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Note

DSC BEHAVIOUR OF POLYAMIDES AND POLYESTERS ANNEALED RESPECTIVELY IN WATER OR HOT AIR

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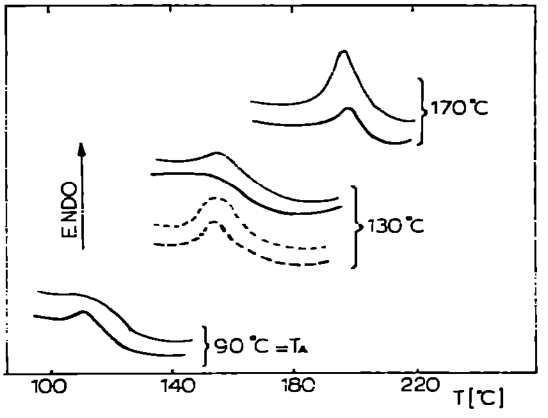
The same thermal process close to the melting point, T_m, is observed during DSC or DTA scans of semicrystalline poly(ethylene terephthalate) (PET) after it has been annealed under isothermal conditions. The position of the process on the DSC curve depends on the prior annealing of the sample. It has been observed by many authors [1—6], but its interpretation has not been agreed and is ambiguous. It is possible to use the position of this process on the DSC curve to specify the so-called "effective setting temperature" of the fibres [7]. The process is not associated with the oriented polymer structure only; it also occurs in the unoriented polymer [8]. The process is "the secondary transition", T_s, and the shape of a DSC curve has the form of an exothermic step or an endothermic peak (Fig. 1). It is suggested that the process is the result of two simultaneous processes, viz. par-



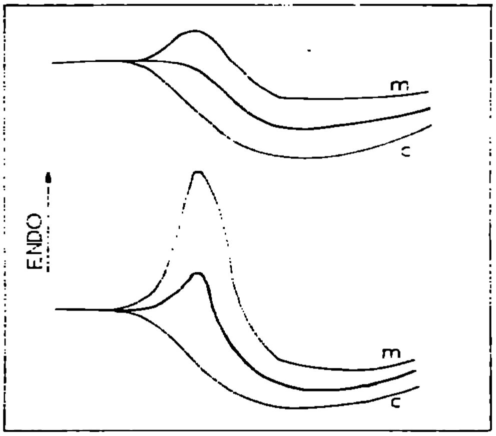


Fig. 1. The shape of the DSC curves in the region of the secondary transition at various annealing temperatures. Heavy line, PET; thin line, PA; full line, oriented sample; broken line, unoriented sample.

Fig. 2. Probable model of a secondary transition of a sample of isothermally annealed PA or PET. The resulting shape of the DSC curve can be considered as a total of two following partial processes: c, crystallization and recrystallization; m, partial melting of imperfect crystals.

tial melting and recrystallization (Fig. 2). The shape of the DSC curve depends on the ratio of the two processes. The aim of this paper is to compare the behaviour of PET and polyamide-6 (PA) from the point of view of such a "secondary transition". The influence of orientation, annealing in water and a combined annealing (boiling water and dry air at higher temperature) have been examined.

EXPERIMENTAL

Materials

Undrawn PA and PET fibres were used. They were routine production fibres with relative viscosities of 1.82 for PET and 1.56 for PA measured in a 1 : 3 phenol—tetrachlorethane solvent mixture. The oriented sample was prepared by drawing fibres using an Instron dynamometer. The test length was 40 mm and the deformation rate was as high as 100 mm min^{-1}. In such a deformation of fibres, the neck was formed and the orientation took place locally until drawing of the total sample was complete. Under such conditions, the drawn PET sample was completely amorphous as tested by X-ray analysis. The PA sample was partially crystalline before drawing because PA-6 is able to crystallise at room temperature. The birefringence of an oriented PA sample was as high as 0.045 and that of the PET sample was 0.160.

