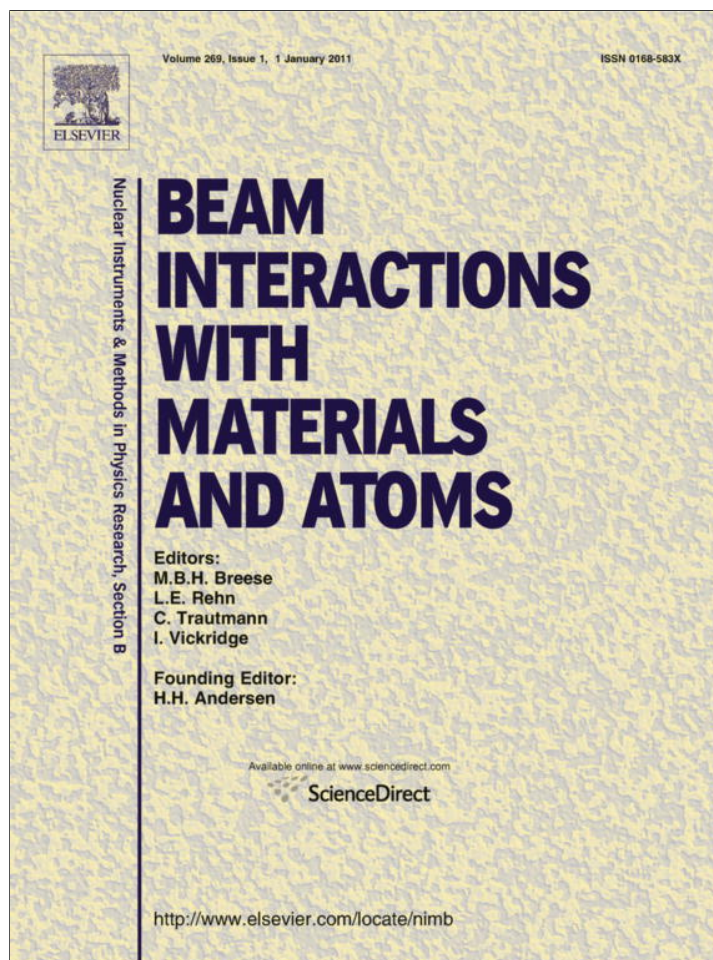


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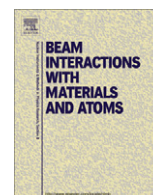
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Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimbDouble melting in polytetrafluoroethylene γ -irradiated above its melting point

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ABSTRACT

PTFE irradiation above its melting point leads to formation of double melting and crystallization peaks in DSC curves. Splitting of melting peaks is connected to dual crystalline morphology typical for PTFE irradiated in the melt. According to electron microscopy, two crystalline types with different size and packing density exist in the irradiated PTFE.

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1. Introduction

γ -Irradiation of sintered polytetrafluoroethylene (PTFE) at temperature above the polymer melting point is a promising technique which imparts unique properties to PTFE [1–5]. But the nature and the structure of PTFE modified in this way are still not enough understood.

Thermal properties of PTFE irradiated at room temperature have been intensively studied for a long time (see [6–9] and references therein). Meanwhile, there are only few papers where PTFE irradiated in the melt was examined with differential scanning calorimetry (DSC) [1,2,10–12]. These investigations focused mainly on changes in temperature and enthalpy of melting transition, although changes in the shape of melting and crystallization peaks can be seen in some reported DSC scans of irradiated PTFE [1,10].

In the present work we study effect of γ -irradiation in the melt on thermal properties of PTFE for low absorbed doses (≤ 200 kGy). Obtained results are compared with morphology analysis by scanning electron microscopy (SEM).

2. Experimental

2.1. Samples

Commercial PTFE sheets ($2 \times 400 \times 400$ mm³) manufactured by Kirovo–Chepetsk chemical plant were used in experiments. The

samples were produced by manufacturer from the polymer powder of PN grade by standard uniaxial molding with further sintering (TU 6-05-810).

2.2. Irradiation

The PTFE samples were irradiated at 335 °C, above the melting point of crystallites (327 °C), in argon atmosphere by ⁶⁰Co γ -quanta with 1.25 MeV mean energy using a KSV-500 γ -ray apparatus located in Karpov Institute of Physical Chemistry (Moscow, Russia). Design of apparatus allows to maintain required irradiation conditions.

