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Investigation of electron irradiation induced-changes in poly(vinylidene fluoride) films

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Abstract

The radiation-induced changes taking place in poly(vinylidene fluoride) (PVDF) films exposed to electron irradiation were investigated in correlation with the applied doses. Samples were irradiated in air at room temperature by a universal electron beam accelerator to doses in the range of 100–1200 kGy. Various properties of the irradiated PVDF films were studied using FTIR, differential scanning calorimetry (DSC) and universal mechanical tester. Unirradiated PVDF film was used as a reference. Electron irradiation was found to induce changes in physical, chemical, thermal, structural and mechanical properties of PVDF films and such changes vary depending on the irradiation dose. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: PVDF; Electron irradiation; Structural changes; Thermal properties; Mechanical properties

1. Introduction

Fluoropolymers are well known for their excellent thermal and chemical stability and mechanical properties [1]. Among them, poly(vinylidene fluoride) (PVDF) —$(CF_2\text{-}CH_2)_n$— has attracted considerable attention in many areas of research and industrial use [2]. This is due to its electrical properties, resistance to weathering, durability, biocompatibility and processibility [3]. Investigation of PVDF morphology and piezoelectric properties has become a subject for active research in the last 4 decades [4–7].

PVDF is a semicrystalline polymer, which has several crystalline phases known as α, β, γ and δ phases (or II, I, III and IV). The α (II) phase in which the polymer chains are in non-polar conformation (TGTG′) is the most common phase appearing under normal circumstances. The polar crystalline phase β (I), which has a zigzag (all-trans) confirmation is obtained by straining, stretching or quenching [3]. The intermediate polar confirmation γ (III) results when the polymer is moderately stressed. The last phase δ (IV) appears only under special crystallization temperature and pressure.

Irradiation by ionizing radiation has been found to induce changes in the chemical structure and physical properties of polymers [8]. Such changes may be in the form of crosslinking, main chain session, or evolution of hydrogen depending upon the chemical as well as physical nature of the polymer and the radiation. Radiation crosslinking and radiolysis of fluoropolymers have been reviewed in Refs. [1] and [9], respectively.

The effect of electron radiation on the inherent properties of the PVDF has been studied in various occasions [10–14]. However, some of the reported results, particularly those related to crystallinity, crosslinking and melting temperature are contradictory and as a result further clarification studies are needed. The present work aims to investigate various changes taking place in the properties of PVDF films after exposing to electron radiation at different doses.

2. Experimental

2.1. Materials and electron irradiation

The PVDF films were supplied by Goodfellow Cambridge (England). The film has a thickness of 0.08 mm and density of 1.76 gm/cm^3. The irradiation experiments were

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carried out using a universal electron beam accelerator (NHV-nissin high voltage, EPS 3000, Cockroft Walton type, Japan) located at Malaysian Institute for Nuclear Technology Research. The specifications of the electron beam accelerator and conditions of irradiation are given in Table 1. The samples were irradiated to doses in the range of 100–1200 kGy in air at room temperature on a step by step basis using an irradiation dose of 100 kGy per pass.

2.2. FTIR measurements

FTIR measurements were carried out using a Nicolet (Magna-IR 560) spectrometer equipped with ATR (Thunder dome-HATR) having Germanium spherical crystal. The spectra were measured in the wave number range of 4000–500 cm^{-1} and analysed using commercial software.

2.3. Differential scanning calorimetry

Thermograms of irradiated samples were measured by differential scanning calorimetry, DSC, (Perkin Elmer, Pyris-1). Typical samples weighing 3–5 mg were used. Thermograms were obtained from the first heating run in a temperature range of 50–200 °C at a constant heating rate of 20 °C/min and under nitrogen atmosphere. The samples were held at 200 °C for 5 min before they were cooled down to 50 °C at a cooling rate of 20 °C/min. Melting as well as recrystallization temperature and the heat of melting were obtained from the thermograms using commercial software. The degree of crystallinity (X_c) or crystallinity (%) in the samples was calculated using the equation.

$$X_c = (\Delta H_m / \Delta H_{m100}) \times 100 \qquad (1)$$

Table 1
Specifications of the electron beam accelerator and irradiation conditions

Brand: NHV (Nissin high voltage)
Model: EPS 3000 (Cockroft Walton type)
Energy range: 500 eV–3.0 MeV
Beam power through the whole
Energy range: 0.5–9 kW
Beam current: 1–30 mA
Scan range: 30–120 cm
Dose uniformity: ±5%
Conveyor speed: 1–20 m/min
Irradiation conditions:
   accelerating voltage: 2.0 MeV
   beam current: 10 mA
   distance from window: 20 cm
   conveyor speed: 0.94 m/min
   dose per pass: 100 kGy

where, ΔH_m is the heat of melting of PVDF and ΔH_{m100} is the heat of melting of 100% crystalline PVDF polymer, which is equal to 104.7 J/g [14].

