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Mechanistic insights into the room temperature transitions of polytetrafluoroethylene during electron-beam irradiation

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ABSTRACT

In order to recognize the characteristic thermal transitions of polytetrafluoroethylene (PTFE) occurring at 19 °C and 30 °C, PTFE is irradiated on electron beam accelerator at room temperature and analyzed by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The results suggest that the two transition temperatures decrease considerably with increasing irradiation doses. Based on the results of structural analysis, the decrease of the two transition temperatures is supposed to be highly relevant to the structural changes. In particular, the content and structure of the side groups generated in PTFE are responsible for the variations of the two thermal transitions after irradiation, offering fundamental insights into the reaction mechanisms of PTFE during irradiation.

1. Introduction

It is well known that polytetrafluoroethylene (PTFE) exhibits two thermal transitions around 19 °C and 30 °C at atmospheric pressure, as usually referred to "first-order transition" in comparison with the second-order transition occurring in the amorphous regions [1,2]. Since the first observation of room temperature transition for PTFE in 1949, numerous techniques were applied to detect and explain the origin of these changes, and then the solid-solid transitions were postulated [1–7]. It is hypothesized that the transition occurring at 19 °C is the crystal cell transformation caused by the helical conformation of polymer chains from 13 to 15 CF_2 groups with a twist of 180°. The transition at 30 °C is regarded as the further untwisting and loss of a regular conformation of polymer chains along the molecules [8]. With the development of molecular simulation, theoretical modeling of helical symmetry and reversal defects in PTFE are also carried out to explore the crystal structure changes [9–11].

In 1963, Kline et al. [12] demonstrated that the solid-solid transition temperature of PTFE was decreased by high-energy irradiation. Since then, comprehensive investigations concerning the dynamic mechanical properties, specific volume and thermal conductivity have been carried out to explain the phenomenon [8,12–15]. It was assumed that the decrease of the solid-solid transition temperature was attributed to the decrease of molecular weight caused by radiation-induced degradation of PTFE chains and the decline of activation energy for the mobility of chain segments in macromolecules [8,13,15].

Though this room temperature transition is considered rather unique to polymers, it is a common feature among fluorocarbons, especially for such melt-processable polymers as the copolymers of tetrafluoroethylene (TFE) with hexafluoropropylene (HFP) (FEP) and TFE with perfluoropropylvinyl ethers (PPVE) (PFA) [13,16–25]. Pucciariello et al. [16,17] and Funaki et al. [18], for example, have found that the two transitions at 19 °C and 30 °C shifted to lower temperatures in FEP and PFA copolymers with varying monomer concentrations. This implied that the solid-solid transition of PTFE could decrease by the copolymerization of TFE with trace amount of the other perfluorinated monomers.

Recently, we have reported the structural changes of PTFE occurring in irradiation [26]. In the present work, we find that the decreased room temperature transition of irradiated PTFE is somewhat relevant to the newly formed side groups and their content [27–36].

2. Experimental

2.1. Materials

PTFE micropowder was a product of Shanghai 3F New Materials Co., China.

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2.2. Irradiation of PTFE

The irradiation of PTFE was performed on a GJ-2 electron beam accelerator (1.8 MeV, 6.5 mA) at Sichuan Institute of Atomic Energy (Chengdu, Sichuan, China) in air. The PTFE samples in polyethylene (PE) bags were irradiated up to accumulated dose of 0.5, 1, 2, 3, 4, 5 and 6 MGy, respectively. The unirradiated and irradiated samples were thus labeled as PTFE0, PTFE0.5, PTFE1, PTFE2, PTFE3, PTFE4, PTFE5 and PTFE6 according to their applied irradiation dose.

2.3. Characterization

The differential scanning calorimetric (DSC) analysis was carried out on a TA Q200 1747 (TA Instruments, USA) thermal analyzer between −50 °C and 350 °C with heating/cooling rate of 10 °C/min under nitrogen atmosphere.

The Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 6700 (Thermo Electron Co., USA) spectrometer over the range of 400–4000 cm^{-1} with a resolution of 0.09 cm^{-1}. The samples for the measurements were prepared by cold-pressing PTFE into films under a pressure about 10 MPa at room temperature.

The wide-angle X-ray diffraction (WAXD) measurements were performed on an Empyrean X-ray diffractometer (PANalytical B. V., Holland) using Cu Kα radiation (λ = 1.54 Å). The data at 2θ degrees from 10° to 90° were collected.

