Influence of the Antimony Catalyst Remnants on the Melt Crystallization of PET

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SYNOPSIS

The nucleating activity of antimony catalyst remnants on the melt crystallization of poly(ethylene terephthalate) (PET) is proved through comparisons, for samples with Sb concentrations in the range 180–1850 ppm, of the crystallization behaviors before and after a complete extraction of the catalyst remnants. These comparisons are performed by analysis of the crystallization peaks of differential scanning calorimetry (DSC), by the study of isothermal crystallization kinetics from X-ray diffraction experiments, and by optical microscopy observations of the size of the spherulites. The dependence of the crystallization temperature (T_c, as evaluated by the position of the DSC peak) on the Sb concentration, reported in the literature, is shown to be largely overestimated. In particular, it is found that the T_c of commercial samples are essentially unaffected by the presence of the standard concentrations of Sb catalyst remnants. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The influence of the catalyst remnants on the crystallization of poly(ethylene terephthalate) (PET) was recognized several years ago in papers that did not declare the chemical nature of the catalysts.[1,2] More recently, detailed studies on this subject have been reported, which dealt mainly with the nucleating activity of calcium acetate,[3–5] which is added as a transesterification catalyst.

There are also some papers that recognize the influence of antimony, added as a polycondensation catalyst (as antimony glycolate), on the crystallization of PET.[6–8] In Ref. 6 it is specified that the used catalytic system contains Mn rather than Ca in the transesterification catalyst. According to the reported calorimetric analysis, the crystallization temperature (T_c) and the enthalpy of crystallization would depend on the Sb concentration as well as on the diethylene glycol (DEG) comonomer concentration and would be substantially independent of the Mn concentration.[6]

In this study, the influence of Sb on the crystallization of PET is more thoroughly studied by calorimetry, X-ray diffraction, and optical microscopy. In particular, samples without Ca, containing different amounts of Sb, are compared with samples in which the catalytic remnants have been completely extracted by a suitable procedure.

EXPERIMENTAL

Materials

A commercial and two laboratory PET samples have been used. The commercial PET powder is obtained by the terephthalic acid (TPA) process, with Sb as the polycondensation catalyst. The inherent viscosity determined at 35°C in o-chlorophenol is 0.64 dL/g; the diethylene glycol content, 1.2%; the Sb content, 180 ppm; and the TiO$_2$ content, 0.3 wt %. The two considered PET laboratory samples of lower molecular weight contain nearly 360 and 1850 ppm of Sb. The inherent viscosities of the two samples are 0.44 and 0.41 dL/g and the dietheylene glycol content, 0.91 and 0.97%, respectively. In all cases, Sb was added as an antimony glycolate solution in ethylene glycol.

The removal of the catalyst remnants in the polymers was performed by a glacial acetic acid extraction for 5 h in a Kumagawa extractor. The polymer was then washed in water and dried in vacuum for 24 h at 140°C.

The Sb content in the as-prepared and in the treated samples was determined, after dissolution of the polymer into a mixture of nitric, perchloric, and sulfuric acid, by an atomic absorption spectrophotometer (Perkin-Elmer, 3030 B). The measurements were performed at wavelength 217.6 nm, with an accuracy of nearly ±3%. The complete removal of Sb from the polymer samples by the extraction procedure was also confirmed by the analyses of the Sb content in the acetic acid used for the extractions.

The substantial invariance of the polymers after the extraction procedures was verified by measurements of the melting temperatures and of the inherent viscosities. The invariance of the molecular weight distributions was also verified, by comparisons of gel permeation chromatograms before and after the extraction procedures.

Kinetics of Isothermal Crystallization by X-ray Diffraction

The X-ray diffraction patterns at different temperatures were obtained with an automatic Philips powder diffractometer (Ni-filtered CuKα radiation), with a temperature control of ±0.5°C.

