using following equations:

$$C' = \left|C_p^*\right|\cos\phi, \tag{3}$$

and

$$C'' = \left|C_p^*\right|\sin\phi, \tag{4}$$

where ϕ represents a phase angle between the calorimeter response function and time derivative of a modulated temperature program [21,23], which result from a relaxation processes in the sample. According to the Weyer's report [21], the calibration of C'' was also carried out using optimal method for a more realistic phase angle correction.

2.5. Quasi-isothermal measurement using TMDSC

Second, quasi-isothermal processes were carried out to measure the apparent heat capacity. The 20 min long isothermal measurements were carried out every 2 °C, over the temperature range of 0–300 °C. The T_a was set to 0.5 °C with $t_p = 60$ s. We assume that the average heat capacity decreases, within 1% of the value, at 20 min. The analysis time was assumed until all irreversible processes completed. The measurements were applied to blank

Table 1
The sample number, group, treated condition, draw ratio, glass transition temperature, cold crystallization temperature, heat capacity change, heat of fusion mobile amorphous fraction, rigid amorphous fraction, crystallinity and characteristic length of CRR for PET films.

No.	Group	Treated condition	Draw ratio λ	T_g (°C)	T_{cc} (°C)	$\Delta C_{p,\text{obs}}$ (Jg^{-1} mol^{-1})	ΔH_m(Jg^{-1})	$X_{\text{mobile am.}}$ (%)	$X_{\text{rigid am.}}$ (%)	X_{crystal} (%)	ξ_α (nm)[a]
A	Undrawn	Neat	Undrawn	78.1	140.3	0.33	0.0	80	20	0	3.2
B	Annealed	Anneal, 110 °C, 15 min	Undrawn	78.4	136.3	0.29	8.8	71	22	6	2.9
C		Anneal, 110 °C, 30 min	Undrawn	78.1	134.3	0.26	21.5	62	22	15	2.6
D		Anneal, 120 °C, 60 min	Undrawn	89.6	147.4	0.18	42.2	44	26	30	1.4
E	90 °C low strain rate	Uniaxially drawn, 90 °C, 300% min^{-1}	2.00	78.2	115.4	0.31	6.7	76	19	5	3.0
F		Uniaxially drawn, 90 °C, 300% min^{-1}	2.20	78.2	109.9	0.31	12.0	76	15	9	3.1
G		Uniaxially drawn, 90 °C, 300% min^{-1}	2.30	78.0	106.7	0.30	17.0	73	15	12	3.0
H		Uniaxially drawn, 90 °C, 300% min^{-1}	2.50	78.9	99.0	0.30	20.1	74	12	14	2.7
I		Uniaxially drawn, 90 °C, 300% min^{-1}	2.75	83.3	99.5	0.19	23.9	47	36	17	1.9
J		Uniaxially drawn, 90 °C, 300% min^{-1}	3.00	83.8	99.4	0.20	24.7	50	33	18	1.7
K	90 °C high strain rate	Uniaxially drawn, 90 °C, 7000% min^{-1}	2.25	77.9	118.9	0.36	2.6	88	10	2	3.1
L		Uniaxially drawn, 90 °C, 11,000% min^{-1}	2.50	78.1	109.9	0.29	6.6	71	24	5	2.4
M		Uniaxially drawn, 90 °C, 15,000% min^{-1}	2.75	78.3	109.6	0.25	9.4	60	33	7	2.3
N		Uniaxially drawn, 90 °C, 22,000% min^{-1}	3.00	80.5	99.1	0.18	15.8	45	44	11	1.6
O		Uniaxially drawn, 90 °C, 28,000% min^{-1}	3.25	77.6	98.0	0.17	26.2	42	39	19	1.3
P		Uniaxially drawn, 90 °C, 34,000% min^{-1}	3.50	69.3	97.3	0.17	29.4	42	37	21	1.4
Q	95 °C low strain rate	Uniaxially drawn, 95 °C, 300% min^{-1}	2.20	78.0	119.0	0.34	2.7	83	15	2	3.2
R		Uniaxially drawn, 95 °C, 300% min^{-1}	2.40	78.0	115.7	0.33	7.1	82	13	5	3.1
S		Uniaxially drawn, 95 °C, 300% min^{-1}	2.50	78.0	114.2	0.34	9.5	83	10	7	3.2
T		Uniaxially drawn, 95 °C, 300% min^{-1}	2.75	78.4	107.1	0.29	10.9	71	21	8	2.7
U		Uniaxially drawn, 95 °C, 300% min^{-1}	3.00	78.4	105.1	0.30	13.0	74	16	9	2.6
V	100 °C low strain rate	Uniaxially drawn, 100 °C, 300% min^{-1}	2.00	78.1	140.3	0.33	0.0	82	18	0	3.1
W		Uniaxially drawn, 100 °C, 300% min^{-1}	2.30	78.0	140.3	0.34	0.6	83	16	0	3.2
X		Uniaxially drawn, 100 °C, 300% min^{-1}	2.50	78.1	142.3	0.33	2.6	82	16	2	3.1
Y		Uniaxially drawn, 100 °C, 300% min^{-1}	2.75	78.0	144.3	0.34	5.1	83	13	4	3.2
Z		Uniaxially drawn, 100 °C, 300% min^{-1}	3.00	78.1	145.3	0.34	6.0	84	12	4	3.0

[a] The accepted error bars are 10% as proposed in the Ref. [4].