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DSC INVESTIGATION OF AN ISOTHERMAL CRYSTALLIZED POLY(ETHYLENE TEREPHTHALATE)

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ABSTRACT

Two samples of poly(ethylene terephthalate), oriented and unoriented (annealed for several times and temperatures), were scanned by DSC. The density of the samples was also determined. A thermal process was observed in the region between the glass transition and the melting temperature. The position of this thermal process is related to the annealing temperature. The model of the process was proposed as a simultaneous partial melting and recrystallization. The shape of the heating curve depends on the rate of both processes.

INTRODUCTION

A number of authors have been engaged in the thermal analysis of poly(ethylene terephthalate) (PET). Recently, a paper was published by Berndt and Bossmann[1]. In the case of an unoriented amorphous PET either a step or a peak is observed in the region of a glass transition on the DSC curve, then an outstanding peak of a cold crystallization and either a simple or multiple melting peak. When measuring a crystalline sample, a peak of another thermal process is observed and its position depends on both the temperature and time of crystallization to which the sample was exposed before DTA scanning[1, 3–7]. However, the interpretation of this is not uniform. According to some authors there is an endothermic process[3–5], whereas according to others the process is exothermic[6, 7]. However, one group of investigators do not attach any weight to this process although it is perceptible on the heating curve[2]. Generally, the process has a relatively small thermal effect.

The aim of the present study was to decide if the above process was exothermic and if so under what conditions an endothermic peak might be produced. According to our hypothesis this process is caused by a recrystallization (or by a partial melting and a subsequent crystallization) so samples were selected in which it was possible to assume that there was a different rate for both these partial processes. Some results of this work have already been published in a preliminary paper[10].

TABLE 1

SOME PROPERTIES OF THE SAMPLES

Sample	*Fibre diam. (μm)*	*Birefringence*	*R.T.G. crystallinity*	*Density (g cm^{-3})*
1	38.4	0.0048	0	1.3336
2	21.8	0.1673	0	1.3473

EXPERIMENTAL

Materials

An undrawn PET yarn having the intrinsic viscosity 72.2 ml g^{-1} (measured in a mixture of phenol/tetrachlorethane 1:3 at 30 °C) was used for measuring on DSC. The fibre was selected from the routine production. Using this material, another sample was prepared by drawing this undrawn yarn on the Instron dynamometer (deformation rate 100 mm min^{-1}, test length 40 mm). During the deformation, a neck arose on the fibre and the deformation was increasing to the natural draw ratio value (i.e. to the disappearance of the neck). The amorphous highly drawn oriented fibre was thus prepared. The amorphous character of these fibre samples was checked by using wide and small angle X-ray techniques. The properties of the samples are listed in Table 1. Both the fibre diameter and the birefringence were measured by a microscope, the birefringence was measured by means of a Bereks compensator.

Methods

Annealing of samples. Both samples were annealed for 10, 10^2 and 10^3 min at 90, 130, 180 and 220 °C, respectively, in a nitrogen atmosphere. In order to prevent undesirable deformation of crystallized samples, they were formed, before annealing, to the shape required for DSC and density gradient column measurement.

Density measurements. The density measurements were carried out by using a density gradient column in a *n*-heptane/CCl_4 system at 30 °C, the stated values are the averages of five samples.

Thermal analysis. The thermal analysis was carried out on the Differential Scanning Calorimeter DSC-1B (Perkin-Elmer). In most cases a scanning rate of 16 K min^{-1} was used during the measurements. Each measurement was repeated three times. The character of the partial thermal processes was well reproducible, especially with regard to the shape and position of the peaks. The polymer sample was 10 mg, the measurement range was 33.5×10^{-6} J sec^{-1}.