2.3. DSC

Differential scanning calorimetry (DSC) analysis was carried out with using a Netzsch DSC 204 F1 Phoenix calorimeter. During DSC experiments the samples were purged with helium gas at flow rate of 25 ml/min. Melting and crystallization temperatures were determined as maximums of corresponding peaks. Heats of melting and crystallization were determined by integrating the peaks in the DSC curves. The calorimeter was calibrated according to ISO 11357 by using standard materials with known heat of melting.

2.4. SEM

Morphology of PTFE samples was examined by scanning electron microscopy (SEM). Fracture surfaces were produced at liquid nitrogen temperature. A JEOL JSM-7500F high resolution scanning

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electron microscope with a field-emission cathode was used to obtain images of the fracture surfaces. The images were obtained in the mode of low-energy secondary electrons because the highest resolution can be obtained in this case (the resolution was 1.5 and 1 nm at primary beam energy of 1 and 5 keV, respectively). To eliminate charging and destruction of analyzed surface by electron beam, the following technical approaches were applied: (1) low electron beam current (3×10^{-11} A) from a cathode with cold field emission was used; (2) a special Gentle Beam mode decelerating incident electrons near the sample surface was used; as a result, on the one hand, energy of incident electrons decreases to the ultra-low values reducing charging effects and eliminating destruction of the sample, and, on the other hand, diameter of incident electron beam remains small, maintaining high resolution; (3) the fracture surface was coated with thin platinum film by magnetron deposition.

3. Results and discussion

Figs. 1 and 2 show the melting and crystallization curves of the original and irradiated PTFE samples. An increase in the absorbed dose shifts melting and crystallization temperatures to the lower values. Similar temperature shift to the lower temperatures under PTFE irradiation in the melt has been observed previously [1,2,10–12] and explained by a decrease in crystallite sizes [1] and a decrease in the polymer molecular weight due to radiation-induced scission of the macromolecular chains [10].

In addition, melting and crystallization curves of the irradiated samples split into double peaks (Figs. 1 and 2). An occurrence of double peaks for PTFE reported in Ref. [13] was due low penetration depth of α -particles and, consequently, presence of both irradiated and non-irradiated regions with different melting temperatures in the analyzed sample. In our work high penetration capability of γ -quanta provides a highly uniform spatial distribution of γ -radiation over an irradiated sample. This allows us to attribute the double peaks to the double-melting phenomenon. Some evidences for this can be seen from DSC curves reported in earlier papers [1,10]. Fig. 7 in Ref. [1] shows splitting of crystallization peak of PTFE irradiated by electron beam under vacuum at 340 °C with dose of 100 kGy. Similarly, in Fig. 1 of Ref. [10] the melting peak of PTFE irradiated in oxygen-free atmosphere at 385 °C with dose of 500 kGy exhibits inflection point, suggesting the complex nature of the melting. However, this complex structure of DSC curves was not discussed earlier.

Temperatures and enthalpies of the transitions are given in Table 1. Compared to the initial sample, enthalpy of PTFE sample irradiated with 10 kGy dose increases stepwise and then varies a little at higher doses.

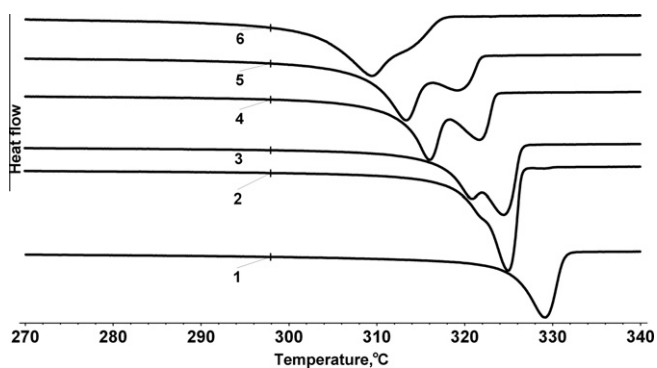


Fig. 1. DSC melting curves of PTFE irradiated with (1) 0, (2) 10, (3) 20, (4) 50, (5) 100, and (6) 200 kGy. Scan rate 5 K/min.

