

Effect of Moisture on the Crystallization Behavior of PET from the Quenched Amorphous Phase

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SYNOPSIS

The dependence on the moisture content of the glass transition temperature (T_g) and of the crystallization temperature from the quenched amorphous phase (T_c) for poly(ethylene terephthalate) (PET) samples is studied by differential scanning calorimetry.

For low moisture contents, very large and reversible decreases of T_c but small decreases of T_g are observed. This indicates that the strong increase of nucleation rate observed for PET in the presence of moisture is not related to the plasticizing effect that produces significant T_g changes.

INTRODUCTION

Very little has been published concerning the effect of moisture on the crystallization behavior of poly(ethylene terephthalate) (PET) from the quenched amorphous phase. When heating from the glassy state, crystallization peak temperatures (T_c) in the range 120–140°C, which depend on the molecular weight and on the moisture content, have been reported.¹ In particular, pronounced decreases of the glass transition and crystallization temperatures (T_g and T_c) of PET, due to the absorbed moisture, have been described.¹ The observed decreases of these temperatures (up to 16°C and 9°C for T_g and T_c , respectively) were nearly linear and independent of the molecular weight.

A recent study of isothermal crystallizations of PET from the glassy state has also shown an increase of the overall rate of crystallization for wet samples, primarily due to an increase in the nucleation rate. The spherulite growth rate appeared, in fact, to be independent of the moisture content.²

On the basis of these results, it has been suggested that the increases in the nucleation rate (as well as the reduction of T_c) would be caused by the plasti-

cizing effect of the absorbed water, which reduces the glass transition temperature.²

Here it is shown that quenched PET samples, dried in suitable conditions, can present T_c values as high as 171°C and reversible decreases of T_c up to 40°C, due to the moisture absorption, are possible. For low values of moisture content, very different behaviors of T_c and T_g are observed. This gives some further insight into the influence of the moisture on the nucleation rate of PET.

EXPERIMENTAL

PET pellets obtained by the dimethyl terephthalate (DMT) process, with Sb as the polycondensation catalyst, have been used. The inherent viscosity determined at 35°C in *o*-chlorophenol is 0.625 dL/g; the diethylene glycol content is 1.6 mol %.

The quenching conditions for the pellets are those of the industrial plant: The polymer is obtained by melt condensation at 290°C, extruded, and then quenched in water at 8°C. All the considered samples are amorphous as shown by X-ray diffraction analysis.

Humidity conditioning was achieved by storing samples in controlled temperature chambers with relative humidities ranging from 7 to 89%. These

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humidity conditions were maintained by using various saturated salt or sulfuric acid solutions.

Percent moisture absorbed was measured using a DuPont Moisture Evolution Analyzer 903. Thermal properties were determined using a DuPont Thermal System 9900 by heating samples of about 30 mg at 10°C/min under nitrogen atmosphere. Glass transition temperatures (T_g) were taken as the midpoint of the step change in the base line. Peak crystallization temperatures (T_c) were taken as the maximum displacement of the crystallization exotherm. The T_g and T_c values have been averaged on at least three different samples.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC) scans for PET samples with different equilibrium moisture contents are reported in Figure 1. Although the temperature corresponding to the melting endothermic peak (T_m) is substantially identical for all the considered samples (possibly due to recrystallization phenomena that occur during the DSC scans), the glass transition temperature (T_g) and, particularly, the temperature corresponding to the crystallization exothermic peak (T_c) are largely different. The T_g and T_c values obtained by DSC scans

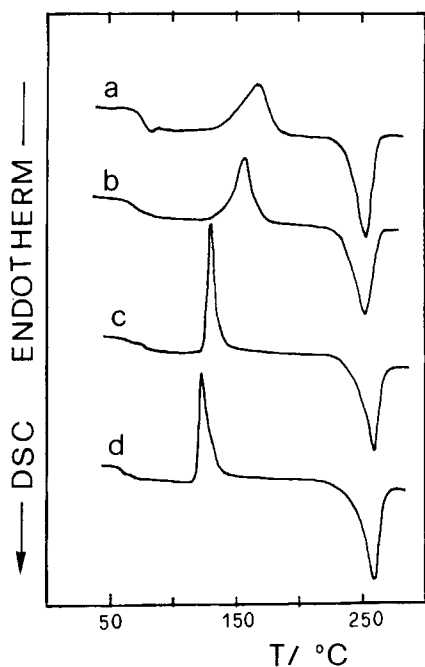


Figure 1 DSC scans of PET samples with different equilibrium moisture contents: (a) 0%, (b) 0.021%, (c) 0.37%, (d) 0.91%.

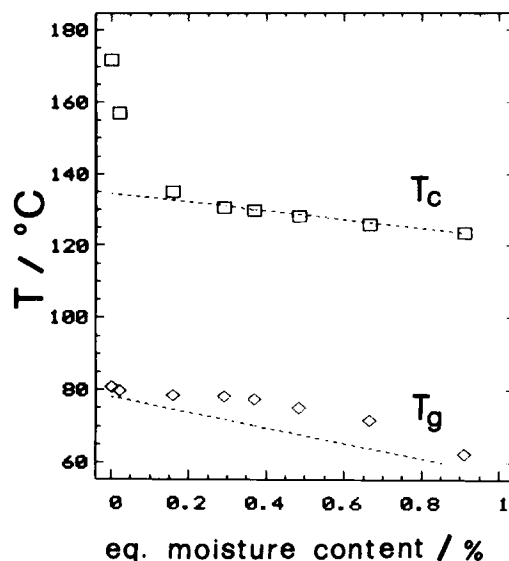


Figure 2 Glass transition temperature (T_g) and crystallization temperature (T_c) of PET samples vs. the equilibrium moisture content. The dashed lines correspond to interpolations of the T_g and T_c data of Ref. 1.

of the kind of Figure 1 are reported versus the equilibrium moisture content in Figure 2. For an easier comparison, broken lines corresponding to interpolations of the T_c and T_g data of Ref. 1, for a sample with inherent viscosity of 0.60 dL/g, are also reported in Figure 2.

