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A STUDY ON THE THERMAL BEHAVIOUR AND STRUCTURAL CHARACTERISTICS OF POLYTETRAFLUOROETHYLENE *

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ABSTRACT

Virgin polytetrafluoroethylene (PTFE) displays three crystal–crystal transitions at 17, 20 and 28 ° C. After sintering at 370 ° C, only the two transitions are present at about 19 and 30 ° C, those usually reported in the literature.

This paper investigates the nature of the 17 ° C transition, using differential scanning calorimetry and wide-angle X-ray scattering.

INTRODUCTION

It is well known that at atmospheric pressure polytetrafluoroethylene (PTFE) displays two solid–solid transitions at 19 and 30 ° C [1,2]. Below 19 ° C it crystallises in a very well ordered phase (phase II) for which a number of structural hypotheses have been proposed [1,3–7], whereas between 19 and 30 ° C it gives a well-known only partially ordered hexagonal phase (phase IV) [1,2]. Lastly, above 30 ° C and up to melting, a pseudo-hexagonal, very disordered phase (phase I) is stable [1,2,8].

PTFE crystalline phases and the corresponding transitions can be clearly illustrated by thermal analysis (differential scanning calorimetry, DSC) or structural analysis (wide-angle X-ray scattering, WAXS). This paper reports the use of both techniques to study the characteristics of PTFE from aqueous emulsion polymerisation. There are, in fact, two types of PTFE: a granular polymer obtained by aqueous suspension polymerisation, consisting of particles with an average diameter of 600 μm; and a fine powder, obtained by aqueous emulsion polymerisation, consisting of particles with an average diameter of 0.2 μm [2]. Starkweather [9] has employed DSC for the in-depth examination of virgin (never-melted) PTFE obtained from aqueous emulsion polymerisation. His DSC curve showed three crystal–

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crystal transitions at about 17, 20 and 28 °C. After heating at temperatures higher than the melting point ($T_m = 340\,°C$), i.e. sintering at 370 °C, only the transitions at about 19 and 30 °C, those usually reported in the literature, are present. Starkweather attributes the third transition to a peculiar, not clearly understood, characteristic of virgin PTFE.

This paper investigates the trend shown by the 17 °C transition with respect to the annealing temperature. Its nature is examined in the light of DSC and WAXS measurements versus temperature.

EXPERIMENTAL

Materials

Virgin PTFE powders obtained by aqueous dispersion polymerisation (DF1, Montefluos) were used for all the measurements.

Thermal analysis

Scans were carried out at −40 °C to +60 °C in a nitrogen atmosphere on a Perkin–Elmer DSC-2C, using a heating rate of 10 °C min^{-1}.

X-ray diffraction

WAXS was performed on a PW 10049/10 Philips diffractometer for wide-angle measurements on microcrystalline powders. Ni-filtered Cu radiation was used ($\lambda_{K\alpha} = 1.5418$ Å). A temperature precision of ±1 °C was assured by blowing nitrogen onto the specimen at a constant temperature.

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves for the first (−40 to +60 °C) second (+60 to −40 °C) and third (−40 to +60 °C) scans, recorded in succession. They confirm the observations of Sperati et al. [2] and make it clear that the typical pattern for this polymer is fully reversible.

The DSC curves for the polymer kept for 5 min at 100, 200, 250, 300 and 370 °C are presented in Fig. 2. After annealing at 100 and 200 °C, all the transitions remain unchanged. After annealing at 250 °C, the first transition, which is a shoulder of the second, becomes less resolved with respect to the latter. This agrees with Starkweather's observation [10] that the thermal linear expansion coefficient relative to the interchain distance begins to rise at 260 °C, showing the onset of pre-melting. At 300 °C, the first transition becomes even less resolved, while at 370 °C (when the polymer is completely

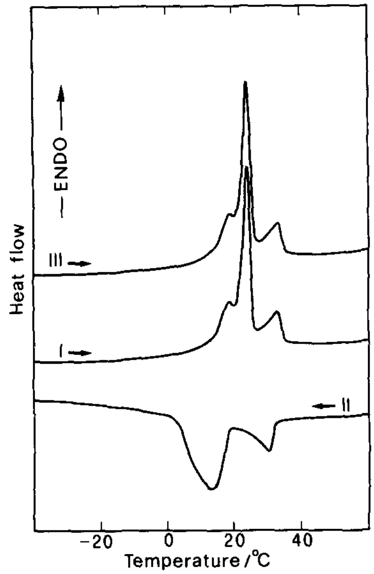

Fig. 1. DSC curves for the first (I), second (II) and third (III) scans of the virgin polymer.

