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Calorimetric study of the room-temperature transitions of tetrafluoroethylene–hexafluoropropylene copolymer: thermal history and crystalline state [1]

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Abstract

Differential scanning calorimetry reveals at least three very clear room-temperature transitions for native tetrafluoroethylene–hexafluoropropylene (TFE–HFP) copolymer, with a composition of 0.3 mol.% HFP, from aqueous dispersion polymerization. The influence of the thermal history on the room-temperature transitions was studied. The enthalpies and the temperatures of each transition were evaluated vs. the annealing temperature. The results are compared with those previously obtained for polytetrafluoroethylene (PTFE). As for the homopolymer, it is suggested that the native copolymer and the copolymer annealed at $T_{ann} < 330$°C are composed of two crystalline components with different morphologies that are responsible for the room-temperature transitions observed.

INTRODUCTION

Polytetrafluoroethylene (PTFE) presents a high melting temperature and a very high melt viscosity and hence requires special processing techniques such as powder stirring and paste extrusion, whereas tetrafluoroethylene and hexafluoropropylene (TFE–HFP) copolymers with a very low comonomer content (i.e. 0.3 mol.%) have useful mechanical and chemical properties and require easier processing conditions (e.g. lower extrusion pressures).

It is well known that at atmospheric pressure, PTFE displays two crystal–crystal transitions at 19°C (transition 1) and 30°C (transition 2) [1,2]. Below 19°C, PTFE is generally thought to crystallize in a very well-ordered triclinic phase [1,3,4], whereas between 19°C and 30°C it gives a well-known only partially ordered hexagonal phase [1,2]. Above 30°C and up to the melting point (equilibrium melting temperature $T_m^0 = 332$°C [5]), a pseudo-

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hexagonal very disordered phase is stable [1,2,5]. These results have been obtained by X-ray diffraction and calorimetric measurements on the melt-crystallized polymer. Differential scanning calorimetry (DSC) has recently revealed a new transition at 17°C (transition 1′) for native PTFE obtained from aqueous dispersion polymerization [6,7]. Our previous in-depth examination by DSC and wide angle X-ray scattering (WAXS) of the room-temperature transitions of native PTFE and the effect of the scanning rate and thermal history on these transitions [8–11] has shown that the transition 1′ is a true crystal–crystal transition, pointing to the coexistence in the native polymer of two crystalline components with different morphologies, presumably responsible for the transitions observed. Three DSC peaks are clearly evident; however, another small not resolved peak, 2′, may be present near that at 30°C. We have suggested that the first two peaks, 1′ and 1, correspond to the triclinic–hexagonal transition and the last two, 2 and 2′, to the hexagonal–pseudohexagonal transition of the two crystalline components respectively.

For melt-crystallized TFE–HFP copolymer, X-ray diffraction and calorimetry have shown that the two transitions at 19°C and 30°C move towards lower temperatures and become a single transition from a composition of 1.8 mol.% of HFP [4]. By contrast, nothing is known about native TFE–HFP copolymers and their morphology, whereas native PTFE morphology has been extensively studied. An electron microscopy study by Luhman and Feiring revealed rod-like, roughly spherical and, in the case of very low molecular weight, small hexagonal particles [12]. The rod-like and the hexagonal particles were single crystals, while the spherical particles were aggregates. DSC, too, disclosed three room-temperature transitions. The authors attribute the lower of the first two transitions to the hexagonal particles, and the second one to the rod-like and spherical particles. Rahl et al. [13] had previously observed rod-like and spherical particles, the former being fully extended chain crystals containing few defects, the latter composed of similar chain crystals wrapped around themselves.

In the present work our DSC approach [8–11] is extended to the room-temperature transitions of native TFE–HFP copolymer with very low contents of HFP (0.3 mol.%) from aqueous dispersion polymerization and their trend vs. the annealing temperature T_{ann}, in the range 150–370°C.

Conclusions are drawn concerning the morphology of the native and the annealed copolymer.

EXPERIMENTAL

Materials

TFE–HFP copolymer (DFC, Montefluos), containing 0.3 mol.% of HFP, from aqueous dispersion polymerization was used. The surfactant was ammonium perfluorooctanoate. The dispersion was coagulated by mechanical stirring, then washed and dried under vacuum.

