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THE INFLUENCE OF ANNEALING AND HEAVY ION IRRADIATION OF MULTIPLE MELTING AND CRYSTALLIZATION IN PBT FILMS

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Abstract

The influence of heavy ion-irradiation (Ar 5.5 MeV amu^{-1}, $5 \cdot 10^{11}$ ion cm^{-2}) on the melting and crystallization of two PBT films subjected to different modes of thermal treatment was investigated. Differences were observed between the processes occurring in both initial films, due to differences in crystalline phase content. The course of melting and crystallization in heavy ion-irradiated films during first heating, cooling and second heating differs from that in the initial films. The density data and DSC results indicate a decreased crystalline phase content in the PBT films after irradiation.

Keywords: crystallization, DSC, heavy ion irradiation, melting, PBT films, poly(butyleneterephthalate) films

Introduction

Heavy ion irradiation induces physico-chemical transformations in dielectric matter [1, 2]. The phenomenon of latent track creation on the ion paths in materials is applied in the construction of nuclear track detectors and in the preparation of particle track membranes (PTMs) by means of the heavy ion irradiation of thin polymer films and successive selective dissolution of the track material. Studies on the effects of heavy ion irradiation on various types of polymer films are included in the search for new materials for nuclear track detectors and for PTM preparation.

The structural and chemical changes are expected to influence the processes occurring on the heating and cooling of polymer films. Earlier studies [3–6] confirmed that DSC is helpful in the investigation of heavy-induced defects in polymer films. Preliminary work [6] on poly(butyleneterephthalate) (PBT) revealed some differences in melting and crystallization between the initial and the heavy ion-irradiated films.

Several melting processes may be observed during the heating of PBT [7, 8]. Cheng *et al.* distinguished three temperature ranges of PBT melting: high, intermediate and low [7], and pointed out that the occurrence of particular processes depends on the presence, within the sample, of a variety of crystals differing in quality. Although the thermal history is known to influence the melting behaviour of PBT [7, 8], little is known about the nature of the particular processes involved.

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In the present work, DSC was applied to study the melting and crystallization processes occurring in PBT films, both initial and heavy ion-irradiated, in the course of heating – cooling – heating cycles. Another problem of interest was the effect of the film preparation conditions on the course of the processes taking place in the initial and the irradiated films. The results of the DSC studies are related to the crystalline phase contents in the films.

Experimental

Sample preparation and irradiation

Two PBT films (ca. 80 μm thick) were prepared from commercial granules of 'Eldur Pure', a product of Jelchem, Poland (mean molecular mass M_n ca. 25 000). The films were obtained by melting the granules and calendering the ribbons in the commercially available PLE330 (Brabender) plasticorder. Use of this equipment allows very fast cooling of the polymer erupting from the melting chamber. Sample PBT1 was prepared at a melting chamber temperature of 240°C and a cooling tumbler temperature of 90°C (cooling of the resulting film from 90°C to ambient temperature occurred within ca. 2 min). The PBT2 film was prepared by melting at 260°C, cooling on tumblers kept at 20°C and subsequent recrystallization at 200°C for 2 h in a vacuum dryer. The film was then cooled from 200 to 100°C in the dryer for ca. 2 h, removed from the dryer and cooled to ambient temperature for ca. 5 min.

The films were irradiated in a cyclotron installed in the Centre de Recherches du Cyclotron (Watman Company) in Louvain-la-Neuve, Belgium, with Ar ions (5.5 MeV amu^{-1}), using a fluence of $5 \cdot 10^{11}$ ion cm^{-2}. The calculated dose [4] amounted to about $1.5 \cdot 10^6$ Gy.

Methods

The DSC measurements were performed during heating – cooling – heating cycles (with samples situated in closed Al pans) in dry nitrogen in the temperature range 30–270°C, using a DSC7 Perkin-Elmer instrument of power compensation type. The instrument was calibrated with tin and indium. The heating – cooling – heating rates were 10,–10 and 10°C min^{-1}, respectively. The crystallinity indices x_{dsc} were calculated on the basis of the heat of fusion measured during the first heating, on the assumption that the equilibrium heat of fusion of PBT crystals is 142 J g^{-1} [9].

Density measurements were performed by means of a density gradient column consisting of sodium iodide solution and water. The volume crystallinity indices, x_v, were calculated on the basis of the density data, values of 1.280 and 1.400 g cm^{-3} being taken for the amorphous and the crystalline regions, respectively [10].

Results and discussion

The volume crystallinity indices were 0.158 for PBT1 and 0.266 for PBT2 initial films (the densities were 1.299 and 1.312 g cm^{-3}, respectively). The corresponding values of the crystallinity indices x_{DSC}, determined from the DSC results, were 0.362 and 0.415.