RESULTS AND DISCUSSION

The density changes

The results obtained show the difference in behaviour between the oriented

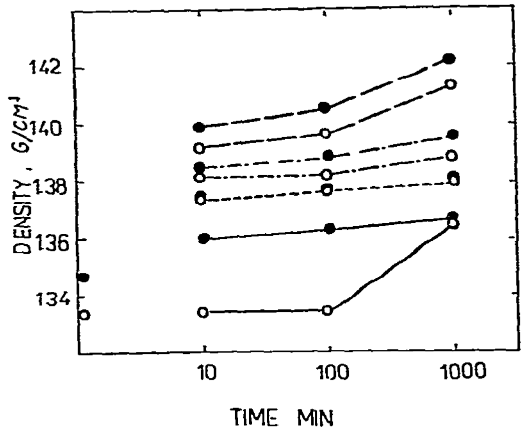

Fig. 1. The density changes of an oriented (●) and unoriented (○) PET sample depending on the annealing time at various temperatures: 90°C (———), 130°C (– – – –), 170°C (—.—.—) and 220°C (———). The densities of the original samples are also plotted.

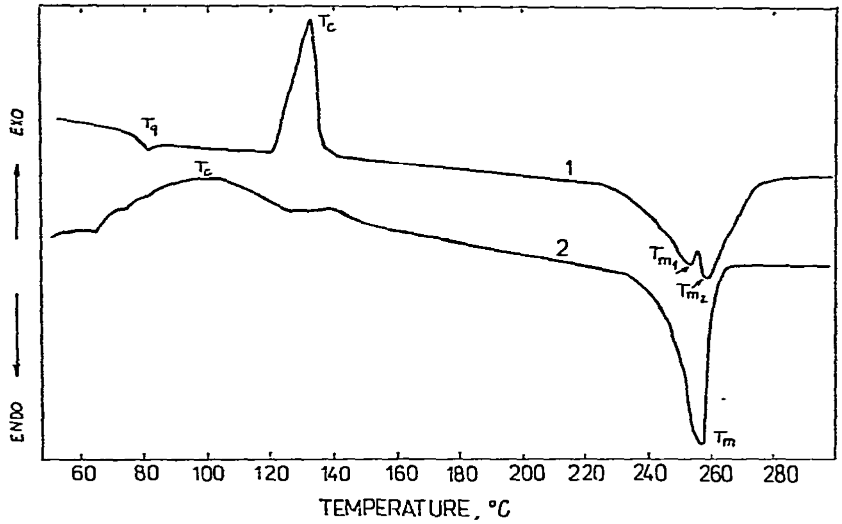

Fig. 2. The DSC trace of an original unoriented (1) and oriented (2) PET sample.

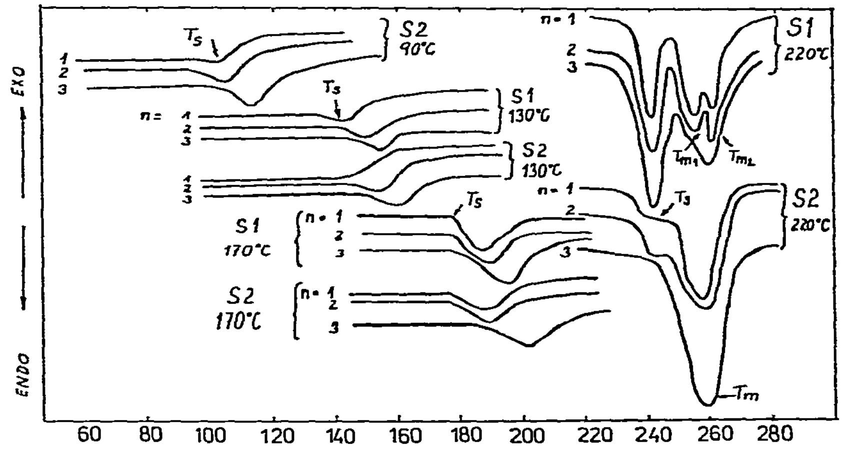

Fig. 3. The DSC heating curve in the region of a secondary transition (T_S) after annealing at various temperatures for 10^n min ($n = 1,2,3$) of an unoriented (S 1) oriented (S 2) sample.

and unoriented samples. Sample 1 has some initial orientation, but this orientation immediately disappears after heating above T_g (e.g., see ref. 11). The results of density measurements are plotted in Fig. 1. The different crystallization rates of the oriented and unoriented PET have been described[8]. At the annealing temperature 90°C, a higher density of sample 2 is affected by its greater orientation. An outstanding crystallization of an unoriented sample will take place after annealing for 10^3 min. After annealing at 130°C, the densities of both samples are practically the same. Only when the samples were annealed at higher temperatures (170 and 220°C), did the greater crystallization rate of an oriented sample become evident.