Differential scanning calorimetry

All runs were performed on 10 ± 0.5 mg from −30°C to +50°C in a nitrogen atmosphere on a Perkin–Elmer DSC 2, using a heating rate of 10°C min^{-1}. The apparatus was calibrated using the melting temperatures of mercury (−38.9°C), indium (156.4°C), lead (327.4°C) and their melting enthalpies. The copolymer, either native or annealed for 10 min at 150, 200, 250, 260, 270, 280, 290, 300, 330 and 370°C, was examined. We have verified that longer annealing times did not change the results. The annealing was carried out in the DSC apparatus, in a nitrogen atmosphere at a heating and cooling rate of 10°C min^{-1}. The transition temperatures correspond to the maxima of the peaks and their uncertainty is ±0.5°C. The enthalpy of each transition was evaluated by a computer program of integration of partial areas; using different integration limits the uncertainty has been evaluated as ±0.05 J g^{-1}.

RESULTS AND DISCUSSION

The DSC curves of the room-temperature transitions for the melt-crystallized ($T_{\text{ann}} = 370°\text{C}$) copolymer (curve A) and homopolymer (curve B) (Fig. 1) show two clear endothermic peaks corresponding to the triclinic–hexagonal (lower temperature, sharp peak, 1) and the hexagonal–pseudohexagonal (higher temperature, broad peak, 2) transitions. The curves are

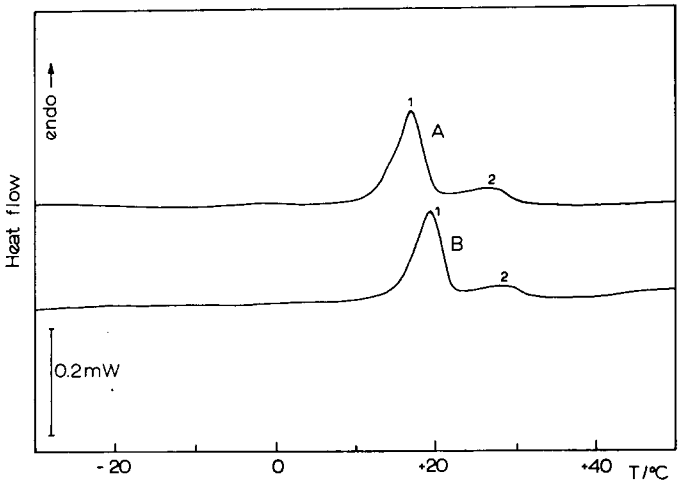

Fig. 1. DSC curves for melt-crystallized ($T_{\text{ann}} = 370°\text{C}$) TFE–HFP copolymer (curve A) and PTFE (curve B). Transitions 1 and 2 are shown.

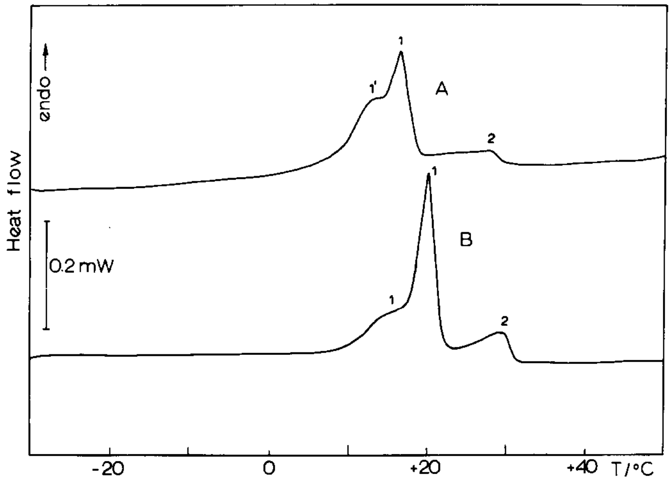

Fig. 2. DSC curves for native TFE–HFP copolymer (curve A) and PTFE (curve B), from aqueous dispersion polymerization. Transitions 1′, 1 and 2 are shown.

very similar, except for the transition temperatures, which are slightly lower for the copolymer ($T_1 = 17°C$ and $T_2 = 27°C$) than for the homopolymer ($T_1 = 20°C$ and $T_2 = 30°C$). This agrees with the trend of the room-temperature transitions vs. the comonomer concentration (0.8–6.9 mol.% HFP) described by Eby and coworkers [4]. The enthalpy of each transition is the same for both the copolymer and homopolymer ($\Delta H_1 = 5.0$ J g^{-1} and $\Delta H_2 = 1.2$ J g^{-1}).

The temperature decrease and constant transition enthalpies, bearing in mind that the degrees of crystallinity of the copolymer and homopolymer are substantially the same (enthalpy of fusion 27.6 J g^{-1} and 30.5 J g^{-1} respectively), may imply an increase in the transition entropy on passing from the homopolymer to the copolymer. This would correspond to a higher degree of disorder of the pseudohexagonal, e.g. greater comonomer inclusion [14–16] with respect to the triclinic phase, on passing from the homopolymer to the copolymer.