The thermal treatment

Both the samples were annealed in a nitrogen atmosphere in an annealing block at 90, 100, 130, 170 and 220°C (the last temperature for PET only), and in boiling water (100°C). The sample of PA contained only 3% monomer and before measuring it was kept over P_2O_5 to remove moisture. Thermal treatment was carried out for 10, 10^2 and 10^3 min. In order to consider the influence of the combined annealing, the samples were annealed at 100°C for 10 min in hot air or boiling water and then annealed at 110, 130, 150 and 170°C in a N_2 atmosphere for 10, 10^2 and 10^3 min.

Density measurements

The density determinations were carried out by using a density gradient column with the mixture *n*-heptane—carbon tetrachloride for PET and toluene—carbon tetrachloride for PA. All the stated values are an average of 5 parallel results. The fraction of crystals, β, was calculated assuming that the density of the amorphous polymer is 1335 and 1084 kg m^{-3} and that of the crystalline polymer is 1460 and 1230 for PET or PA, respectively.

DSC measurements

DSC measurements were performed with a Perkin-Elmer differential scanning calorimeter Model DSC-1B. A heating rate of 16 K min^{-1} was chosen and every measurement was repeated three times. A good reproducibility at all points of the thermal process was obtained. A sample weight of 10 mg was used at a calorimetric sensitivity of 33.5×10^{-6} J s^{-1}. The T_s value was read on the DSC thermogram either as the position of a curve flexure, in the case of "step", or as the position of an endothermic peak maximum.

RESULTS AND DISCUSSION

The relation between T_s and temperature, T_A, and time, t_A, of annealing is plotted in Fig. 3 for oriented PET and PA fibres. It is very interesting that the T_s value seems to be almost the same for both polymers if the same thermal treatment conditions have been used. The plots of T_s vs. t_A have almost the same slope at all the annealing temperatures used for both PA and PET.

When annealed in water, the polymers show a very different behaviour. While in the case of a polyester, an increase in T_s of about 16 K occurs after annealing for the arbitrary time range studied [see Fig. 3 (a)], in the case of polyamide-6, the secondary transition does not occur at all after annealing in water at temperatures up to the melting temperature. In the case of PET, the increase in T_s of about 16 K was also noted when samples had been annealed in water at 110°C or 130°C under pressure.

Even when the thermal treatment is the same, we obtain different values of T_s and also a different shape of thermogram for the oriented and the unoriented samples. The values of T_s are always lower in the case of an unoriented sample. As has been stated [8] and can be seen from Fig. 1, the DSC curve of an oriented sample has a characteristic shape of exothermic step. This fact is connected with the greater rate of an exothermic recrystallization in an oriented state [8].

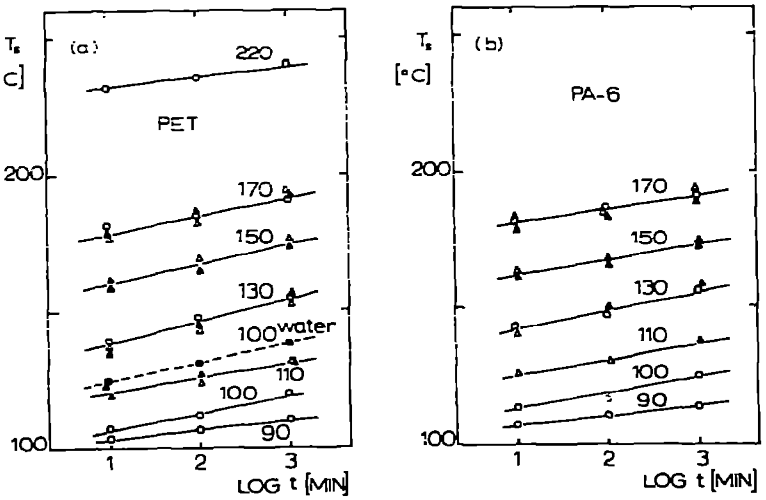


Fig. 3. The dependence on the time and temperature of annealing in a N_2 atmosphere of the secondary transition temperature (T_S) of (a) oriented PET and (b) oriented PA-6 exposed to initial annealing at 100°C for 10 min in air (△) or water (▲) or with no initial annealing treatment (○).