2.4. Mechanical properties measurements

Tensile strength and elongation percent at break point of the irradiated films were measured using a universal mechanical tester (Instron, model 4301, UK) at room temperature. Dumbbell-shaped specimens of 50 mm long with a neck of 28 and 4 mm wide (ASTM D882) were used. The cross-head speed was fixed at 50 mm/min.

3. Results and discussion

3.1. Changes in physical properties

The unirradiated PVDF film exhibited a faint opaque white colour as result of processing. Electron irradiation of the film did not bring about any visible changes until a dose of 800 kGy, beyond which the film colour turned to faint yellow. This indicates that electron beam irradiation has induced certain changes in the properties of the films and such changes can be physically seen at doses higher than 800 kGy.

3.2. Changes in chemical properties

Fig. 1 shows typical FTIR spectra of unirradiated and electron irradiated PVDF films. The unirradiated film is characterised by the presence of symmetric and asymmetric stretching vibrations of CH$_2$ groups at 2854 and 2923 cm^{-1}, respectively. The strong band at 1211 cm^{-1} is assigned for CF$_2$ groups. The spectra of irradiated films did not show major changes in the main absorption bands compared to the unirradiated film. However, two small adjacent bands at 1725 and 1741 cm^{-1} can be identified. The former is assigned to C=C bond resulting from dehydrofluorination (removal of HF) and the subsequent crosslinking, whereas the latter is assigned to C=O (carbonyl) resulting from the formation of hydroperoxide radicals initiated by irradiation in air. The band at 3300 cm^{-1} is characteristic for –OH (hydroxyl group). More detailed FTIR analysis including samples irradiated at low doses (20–100 kGy) is shown in Fig. 2. The bands representing C=C and C=O were found to decrease as the dose goes as high as 800 kGy. The C=O band almost vanished at a dose of 1200 kGy. This most likely due to the dominance of the crosslinking in the film structure. Based on FTIR results, the following plausible mechanism is suggested for the chemical changes taking place in the surface of electron irradiated PVDF film:
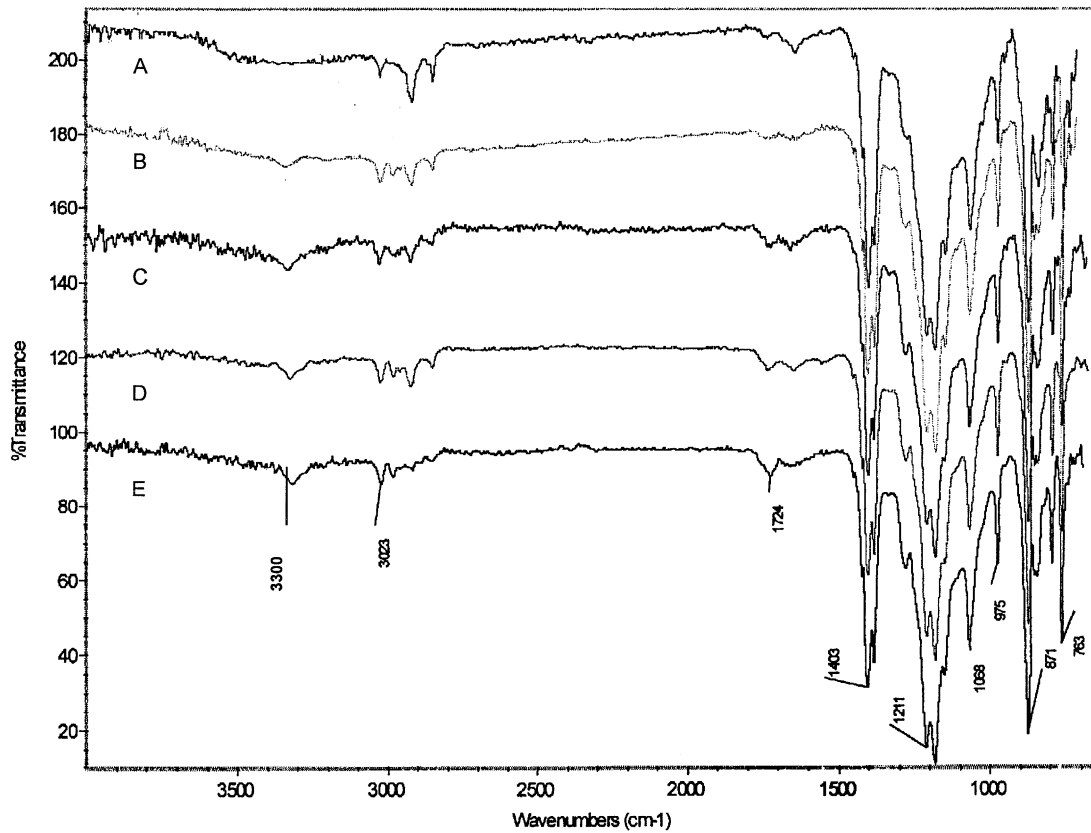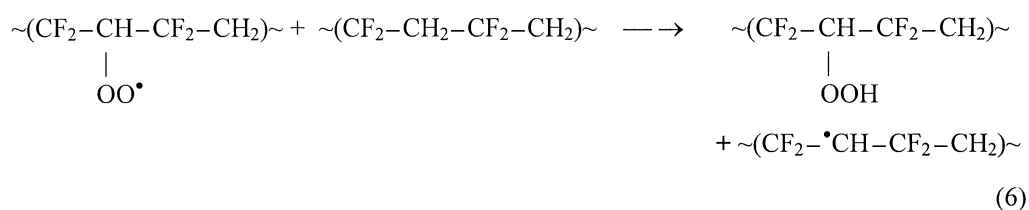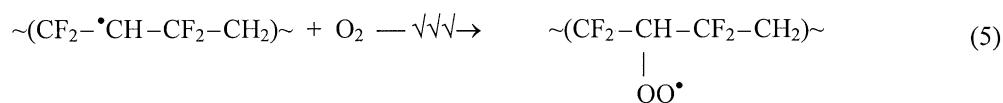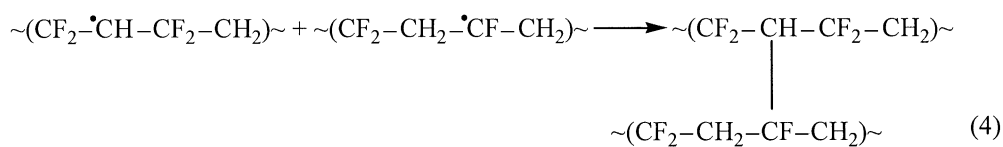
Fig. 1. Typical FTIR spectra of unirradiated PVDF film (A) and PVDF films irradiated at various doses: (B) 100 kGy; (C) 400 kGy; (D) 800 kGy; (E) 1200 kGy.

