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Study on the double cold crystallization peaks of poly(ethylene terephthalate) (PET):

2. Samples isothermally crystallized at high temperature

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Abstract

The exothermic peak during the heating scan of differential scanning calorimeter (DSC) analysis is called the cold crystallization peak, originating from the crystallization of the amorphous regions. In this work, we further use the cold crystallization peak in DSC scans as a probe to study the structure in the amorphous regions of poly(ethylene terephthalate) (PET). For PET samples properly treated at high temperature near the melt temperature, double cold crystallization peaks also appear in DSC scanning. This fact may have a relation to the co-existence of two kinds of amorphous regions: interlamellar amorphous regions and complete amorphous regions between spherulites. The difference and changes in position, height and shape of peaks reflects the change in structure of amorphous regions under treatment conditions. The difference in cold crystallization behavior between samples treated at low temperature and at high temperature is also discussed. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Poly(ethylene terephthalate) (PET), a semicrystalline polymer which crystallizes at a moderate rate. It can be quenched from the melt to produce material which is amorphous at room temperature. It can also be crystallized to get a rather high crystallinity under thermal treatment conditions. The structure in amorphous regions of PET has been of considerable interest [1–7]. Recent studies have indicated that the amorphous phase in high performance semicrystalline PET is complex [8]. In the previous work [9], we have used the cold crystallization peak(s) in differential scanning calorimeters (DSC) as a probe to study the structure in the amorphous regions of PET. The appearance of double cold crystallization peaks for PET properly treated at low temperatures (just above the glass transition temperature) reveals the co-existence of two kinds of amorphous regions: an interlamellar amorphous region with some order and a complete amorphous region between spherulites.

In this paper, we further report the results of work for PET samples isothermally crystallized at high temperatures. Our attention is particularly paid to the difference in cold crystallization behavior of these PET samples from those treated at low temperatures.

2. Experimental

Thermal treatment of samples was preformed in this way by isothermal crystallization at high temperature (just below the melt temperature) from the melt. At given time intervals, the crystallization was stopped by quenching the samples in ice-water. The original PET was directly quenched from the melt, which is amorphous and unoriented. The thermal analysis was carried out on a Perkin–Elmer DSC-2C differential scanning calorimeter. The heating rate used was

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20°C/min. Densities were measured at 20°C using a conventional density gradient column filled with a carbon tetrachloride/xylene mixture.

3. Results

The original PET sample quenched from the melt has one narrow cold crystallization peak during DSC analysis. However, after isothermal crystallization at high temperature from the melt for certain times, the samples no longer show only one peak, but two peaks, and the peaks broaden obviously compared to the original PET sample. The position, height and shape of double cold crystallization peaks are influenced regularly by the thermal history (crystallization temperature and crystallization time). The detailed experimental results are related as follows.

3.1. Effects of crystallization time

Fig. 1 shows the representative DSC thermograms of PET samples which have been crystallized at 230°C from the melt. The original PET shows a pronounced narrow peak T_{co} (curve A in Fig. 1). After isothermal crystallization at 230°C from the melt for a short time, the peak(s) broaden obviously. Furthermore, there appears a shoulder peak at a lower temperature (T_{cl}). It can be seen that as the crystallization time (t_c) lengthens, the peak located at the higher temperature (T_{ch}) weakens gradually. Two peaks overlap in most cases. While t_c lengthens more, only one weak crystallization peak appears in the DSC thermogram. The related calorimetric data, density and crystallinity are listed in Table 1.

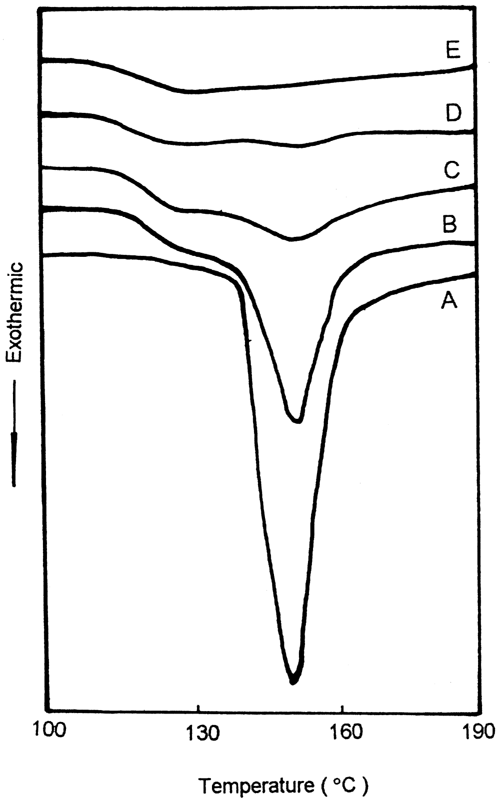

Fig. 1. The cold crystallization peak(s) for PET samples crystallized at 230°C for various times: (A) 0 min,amorphous; (B) 7 min; (C) 10 min; (D) 15 min; (E) 20 min.