The DSC curves show three clear peaks (1′, 1 and 2) for both the native copolymer (curve A) and homopolymer (curve B) (Fig. 2). The shape of the higher temperature peak (strongly asymmetric, with a plateau towards the low temperatures) suggests that another small and broad not resolved and not quantifiable peak, 2′, may be present. We suggest that the native copolymer, as the homopolymer, is composed of two crystalline components with different morphologies giving transitions at different temperatures. Peaks 1′ and 2′ belong to the low-transient crystalline component and peaks 1 and 2 to the high-transient component. In particular, peaks 1′ and 1 correspond to the triclinic–hexagonal transition and peaks 2 and 2′ to the hexagonal–pseudohexagonal transition of the two crystalline compo-

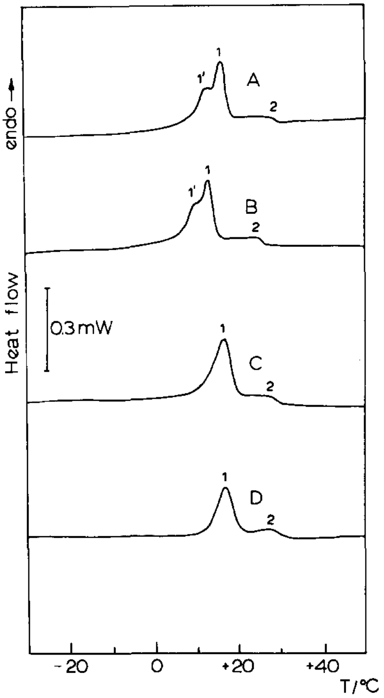

Fig. 3. DSC curves for TFE–HFP copolymer annealed at 200°C (curve A), 250°C (curve B), 300°C (curve C) and 330°C (curve D). Transitions 1', 1 and 2 are shown.

nents respectively. The temperatures (°C) and the enthalpies (J g^{-1}) of each resolved transition are $T_{1'} = 14$, $T_1 = 16$, $T_2 = 27$ and $\Delta H_{1'} = 1.0$, $\Delta H_1 = 3.8$, $\Delta H_2 = 1.2$ for the copolymer, and $T_{1'} = 15$, $T_1 = 20$, $T_2 = 30$ and $\Delta H_{1'} = 1.7$, $\Delta H_1 = 6.7$, $\Delta H_2 = 1.2$ for the homopolymer. It should be stressed that the transition temperatures for peaks 1 and 2 are lower for the copolymer, according to Eby and coworkers [4], whereas that of peak 1' is constant. Moreover, while the total heat of transition $\Delta_t H$ is the same (9.2 J g^{-1}), the ratio $\Delta H_{1'}/\Delta H_1$ of the peaks 1' and 1 is very different: 1.0 for the copolymer and 0.25 for the homopolymer, suggesting that the low-transient component has a very similar crystalline state but is present to different extents.

The DSC curves for the copolymer annealed at 200°C (curve A), 250°C (curve B), 300°C (curve C) and 330°C (curve D) are shown in Fig. 3. Transitions 1', 1 and 2 are evident for $T_{ann} < 330$°C whereas only transitions 1 and 2 are present at $T_{ann} = 330$°C. As in the case of the homopolymer, annealing at $T_{ann} < 330$°C does not substantially modify the crystalline morphology, whereas annealing at $T_{ann} = 330$°C causes a profound irreversible modification.

In Fig. 4, the peak temperatures and the enthalpies of each transition are reported vs. T_{ann}. For $T_{ann} < 330$°C both the parameters are about