$$\sim(CF_2-CH_2-CF_2-CH_2)\sim \quad —\sqrt{}\sqrt{}\sqrt{}\rightarrow \quad \sim(CF_2-{}^{\bullet}CH-CF_2-CH_2)\sim + {}^{\bullet}H \quad (2)$$

$$\sim(CF_2-CH_2-CF_2-CH_2)\sim \quad —\sqrt{}\sqrt{}\sqrt{}\rightarrow \quad \sim(CF_2-CH_2-{}^{\bullet}CF-CH_2)\sim + {}^{\bullet}F \quad (3)$$

$$\sim(CF_2-{}^{\bullet}CH-CF_2-CH_2)\sim + \sim(CF_2-CH_2-{}^{\bullet}CF-CH_2)\sim \longrightarrow \sim(CF_2-CH-CF_2-CH_2)\sim$$
$$|$$
$$\sim(CF_2-CH_2-CF-CH_2)\sim \quad (4)$$

$$\sim(CF_2-{}^{\bullet}CH-CF_2-CH_2)\sim + O_2 \quad —\sqrt{}\sqrt{}\sqrt{}\rightarrow \quad \sim(CF_2-CH-CF_2-CH_2)\sim$$
$$|$$
$$OO^{\bullet} \quad (5)$$

$$\sim(CF_2-CH-CF_2-CH_2)\sim + \sim(CF_2-CH_2-CF_2-CH_2)\sim \quad \longrightarrow \quad \sim(CF_2-CH-CF_2-CH_2)\sim$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$OO^{\bullet} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad OOH$$
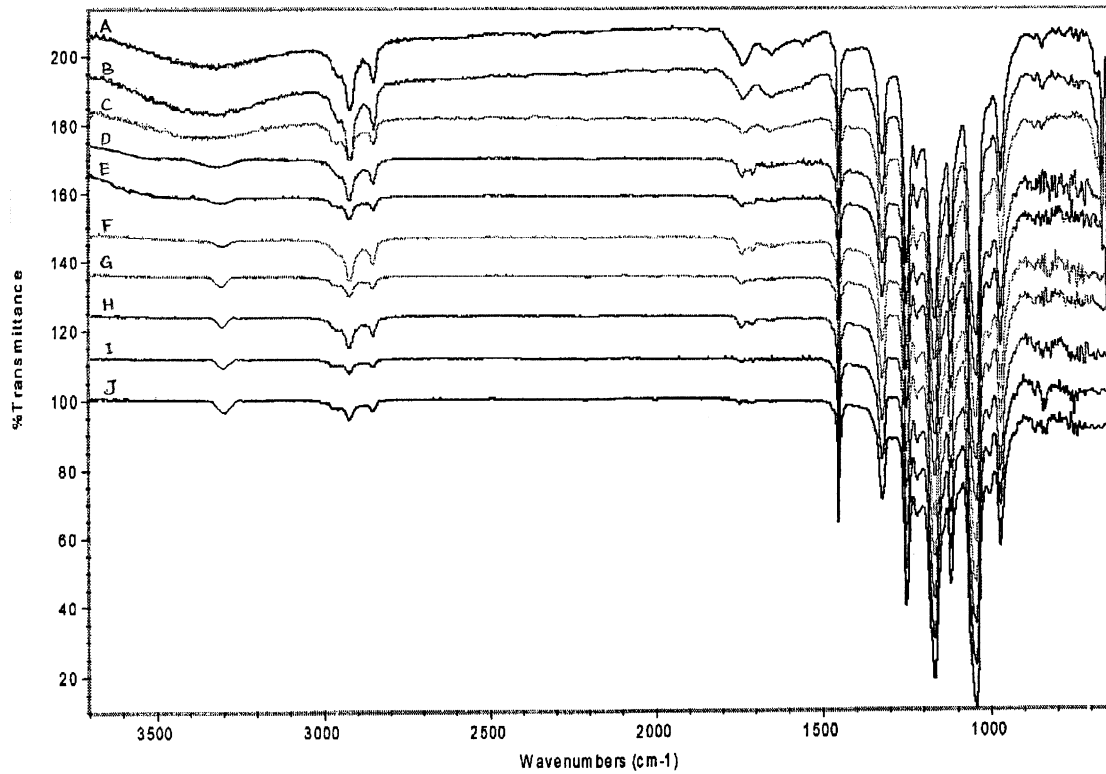$$+ \sim(CF_2-{}^{\bullet}CH-CF_2-CH_2)\sim$$
$$(6)$$

Fig. 2. Typical FTIR spectra of unirradiated film (A) and PVDF films irradiated at various doses: (B) 20 kGy; (C) 40 kGy; (D) 60 kGy; (E) 80 kGy; (F) 100 kGy; (G) 200 kGy; (H) 400 kGy; (I) 800 kGy; (J) 1200 kGy.
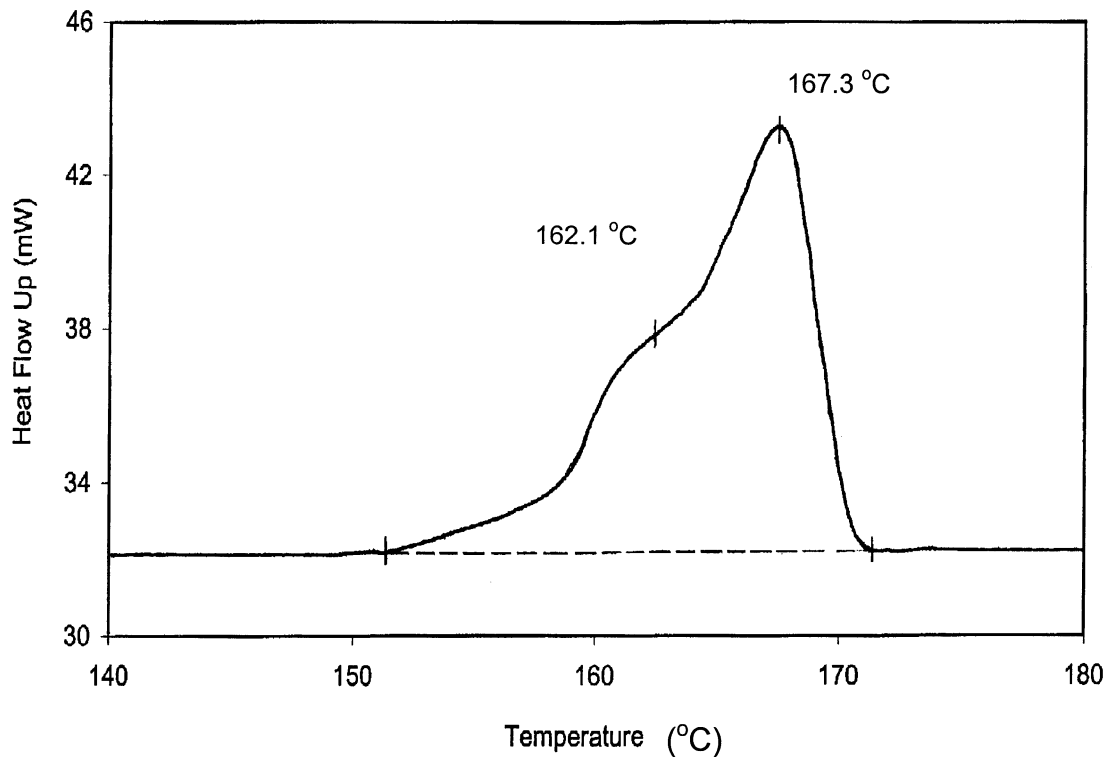

