

THERMAL PROPERTIES AT ROOM TEMPERATURE OF POLYTETRAFLUOROETHYLENE

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Through Differential Scanning Calorimetry (DSC), at least three room temperature transitions are clearly observable for native polytetrafluoroethylene (PTFE). The influence of the thermal history on the room temperature transitions has been investigated. Possible interpretations for the lowest room temperature transition are suggested.

Introduction

It is well known that, at atmospheric pressure, PTFE displays two crystal-crystal transitions at 19 and 30° [1, 2]. It is a general opinion that, below 19°, PTFE crystallizes in a very well ordered triclinic phase [1, 3, 4], whereas, between 19 and 30°, it gives a well known, only partially ordered hexagonal phase [1, 2]. Lastly, above 30° and up to the melting point (equilibrium melting temperature $T_m^0 = 332^\circ$ [5]), a pseudo-hexagonal very disordered phase is the stable one [1, 2, 5]. Moreover, it is known from the literature [6] that the presence of reticular defects (for example hexafluoropropene comonomer units) makes the two transitions at 19 and 30° move towards lower temperatures. In case of higher defects concentration only a single transition can be observed. These results have been obtained through X-ray diffraction and calorimetric measurements on the melt-crystallized polymer. Recently [7] through DSC a new crystal-crystal transition at 17°, has been shown for the native polymer, obtained from aqueous dispersion polymerization. This transition disappears after a thermal annealing at $T > T_m^0$ (irreversible transformation). In previous papers [8–10] we have performed an in-depth examination, through Wide Angle X-ray Scattering (WAXS) and DSC, of the room temperature transition of native PTFE and the effect of the scanning rate and of the thermal history on the transitions themselves. Our studies con-

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firmed Starkweather's observations [7] and the independence of the lowest room temperature transition on the heating kinetics suggested that it is a true crystal-crystal transition.

The morphology of native and melt-crystallized PTFE has been extensively studied. Recently Luhman *et al.* [11], through electron microscopy, have observed, in native PTFE, three types of particles with different morphology: rod-like, roughly spherical and, in case of very low molecular weight, small hexagonal particles. The rod-like particles and the hexagons are single crystals, while the spherical particles are aggregated of a number of crystals. Through DSC the authors have observed three room-temperature transitions and have hypothesized that the lower temperature one is due to the hexagonal particles, while the second to the rod-like and spherical ones. Previously Rahl *et al.* [12], through electron microscopy, observed, for native PTFE, two types of particles with different morphology: rod and spherical ones. The first ones are fully-extended chain crystals, containing few defects; the second appear to be composed of similar entities which wrap around themselves.

For the melt-crystallized polymer and presence of extended-chain crystals with very thick lamellae has been observed [13, 14].

In this paper, using native PTFE from aqueous dispersion, the room temperature transitions and their trend versus the annealing temperature (T_{ann}), in the range from 150 to 370° have been studied, through DSC. The enthalpy of each transition was evaluated both by the conventional partial areas method and the deconvolution of the curves $C_p(T)$, performed using Pearson VII type functions [15] and the Marquardt's non-linear least squares method [16]. Hypotheses about the morphology of the native and the annealed polymer are proposed.

Experimental part

Materials

Native PTFE, obtained from aqueous dispersion polymerization (DF200-Montefluos), was used. The surfactant was ammonium perfluorooctanoate. The dispersion was coagulated with mechanical stirring, washed and dried under vacuum.

Thermal analysis

All runs were performed at -30° to $+50^{\circ}$ in a nitrogen atmosphere on a Perkin-Elmer DSC 2, using a heating rate of 10 deg/min and samples of 10 ± 0.5 mg. The polymer, either native or annealed for 10 minutes at 150, 200, 250, 260, 270, 280, 290, 300, 330 and 370° , 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, going to the annealing temperature at a heating rate of 10 deg/min and cooling the samples at the same rate. The transition temperatures correspond to the maxima of the peaks. The enthalpy of each transition was evaluated either using a conventional partial areas method or by performing the deconvolution of the curves $C_p(T)$, using Pearson VII type functions [15] and the Marquardt's non-linear least squares method [16]. The curves $C_p(T)$ were obtained using aluminium oxide (sapphire) as a standard. Data were sampled every 0.1° . At least two measurements over the whole temperature range were made for each sample. Average data points were used [5].

