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# Effect of milling on the thermal behaviour of poly(ethylene terephthalate)

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## Abstract

The solid state amorphization of poly(ethylene terephthalate), applying mechanical milling, is described. Their effect on samples quenched or slowly cooled after the melt as well as in samples with different crystallinity degrees, attained from annealing treatments, is characterized using differential scanning calorimetry and X-ray diffraction at room temperature. In previously annealed poly(ethylene terephthalate) at several temperatures some differences appear in the amorphization after milling. However, effects other than the crystallinity degree have to be taken into account to explain them.

*Keywords:* Poly(ethylene terephthalate); Ball milling; Amorphous material; Differential scanning calorimetry; X-ray diffraction

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## 1. Introduction

Ball milling is being used widely to improve the physical properties of materials. This technique can be applied to elemental crystalline powders (mechanical milling) with different objectives: particle size reduction, amorphization, obtainment of nanocrystalline structures, etc. It can be also used for alloying powders in the solid state (mechanical alloying). Most of the studies employing this technique have been limited to metallic systems [1–3].

More recently, ball milling has begun to be applied to polymeric materials. First studies reveal the possibility of alloying incompatible polymer mixtures. Farrell et al. [4] obtained blends of polypropylene with a thermotropic crystalline polymer, resulting in unique structures and altered mechanical properties. Alloys of polytetrafluoroethylene and polyethylene were prepared by Ishida [5] using the same technique. A work performed by Castricum et al. [6] in amorphous polystyrene showed the formation, after milling, of a second glass transition. Also a complete structural phase transformation was driven by mechanical milling in partially crystalline high density polyethylene. In polyethylene glycol neither chemical nor physical changes were induced.

Our previous studies applying ball milling to organic materials showed the formation, in the solid state, of binary alloys of plastic crystals derived from neopentane [7,8]. In another paper [9] we analysed the behaviour of sucrose and poly(ethylene terephthalate) (PET) previously submitted to mechanical milling. Different amorphization levels were observed between both organic compounds.

In the present work we complete our study of PET analyzing the effect of milling on the behaviour of this polymer having different crystallinity degrees obtained from several thermal treatments.

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## 2. Experimental

Pellets of PET were supplied by Aldrich, with a number-average molecular mass $M_n$ about 13 000. The polymer was milled in a Fritsch (Pulverisette 6) centrifugal ball mill, working with a rotation speed of 50% of its maximum value. We used a cylindrical stainless steel grinding jar of 80 $cm^3$ with two balls 2 cm in diameter made of the same material. The sample mass into the vial was 5 g, giving rise to a product to ball ratio of 1:12. The vial was maintained at room temperature.

The samples were thermally analysed by means of differential scanning calorimetry (Setaram DSC92). Sample masses about 50 mg were placed in open aluminium crucibles. The heating rate used was 5 K $min^{-1}$. Room temperature X-ray diffractions were performed on a D-500 Siemens diffractometer operating with a goniometer speed of 0.005° ($2\theta$) $s^{-1}$ with Cu K$\alpha_1$ radiation $\lambda$=0.154 nm.

## 3. Results and discussion

Poly(ethylene terephthalate) melted and quenched to liquid nitrogen (almost fully amorphous) showed on heating a glass transition at 350 K followed by the crystallization at 405 K and the melting at 535 K. When the sample was melted and slowly cooled (at 0.2 K $min^{-1}$) to room temperature we obtained a degree of crystallinity of 45%, determined from the enthalpy variation of melting (accepting an enthalpy change for fully crystalline PET of 118 kJ $kg^{-1}$ [10]).

The sample previously quenched was submitted to mechanical milling. Fig. 1 shows the DSC curves corresponding to the heating runs from room temperature to liquid state after 1 and 15 h of grinding, respectively. The crystallization in the quenched PET (exothermic peak in curve a) is split into two processes (see curves b and c). For 15 h of milling we detect a slight exothermic effect near the glass transition followed by another crystallization, more intense, at the beginning of the melting (curve c). No further evolution was observed for longer milling times.

As we can see from Fig. 2, a very similar final state was obtained in semicrystalline PET milled 15 h (compare the DSC curve c in Fig. 1 with b in Fig. 2). X-ray diffraction patterns included in Fig. 3 point out the amorphization of semicrystalline PET produced by ball milling (see curve a). Curves b and c, in the same figure, are the diffraction patterns of samples slowly cooled to room temperature from 420 and 535 K respectively, temperatures corresponding to the end of the first and second exothermic effects showed in Fig. 2, curve b. The increase in the crystallinity degree, revealed by Fig. 3, confirms that both exothermic peaks are due to a partial crystallization of PET amorphized by ball milling.

