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Physical ageing studies in semicrystalline poly(ethylene terephthalate)

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The physical ageing of semicrystalline poly(ethylene terephthalate) (c-PET) of different crystallinities and morphological structures was studied using differential scanning calorimetry. Samples of c-PET of crystallinity content $\varkappa_c = 0.12$, crystallized at low temperatures (105 °C for 13 min), submitted to physical ageing in a temperature range between 50 and 65 °C for different periods of time, showed two endothermic peaks. The first peak (P_1) of higher intensity, appeared at a temperature close to the glass transition temperature, T_g, of the amorphous PET, and the other peak (P_2) of lower intensity, merged as a shoulder of the first one, at a higher temperature. These peaks have been attributed to the enthalpy relaxation process of two different amorphous regions: one amorphous phase outside the spherulitic structure (interspherulitic amorphous region) and another amorphous phase inside the spherulites (interlamellar amorphous region). The separation between P_1 and P_2 indicates that DSC, via enthalpy relaxation, is a good technique to detect the real double glass transition of the semicrystalline PET. However, the physical ageing of a semicrystalline PET of $\varkappa_c = 0.32$, crystallized at 114 °C during 1 h, showed a main endothermic peak shifted to a higher temperature, which probably corresponds to the enthalpy relaxation of the more restricted interlamellar amorphous region, and a small endothermic peak at lower temperature which could be a reflection of the hindered interspherulitic amorphous region.

1. Introduction

The presence of the crystals in a semicrystalline polymer is known to constrain the amorphous phase and to influence the glass transition region [1]. The segmental mobility of the amorphous phase near the crystals will be reduced, whereas at large distances from the crystals, the amorphous phase will have the same properties as in the bulk amorphous polymer. According to Struik [2–4], the view of this picture is that the glass transition of the semicrystalline polymer is broader than in the amorphous one and extends towards the high-temperature side.

Illers and Breuer [5], in studies of semicrystalline poly(ethylene terephthalate) (c-PET), demonstrated that the glass transition region depends not only on the crystallinity content but also on the morphological structure of the polymer. More recently, Schick *et al.* [6] observed that the glass transition in undrawn semicrystalline PET is influenced by the thickness of the amorphous layers between neighbouring lamellae.

Measurements of small-angle X-ray diffraction, electron microscopy, and viscoelastic analysis performed by Groeninckx *et al.* [7] in a PET of low crystallinity degree (obtained by isothermal crystallization from the glassy state) displayed the presence of two amorphous regions. One of them was attributed to an amorphous interspherulitic region and the other to an amorphous intraspherulitic region located between the crystalline lamellae. Two glass transition temperatures, T_g, could have been expected in this semicrystalline PET: one for the amorphous region between the lamellae inside the spherulites and the other for the amorphous region between the spherulites. However, only one glass transition temperature (measured by the inflexion temperature of the modulus–temperature curves) was observed, probably due to the proximity of these two T_{gs}.

As Boyer pointed out [8], there are other polymers in which the double glass transition can be observed. The glass transition in a semicrystalline polymer takes place in the amorphous phase, and a real double T_g requires isolated amorphous domains. Illers [9] suggested that lower levels of crystallinity in PET might provide such a system. The simultaneous detection of the two T_g's, which is termed a real double T_g, is, however, very difficult to obtain by thermal analysis techniques.

Recently, a double α relaxation associated with the glass transition in a c-PET of a crystallinity degree of 32% has been observed using a thermally stimulated current (TSC) technique. One relaxation was observed at 80–82 °C and the other at 88 °C. These relaxations were attributed to the amorphous interspherulitic region and interlamellar region, respectively [10]. TSC has proved to be an excellent technique to characterize the microstructure of polymers [11, 12].

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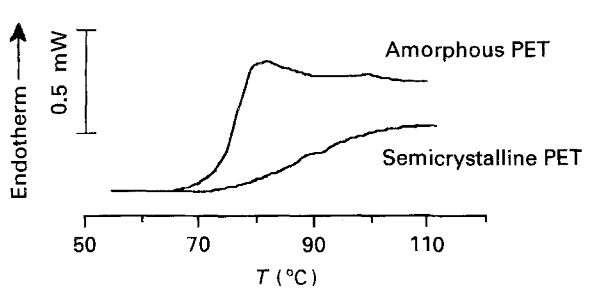

Figure 1 DSC curves of amorphous PET and semicrystalline PET ($\varkappa_c = 0.32$).