Results and discussion

In Fig. 1A the DSC curve of the room temperature transitions for melt-crystallized PTFE is reported. The well known two endothermic peaks corresponding to the triclinic-hexagonal (lower temperature, sharp peak) and to the hexagonal pseudo-hexagonal (higher temperature, broad peak) transitions are clear. In Fig. 1B the DSC curve for native PTFE is reported. Three well evident peaks are present. The shape of the higher temperature peak

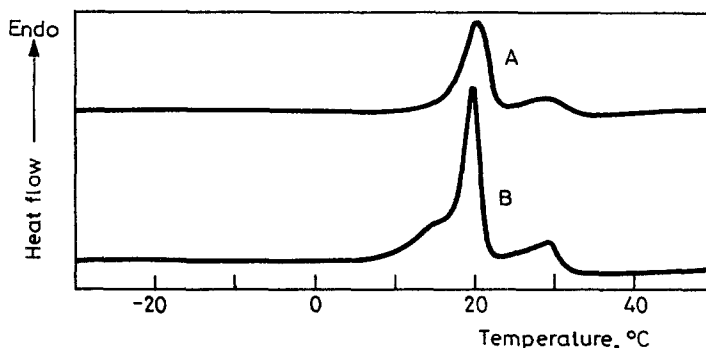


Fig. 1 DSC curves for: A) melt-crystallized PTFE ($T_{\text{ann}} = 370^{\circ}\text{C}$); B) native PTFE, from aqueous dispersion polymerization

(strongly asymmetric, with a plateau towards the low temperatures) suggests that another, small, not resolved and not measurable peak is present.

In Fig. 2 The DSC curves PTFE annealed at 200 (A), 250 (B), 300 (C) and 330° (D) are shown. Three room temperature transitions are evident for $T_{\text{ann}} \leq 300^\circ$, while only two transitions are present at $T_{\text{ann}} = 330^\circ$.

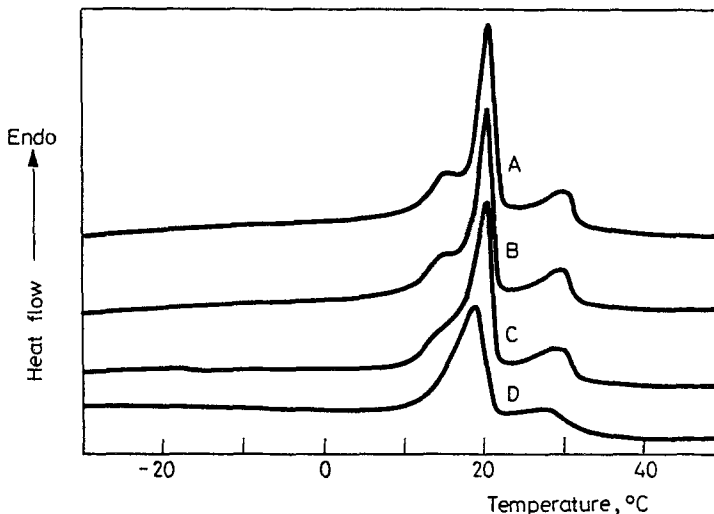


Fig. 2: DSC curves for PTFE annealed at : A) 200, B) 250, C) 300 and D) 330°C.

The deconvolution analysis confirms three results. In fact the best fitting resolved the curve $C_p(T)$ in three contributions for the native polymer and for the polymer annealed at $T_{\text{ann}} \leq 300^\circ$. For the polymer annealed at $T_{\text{ann}} \geq 330^\circ$ it was not possible to resolve the curves in three contributions, but, in these cases, the best fitting was obtained by admitting the presence of only two transitions.

In Table 1 the peak temperatures (T_1 , T_2 and T_3) and the enthalpy of each resolved transition (ΔH_1 , ΔH_2 and ΔH_3), evaluated through both the partial areas and the deconvolution methods, are reported versus T_{ann} . The differences between the enthalpies calculated through the two methods can be ascribed to the major accuracy of the last one with respect to the first. However, the same remarks can be done by taking into account both the data sets. T_1 and ΔH_1 are constant for $T_{\text{ann}} < 330^\circ$. For $T_{\text{ann}} > 330^\circ$ the first transition disappears, as we have previously said. T_2 and T_3 are practically constant in the whole range of T_{ann} . ΔH_2 and ΔH_3 are constant for $T_{\text{ann}} < 330^\circ$, while there is a strong decrease for $T_{\text{ann}} > 330^\circ$.

Table 1 Temperatures and enthalpies of the room-temperature transitions of PTFE

T_{ann} (°C)	T_1	T_2 (°C)	T_3	ΔH_1	ΔH_2 J/g	ΔH_3
*	15.4	20.5	29.9	1.84	6.65	1.38**
				2.22	5.56	1.51***
150	16.0	21.4	30.5	1.63	7.00	1.38
				2.64	7.00	1.38
200	15.0	20.4	29.7	1.80	7.74	1.17
				2.89	5.90	2.05
250	15.1	20.7	29.9	2.13	7.45	1.42
				2.68	6.28	2.05
260	15.3	20.4	29.6	2.13	7.11	1.42
				2.68	5.98	2.01
270	15.5	20.5	29.6	2.01	7.28	1.21
				2.47	6.19	1.84
280	14.8	20.4	29.3	2.18	7.36	1.38
				2.85	6.19	1.84
290	13.8	20.0	29.3	2.22	7.24	1.17
				2.09	6.11	1.97
300	13.5	20.2	29.3	2.26	7.28	1.34
				2.01	6.74	2.13
330	—	18.6	27.8	0.0	7.45	1.30
				0.0	7.45	1.30
370	—	19.6	28.3	0.0	4.64	0.84
				0.0	4.64	0.79

