EFFECT OF γ IRRADIATION ON THE MECHANICAL PROPERTIES OF CRYSTALLINE PET

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EFFECT OF γ IRRADIATION ON THE MECHANICAL PROPERTIES OF CRYSTALLINE PET

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Résumé - On a étudié, par moyen d'expériences de frottement interne, les effets de la cristallisation et de l'irradiation gamma d'échantillons fortement cristallisés de poly-éthylène-térephthalate (PET). Un augmentation du degrée de cristallinité (obtenue par des traitements thermiques à des températures croissantes) conduit à une diminution de la partie température élevée du pic de relaxation β et aussi du pic α. Plusieurs échantillons fortement cristallisés présentent une anomalie (à 250 K) dans l'amortissement et le module. Après irradiation jusque 300 Mrad, on observe une décroissance graduelle du frottement interne, tandis que le module présente une croissance initiale avant de décroître graduellement. Une tendance analogue à la baisse se retrouve dans la chaleur de fusion et la température de fusion.

Abstract - The effects of crystallization treatments and of gamma irradiation of highly crystallized specimens of polyethylene terephthalate (PET) have been studied by means of internal friction experiments. Increasing crystallinity (resulting from thermal treatment at increasing temperatures) results in a decrease of primarily the high temperature part of the β relaxation and in a decrease of the α peak height. In some highly crystallized specimens, an anomaly is observed at 250 K in both damping and modulus. Irradiation fluences up to 300 Mrad lead to a gradual decrease of the damping, whereas the modulus, following an initial increase, also decreases slightly. A similar decreasing trend is observed in the heat of fusion and the melting point.

INTRODUCTION

Polyethylene terephthalate (PET) is a polymer prepared by condensation of terephthalic acid and ethylene glycol. The repeat unit of the molecule has the average structure $-CO-O-CH_2-CH_2-O-CO-C_6H_4-$, but occasionally (2-8 wt % of the polymer) two molecules of the glycol are combined as the structure $-CO-O-CH_2-CH_2-O-CH_2-CH_2-O-CO-O_6H_4-$. The predominant end groups are $-CH_2-CH_2-OH$ and -COOH. During processing PET can be stretched uniaxially, to yield fibres, or biaxially, to produce films; this results in orientation of the polymer molecules. Recently crystallization studies of oriented PET have been reported e.g. by Pereira and Porter [1], Tong Sun et al. [2] and Desai and Abhirman [3]. Fig. 1 shows the arrangement of molecules in a PET crystal [4].

As mentioned in the preceding paper [5], the effect of irradiation of PET has been reported by Charlesby [6] who found that the polymer cross-links, and by Little [7] and Todd [8] who found that it degrades.

In the present work internal friction has been used to contribute to the elucidation of the effect of γ irradiation on well-crystallized PET.

SPECIMEN PREPARATION

Amorphous PET films were prepared by melt pressing of commercial PET pellets and quenching in cold water. Crystallization of this material has been carried out by sealing amorphous specimens in an evacuated (10^{-2} Pa) quartz tube and heating to various temperatures ranging from 150-245°C. The crystallization time was 20 h,

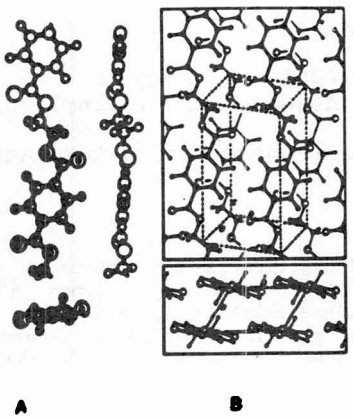

FIG. 1a,b
Configuration (a) of molecules and arrangement (b) of molecules in crystalline PET. Upper part: projection along the a-axis; lower part: projection along the c-axis. (large dots carbon; smaller dots, hydrogen; open circles, oxygen)

which is long enough to ensure reaching the equilibrium degree of crystallization. Fig. 2 shows DSC scans of the melting behaviour of an amorphous PET and of PET crystallized by annealing at 245°C.

A comprehensive study of the melting behaviour of PET and of the effects of heat treatments has been reported by Groeninckx and Berghmans [9], by Groeninckx et al. [10] and by Peszkin and Schultz [11].

EXPERIMENTAL ASPECTS

For studying the internal friction of the material, two types of systems were used working at two distinct ranges of frequencies. They have been described in the preceding paper [5]. The degree of crystallinity can be determined from density measurements using the following equation:

$$\chi d = (\rho-\rho_\alpha)/(\rho_c-\rho_\alpha)$$

where ρ is the density of a semicrystalline sample, ρ_c is the density of a perfect crystal of the polymer (ρ_c = 1.445 g/cm^3 at 250°C [4]) and ρ_α is the density of amorphous PET (ρ_α = 1.335 g/cm^3 at 25°C [4]). The density of the specimen annealed at 245°C was found to be 1.41 g/cm^3, hence χd = 68.4 %.