3.2. Effect of crystallization temperature

Different cold crystallization behaviors are not only obtained by changing the crystallization time at one temperature, but also by changing the crystallization temperature (T_a). Compare the cold crystallization behavior of three samples which had been isothermally crystallized at 225°C, 230°C and 235°C for same amount of time (such as 7 min) as demonstrated by Fig. 2 and Table 2. The crystallization behaviors are considerably different. This phenomenon reveals the effect of treatment temperature on the structure of amorphous regions.

4. Discussion

The literature [10] has shown that, in several semicrystalline polymer systems, the glass transitions are shifted upward by tens of degrees due to constraining

Table 1
Calorimetric date, density and crystallinity of PET samples crystallized at 230°C for various times

t_c (min)	T_g (°C)	T_{co} (°C)	T_{cl} (°C)	T_{ch} (°C)	T_m (°C)	d (g/cm^3)	$X_{c,d}$ (%)
0	83	150	–	–	258	1.338	1.8
7	83	–	127	150	257	1.340	3.6
10	82	–	127	150	258	1.346	9.1
15	80	–	126	150	256	1.350	12.7
20	80	–	127	–	258	1.364	25.1

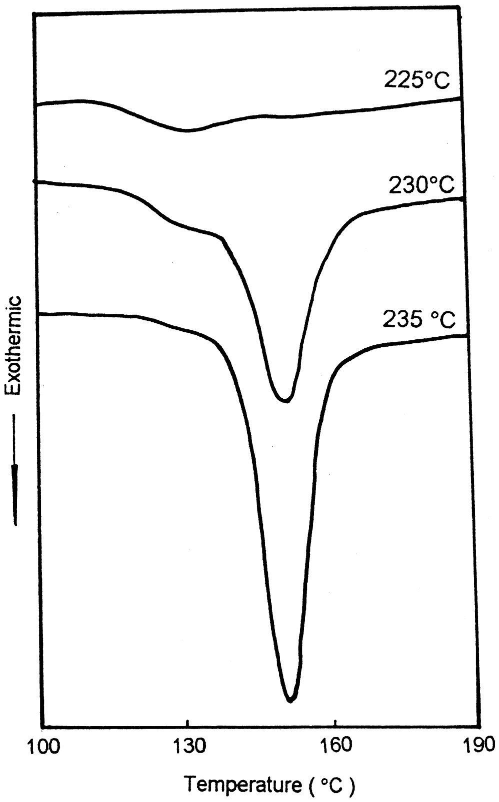

Fig. 2. The cold crystallization peak(s) for PET sample crystallized at different temperatures for the same time (7 min).

effects of crystallites on adjoining non-crystalline or amorphous regions. This represents a large fraction of the "rigid amorphous phase" or RAP. When RAP is removed [8], the glass transition temperature (T_g) decreases; when RAP is restored, T_g increases again. In our results (shown in Table 1), PET samples crystallized at 230°C for various times, didn't show any increase in T_g over that for the purely amorphous sample. What our present study implies is that thermal treatment in the way performed in this work initially causes RAP to nearly disappear. Our results conform well with prior studies [11–13], which show that the weight fraction of RAP tends to decrease, as the crystallized temperature increases. So in the subsequent discussion, the influence of RAP is neglected.

The original PET (completely amorphous) shows a pronounced narrow peak at 150°C. After being crystallized at 230°C for 7 min, the sample shows two peaks, one is at 150°C which is very similar to the original amorphous PET, the other is a shoulder peak at about 127°C. With longer treatment, the peak at 150°C (T_{ch}) weakens gradually. The cold crystallization peak in DSC analysis originates only from the amorphous regions left over after thermal treatment. Obviously, the state of the amorphous regions clearly changes due to thermal treatment. Two kinds of amorphous regions coexist: the remaining complete amorphous regions between spherulites and interlamellar amorphous regions. This interlamellar phase is composed of chain folds, molecular segments going from one lamellae to another, chain ends, and low molecular weight material rejected during crystallization [5]. In the subsequent DSC analysis, the crystallization from the interlamellar amorphous region is supposed to be easier than that from the interspherulitic amorphous region [9]. So the two cold crystallization peaks T_{cl}, T_{ch} reflect the crystallization from the interlamellar and interspherulitic amorphous region, respectively. Our results conform very well with the point of Groeninckx et al. [5] from stress relaxation experiments and of Qi et al. [3] from dynamic mechanical testing.