The thermal behaviour

The heating curves of samples 1 and 2 are plotted in Fig. 2. Whilst a glass transition temperature T_g of an unoriented sample was as high as 82°C and the cold crystallization peak arose at 132°C, the heating curve of sample 2 shows a quite unrepresentative course. The intense bending of a curve toward an exotherm at 67°C is evidently due to a partial disorientation (retraction) due to an increased mobility of chains. As the cold crystallization takes place at 76°C, having the maximum at 97°C, it is to be thought that for an oriented amorphous sample T_g is decreased. A lower temperature of a cold crystallization peak corresponds to a higher crystallization rate of an oriented polymer[14].

The differences in the shape of the melting peak of both the samples are quite characteristic. Such differences were to be observed after all kinds of annealing, up to 220°C (see also Fig. 3). As for the unoriented sample, the peak melting double had a maximum at T_{m1} = 248–249°C and T_{m2} = 251–253°C. The single melting peak of oriented samples had a maximum at temperature T_m = 251–252°C and, evidently, this peak is to be identified with peak T_{m2} of the unoriented sample. Such a variation in behaviour of both types of fibre samples can be explained as being due to the influence of the different recrystallization rate during the heating on DSC. When measuring unoriented samples, the double melting peak is evidently due to the lower crystallization rate. Thus T_{m1} corresponds to a melting of imperfect crystals originating at lower temperatures. This fact was confirmed by measurements made using scanning rates of only 1 or 2 K min^{-1}, respectively. Under such conditions only one melting peak appeared and its position corresponded to temperature T_{m2} or T_m, respectively.

In Fig. 3 the related parts of various samples are plotted, the samples having been annealed at various temperatures for various times. Some further thermal process is observed in the region between the glass transition and melting temperatures. In this paper this process is called "the secondary transition" and its position is indicated as T_s. As for the thermal analysis of synthetic fibres, this temperature is sometimes called "the effective setting temperature". As shown in Fig. 3, the shape of a DSC curve in the region of T_s varies according to fibre orientation and annealing conditions, i.e. the temperature and time of annealing. The shape of the curve can be compared with "a step" and is characteristic of a second order transition. In

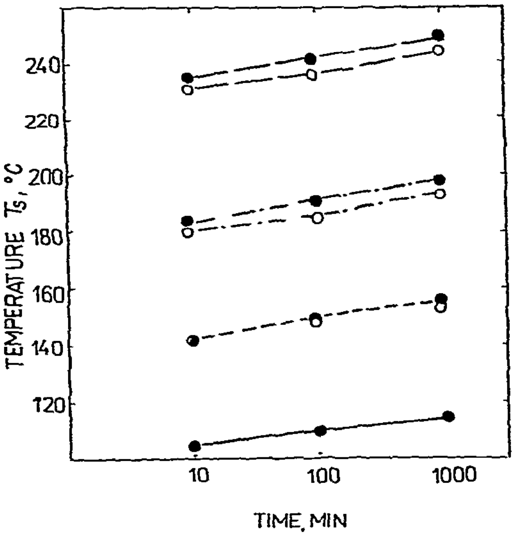

Fig. 4. The relation between the start of a secondary transition (*Ts*) of an oriented (●) and unoriented (○) sample and the annealing time at various temperatures: 90°C (———), 130°C (– – –), 170°C (—·—·—) and 220°C (— — —).

contrast to T_g, there is a bending in the direction of an exotherm. Another typical form of the curve is an exothermic peak. In Fig. 4, T_s is plotted as a function of time and the temperature of annealing. The influence of a molecular orientation is also visible in this figure. In the case of an unoriented sample it is not possible to read the temperature T_s after annealing at 90°C because the heating curve of such a sample is similar to that of an original amorphous sample (see Fig. 2, curve 1). As for the influence of annealing conditions on this secondary transition, the results can be summarized as follows.

