



PERGAMON

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Radiation Physics and Chemistry 68 (2003) 875–883

Radiation Physics
and
Chemistry

www.elsevier.com/locate/radphyschem

Electron beam irradiation effects on ethylene-tetrafluoroethylene copolymer films

Mohamed Mahmoud Nasef^{a,*}, Hamdani Saidi^b, Khairul Zaman M. Dahlan^c

^a *Business & Advanced Technology Centre (BATC), Universiti Teknologi Malaysia, Jalan Semarak, Badar Seri Iskandar, Kuala Lumpur 54100, Malaysia*

^b *Membrane Research Unit (MRU), Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia*

^c *Radiation Processing Technical Division, Malaysian Institute for Nuclear Technology Research (MINT), Bangi, Kajang 43000, Malaysia*

Received 3 October 2002; accepted 2 March 2003

Abstract

The effects of electron beam irradiation on ethylene-tetrafluoroethylene copolymer (ETFE) films were studied. Samples were irradiated in air at room temperature by a universal electron beam accelerator for doses ranging from 100 to 1200 kGy. Irradiated samples were investigated with respect to their chemical structure, thermal characteristics, crystallinity and mechanical properties using FTIR, differential scanning calorimeter (DSC) and universal mechanical tester. The interaction of electron irradiation with ETFE films was found to induce dose-dependent changes in all the investigated properties. A mechanism for electron-induced reactions is proposed to explain the structure-property behaviour of irradiated ETFE films.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: ETFE; Electron beam irradiation; FTIR; Thermal analysis; Mechanical properties

1. Introduction

In the recent years, there has been an increasing interest in the development and the usage of fluoropolymers. This is due to their excellent thermal resistance, chemical stability and mechanical strength (Feiring, 1989). Ethylene-tetrafluoroethylene copolymer (ETFE) occupies a special position among fluoropolymers as it contains alternating structural units of polyethylene and poly(tetrafluoroethylene) $[-(\text{CF}_2-\text{CF}_2-\text{CH}_2-\text{CH}_2)_n-]$ that confers it a unique combination of properties imparted from both fluorocarbon and hydrocarbon polymers (Forsythe and Hill, 2000). For instance, ETFE is less dense, tougher, stiffer and exhibit high-tensile

strength, flexural modulus and creep resistance than the fully fluorinated polymer i.e. poly(tetrafluoroethylene) (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) and poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA) (Mark et al., 1988). It also offers an excellent thermal stability and superior resistance to common solvents (as does PTFE) in addition to high resistance to radiation and fatigue (Carlson and Schmiegel, 1988). This has made ETFE a good candidate for preparation of membranes, polymer electrolytes, ion exchange resins and advanced composite materials (Brack et al., 2000) beside its common uses in cable and fine wire insulation, sealing, pipe plugs, etc. (Anderson and Punderson, 1979).

Studying the effects of electron beam and gamma irradiation on fluorinated polymers such as PTFE (e.g. Oshima et al., 1995; Lappan et al., 1997; Fischer et al., 1998), FEP (e.g. Iwasaki and Toriyama, 1967; Iwasaki et al., 1967), PFA (e.g. Forsythe et al., 1997a, b), and

*Corresponding author. Tel.: +6-03-2691-4020; fax: +6-03-2691-1294.

E-mail address: mahmoudeithar@mailcity.com (M.M. Nasef).

poly(vinylidene fluoride) (PVDF) (e.g. Adem et al., 1999; Nasef et al., 2002) have been reported in many occasions and the subject has been recently reviewed (Lyons, 1995; Forsythe and Hill, 2000). However, reports on the effect of electron radiation on ETFE and its consequent radiation induced changes on the copolymer inherent properties are scarce despite their extensive use (Rosenberg et al., 1992; Oshima et al., 1997).

The objective of this study is to report on the various changes taking place in the inherent properties of ETFE copolymer under the influence of electron beam irradiation for doses in the range of 100–1200 kGy. A study of such kind may help in understanding the mechanism of radiolysis of ETFE films and the extent of irradiation induced changes in their various properties.