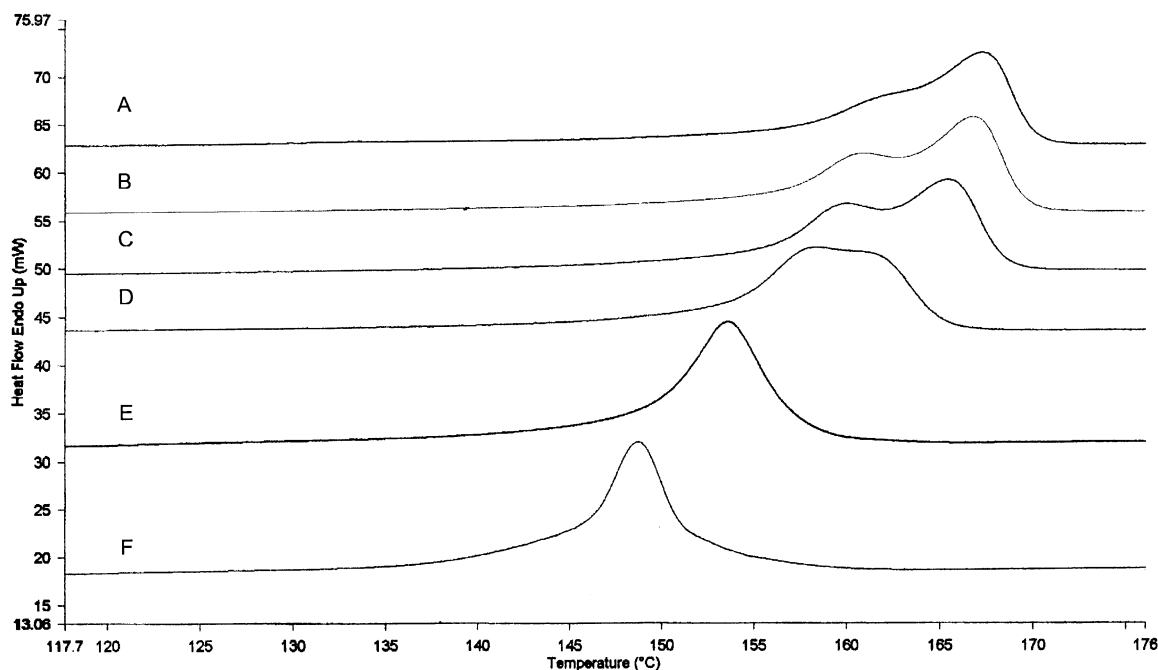Fig. 3. A typical melting thermogram of unirradiated PVDF film.

Fig. 4. Typical melting thermograms of unirradiated PVDF film (A) and PVDF films irradiated at various doses: (B) 100 kGy; (C) 200 kGy; (D) 400 kGy; (E) 800 kGy; (F) 1200 kGy.