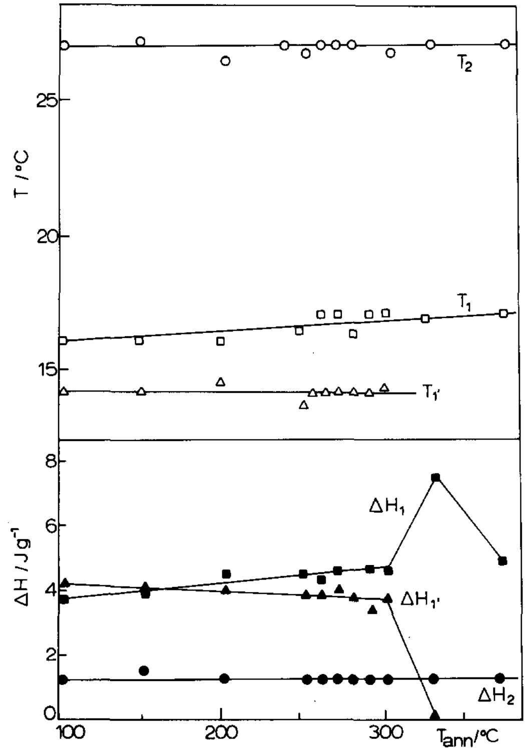

Fig. 4. Values of the temperatures, $T_{1'}$ (△), T_1 (□), T_2 (○), and the enthalpies, $\Delta H_{1'}$ (▲), ΔH_1 (■), ΔH_2 (●), of the resolved room-temperature transitions for TFE–HFP copolymer vs. T_{ann}. The first point always represents the value for the native copolymer.

constant, as for the homopolymer, though T_1 tends to increase slightly, while $\Delta H_{1'}$ and ΔH_1 tend to decrease and increase respectively to approximately the same extent. At $T_{ann} = 330°C$, $\Delta H_{1'}$ passes from 3.8 to 0.0 J g^{-1} and ΔH_1 from 4.2 to 7.5 J g^{-1} and ΔH_2 is constant. Then $\Delta_t H$ remains about constant, whereas for the homopolymer $\Delta H_{1'}$ goes to zero and ΔH_1 as well as ΔH_2 are constant, implying a substantial decrease in $\Delta_t H$ [9–11]. The behaviour at $T_{ann} = 330°C$ indicates that the irreversible modification in the homopolymer is not a recrystallization, but occurs with the loss of an appreciable crystalline fraction, whereas the decrease in $\Delta H_{1'}$ for the copolymer corresponds to an increase in ΔH_1 of about the same extent. We suggest that in the homopolymer the crystalline melted low-transient component is unable to recrystallize and passes into the amorphous phase (clear decrease in $\Delta_t H$), whereas in the copolymer almost total recrystallization occurs. The strong decrease in $\Delta_t H$ for both the homopolymer and copolymer after annealing at 370°C shows [17] that their melting and melt-crystallization result in a marked decrease in their crystallinity.

We have verified that by contrast with the room-temperature transitions the melting behaviour is scarcely affected by the modifications of the crystalline state, which take place after annealing at 330°C. After annealing at 370°C, strong modifications in the shape of the melting curve and a strong decrease in the temperature and heat of fusion (decrease in crystallinity) in keeping with the behaviour of the melt-crystallized homopolymer occur [17].

CONCLUSIONS

In the light of the previous studies of the homopolymer [8–11] and its morphology [12,13], these findings indicate that the native copolymer and the copolymer annealed at $T_{ann} < 330°C$ consist of two crystalline components giving transitions at different temperatures as a result of their different morphologies. The first transition peak could correspond to the triclinic–hexagonal transition of the low-transient crystals (a much smaller possible transition from the hexagonal to the pseudohexagonal phase of the same crystals is unquantifiable by our analysis), the second to the triclinic–hexagonal transition of the high-transient crystals, and the third to their hexagonal–pseudohexagonal transition.

The low-transient crystals of the homopolymer and the copolymer give transitions at the same temperatures, pointing to a very close similarity in their morphological–structural features.

The high-transient crystals of the native and melt-crystallized copolymer give transitions at the same temperatures, and a strong similarity in their crystalline state may be supposed. The same occurs for the homopolymer.

The crystalline state of the copolymer remains substantially unaltered for $T_{ann} < 330°C$, as for the homopolymer.

At $T_{ann} = 330°C$, the low-transient crystals strongly modify themselves. They melt and recrystallize almost completely. After annealing at 330°C, the copolymer is composed of native crystals (the high-transient ones), and melt-crystallized crystals, which give a transition at the same temperature. The behaviour of the homopolymer is quite different: the low-transient crystals melt, are unable to recrystallize and pass into the amorphous phase. The homopolymer at this temperature consists of the native high-transient crystals and an amorphous fraction [10,11]. This strong difference is related to the different melt-crystallizing abilities of the copolymer and homopolymer, which could be correlated with the lower intrinsic macromolecular mobility of the homopolymer (very stiff chains) [18,19].

Our results indicate that the morphology of native TFE–HFP copolymer containing 0.3 mol.% of HFP is very similar to that of the native PTFE.

The differences between the transition temperatures of the two crystalline components agree with both the morphologies for the homopolymer described by Luhman [12] and Rahl [13]. Both the low molecular weight chain and defect-rich crystals would give lower transition temperatures than high molecular weight chain and defectless crystals [1,4].

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