The measurements were performed on sheets 1 mm thick, obtained by compression molding. The
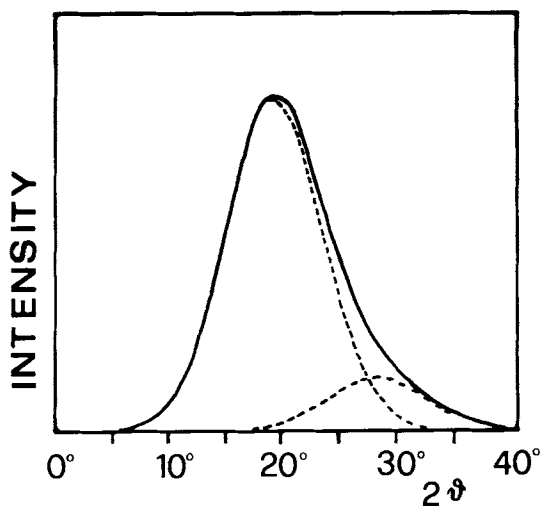
Figure 1 X-ray diffraction pattern of the commercial PET sample at 270°C. The experimental pattern can be described as a sum of two Gaussian peaks (dashed lines) with maxima at nearly 18.5° and 27.5°.
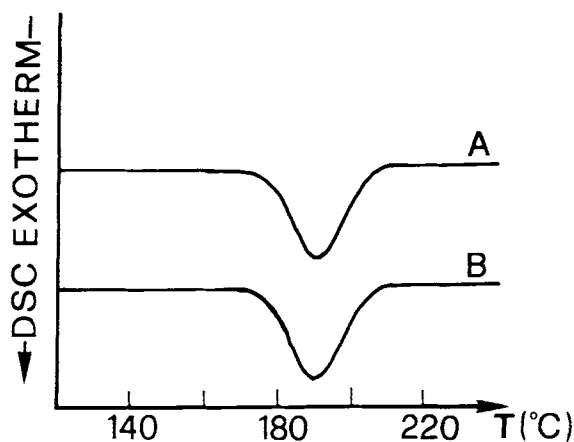
Figure 2 DSC scans on cooling from the melt for the commercial sample of PET (A) before and (B) after Sb extraction.

samples were heated at 300°C and maintained at that temperature for 10 min, then rapidly cooled to the temperature of isothermal crystallization.

The degree of crystallinity, X_c, at different crystallization times was evaluated by comparing the area of the amorphous halo in the crystallizing sample at time $t[A_{am}(t)]$ with the area of the completely amorphous sample (A_{am}^0)[9]:

$$X_c(t) = 1 - [(A_{am}(t)/A_{am}^0)] \qquad (1)$$

For each kinetic measurement, the value of A_{am}^0 was taken from previous measurements at 270°C, where the crystallization is sufficiently slow.

The area of the amorphous halo in the crystallizing samples is obtained by diffraction intensity measurements (10 s) at $2\theta = 9°$, $12°$, $14°$, $19.6°$, $19.8°$, $29.8°$, and $36°$, i.e., at diffraction angle values for which no crystalline peak is present also in the fully crystallized samples. The line connecting the measured values at $2\theta = 9°$ and $36°$ is assumed as base line. The profile of the amorphous halo is then obtained by interpolation, between these measured values, of the profile of the amorphous halo measured for the melt at 270°C.

This profile has been described as due to two Gaussian functions centered at $2\theta = 18.5°$ and $27.5°$ (Fig. 1). The positions, the half-widths, and the ratio of the heights of the two Gaussian peaks have been maintained as fixed in the profile fitting procedure.

Optical Microscopy

The size of the spherulites was measured using a Leitz polarizing microscope (Laborlux 12 pol) with
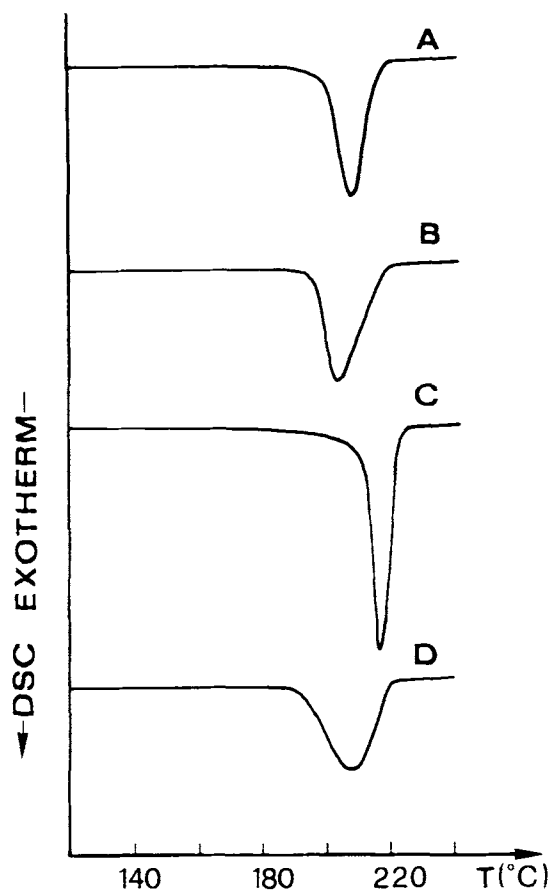
Figure 3 DSC scans on cooling from the melt for two laboratory PET samples of lower molecular weight: (A) with 350 ppm of Sb; (B) sample A after Sb extraction; (C) with 1850 ppm of Sb; (D) sample C after Sb extraction.

an attached Leitz camera and a Linkam TH600 hot stage. Specimens were prepared by placing the powders between a glass plate and a coverglass. The polymer was melted at 310°C for 5 min in the hot stage, then cooled to room temperature with a cooling rate of 50°C/min.