3.3. Changes in thermal and structural properties

The changes in thermal and structural properties of irradiated PVDF films were studied by DSC. The melting and cooling thermograms were recorded for various samples exposed to electron beam irradiation at different doses. The glass transition temperature could not be detected in the first heating run. Fig. 3 shows a typical melting thermogram of unirradiated PVDF film (control sample). As can be seen a bimodal melting endotherm is detected with two melting temperatures (high and low melting peaks) at 167.3 and 162.1 °C, respectively. The two melting temperatures were caused by a temperature dependent bimodal distribution of lamellar thicknesses. The lower melting temperature is attributed to melting of crystals originally present (small crystals) and the higher melting peak is due to melting of crystals reorganised upon heat treatment (big crystals) [15,16]. These results are in an excellent agreement with those reported in literature for PVDF films treated at similar thermal conditions [12,17]. From melting thermograms of the unirradiated PVDF sample, it also possible to evaluate the heat of melting (34.3 J/g) by taking the total area under the two peaks (183.3 mJ) into consideration. From this value, the degree of crystallinity can be calculated by taking the heat of melting of 100% crystalline PVDF into account.

Fig. 4 shows typical melting thermograms of PVDF films irradiated at various doses in the range of 100–1200 kGy. A bimodal melting endotherm can be clearly observed in all the thermograms of the irradiated PVDF

films (except for the film irradiated at 800 kGy and above). The shape of the bimodal melting endotherm changed with the variation of the irradiation dose. For instance, the area under the lower melting peak increased and that under the higher melting peak decreased with the increase in the irradiation dose up to 400 kGy. As the irradiation dose further increased to 800 kGy and above, the higher melting peak completely disappeared. A similar melting behaviour for electron irradiated PVDF films was reported in the literature, but the higher melting peak completely disappeared at a dose of 500 kGy [18,13]. The decrease in high melting peak with the irradiation dose up to 400 kGy in this work can be ascribed to the decrease in the melting of the reorganised thicker lamellae, which leads to inhibition of the lamellar growth in this melting region. Further increase in the irradiation dose enhances the

Table 2
Variation of heat of melting and melting temperature of PVDF films with the irradiation dose

Irradiation dose (kGy)	Heat of melting (J/g)	Melting temperature (°C)	
		Higher peak	Lower peak
0	34.3	167.3	162.1
100	38.2	166.8	160.7
200	40.6	165.4	159.8
400	39.1	158.5	158.2
800	39.9	–	153.5
1200	40.2	–	148.7

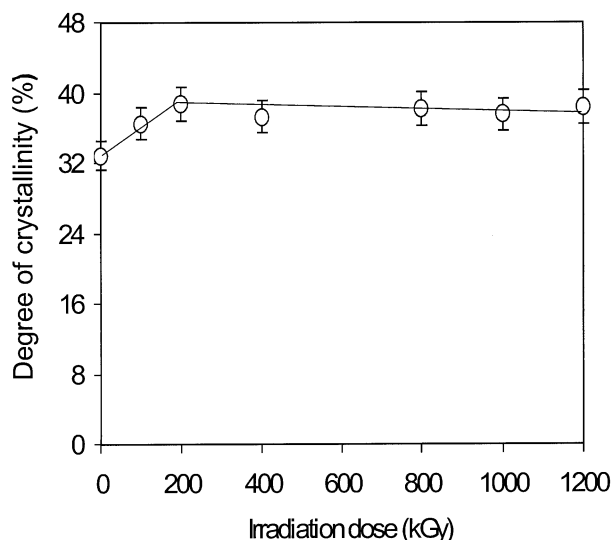Fig. 5. Variation of the degree of crysallinity with the irradiation dose.

crosslinking and the oxidative degradation in the films (elimination of HF and peroxidation) leading to formation of a single crystalline structure in which the reorganised thicker lamellae completely vanished. According to Pae et al. [12], one possible explanation for the disappearance of the high-temperature melting peak at high irradiation doses stems from the possible annealing effects during thermal scanning itself.