melted), there is a marked change and only the two usual transitions at 19 and 30 °C remain. As annealing approachs the melting point (340 °C), the characteristic transition gradually disappears. This trend can be ascribed to the gradual loss of the highly ordered state characteristic of the native polymer as it is sintered and pre-sintered.

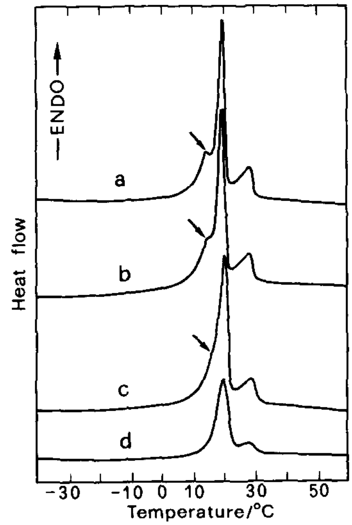

Fig. 2. DSC curves for the polymer after thermal annealing at: a, 100 and 200; b, 250; c, 300; and d, 370 °C.

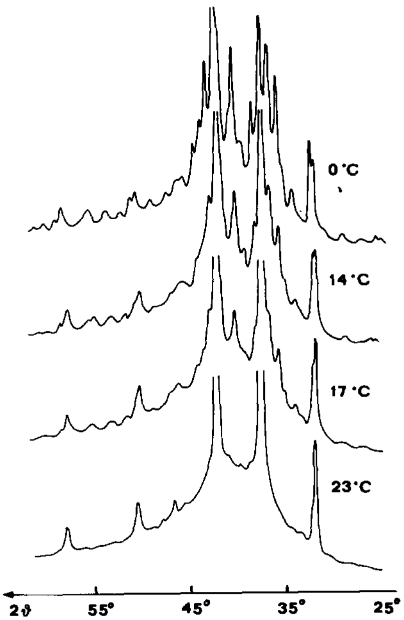

Fig. 3. Wide-angle X-ray diffraction patterns for the virgin polymer at different temperatures.

Figures 3 and 4 show the WAXS measurements versus temperature (0–23° C) for the virgin and the sintered polymer respectively. There is a gradual transition from the highly ordered (0° C) to the disordered phase (23° C) in the case of the virgin polymer and the temperature at which the intermediate states of order take place corresponds to its characteristic transition. The sintered polymer has a lower degree of crystallinity. Here

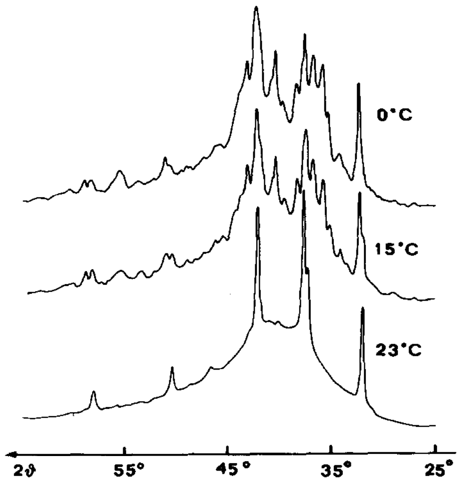

Fig. 4. Wide-angle X-ray diffraction patterns for the sintered polymer at different temperatures.

there is a distinct transition from the monoclinic to the hexagonal phase. This trend corresponds to the absence of the transition at 17 ° C.

CONCLUSIONS

Our results indicate that the transition at 17 ° C can be ascribed to a highly ordered state present during the polymerisation only and no longer accessible once the polymer has been taken to the liquid state.

If account is taken of the folded 'ribbons' morphology (the lamellae fold a number of times on themselves [11,12]) for virgin PTFE obtained from aqueous and dispersion polymerisation, it may be suggested that this transition can be related to the folding regions as these are less ordered and have a greater superficial energy than the rest of the crystal.

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