Differential Scanning Calorimetry

The DSC scans were carried out in a Perkin-Elmer DSC 7 calorimeter, in a flowing N_2 atmosphere. For the reproducibility of the crystallization behaviors, it is essential to control the moisture in the samples. For this reason, immediately before the DSC measurements, the samples were dried in a vacuum oven at 140°C for at least 14 h. The scans of melt crystallization were obtained, after melting in the apparatus at 290°C for 5 min, at a cooling rate of 10°C/min. The melting of these samples was characterized

in succession by scans with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The DSC scans on cooling from the melt for the PET commercial sample, before and after Sb extraction, are compared in Figure 2. The two crystallization peaks are very similar; in fact, only a shift smaller than 1°C toward lower temperatures is observed for the sample deprived of the catalyst remnants. We observed a similar behavior for standard commercial samples obtained by the dimethyl terephthalate (DMT) process (typically with nearly 350 ppm of Sb).

This behavior is in contrast to the relation proposed in the literature for the dependence of T_c on the Sb concentration[6]:

$$T_c = 182.8 + 0.0351[Sb] - 23.1[DEG] \quad (2)$$

where T_c is in °C and the concentrations in ppm. This relation, in fact, would predict differences of T_c between extracted and unextracted samples higher than 5°C for the standard commercial samples.

The disagreement of our results with the literature relationship (eq. (2)) could be, in part, explained by the fact that it was derived by the measured T_c values for samples all having lower molecular
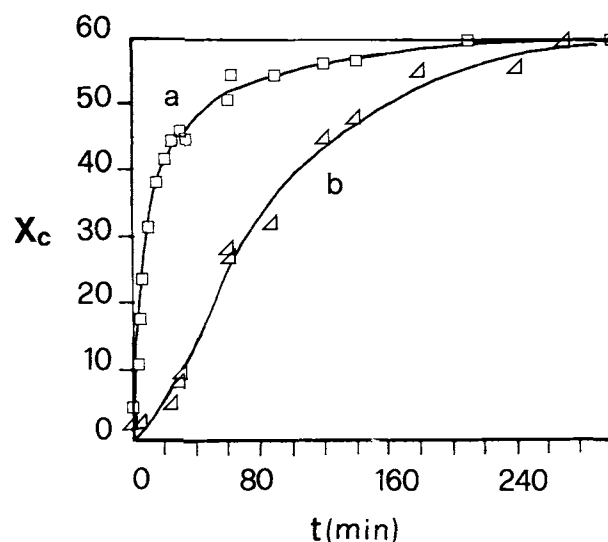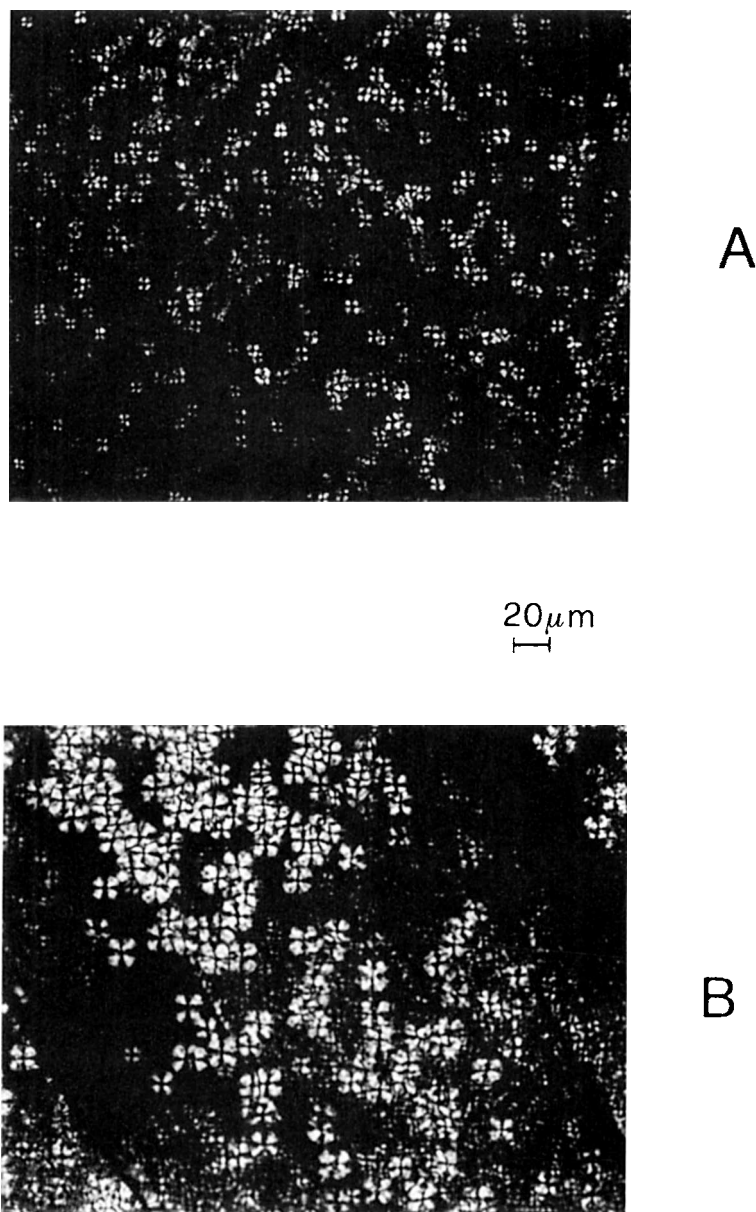