The variation of heat of melting and melting temperatures of PVDF films with the irradiation dose is shown in Table 2. The heat of melting which is obtained from the area under the peaks is found to decrease with the increase in the irradiation dose up to 200 kGy beyond which it tends to show a very small shift towards lower values depending on the irradiation dose. This was accompanied by a decrease in the melting temperatures with the increase in the irradiation dose. Moreover, the degree of crystallinity increased with the initial doses (up to 200 kGy) and then tended to marginally decrease with the increase in the irradiation dose as depicted in Fig. 5. This behaviour can be explained by taking the nature as well as the location of the radiation-induced structural changes taking place in PVDF films into consideration. At low irradiation doses, scission reaction (free radical formation) takes place causing an increase in molecular mobility and allowing polymer molecules in the amorphous region to crystallise during the irradiation process [14]. This leads to mutual increase in the heat of melting and the degree of crystallinity. Further increase in the irradiation dose causes some damages in the crystalline structure under the influence of electron irradiation leading to a marginal decrease in both heat of melting and degree of crystallinity. Since PVDF crosslinks rapidly when exposed to ionising radiation [9], it can be concluded that radiation-induced crosslinking takes place mainly in the whole amorphous region and also in areas close to the crystallite surfaces of the lamellae. However, the decrease in the melting temperatures with the irradiation dose as shown in Table 2 is a sign of crystallite defects, which is responsible for the decrease in the crystallinity. This suggests that crystalline damage (distortion) is mainly taking place in the newly formed crystallites. Moreover, the variation of melting tem-
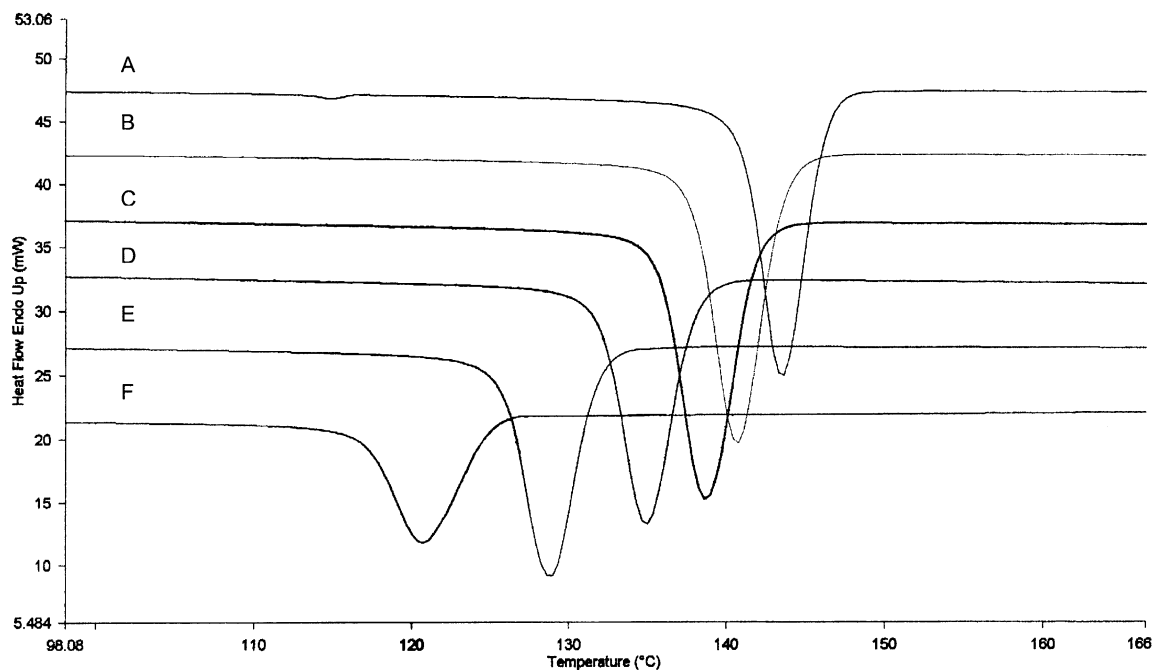