The objective of this work was to study the real double glass transition in a PET of low crystallinity degree by differential scanning calorimetry (DSC) via the physical ageing of the polymer, carried out at temperatures below the glass transition region for different periods of time.

2. Experimental procedure

PET samples of low degree of crystallinity ($\varkappa_c = 0.12$) were obtained by isothermal treatment of an amorphous commercial PET ($M_n = 20000$) at 105 °C for 13 min. The original amorphous PET had a degree of crystallinity of $\varkappa_c = 0.03$, and the glass transition temperature, T_g, measured as the mid-point between the rubbery and glassy lines was between 76 and 77 °C. The c-PET ($\varkappa_c = 0.12$) showed a unique T_g about 77–78 °C. A PET with a higher degree of crystallinity ($\varkappa_c = 0.32$) was obtained by isothermal crystallization of the amorphous PET at 114 °C for 1 h. The T_g of this c-PET ($\varkappa_c = 0.32$) was 92 °C, as shown in Fig. 1. The ΔC_p was of 0.42 and 0.16 $\text{J g}^{-1}\text{K}^{-1}$ for the amorphous PET and the c-PET ($\varkappa_c = 0.32$), respectively.

The DSC curves were obtained with a Mettler Thermoanalyser TA4000 equipped with a low-temperature-range DSC 30 Differential Scanning Calorimetry module, a TC 11 processor, and the software Graphware TA72.2.5. The density was measured at 23 °C by a density gradient column filled with *n*-heptane/carbonium tetrachloride. From the density, the degree of crystallinity, $\varkappa_c$, was estimated, assuming for the density of the crystals a value of $\rho_c = 1.455\,\text{g cm}^{-3}$ and for the amorphous phase a value of $\rho_a = 1.335\,\text{g cm}^{-3}$.

The c-PET ($\varkappa_c = 0.12$) samples were submitted to physical ageing at the ageing temperatures of 50, 60, 63 and 65 °C, for periods of time between 1 and 264 h. The aged samples were quenched to room temperature and scanned in the DSC equipment from 10–110 °C at a heating rate of 10 K min^{-1}, and then cooled again to 10 °C. A second scan was obtained at the same heating rate until 110 °C. The c-PET ($\varkappa_c = 0.32$) samples were aged at 60 °C.

3. Results and discussion

The DSC curves obtained from the aged c-PET of low crystallinity degree ($\varkappa_c = 0.12$) are shown in Fig. 2. For ageing temperatures $T_a \geq 50$ °C, two endothermic peaks of different intensity appear. The first peak, P_1, which appears in the DSC trace is higher than the second peak, P_2. For $T_a = 50$ °C, P_1 is between 75 and 76 °C, while P_2 is between 82 and 85 °C.

The intensity of the first peak, P_1, estimated by the specific heat capacity at the maximum of the peak, $C_{p_{max}}$, tends to increase with the ageing time similar to what happens in the amorphous poly(ethylene terephthalate) [13, 14]. The intensity of P_1 for $T_a = 63$ °C and 65 °C is lower than at 60 °C. This behaviour is similar to that observed in amorphous samples of PET [13, 14]. On the other hand, contrary to the behaviour in amorphous PET, for $T_a = 60$ and 63 °C, the intensity in semicrystalline PET decreases for ageing times higher than 48 h. Equally, the intensity of the second peak, P_2, tends to increase with ageing time, showing lower intensity than in P_1. Similar to in P_1, the intensity for $T_a = 63$ and 65 °C is lower than for 60 °C, and the intensity of P_2 at 60 °C decreases approximately from 100 h ageing (Fig. 3).

For low ageing times, the second peak merges as a shoulder of P_1, and with the ageing time becomes a more intensive peak depending on the ageing conditions. The separation between P_1 and P_2 increases slightly with the ageing time. For $T_a = 50$ °C, the separation between the peaks increases from 2.5 °C to 6 °C when the ageing time passes from 10 h to 264 h.

