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DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS OF IRRADIATED POLYTETRAFLUOROETHYLENE FILMS

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Crystalline content of polytetrafluoroethylene (PTFE) can be substantially increased by electron beam irradiation. These changes as a function of radiation dose were examined in PTFE films by differential scanning calorimetry (DSC). Surprisingly small radiation doses (<0.002 Mrad) were found to cause a fairly substantial increase (25%) in their heat of fusion. Variations in the heat of fusion and the peak melting temperature of PTFE films with radiation dose, in the range of 0.0017 to 16 Mrad, are examined.

Several different linear polyethylenes including (and especially) ultra-high molecular weight linear polyethylene have been shown to experience, upon exposure to high energy radiation, a significant increase in their heat of fusion and hence the degree of crystallinity [1–4]. The present communication reports on the change in the heat of fusion of PTFE films caused by electron beam radiation. High energy radiation has indeed been shown in the past to induce crystallinity changes in PTFE [5–10]. However, as demonstrated in the present communication, surprisingly small radiation doses (< 0.002 Mrad) were found to cause a fairly substantial (approximately 25%) increase in the heat of fusion. Variation in the heat of fusion and the melting temperature of PTFE films with radiation doses from 0.0017 to 16 Mrad is presented.

Experimental

The PTFE films employed in the present work were 5 mil thick and were obtained from Chemplast, Inc., N. J. The films were exposed at ambient conditions to a 2MeV electron beam in a van de Graaff accelerator, the radiation doses employed ranging from 0.0017 to 16 Mrad. The melting behavior of resulting samples was evaluated in a Mettler TA 2000 differential thermal analyzer (DSC). All specimens, 3 mg in size, were scanned from 190 to 390° at the rate of 10 deg/min, cooled down to 190° at a fast rate (100 deg/min) and rescanned to 390 deg/min. The data are presented in the next section in terms of the heat of fusion and the peak melting temperature obtained from the DSC scans.

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Results and discussion

Figure 1 shows the DSC scan, during first melting, of both virgin, unirradiated and irradiated (16 Mrad) samples. The heat of fusion can be seen to double from 35 to 70 J/g upon irradiation to 16 Mrad. However, the irradiated film was extremely brittle. In fact, it was so brittle and friable that it fractured into many pieces during irradiation itself. Therefore, it was decided to examine the effect of lower doses. The complete set of melting data (during first and second melting) as a function of radiation dose are shown in Figs 2 and 3. As can be seen from Fig. 3, the peak melting temperature is essentially independent of the radiation dose. However, radiation dose has a substantial effect on the heat of fusion of PTFE films, Fig. 2. Surprisingly, even at the low dose of 0.0017 Mrad, the heat of fusion on first melting increases from 35 to 43.5 J/g – approximately 24% increase. It then stays essentially constant until a dose of approximately 0.04 Mrad, followed by an increase to approximately 50 J/g at 0.1 Mrad, to approximately 63 J/g at 0.5 Mrad, and finally to approximately 75 J/g at 5 Mrad.

Since the heat of fusion is directly proportional to the degree of crystallinity, the significance of the changes observed is obvious, especially since the degree and type of crystallinity govern the macroscopic properties of a given polymer. It should also be pointed out that relatively low radiation doses cause a large increase in crystallinity. For instance, a dose as low as 0.1 Mrad causes a 43% increase in crystallinity while a dose of 0.5 Mrad causes an 80% increase.

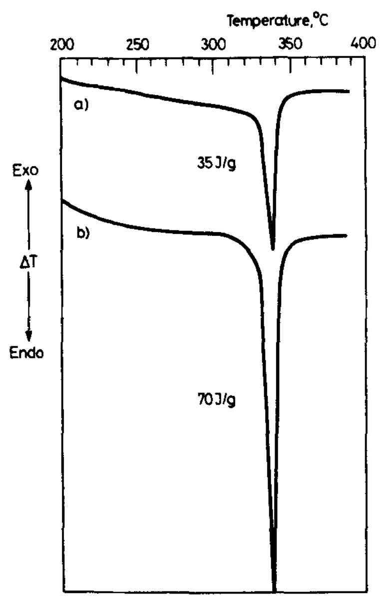

Fig. 1 DSC scans of (a) unirradiated and (b) irradiated (16 Mrad) films

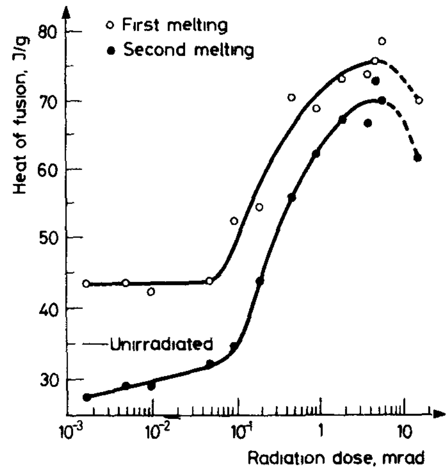

Fig. 2 Effect of radiation dose on the heat of fusion

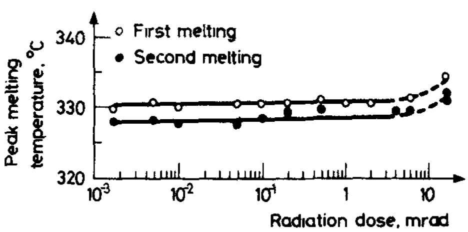

Fig. 3 Effect of radiation dose on the peak melting temperature

The heat of fusion during second melting also rises monotonically with radiation dose, although the magnitude at any given dose is lower than that during first melting. The heat of fusion at 16 Mrad (during first and second melting) is significantly reduced, which probably results from extensive degradation.

One obvious interpretation of the data presented is that radiation causes main-chain scission of strained molecules in the amorphous regions, followed by subsequent recrystallization of broken chains. This explanation has been proposed and examined in varying degrees of detail by different researchers [8–12].

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Zusammenfassung — Der kristalline Anteil von Polytetrafluoroäthylen (PTFE) kann durch Bestrahlung mit Elektronen wesentlich erhöht werden. In PTFE-Filmen wurden diese Veränderungen in Abhängigkeit von der Strahlungsdosis mittels DSC untersucht. Überraschend kleine Strahlungsdosen (< 0.002 Mrad) verursachen bereits eine wesentliche Erhöhung (25%) der Schmelzwärme. Veränderungen der Schmelzwärme und der dem Schmelzpeak von PTFE-Filmen zuzuordnenden Temperatur in Abhängigkeit von der Strahlungsdosis wurden im Bereich von 0.0017 bis 16 Mrad untersucht.

Резюме — Содержение кристаллического политетрафторэтилена (ПТФЭ) может быть значительно увеличено облучением его электронами. Такие изменения исследованы методом ДСК в пленках ПТФЭ в зависимости от дозы облучения. Найдено, что даже малая доза облучения (< 0,002 Мрад) приводи к довольно значительному увеличению (25%) их теплоты плавления. Исследованы изменения теплоты плавления и пиков температур плавления пленок ПТФЭ в зависимости от дозы облучения в области от 0,0017 до 16 Мрад.