When thermal treatment progressed at high temperature (low degree of undercooling), the diffusion rate of the segment is high, but the formation of the interlamellar links is strongly reduced because of the decrease in nucleation density, so a large number of interspherulitic regions remain during the initial stage of crystallization. So, for samples crystallized for a short time, the peak T_{ch} is considerably strong, meanwhile the peak T_{cl} is weak, reflecting the cold crystallization from a small amount of interlamellar, amorphous region. As the diffusion of the amorphous chains from the growing crystal surface is easy, the formation of a regular fold surface is, therefore, expected. So as the thermal treatment proceeds, the increase of crystallinity occurs in the increase of nucleation density. Consequently, peak T_{ch} weakens gradually with t_c

Table 2
Calorimetric data, density and crystallinity of PET samples crystallized at different temperatures for the same length of time (7 min)

T_a (°C)	T_g (°C)	T_{cl} (°C)	T_{ch} (°C)	T_m (°C)	d (g/cm^3)	$X_{c,d}$ (%)
225	83	128	154	257	1.349	11.8
230	83	127	150	257	1.340	3.6
235	84	127	151	258	1.339	2.7

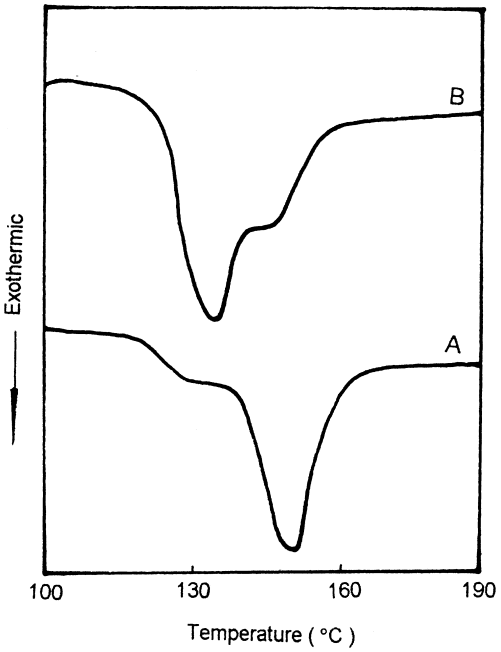

Fig. 3. A comparison of cold crystallization peaks for PET samples with the same crystallinity (3.6%): (A) treated at 230°C for 7 min; (B) treated at 105°C for 10 min.

lengthening because of the decrease of the interspherulitic region.

For samples crystallized at different temperatures (still at a low degree of undercooling) for the same length of time, the difference in cold crystallization peak(s) may be due to the temperature dependence of the crystallization rate.

It is interesting to compare the cold crystallization behavior of two samples with the same crystallinity, one has been crystallized at 105°C for 10 min, the other at 230°C for 7 min., shown in Fig. 3. The sample treated at low temperature (high degree of undercooling) leaves more interlamellar amorphous regions, but for samples treated at high temperature (low degree of undercooling), more interspherulitic amorphous regions remain. These differences are related to the temperature dependence of nucleation and chain diffusion. At low temperatures (close to the glass transition temperature), the growth nucleation probability is fairly high, meanwhile the diffusion is difficult. Otherwise, at high temperatures (close to the melt temperature), the diffusion of amorphous chains from the growing crystal surface becomes easier, moreover the nucleation density decreases because of the low nucleation probability.

The original amorphous PET sample has one narrow cold crystallized peak located at 150°C during the DSC heating scan [Fig. 1(A)]. After being treated at 230°C for 20 min, the crystallinity increases to 25.1%, the semi-crystalline sample has one weak cold crystallized peak located at 127°C, with the 23°C separation from the amorphous sample. But the glass transition temperatures, measured by normal DSC testing, remains almost unaffected. It is also noted that two glass transition temperatures should be expected [5]: one for the amorphous phase between the lamellae within the spherulites, and the other one for the interspherulitic region. Nevertheless, these two T_gs are too close to each other to be detected by normal DSC testing.

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