It is apparent that the similarity in the behaviors of T_c and T_g , observed in Ref. 1, is found in our case only for high equilibrium moisture contents (> 0.3%). According to our results, low moisture contents produce very small decreases of T_g but very large decreases of T_c , with respect to the completely dry sample (e.g., for the 0.3% equilibrium moisture content, decreases of T_g and T_c of 3°C and 40°C, respectively).

Some DSC scans for samples held at a fixed relative humidity condition (51%) for different exposure times (i.e., for samples that have not yet reached the equilibrium moisture content) are reported in Figure 3. Two crystallization peaks are generally present, and, with the exposure time, the area of the peak at lower temperature increases at the expense of the area of the peak at higher temperature. Correspondingly, the T_g remains substantially constant. The lower crystallization peaks possibly correspond to the material behind the humidity front in the samples, and the higher peak, to the material ahead of this front. These data confirm that strong variations of T_c are possible also in the absence of any significant T_g decrease.

Samples originally with an equilibrium moisture content of 0.3% have been desiccated at 40°C with a dry nitrogen draft or with a vacuum pump (pressure lower than 10 mbar), for different times. The drying procedure with the nitrogen draft is much more efficient than with a standard vacuum pump, e.g., after 14 days the residual solvent content is of 0.005% and 0.15%, respectively. This, in particular, could be a possible reason for the large differences in the T_c values for dry PET samples between the present study and Ref. 1. Some DSC scans of samples subjected to the above-described drying procedures are reported in Figure 4. It is apparent that the described large variations of T_c , with the moisture content, are reversible.

The very different behaviors of T_c and T_g for low moisture contents in PET samples indicate that the large decrease of T_c already for low moisture contents (possibly corresponding to a large increase of nucleation rate) is not related to the plasticizing effect that produces significant T_g changes.

Only tentatively, we suggest that a drastic in-

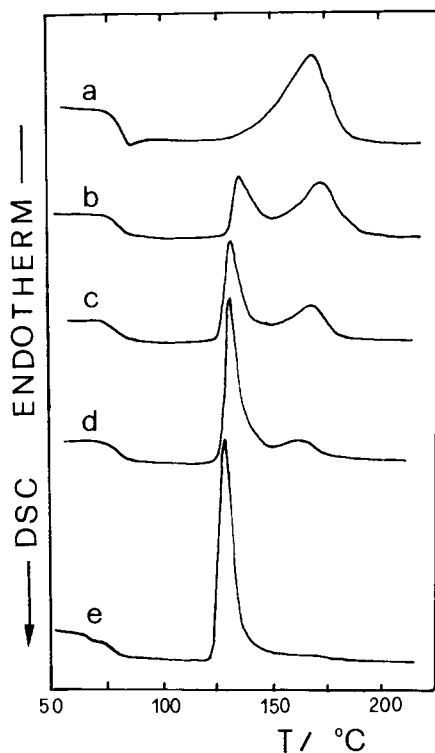


Figure 3 DSC scans of samples held at the relative humidity of 51% for different times: (a) 0 h, (b) 1 h, (c) 4.5 h, (d) 16.5 h, (e) 72 h.

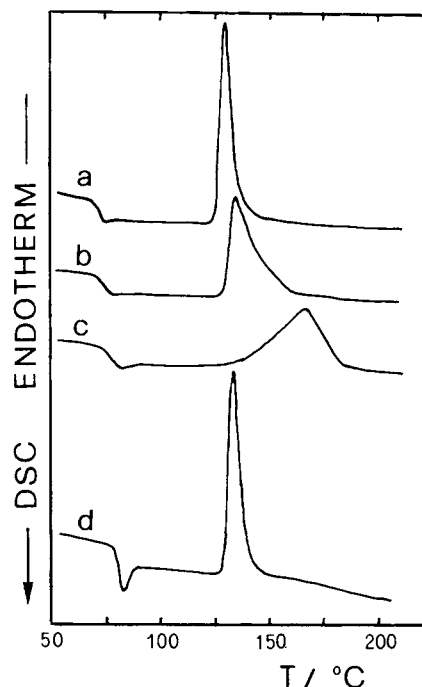


Figure 4 DSC scans of a PET sample with an equilibrium moisture content of 0.3%: (a) not dried, (b) after drying with a nitrogen draft for 2 days, (c) after drying with a nitrogen draft for 14 days, (d) after drying with a vacuum pump for 14 days.

crease in the nucleation rate could be related to some local mobility generated by a different sorption state of water, when it is present in a very low amount. A different sorption state of water for content below 2% b.w. has been suggested, for instance, for nylon-6, in order to explain the effect of sorbed water on the density, on the Young's modulus,³ and on the glass transition temperature.^{4,5}

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