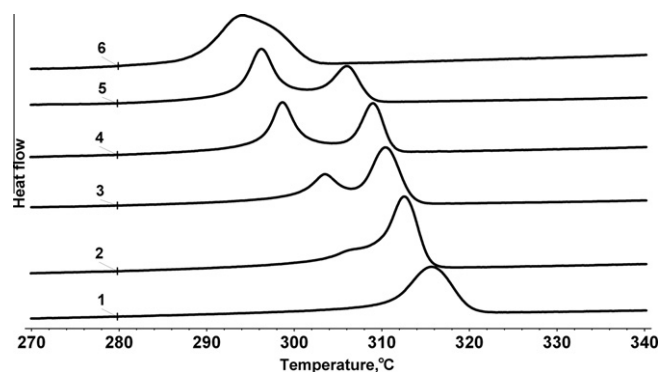


Fig. 2. DSC crystallization curves of PTFE irradiated with (1) 0, (2) 10, (3) 20, (4) 50, (5) 100, and (6) 200 kGy. Scan rate 5 K/min.

Table 1

Thermal characteristics of the original and irradiated PTFE.

Sample	D (kGy)	T_m (°C)	T_c (°C)	ΔH_m (J/g)
PTFE	0	329.2	315.6	29.3
	10	Not resolved	325.0	Not resolved
	20	320.8	324.4	312.5
	50	316.0	321.7	310.4
	100	313.4	319.2	309.0
	200	309.4	Not resolved	298.7
			296.3	305.9
			294.3	Not resolved
				37.6

D – absorbed dose, T_m – melting temperature, T_c – crystallization temperature, ΔH_m – total heat of melting.

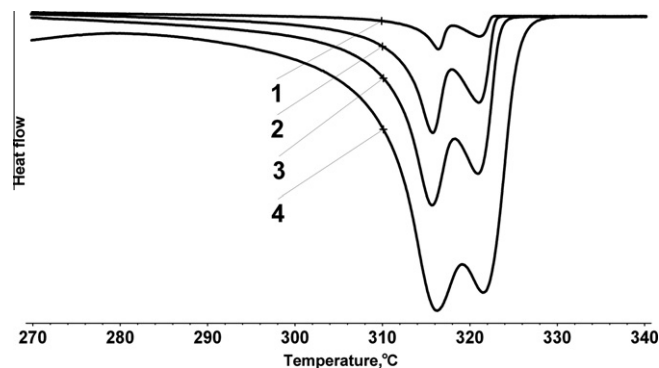


Fig. 3. DSC melting curves for the PTFE irradiated with 50 kGy and scanned at rate of (1) 1, (2) 5, (3) 10, and (4) 20 K/min.

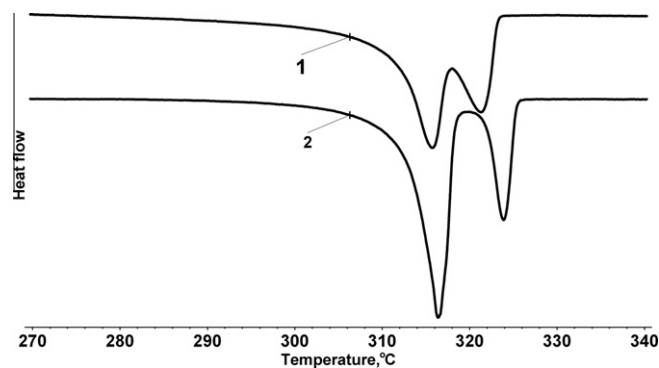


Fig. 4. DSC melting curves of PTFE irradiated with dose 50 kGy (1) before and (2) after annealing at 319 °C. Scan rate 5 K/min.