Some differences were observed between the DSC curves recorded for the initial films with different crystallinities (Figs 1 and 2, Table 1). In particular, considerable differences were observed between the melting endotherms recorded on first heating. Higher values of fusion and crystallization heats (Table 1, Column IV) were found for the PBT2 film recrystallized at 200°C than for the PBT1 quenched film.

Noteworthy differences were found between the courses of melting and crystallization during the first heating, the cooling and the second heating of the initial and the irradiated films.

A single endothermal high-temperature melting effect with maximum at 223.3°C was observed during the first heating of the initial PBT1 film (Fig. 1). The decrease in heat flow observed in the temperature range preceding the endothermal melting effect, however, indicates the occurrence of exothermal process, probably due to recrystallization [7]. For the irradiated film, two melting processes are observed. Besides the high-temperature effect with maximum at 221.2°C connected with the melting of PBT crystals with a well-developed structure, an intermediate-temperature endothermal effect with maximum at 212.2°C was detected (Fig. 1).

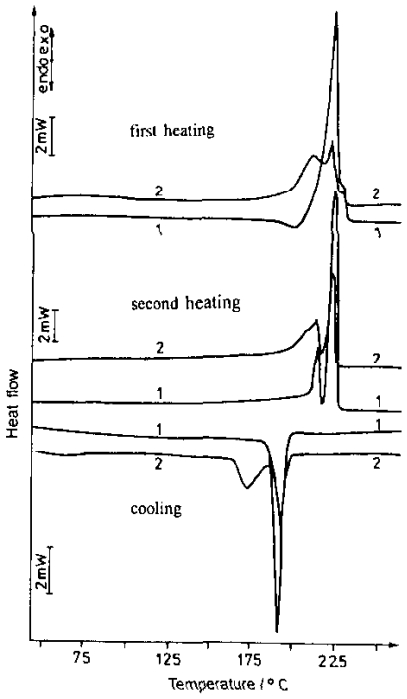

Fig. 1 Comparison of DSC curves recorded during first heating, cooling and second heating at rates of 10, −10 and 10°C min^{-1}: Curves denoted 1 relate to initial PBT1 film; curves 2 relate to the irradiated film (Ar 5.5 MeV amu^{-1}, $5 \cdot 10^{11}$ ion cm^{-2}; calculated dose equal to $1.5 \cdot 10^6$ Gy)

Table 1 DSC results obtained on the initial and the irradiated PBT films during first heating, cooling and second heating. The measurements were carried out in the temperature range 30–270°C at heating – cooling – heating rates of 10, –10 and 10°C min^{-1}. Columne IX presents the temperatures of the additional weak maxima observed in the DSC melting effects (nd=not detected, sh=shoulder). For the initial PBT1 sample, the exothermal effect was observed in the temperature range from 185°C up to the beginning of the endothermal effect connected with melting at 198.6°C. Crystallinity indices x_{DSC} were calculated via the heat of fusion determined for the first heating, assuming that the equilibrium crystal heat of fusion is 142 J g^{-1} [9]. Values of 0.362 and 0.278 were found for the initial and the irradiated PBT1, respectively, and values of 0.415 and 0.336 for the initial and the irradiated PBT2 samples, respectively

No.	Process	Sample	Total heat of fusion/J g^{-1}	High-temperature effects		Low and intermediate temperature effects		Additional endothermal maxima/°C
				peak temperature/°C	height of effect/W g^{-1}	peak temperature/°C	height of effect/W g^{-1}	
I	II	III	IV	V	VI	VII	VIII	IX
1	I heating	PBT1 initial	51.4±0.2	223.3±0.3	1.01±0.01	none	–	228.0
2	I heating	PBT1 irradiated	39.5±1.0	221.6±0.6	0.29±0.01	212.0±0.1	0.26±0.01	228.2
3	cooling	PBT1 initial	51.0±0.5	192.2±0.3	1.55±0.01	none	–	nd
4	cooling	PBT1 irradiated	38.4±1.0	193.8±0.2	0.59±0.01	175.6±0.1	0.19±0.03	nd
5	II heating	PBT1 initial	52.4±1.0	224.0±0.2	1.24±0.01	214.0±0.1	0.32±0.04	197.3 (sh)
6	II heating	PBT1 irradiated	39.3±2.0	222.5±0.3	0.51±0.01	212.8±0.1	0.26±0.01	207.6 (sh)
7	I heating	PBT2 initial	59.0±0.2	223.8±0.5	0.99±0.03	199.8±0.2	0.12±0.01	nd
8	I heating	PBT2 irradiated	47.7±0.7	221.6±0.1	0.38±0.05	187.5±0.5 210.9±0.1	0.10±0.01 0.22±0.01	227.0
9	cooling	PBT2 initial	51.8±0.5	191.3±0.1	1.45±0.02	none	–	nd
10	cooling	PBT2 irradiated	42.3±1.3	193.4±0.1	0.73±0.05	173.4±0.1	0.17±0.01	nd
11	II heating	PBT2 initial	54.5±1.0	224.2±0.1	1.15±0.01	210.5±0.3	0.26±0.01	nd
12	II heating	PBT2 irradiated	42.7±1.0	222.4±0.1	0.65±0.01	212.5±0.1	0.24±0.01	207.6 (sh)