The degree of crystallinity can also be obtained from the heat of fusion δH_{exp} measured by means of DSC using the relationship:

$$\chi_{DSC} = \delta H_{exp}/\delta H^o$$

where δH^o is the heat of fusion of fully crystalline PET and is equal to 28.1 cal/g [12]. The heat of fusion for a specimen annealed at 245°C was found to be equal to 18.8 cal/g, so that the corresponding degree of crystallinity of that specimen is χ_{DSC} = 67 %, which agrees well with the value derived from the density. Annealing to 245°C yields the highest degree of crystallinity obtainable in PET. Such specimens were used for studying the effect of γ irradiation. The irradiation conditions were the same as described in the preceding contribution [5].

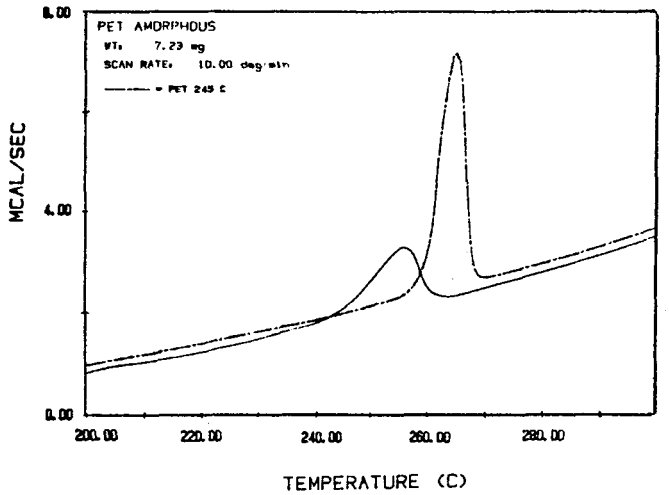

FIG. 2
DSC scans of melting behaviour of amorphous PET (—) and of PET crystallized by annealing at 245°C (—.—)

RESULTS AND DISCUSSION

The mechanical relaxation spectrum of PET annealed at various temperatures is shown in Fig. 3. The decrease of the α peak relaxation strength is consistent with the decrease in the fraction of amorphous material with increasing degree of crystallinity. The β peak also decreases in magnitude with increasing crystallinity and furthermore shifts slightly to lower temperature, suggesting that the higher temperature component of the β peak is reduced by crystallization. The reorientation of hydroxyl groups in the non-crystalline phase, which was suggested by Reddish [13] to be responsible for part of the β relaxation process would then more particularly be related with the high temperature components of the β peak. The activation enthalpy was found to be equal to 0.7 eV (comparable to the value of 0.69 eV in the amorphous material) and the preexponential is $f_o = 4.4 \times 10^{17}$ Hz, which is considerably higher than in the amorphous phase.

For the most highly crystallized material, the data taken at higher temperature are also shown in Fig. 4, indicating the existence of a small peak at the annealing temperature, T_a. The determination of the glass transition temperature of the remaining amorphous phase is rather imprecise but suggests a slight increase in T_g with increasing crystallinity. This is consistent with the decrease in free volume in the amorphous fraction which accompanies the structural reorganization taking place during the annealing treatments.

In several crystallized specimens, both the modulus and the internal friction exhibited anomalous behaviour near 250 K (Fig. 5), characterized by a very sharp damping peak and an increase in the modulus with increasing temperature, occurring at roughly the same temperature for a frequency of both 1 Hz and 270 Hz. The precise conditions required for observing this phenomenon could not yet be determined; an interpretation is also still lacking.

The effect of γ irradiation on the relaxation behaviour of crystallized PET is summarized in Fig. 6. Whereas the modulus measured in the β region at 210 K appears to increase first and then to decrease with increasing fluence, the β peak height follows a monotonously decreasing trend. Such a monotonous trend appears to be followed also by the thermal data (heat of fusion, melting point), which also appear to go through an initial increase (Table I).