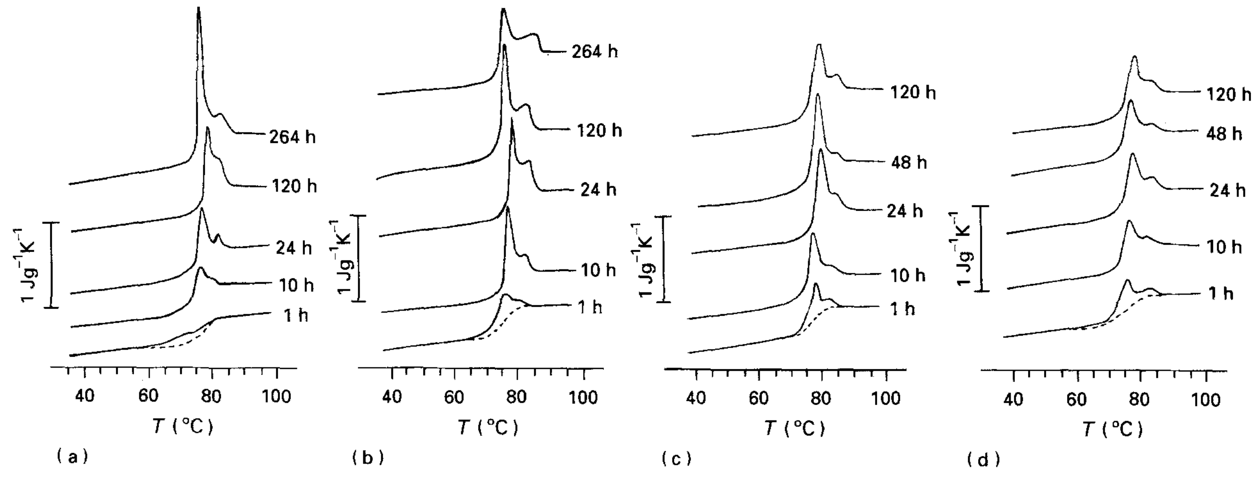

Figure 2 DSC curves of aged c-PET of low crystallinity ($\varkappa_c = 0.12$), for different ageing temperatures, T_a, at a heating rate of 10 K min^{-1}. (a) 50 °C, (b) 60 °C, (c) 63 °C, (d) 65 °C.

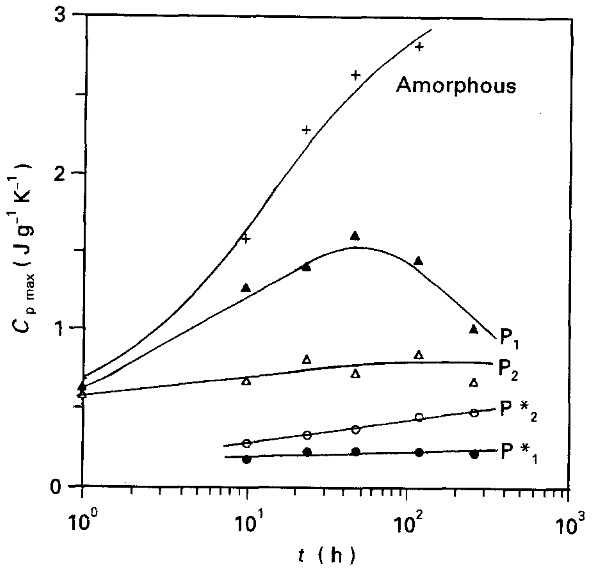

Figure 3 Dependence of C_p of the maximum of the endothermic peak, $C_{p_{max}}$, on ageing time at $T_a = 60$ °C for (+) amorphous PET; semicrystalline PET ($\varkappa_c = 0.12$): (▲) P_1 and (△) P_2; semicrystalline PET ($\varkappa_c = 0.32$): (●) P_1^* and (○) P_2^*.