For the initial PBT2 film, two endothermal effects of melting, with maxima at 199.8 and 223.8°C (low-temperature melting and high-temperature melting), were recorded on first heating, whereas at least three melting processes occurred for the irradiated film, as indicated by the endothermal maxima at 187.5, 210.9 and 221.6°C (Fig. 2).

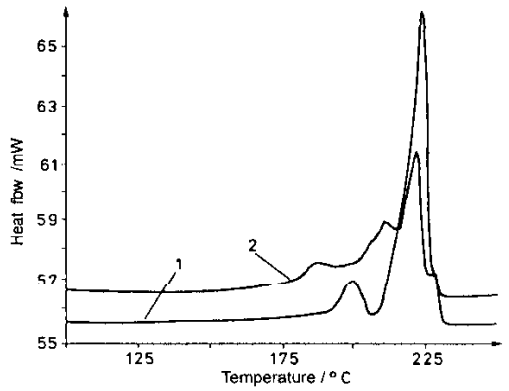

Fig. 2 Comparison of DSC curves recorded during first heating at a rate of 10°C min^{-1} for the initial PBT2 film (Curve 1) and the film irradiated with Ar ions (5.5 MeV amu^{-1}, $5 \cdot 10^{11}$ ions cm^{-2}, calculated dose $1.5 \cdot 10^6$ Gy)

Differences were also observed between the course of crystallization and the second melting processes in the initial and the irradiated films. Thus, a single, sharp exothermal effect due to crystallization was observed during the cooling of molten PBT1 and PBT2 initial films, while for the irradiated films treated under identical conditions two crystallization processes could be distinguished. During the second heating, two narrow effects of melting were observed for the PBT1 and PBT2 initial films. The height of the first (medium-temperature) effect was small, while that of the second (high-temperature) effect was large. For the irradiated films, the first effect, with maximum at 212.3–212.8°C, was wide and relatively large as compared with the high-temperature melting effect. Moreover, the shape of the effect recorded for the irradiated PBT2 samples (additional slight maximum at 207.6°C) demonstrate the occurrence of the additional premelting process.

The peak temperatures of the melting effects recorded during the first and the second heating were smaller for both irradiated films than for the corresponding initial films, while the peak temperature of the crystallization effect was higher for the irradiated films than for the initial ones (Table 1, columns V and VII).

The total heats of fusion and crystallization during the first heating, second heating and cooling were smaller for the irradiated samples than for the initial films (Table 1, column IV). Therefore, the total crystallinity indices x_{DSC} were smaller for the irradiated than for the initial samples. Values of 0.278 and 0.336 were found for the irradiated PBT1 and PBT2 films, respectively, as compared with 0.362 and 0.415 calculated for the corresponding initial films.

A decrease in the crystalline phase content of both films was confirmed by the volume crystallinity data. Crystallinity indices x_v, of 0.095 and 0.158 were determined for the irradiated PBT1 and PBT2 films, respectively (the densities were 1.291 and 1.299 g cm^{-3}). These x_v values were smaller than those found for the corresponding initial films: 0.158 and 0.266, respectively. The results confirm the conclusion drawn from the X-ray diffraction data [4].

The results of the present investigations demonstrate that the crystal reorganization caused by the irradiation leads to a decrease in the content of the phase melting at higher temperatures and increases in the contents of the phases melting at low and intermediate temperatures. The differences between the courses of melting during the first and the second heating processes are connected with crystal reorganization caused by destruction of the ordering on melting, followed by recrystallization.

Conclusions

The presence of different types of crystalline regions in PBT films as a consequence of different treatment conditions is indicated by the various melting and crystallization processes that occur in PBT films during heating and cooling. Differences in melting and crystallization were observed in initial films subjected to different modes of thermal treatment during preparation and differing in crystalline phase content. Some differences were also detected between the processes occurring in the initial and heavy ion-irradiated films during first heating, cooling and second heating. The density data and the results of DSC studies indicate a decreased crystalline phase content in the PBT films after irradiation.

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