Figure 4 Isothermal crystallization kinetics at 247°C for the PET sample with 1850 ppm of Sb (a) before and (b) after Sb extraction. The degree of crystallinity (X_c) was obtained by X-ray diffraction measurements according to eq. (1).

weights (inherent viscosity in the range 0.48–0.53 dL/g).

The DSC scans, on cooling from the melt, of a PET laboratory sample with inherent viscosity $[\eta]$ = 0.44 and $[Sb]$ = 350 ppm, before and after the Sb extraction, are compared in Figure 3(A) and (B), respectively. The nucleating effect of Sb on the melt crystallization is, in this case, apparent. In fact, for the sample still including the catalyst remnants [Fig. 3(A)], the crystallization exothermic peak not only is shifted toward higher temperatures of nearly 3°C

but is also sharper. This effect becomes, of course, more evident in the sample of analogous inherent viscosity, richer in Sb (1850 ppm). For this sample [Fig. 3(C) and (D)], the crystallization peak after the antimony extraction is shifted toward a lower temperature of nearly 8°C. The shifts of T_c in the presence of Sb catalyst remnants are, however, also for these samples of lower molecular weight, much smaller than (roughly lower than one-third of) those predicted from the literature relationship (eq. (2)).

The nucleating activity of Sb catalyst remnants

Figure 5   Optical micrographs of the commercial PET sample, crystallized on cooling from the melt, (A) before and (B) after Sb extraction.

can also be determined by comparisons of the kinetics of isothermal crystallization obtained by X-ray diffraction measurements on unextracted and extracted samples. This is, for instance, shown for the case of the sample with 1850 ppm of Sb, for which the kinetics of the crystallization at 247°C, before and after Sb extraction, are compared (curves a and b of Fig. 4). In both cases, a degree of crystallization close to 60% is reached, whereas the half-times of crystallization are close to 10 and 80 min, before and after Sb extraction, respectively. The differences in the kinetics of crystallization, before and after the Sb extraction, for the investigated commercial sample are small and below the precision of our measurements.

The nucleating activity of Sb catalyst remnants can be shown, however, also for samples with low Sb concentrations like the commercial PET samples by optical microscopy measurements. As an example, optical micrographs of the commercial PET sample from the TPA process crystallized on cooling from the melt (as described in the Experimental part), before and after the Sb extraction, are reported in Figure 5(A) and (B), respectively. A difference in the average sizes of the spherulites is immediately apparent. In particular, they are in the range 8–10 μm for the unextracted sample, while in the range 12–16 μm for the extracted sample.

In summary, our set of experiments on unextracted and extracted PET samples confirms a nucleating activity of the Sb catalyst remnants. This is apparent by DSC crystallization scans, isothermal crystallization kinetics, and optical microscopy observations of the size of the spherulites. The quantitative dependence of T_c on the Sb concentration, reported in the literature is, however, according to our results, largely overestimated. In particular, we

have found that the T_c of commercial samples are little affected by the presence of standard concentrations of Sb catalyst remnants (150–350 ppm), which should, instead, generate, according to eq. (2), shifts of T_c higher than 5°C. The microscopy observation of the size of the spherulites makes, instead, the nucleating activity of Sb easily detectable also for the typical low Sb concentrations of the commercial samples.

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