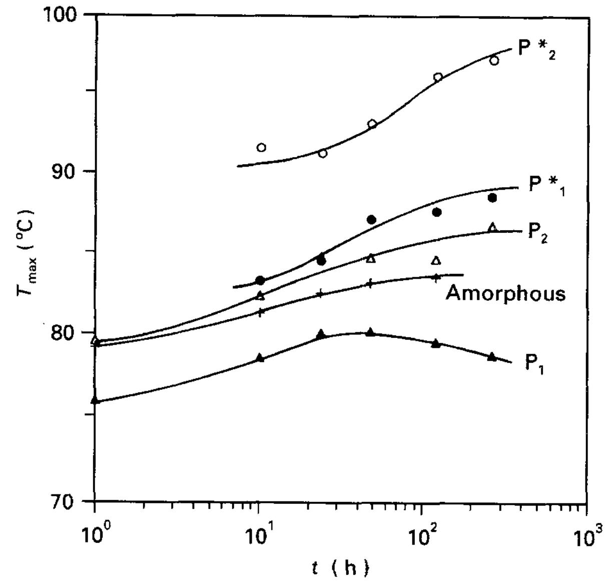

Figure 4 Dependence of temperature of the maximum of the endothermic peak, T_{max}, on ageing time at $T_a = 60$ °C for (+) amorphous PET; semicrystalline PET ($\varkappa_c = 0.12$): (▲) P_1 and (△) P_2; semicrystalline PET ($\varkappa_c = 0.32$): (●) P_1^* and (○) P_2^*.

The position of the endothermic peak determined by the temperature of the maximum, T_{max}, tends in both cases to show a similar behaviour as in the amorphous PET [13, 14]. T_{max} tends to increase with ageing time, with the exception of the temperature of peak P_1 for $T_a = 60$ °C which increases up to an ageing time of 48 h and then decreases slightly (Fig. 4).

These results show peak P_1 within the range 76–80 °C, close to the region of the glass transition of the amorphous PET (76–77 °C), while peak P_2 is in the range 80–87 °C, closer to the region of the glass transition of the c-PET with a crystallinity degree of 0.32 (90 °C). These results agree with others recently reported by Benatmane [15] and Vigier *et al.* [16].

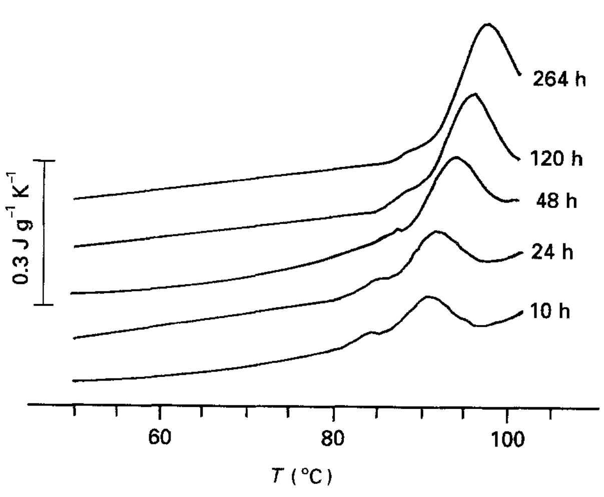

Figure 5 DSC curves of aged c-PET of medium cyrstallinity degree ($\varkappa_c = 0.32$) for an ageing temperature of 60 °C, at a heating rate of 10 K min^{-1}.

The physical ageing of the c-PET of crystallinity degree $\varkappa_c = 0.32$ at 60 °C shows quite a different behaviour. The DSC curves of aged samples show a main endothermic peak, P_2^*, situated between 92 and 98 °C according to the ageing time, and a small endothermic peak, P_1^*, situated between 83 and 89 °C, which merges as a previous shoulder of the main peak (Fig. 5). The intensity of the main peak is lower than the intensity of both peaks P_1 and P_2 of the c-PET ($\varkappa_c = 0.12$) aged at the same temperature (Fig. 3). On the other hand, the temperature of the main endothermic peak is sensibly higher than the T_{max} of P_1 and P_2. In c-PET ($\varkappa_c = 0.32$), both parameters (intensity and position) increase continuously with log(time) and do not show any decrease, as in c-PET ($\varkappa_c = 0.12$).

Other authors [5, 7, 9, 15–17] indicate that the growth of spherulites is not completed when the amorphous PET is crystallized at relatively low temperatures for short periods of time. Spherulites grow from the existing nuclei, and gradually fill the volume of the material. These samples of c-PET ($\varkappa_c = 0.12$) show the following morphological elements: the crystalline lamellae and the amorphous interlamellar region constituting the spherulites, and the interspherulitic amorphous region. The physical ageing of this c-PET leads to a double relaxation process: one in the interspherulitic amorphous region, displayed in peak P_1, and another in the intraspherulitic amorphous region, situated between the crystalline lamellae and displayed in peak P_2.