2. Experimental

2.1. Materials and electron irradiation

The ETFE samples used in this work were in a film form of 0.125 μm thickness and 1.9 g cm^{-3} density (Goodfellow, Cambridge, England). Electron irradiation was performed using a universal electron beam accelerator (NHV-Nissin High Voltage, EPS 3000, Cockcroft Walton type, Japan). The samples were placed on a tray on a conveyer and irradiated in air at room temperature on a stepwise basis. The conveyer speed was kept constant at 0.94 m/min. An acceleration voltage of 2.0 MV was used with a current of 10 mA in order to obtain an irradiation dose of 100 kGy per pass. The applied doses were varied from 100 to 1200 kGy by increasing the number of passes. The doses were verified using Cellulose Triacetate (CTA) dosimeter film based on ASTM E 1650–97 and JAERI-Memo 6948 (Tanaka et al., 1984). Details of the specifications of the electron beam accelerator were described elsewhere (Nasef et al., 2002).

2.2. FTIR measurements

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

2.3. Differential scanning calorimetry

Thermograms of heating and cooling of ETFE samples were obtained using a differential scanning calorimeter (DSC) (Perkin Elmer, Pyris-1) operated at constant heating and cooling rates of 20 min^{-1} in nitrogen atmosphere. The heat of melting and the heat

of crystallisation were calculated from the areas under the melting and cooling peaks, respectively. The degree of crystallinity was calculated using the following equation:

$$\text{Degree of crystallinity(\%)} = (\Delta H_m / \Delta H_{m100}) \times 100,$$

where, ΔH_m is the heat of melting of ETFE films which is proportional to the area under the melting peak and ΔH_{m100} is the heat of melting of 100% crystalline ETFE polymer, which equals 113.4 J/g (Brack et al., 2000).

2.4. Mechanical properties measurements

Tensile strength and elongation percent at break point were recorded on an Instron (model 4301, UK) operated with crosshead speed of 50 mm min^{-1} at room temperature.

3. Results and discussion

3.1. FTIR spectral analysis

Fig. 1 shows typical FTIR spectra of unirradiated and electron irradiated ETFE films. The unirradiated film is initially characterised by the presence of symmetric and asymmetric stretching vibrations of CH_2 groups at 2852 and 2921 cm^{-1} , respectively. The sharp band at 1452 cm^{-1} represents the CH deformation whereas the strong bands in the range 1000–1400 cm^{-1} are characteristics for CF_2 groups. The FTIR spectra of the irradiated ETFE samples in the range of 500–4000 cm^{-1} do not present significant alterations in the absorption bands at all doses of irradiation. However, two small adjacent bands at 1741 and 1654 cm^{-1} can be identified and their amplitude increases with increasing of irradiation dose. These two bands are assigned for C=O and C=C groups, respectively. The stretching vibration located at 3300 cm^{-1} is characteristic for OH groups. Details of these chemical changes can be clearly seen in FTIR spectrum of ETFE film irradiated at 1200 kGy shown in Fig. 2. The co-existence of C=O and OH groups suggests that the presence of oxygen induces the formation of peroxide radicals on the polymer backbone, which were subsequently converted to hydroperoxides by abstraction of hydrogen from the adjacent ethylene comonomer unit. This was confirmed by the thermal decomposition of the hydroperoxides upon heating the irradiated samples in a vacuum oven at 150 °C for 15 min, which causes the disappearance of hydroxyl characteristic peak from their FTIR spectra.