Fig. 6. Typical cooling thermograms of unirradiated PVDF film (A) and PVDF films irradiated at various doses: (B) 100 kGy; (C) 200 kGy; (D) 400 kGy; (E) 800 kGy; (F) 1200 kGy.
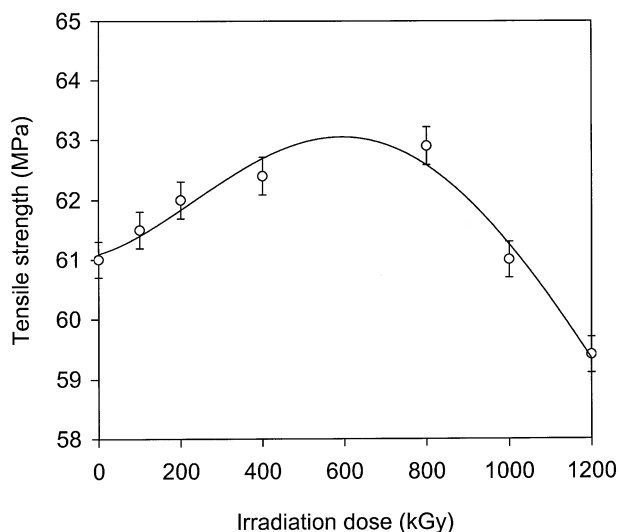
Fig. 7. The effect of irradiation dose on the tensile strength of PVDF films.
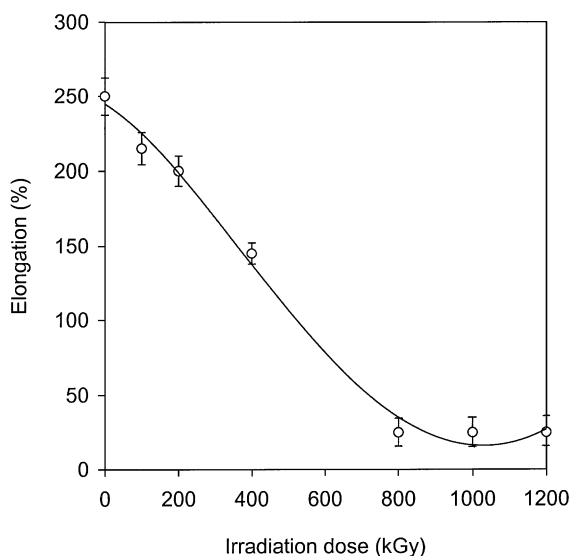

Fig. 8. The effect of irradiation dose on the elongation (%) at break of PVDF films.

peratures is suggested to be a result of three cumulative parameters i.e. radiation-induced crosslinking, crystallite distortion and radiation oxidative degradation of PVDF films.

Fig. 6 shows the cooling thermograms of PVDF films irradiated at various doses in the range of 100–1200 kGy. The recrystallization temperature decreased gradually with the increase of the irradiation dose. It decreased from 143.2 °C in the unirradiated film to 120.8 °C in the film irradiated at 1200 kGy. This most likely due to the mixing of both original and reorganised crystals which lead to formation of a singly crystalline phase of lower crystallisation temperature upon cooling.

The results of the present study are in a complete agreement with those reported by Pae et al. [12], Zhudi et al. [14] and Adem et al. [13], respectively. However, they are in direct contrast with those reported for single crystals of PVDF, which were found to undergo serious loss of crystallinity upon electron beam irradiation [19].

3.4. Changes in mechanical properties

The effect of irradiation dose on mechanical properties such as tensile strength and elongation (%) at break of the PVDF films is given in Figs. 7 and 8, respectively. The tensile strength increases until a dose of 800 kGy then decreases as the irradiation dose goes higher (800 kGy <). It increases to 62.9 (MPa) then drops until it reaches 59.4 (MPa), which represent 97% of its original value (61.0 MPa) after receiving a dose of 1200 kGy. The elongation% at break decreases sharply with the increase in the irradiation dose up to 800 kGy beyond which it tends to level off. It drops from 250% for the unirradiated sample to about 25% at irradiation dose of 800 kGy. Further increase in the dose does not cause any change in the elongation% at break. The variation in the investigated mechanical properties of the PVDF films under the influence of electron beam radiation can be attributed to oxidative degradation, crystal disruption and crosslinking, which becomes predominant above 800 kGy. This results in a limited movement of the chain segments in the crosslinked structure of the PVDF films. These results are in a good agreement with FTIR spectral analysis, which showed a disappearance of the peak representing C=O at doses higher than 800 kGy.

A similar investigation for mechanical properties by Sands et al. [20] showed that the tensile strength of γ-irradiated PVDF increase by about 40% at a dose of 1000 kGy above which it decline to about 80% of the original value. The elongation% also dropped by 80% of its original value after 1000 kGy.

4. Conclusions

The effect of electron beam irradiation on the properties of PVDF films was investigated in this work. FTIR spectral analysis showed absorption bands due to C=C and C=O, which suggest the occurrence of oxidative degradation and the formation of crosslinked structures. Such structural changes were found to have a strong impact on the thermal properties such as melting and recrystallization temperatures which decreased with increase in the irradiation dose as revealed by DSC measurements. The crosslinking was found to occur mainly in the whole amorphous area and near the surface of the crystallites and the crystalline distortion affects only the newly formed crystals. The variation in tensile

strength and elongation percent at break especially at high doses (800 kGy and above) is due to the limited movement of the polymer chain segments resulted from the dominance of crosslinking. Finally, it can be concluded that the deterioration in the properties of the irradiated PVDF films is mainly attributed to three cumulative parameters i.e. oxidative degradation, crystal disruption and crosslinking.

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