(a) The temperature T_s depends above all on the annealing temperature.

(b) T_s is slightly increased by an increase in annealing time.

(c) The T_s value is always greater for an oriented sample.

(d) The endothermic peak of a secondary transition is a typical form of a DSC trace of samples under the conditions of higher temperatures and longer annealing times.

(e) The peak is observed more frequently when measuring unoriented samples.

(f) "The step", which is the region of a secondary transition, is observed in the case of less crystalline samples (lower temperature and shorter time). It is observed more frequently when measuring oriented samples.

According to some authors, the secondary transition process is due to a partial melting[3, 4] or a cohesive force[5]. Other authors prefer a recrystallization[6] or an exothermic molecular relaxation of a polymer[7] as the source of this phenomenon. Holdsworth and Turner-Jones[2] assume that a recrystallization takes place over the whole heating region. Brendt and Bossmann[1] supposed that both processes, i.e. the recrystallization together with the partial melting, take place simultaneously. At

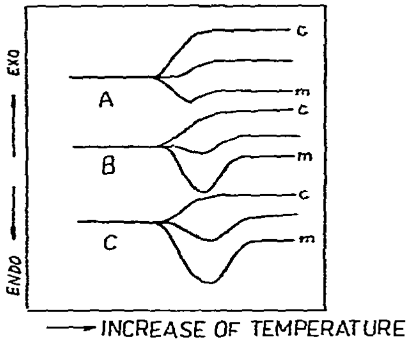

Fig. 5. A probable model of a secondary transition of a PET sample having been isothermally annealed. c, Crystallization and recrystallization; *m*, partial melting of imperfect crystals. The resulting central heating curve is then shaped like "a step" (A), a "peak and step" (B), or "a peak" (C).

the higher heating rate, the partial melting outruns the recrystallization and thus an endothermic peak will occur.

From our results, we proposed a model of the stated process. At the same temperature, we suppose the synchroneous initiation of both processes, i.e. partial melting and recrystallization. The difference in shape of a heating curve is only a result of different forms of the DSC traces and also different intensities of both elementary processes. The three possible events are shown in Fig. 5.

(A) The crystallization rate is greater than the partial melting rate in the whole range of a process. The resulting DSC curve is step-shaped in an exotherm direction. This is so in the case of a low partial melting rate of samples of poor crystallinity or of a large crystallization rate of an oriented sample.

(B) In the first step of a process, the recrystallization rate is less than the partial melting rate but it will reach a greater intensity later. In such cases, the resulting heating curve has a "peak and a step". In fact, it is a continuous change between both variants A and C.

(C) The crystallization rate is smaller than the partial melting rate. The resulting trace of the thermal process has an endothermic peak. Such a course is typical for a more stable crystalline structure, especially for unoriented samples with a poor recrystallization rate.

Furthermore, one other conclusion can be made from the results of this work. Namely, the crystallization rate of an oriented sample is higher than in the unoriented state. A number of authors[9, 12–14] studied the relations between orientation and the rate of crystallization. The crystallization rate of a highly oriented amorphous PET is very high and it increases up to ordinary values of about 10^4. For instance, the orientation of PET having a birefringence 0.08 (in contrast to an anisotropic polymer) provoked the decrease in the crystallization half-time from 660 sec down to values lower than 0.01 sec[14]. Above all, the influence of such an orientation can be explained by some shortening of an induction period. This is also evident from our results when considering the increasing density of an oriented and unoriented sample at 90°C (see Fig. 1). Even the influence of the orientation on the increase of a recrystallization rate is visible from these results (see, for instance, the density differences, T_s value, etc.), but we cannot suppose that the crystallization rate will differ by four numerical orders. It is also difficult to explain the influence of orientation on the rate of a rearrangement of a crystalline structure once it is formed. It means that either the stability of formed crystals is affected by an interaction with a surrounding amorphous structure and then the oriented amorphous fraction will accelerate rearrangement of a crystalline structure already formed, or a great number of imperfect crystals arise during the oriented crystallization and these crystals are able to rearrange themselves at higher temperatures. From these results, it is very difficult to determine which of these hypotheses is acceptable.

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