* as polymerized PTFE

** values obtained through the partial areas method

*** values obtained through the deconvolution method

The described results suggest that for $T_{\text{ann}} \leq 300^\circ$ substantial modifications in the polymer physical (morphological-structural status) do not occur: in fact T_1 and ΔH_1 do not significantly vary. Only at $T_{\text{ann}} = 330^\circ$ the annealing deeply and irreversibly modifies the polymer, as suggested by the disappearance of the first transition ($\Delta H_1 = 0$). The decrease of $\Delta_t H$ ($\Delta_t H = \Delta H_1 + \Delta H_2 + \Delta H_3$), as well as the constancy of ΔH_2 and ΔH_3 indicate that the irreversible modification in the polymer is not a re-crystallization, but it occurs with a loss of an appreciable crystalline fraction. For $T_{\text{ann}} = 370^\circ$

(melt-crystallized polymer) there is a further reduction of the crystallinity as pointed out by the decrease of ΔH_2 and ΔH_3 .

These experimental result would demonstrate that the native and the annealed polymer ($T_{\text{ann}} \leq 300^\circ$) is constituted of two crystalline components with different morphologies, which give transitions at different temperatures. The first peak and the not-resolved one would belong to a low-transient crystalline component, the second and the last one to high-transient component. In particular, the first two peaks would correspond to the triclinic-hexagonal transition and the last two to the hexagonal-pseudo-hexagonal transition of the two crystalline components, respectively. Instead, the crystalline morphology of the polymer annealed at $T_{\text{an}} \geq 330^\circ$ would be constituted of only one crystalline component, the high-transient one, which give the well known transitions at T_2 and T_3 . The absence of the transition at T_1 and the decrease of $\Delta_i H$ suggest that, after the annealing at $T_{\text{ann}} \geq 330^\circ$, the crystalline low-transient component melts and, being not able to re-crystallize, pass into the amorphous phase.

Conclusions

Our experimental results would evidence that native and annealed at $T_{\text{ann}} \leq 300^\circ$ PTFE consists of two crystalline components, which give transitions at different temperatures, because of their different morphologies. The first transition peak could correspond to the triclinic-hexagonal transition of low-transient crystals (a much smaller possible transition of the same crystals from the hexagonal to the pseudohexagonal phase of the same crystals would be measurable by our analysis). The second peak could correspond to the triclinic-hexagonal transition of high-transient crystals and the last one to the hexagonal-pseudohexagonal transition of the same crystals. At $T_{\text{ann}} = 330^\circ$ the low-transient crystals strongly modify themselves. They melt and they are not able to re-crystallize, passing into the amorphous phase. PTFE at this temperature is constituted of the native high-transient crystals and of an amorphous fraction.

Our interpretation is in a good agreement with both the morphologies described by Luhman [11] and Rahl [12]. In fact, both low-molecular weight chain and defect-rich crystals would give lower transition temperatures than high-molecular weight chain and defectless crystals, respectively [1, 6]. Luhman *et al.* [11] described native PTFE as constituted of three types of particles with different morphology: rod-like, roughly spherical and in the case

of very low molecular weight, small hexagons. The small hexagonal single crystals are considered to be responsible for the first transition peak and could correspond to our low-transient crystalline component. That would agree with the literature about the lowering of the transition temperatures passing from PTFE to long chain perfluoroalkanes [1].

Rahl *et al.* described native PTFE as constituted of two types of particles with different morphologies: rod and spherical. The spherical particles, constituted of extended-chain crystals which wrap around themselves, contain crystalline regions that are rich of defects and could correspond to our low-transient crystalline component. That would agree with the literature about the lowering of the transition temperatures in the presence of reticular defects [4].

Our results are also in agreement with the morphology observed [13–14] for the melt-crystallized polymer. In fact only one type of crystals are present (the extended-chain ones), according with our hypothesis with the presence of only one crystalline component (derived from the high-transient one) after annealing at $T_{\text{ann}} \geq 330^\circ$.

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Zusammenfassung – Bei der Untersuchung von nativen Polytetrafluoroethylen (PTFE) lassen sich im Raumtemperaturbereich zumindest drei Umwandlungen eindeutig beobachten. Der Einfluss der thermischen Vorgeschichte von PTFE Proben auf die Umwandlungen im Raumtemperaturbereich wurde untersucht.

Mögliche Erklärungen für den tiefstliegenden Übergang im genannten Temperaturbereich werden vorgeschlagen.