Based on the reported results, it is possible to derive the equation

$$T_s = 0.986\ T_A + 6.46 \log t_A + K_0 + K_E$$

where K_0 is connected with the sample orientation (with a value of zero for an unoriented sample, increasing in such a manner that it can have an average value of 5 K for a highly oriented sample) and K_E is a constant connected with the annealing medium (for dry air, K_E is 6.92 K and for water 23 K in the case of PET). This equation is true for the DSC-1B calorimeter and for a rate of 16 K $\min^{-1}$ only.

In order to find the permanent effect of an annealing treatment (in boiling water) on the DSC behaviour of PA and PET, the samples were exposed to a combined annealing in two stages: (a) annealing in water or air at 100°C for 10 min, and (b) subsequent annealing in air at 110, 130, 150 and 170°C. The measured T_s value of the annealed samples are shown in Fig. 3. It can be seen that the influence of subsequent thermal treatment at 110°C for 10 and 100 min is less marked than the initial influence of annealing in boiling water for PET fibres only. In the case of PA, the secondary transition does not appear after thermal treatment in boiling water [see Fig. 3(b)] nor after subsequent annealing in hot air at 110 and 130°C. The behaviour of samples of PA and PET becomes analogous only if the subsequent thermal treatment has been carried out at 150°C in N_2 atmosphere. In this case, the effects of previous thermal treatments do not manifest themselves. But the densities of samples do not correspond to a thermal behaviour (Fig. 4). While the density of an oriented sample of PET after a previous annealing treatment in boiling water has an even lower value (disorientation), the density of PA increases markedly during annealing in boiling water and only slowly during subsequent treatment in N_2.

We reached a conclusion in our previous paper [8] that the secondary transition is the result of two processes which depend on time and tempera-

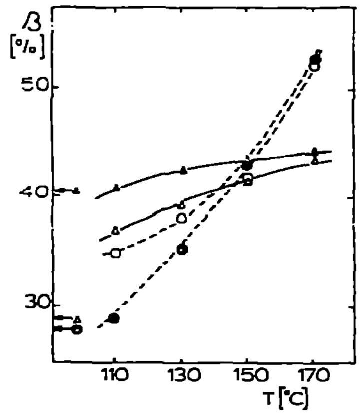


Fig. 4. The influence of annealing temperature (100 min in a N_2 atmosphere) on the crystallinity (β) in samples of PET (○, ●) and PA (△, ▲) having been annealed previously in air (○, △) or in water, (●, ▲) at 100°C for 10 min. The crystallinity of samples after this previous annealing only are indicated by arrows. The PET sample annealed in air at 100°C for 10 min had a crystallinity of 8%.

ture, namely partial melting and recrystallization (Fig. 2). While the course of the partial melting is analogous to an endothermic melting peak shape, the recrystallization occurs continuously over the whole DSC heating range [9]. The resulting shape of the secondary transition DSC curve depends on the ratio of these two processes.

The structural interpretation was also attempted by Oswald et al. [6] who designated this transition as the middle endotherm peak (MEP) and assumed that its inception was a result of melting of nuclei in the highly strained oriented amorphous domains which persist after the thermal treatment of a fibre or film.

According to Holfeld and Shepard [10], the influence of water on PA properties is considered similar to an influence of a carrier on polyester fibres. That is to say, the chains are removed, the physical bonds are broken and a better passage of dyestuff is enabled in such a way. The bonds between molecules of water and PA chains are formed [10]. This bound water is removed only by annealing at 150°C. It should follow that, by a thermal treatment in boiling water, nuclei of an amorphous region of a fibre would be impaired according to the structural idea of Oswald et al. [6]. This is why it is not possible to find the secondary transition (T_s or MEP). One observation is not in keeping with this idea, viz. that the inception of T_s (or MEP) is not confined to an oriented structure but also occurs in an unoriented state but it follows from this and also from the preceding papers [8]. It is also possible to explain the DSC behaviour of PA-6 after annealing in water by using our model. After boiling in water, the highly crystalline structure corresponding to a thermal treatment in air at 200°C is formed. In such a way, partial melting is practically prevented during heating, and limited recrystallization takes place from room temperature due to the hydration bonds. Indeed, the density of a sample annealed in boiling water and then thermally treated in a N_2 atmosphere increases continuously (see Fig. 4). Clarification of all the structural changes taking place during the secondary transition will require further investigation.

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