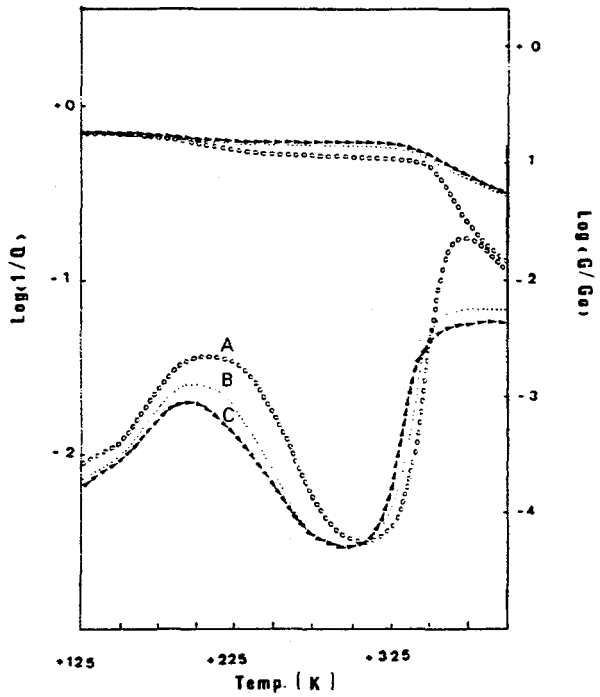

FIG. 3
Mechanical relaxation spectrum (1Hz) of PET annealed at various temperatures A: amorphous; B and C: following 20 h annealing at 228°C and 245°C, respectively

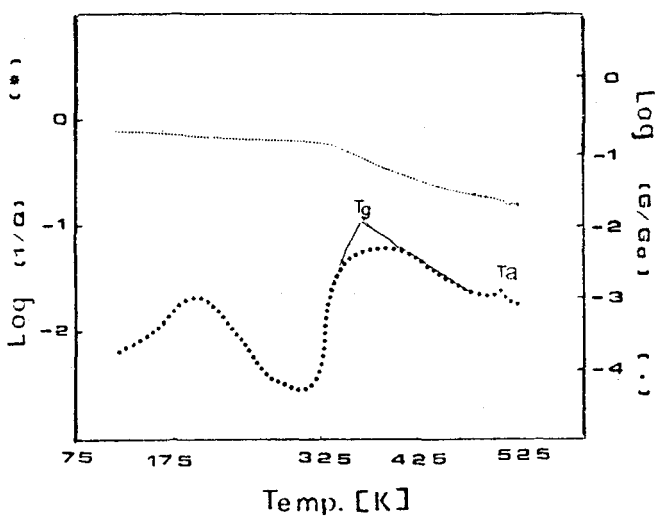

FIG. 4
Mechanical relaxation spectrum at a frequency of 1 Hz of PET annealed at T_a = 245°C

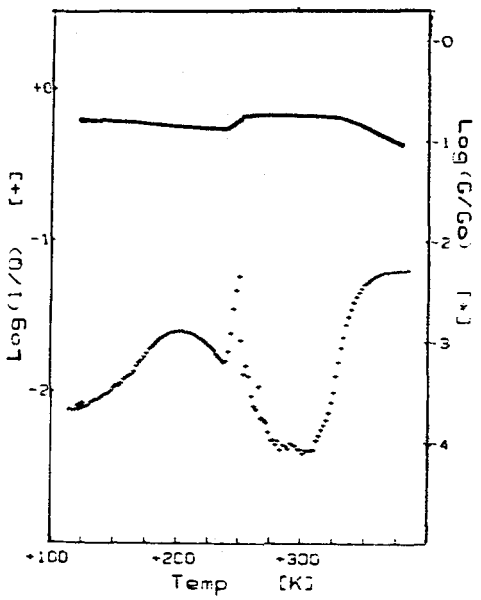

FIG. 5
Mechanical relaxation spectrum for specimen annealed at 245°C. Notice the anomaly near 250 K

TABLE 1. Effect of γ fluence on melting point, T_p and heat of fusion, δH

Fluence (Mrad)	0	1	3	10	30	50	100	300
T_p (°C)	265.2	267.5	268.8	267.4	267	264.6	261.2	257.5
δH (cal/g)	18.8	19.5	19.2	19.35	19.4	19.2	18.1	18.2

As for the amorphous material, it can be concluded that also in the crystalline phase the initial cross linking is gradually overtaken at the higher doses by chain scission. The resulting decrease in crystalline perfection of the crystalline phase leads to the observed decrease in the values of the thermal quantities T_p and δH.

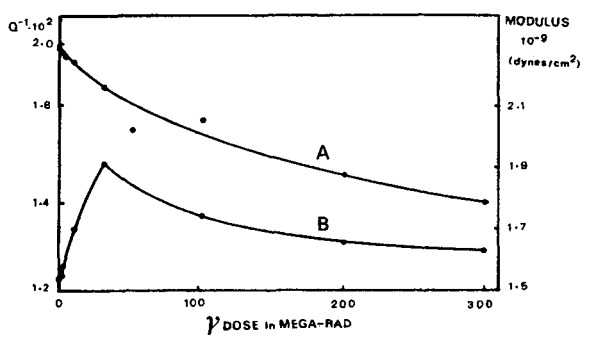

FIG. 6
Effect of γ irradiation of crystallized PET on Q^{-1} (A) and modulus (B) measured at 210 K and 1 Hz

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