The kinetics of the enthalpic relaxation process seems to be different in each amorphous region due to the different mobility of the chain segments. The mobility in the interlamellar amorphous region is more constrained than in the amorphous region outside the spherulites. According to other authors [7, 9, 17, 18], at low crystallization temperatures, the spherulitic growth is initiated by a large number of nuclei. The amorphous interlamellar region is composed of irregular chain folding, chain ends and polymer chains incorporated in several lamellae. Consequently, the segmental mobility will be lower in this region than in the interspherulitic region. Because of this different

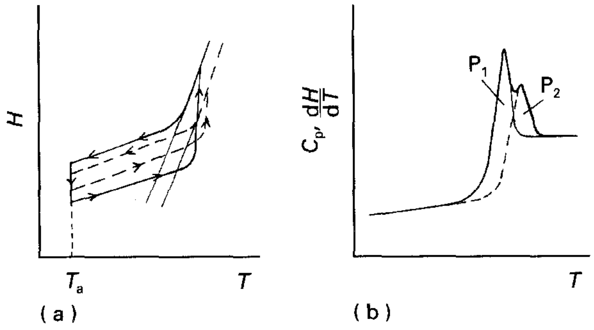

Figure 6 Schematic diagrams of (a) enthalpy versus temperature illustrating the two enthalpic relaxation processes corresponding to two different amorphous regions (interlamellar and interspherulitic), and (b) C_p versus temperature showing the double glass transition (P_1 and P_2).

segmental mobility, the intensity of peak P_2 and its variation with log(time) will be smaller than in P_1, and the peak temperature of P_2 will be higher than in P_1. The overlapping of these two relaxation processes could be the origin of the DSC trace of c-PET ($\varkappa_c = 0.12$), as schematically indicated in Fig. 6.

The higher the crystallization temperature the higher the crystalline content, and the restrictions of the segmental mobility in the interlamellar amorphous region are also greater. As a result, the glass transition appears at higher temperature [5, 7, 9, 17–19]. The c-PET ($\varkappa_c = 0.32$) shows a broader glass transition region with a mid-point T_g (92 °C) higher than in amorphous PET. Inversely, the ΔC_p at T_g is smaller than in amorphous PET. The main endothermic peak of the aged c-PET ($\varkappa_c = 0.32$) samples could be caused by the enthalpic relaxation in the interlamellar amorphous region. The small endothermic peak seems to be a response of the interspherulitic amorphous region where the spherulites practically fill up the whole volume, reducing the amount of this amorphous region, while increasing the restrictions of segmental mobility.

4. Conclusions

1. The physical ageing of a PET of low crystallinity degree can be used to display the different morphological structures of this polymer and contributes to a better understanding of the nature of the double glass transition in the semicrystalline PET.

2. The growth of spherulites in the semicrystalline PET of $\varkappa_c = 0.12$ is not completed, and shows two amorphous regions: one amorphous phase outside the spherulitic structure (interspherulitic amorphous region) and another amorphous phase inside the spherulites (interlamellar amorphous region). The physical ageing of this PET shows two enthalpic relaxation peaks: one of higher intensity, P_1, at a temperature close to the T_g of the amorphous PET, and another with lower intensity, P_2, merging as a shoulder of the first one, at higher temperature. Both peaks P_1 and P_2 are attributed to the enthalpy relaxation of the interspherulitic amorphous region and the interlamellar amorphous region, respectively. The separation between P_1 and P_2 reveals that DSC, via enthalpy relaxation, is a good technique to detect the real double glass transition of the semicrystalline PET.

3. An increase of the crystallization temperature originates an increase of the crystallinity degree and a change in the morphology of the polymer. The physical ageing of the semicrystalline PET of $\varkappa_c = 0.32$ shows a main endothermic peak shifted to a higher temperature, which is probably associated with the enthalpy relaxation of the interlamellar amorphous region. A small endothermic peak is observed which could be associated with the interspherulitic amorphous region.

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