In order to analyse the effect of milling on PET with different degrees of crystallinity we submitted, the

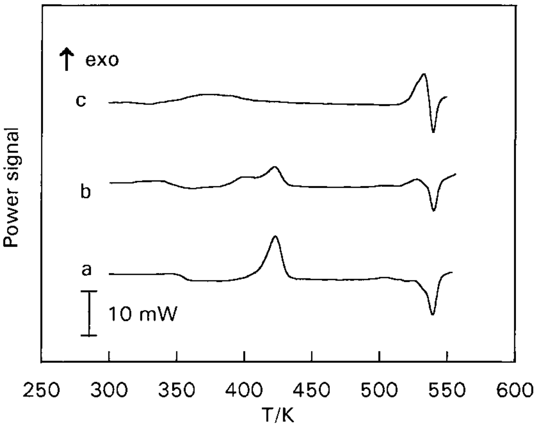

Fig. 1. DSC heating curves, from room temperature to the liquid state, for PET: (a) quenched from the liquid, (b) quenched and 1 h milled and (c) quenched and 15 h milled.

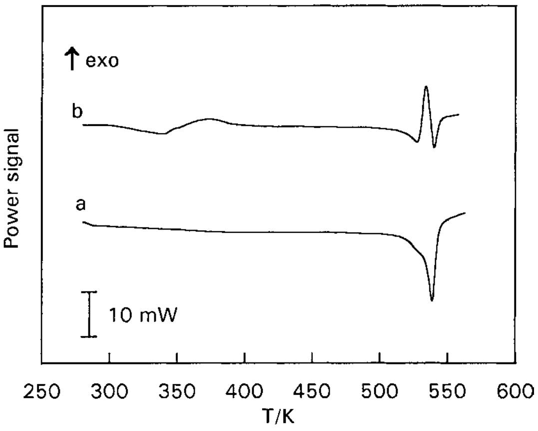

Fig. 2. DSC heating curves, from room temperature to the liquid state, for PET: (a) slowly cooled from the liquid and (b) slowly cooled and 15 h milled.

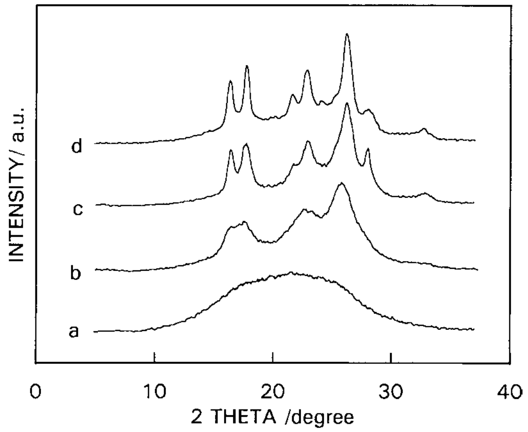

Fig. 3. X-ray diffraction patterns, at room temperature, for PET: (a) slowly cooled from the liquid and 15 h milled, (b) slowly cooled from the liquid, 15 h milled and heated until 420 K, (c) slowly cooled from the liquid, 15 h milled and heated until 535 K and (d) slowly cooled from the liquid.

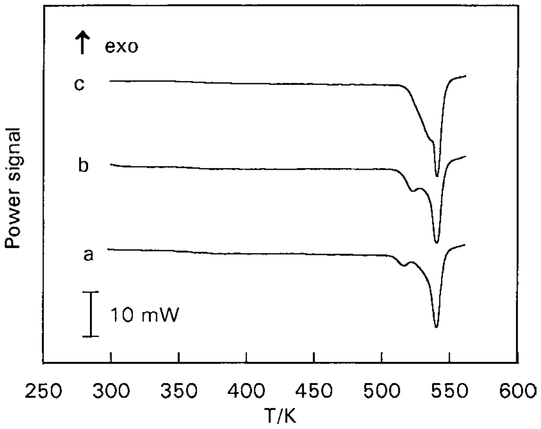

Fig. 5. DSC heating curves, from room temperature to the liquid state, for PET samples quenched and annealed at 503 K during: (a) 1, (b) 3 and (c) 20 h.

samples quenched from the liquid state, to annealing treatments at 473, 488, 503 or 518 K during 1, 3 and 20 h. The maximum degree of crystallinity was 65% obtained with the treatment of 20 h at 518 K. DSC curves for PET annealed are represented in Fig. 4 (20 h at these temperatures) and in Fig. 5 (different times at 503 K). After the annealing treatment the polymer melted in two steps. The first peak, appearing at temperatures above that of the annealing, evolved to higher temperatures when the annealing temperature or the time treatment increased. The second endothermic effect remained always at 535 K. This result is in agreement with the behaviour described in the literature [11,12] for annealed PET.