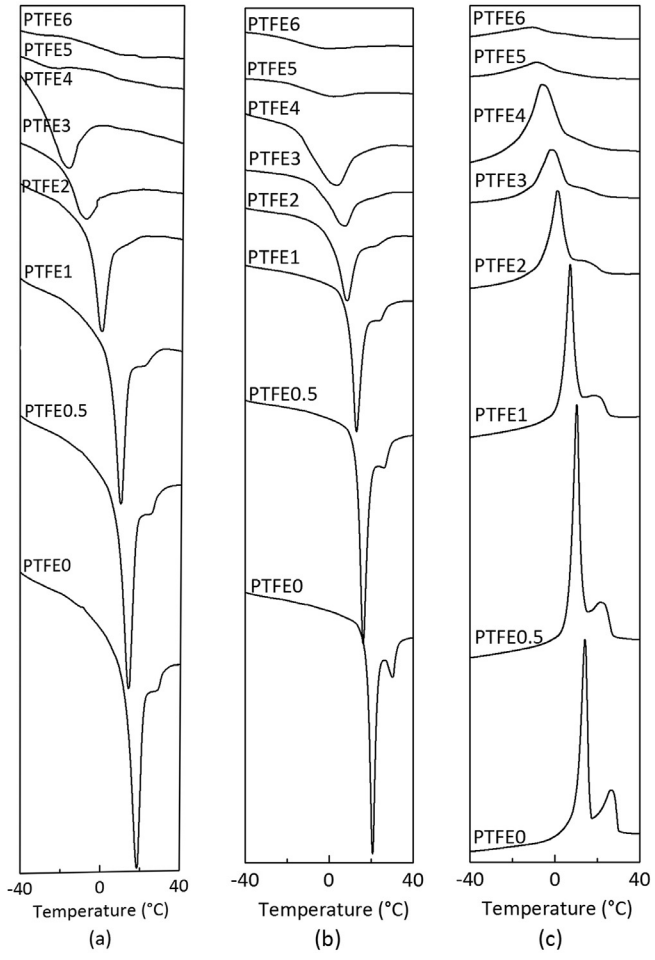

Fig. 1. DSC curves of irradiated PTFE in the range of −40 to +40 °C. (a) First heating, (b) second heating, (c) cooling.

3. Results and discussion

Fig. 1 illustrates the DSC curves of PTFE samples ranging from −40 °C to +40 °C. It is apparent that the samples with low irradiation doses display two transition temperatures, just like the previously reported results [4,8,19,37]. Moreover, the transition peaks become weak, and eventually disappear when increasing irradiation doses further. The detailed transition temperatures and enthalpies from DSC measurements are collected in Table 1.

Table 1 indicates that both the two transitions shift toward the lower temperature with increasing irradiation doses. The results are supported by Kline's work, in which the lowering of transition temperatures was attributed to the combined effects of main chain scission and occlusion of degradation products [13]. Furthermore, the relationship between the transition temperature and irradiation dose was established as the following empirical equation:

$$T = 292\exp(-2.5 \times 10^{-4}D) \quad (1)$$

where T is the temperature in K, and D is the irradiation dose between 1 and 10 MGy [13,38].

Appling the Eq. (1) to our experiments, the calculated transition temperatures are listed in Table 2. It indicates that the calculated temperatures don't coincide with the data in Table 1. For direct comparison, the results of the present work (T_1 of The Second Heating in Table 1) are plotted in Fig. 2. By fitting the lnT-D curve using polynomial regression, an expression in Eq. (2) is given with a correlation coefficient of 0.96.

$$T = 291.2\exp(-1.2 \times 10^{-4}D) \quad (2)$$

where T and D are the same as them in Eq. (1).

The differences of Eqs. (1) and (2) might be caused by different irradiation source, dose rate, starting materials, degradation mechanisms or some other reasons [19,25].

Table 1 also indicates that the enthalpy of the solid-solid transition is not considerably affected by the radiation-induced breakage of polymer aggregation at relatively low doses. This is because the temperature involved is far below the breakage threshold, unable to trigger the long-range molecular movements [8].

To explore the underlying mechanisms affecting the transition temperature in addition to different irradiation source, dose rate,

Table 1
Temperatures and enthalpies for the solid-solid transition of irradiated PTFE.

Sample	The First Heating			The Second Heating			Cooling		
	T_1 (K)	T_2 (K)	$\triangle H$ (J/g)	T_1 (K)	T_2 (K)	$\triangle H$ (J/g)	T_1 (K)	T_2 (K)	$\triangle H$ (J/g)
PTFE0	291.7	301.9	11.1	293.8	303.2	12.2	287.4	299.4	11.3
PTFE0.5	287.3	299.1	6.6	289.4	299.9	11.5	283.5	296.3	10.3
PTFE1	283.1	296.9	7.5	286.2	297.4	12.3	280.5	292.4	10.9
PTFE2	273.4	–	5.4	281.7	296.8	11.2	274.6	290.0	10.0
PTFE3	265.1	–	4.2	280.5	–	8.9	271.4	–	8.6
PTFE4	256.3	–	3.5	276.4	–	7.4	267.0	–	6.2
PTFE5	248.0	–	0.3	274.2	–	5.5	264.7	–	9.5
PTFE6	–	–	–	270.9	–	7.5	262.5	–	8.2