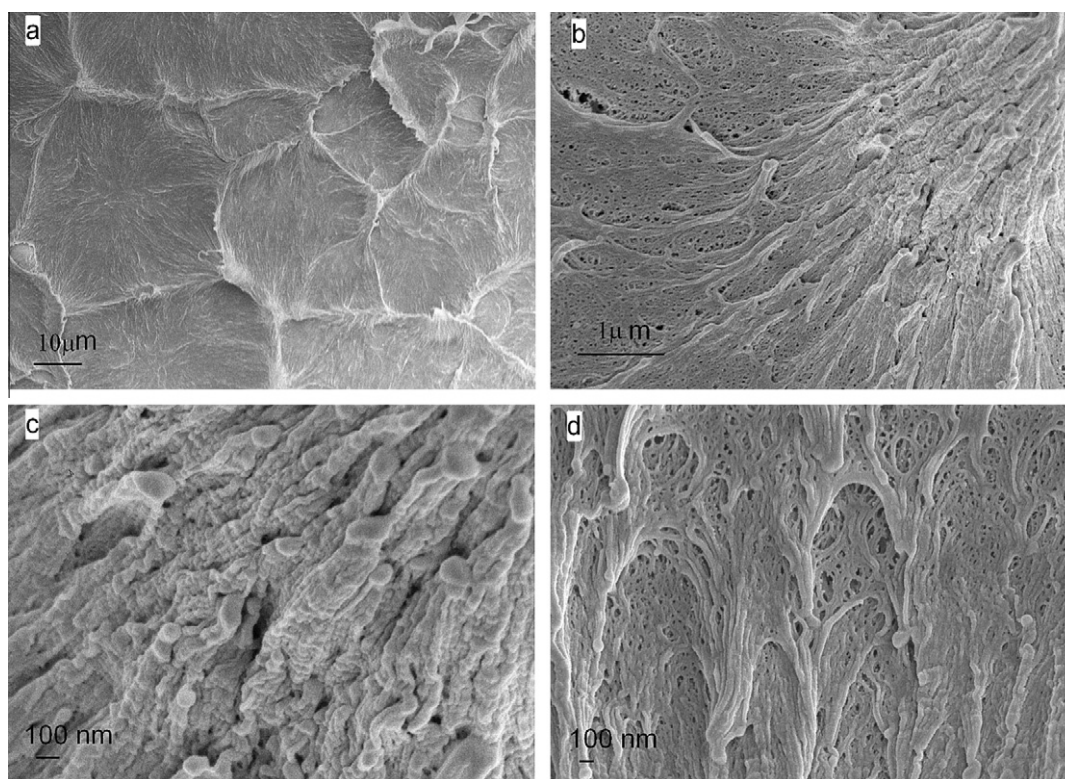


Fig. 5. Typical fracture surface SEM images of the irradiated PTFE: a, b – the spherulites, c – region near the center of spherulite, d – region at the spherulite periphery.

The phenomenon of multiple melting occurs in various polymers and has been a subject of intensive investigations in recent years [14–26]. Two main mechanisms of multiple melting are proposed in literature. The first mechanism involves different structures existing in the polymer at room temperature, having different melting temperatures, and responsible for the individual melting peaks [14,16–23]. The second mechanism assumes that only structures responsible for the low temperature melting peak exist in the polymer at room temperature. Structures responsible for the additional melting peaks at higher temperatures appear during temperature scan as a result of complex melting dynamics, occurrence of various macromolecular rearrangement processes, for example, processes of melting–recrystallization–melting type [15,24–26].

To establish causes of the two melting peaks appearance in our case, we investigated effect of scan rate on melting curves of sample irradiated with dose 50 kGy, at which the splitting of DSC curve in two peaks appears more distinctly. In the case of rearrangement processes, we should observe a change in ratio between high- and low-temperature melting peaks with the change of scan rate [27]. But Fig. 3 demonstrates an independence of the melting curves of scan rate.

The effect of sample thermal history on the high-temperature melting peak represents an additional evidence for the absence of rearrangement process. As seen from Fig. 4, annealing at 319 °C, i.e. above the low-temperature melting peak, shifts the high-temperature melting peak to higher temperatures. This indicates unambiguously that the structures responsible for the high-temperature peak exist at room temperature rather than are formed during temperature scan. Thus, in our case the first double-melting mechanism is realized.

Structures responsible for the two melting peaks could both have a different crystal structure [16,17] and a different morphology (different size and/or shape of crystallites [14,18–22,24]). To establish a nature of these structures, X-ray diffraction analysis

of the original and irradiated PTFE samples was performed. This analysis indicate only existence of single crystalline structure corresponding to the hexagonal packing, with no other polymorphs, particularly monoclinic structure.

Thus, we should attribute the two melting peaks to two different morphologies of crystallites existing in irradiated PTFE.

Morphology of the irradiated PTFE was examined by SEM. Irradiation of PTFE in the melt leads to rearrangement of the polymer supramolecular structure: to formation of spherulites which were absent in the initial polymer (Fig. 5a and b). In addition, two morphology types are clearly observed: dense structures around the center of spherulite (Fig. 5b and c) and loose network structure at the periphery (Fig. 5d). It could be assumed that crystallites in these formations differ by size and, probably, by specific surface energy due to substantially different density of packing. According to the Gibbs–Thompson equation [28], both decrease in crystallite size and decrease in packing density (resulting to an increase in surface energy) lead to a decrease in the melting temperature.

Thus, it can be concluded that the low- and high-temperature melting peaks are associated with the structures shown in Fig. 5d and c, respectively.

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