The samples previously annealed were ground during 15 h. The amorphization induced by mechanical milling is pointed out by Fig. 6 (compare curve $a_2$ with $a_1$ and $b_2$ with $b_1$). The halo-like pattern typical of amorphous material is clearly visible only for the sample annealed at 473 K during 20 h (see curve

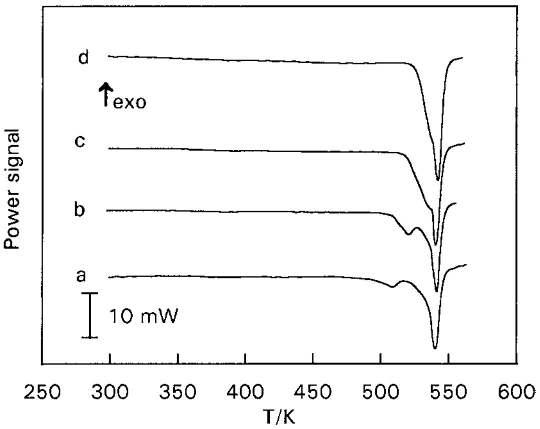

Fig. 4. DSC heating curves, from room temperature to the liquid state, for PET samples quenched and 20 h annealed at: (a) 473, (b) 488, (c) 503 and (d) 518 K.

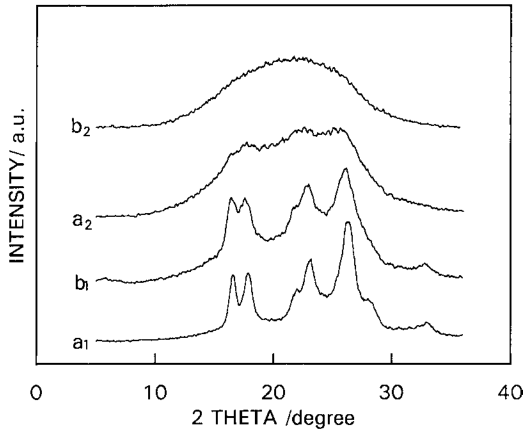

Fig. 6. X-ray diffraction patterns, at room temperature, for PET quenched and 20 h annealed at: ($a_1$) 518K, ($b_1$) 473K, ($a_2$) 518 K plus 15 h milled and ($b_2$) 473 K plus 15 h milled.

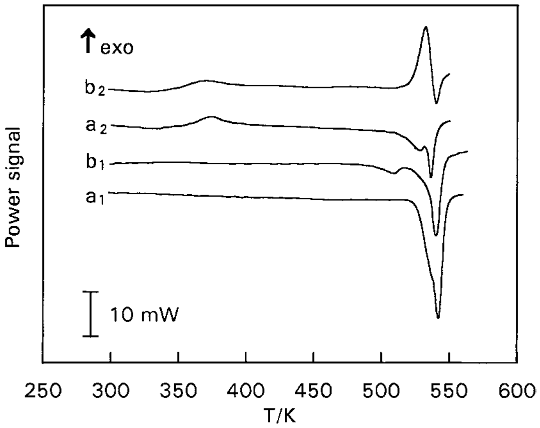

Fig. 7. DSC heating curves, from room temperature to the liquid state, for PET samples quenched and 20 h annealed at: ($a_1$) 518 K, ($b_1$) 473 K, ($a_2$) 518 K plus 15 h milled and ($b_2$) 473 K plus 15 h milled.

$b_2$). The DSC curves corresponding to the heating of these samples are represented in Fig. 7. We can observe that the sample annealed 20 h at 518 K shows a different behaviour after milling. In this case the exothermic peak close to the melting is scarcely visible (see curve $a_2$ in Fig. 7). This result jointly with that of X-ray diffraction pattern (curve $a_2$, Fig. 6), suggest that the amorphization caused by ball milling is lower for the sample submitted to this annealing treatment. However, the sample annealed 20 h at 473 K and milled during 15 h shows the DSC curve characteristic for PET after milling (compare curve $b_2$ in Fig. 7 with c in Fig. 1 or b in Fig. 2).

The level of crystallinity reached after annealing 20 h at 473 K is 55% in front of 65% for 20 h at 518 K. We assume that this difference in crystallinity is not sufficient for explaining the behaviour revealed by Figs. 6 and 7. Other effects induced by annealing, such as differences in crystalline size, may be considered.

The samples, previously annealed and milled, were heated until 535 K (temperature at which the second exothermic process is complete) and then cooled back to room temperature. In the following heating, we observed an unique thermal effect, the melting, with an enthalpy change always lower than that of the sample annealed without milling. To recover the same crystallinity degree an additional annealing treatment was necessary after milling.

## 4. Conclusions

We have studied the effect of mechanical milling on poly(ethylene terephthalate) (PET) with different crystallinity degrees. The energy supplied by grinding the polymer gives rise to an amorphization of the material. The crystallization, on heating the glassy state obtained by milling, takes place in two processes, one near the glass transition and a second just at the beginning of the melting. When PET is previously annealed, some differences in the amorphization produced by mechanical milling are encountered. We assume that other effects in addition to the starting crystallinity level, as for example crystalline size, must be considered to explain this behaviour.

The results of this work provide a necessary information for blending PET with other polymeric materials in solid state, by means of the mechanical alloying technique.

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