The absence of any peaks at wave numbers of 1776, 1810 and 1884 cm^{-1} indicates that COF is mostly not formed in the irradiated ETFE films and there is no hydrolysis with water moisture to form COOH free acid group as happened in poly(tetrafluoroethylene) when it

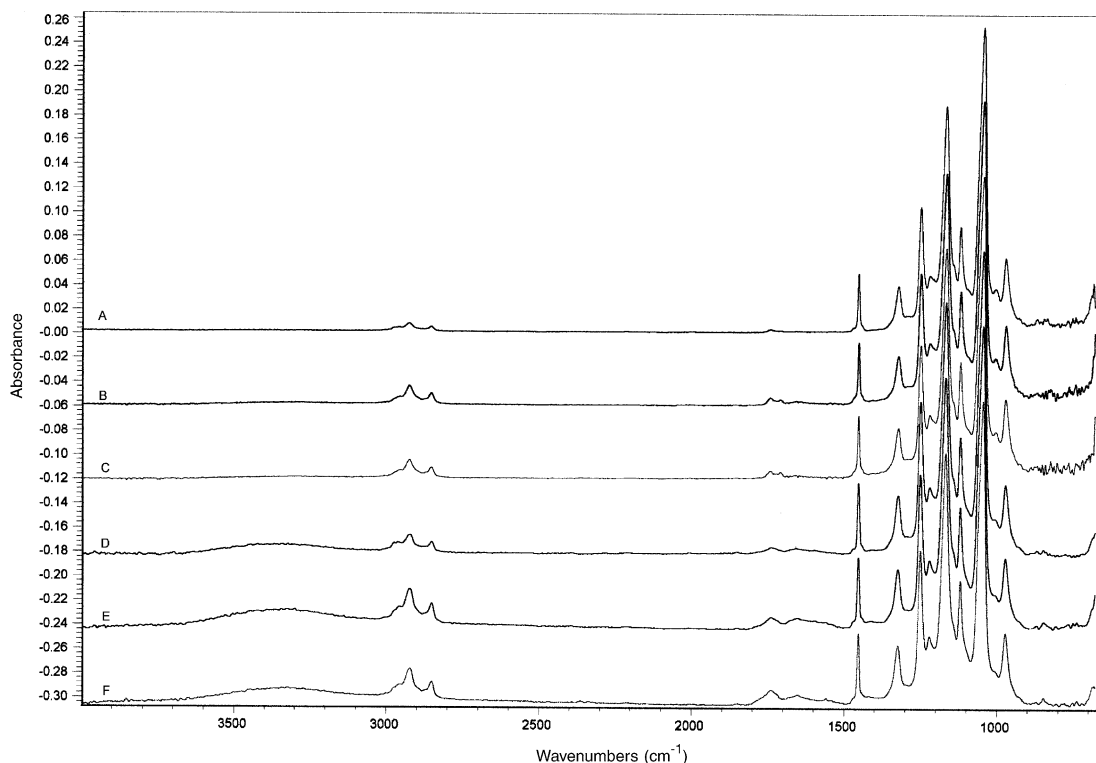


Fig. 1. Typical FTIR spectra of (A) unirradiated ETFE film and ETFE films irradiated at various doses: (B) 100 kGy; (C) 400 kGy; (D) 800 kGy; (E) 1200 kGy.

was irradiated in air using electron beam (Fischer et al., 1998).

The C=C resulted from the removal of HF (dehydrofluorination) after C–C main chain scission leading to the formation of unsaturated structure. The existence of HF, which is a pretty known hydroperoxide scavenger most likely, scavenges a great part of the formed hydroperoxides and this explains the detection of small amount of them as indicated by the size of the characteristic peaks (C=O and OH) at all doses despite their irradiation in air. These results are in accordance with those reported by Adem et al. (1999) who found that the presence of little amount of oxygen induced the formation of C=O and OH in PVDF films although the electron irradiation was conducted under nitrogen atmosphere. Therefore, it can be fairly stated that the contribution of peroxidation and unsaturation reactions in this system is small compared to other radiation-induced reactions, i.e. main chain scission and cross-linking. Eventually, it can be suggested that when ETFE films are exposed to electron irradiation the initial reaction involves scission of C–F, C–H and C–C bonds leading to the formation of macroradicals, which undergo the following competitive reactions: (1) peroxidation by reaction with atmospheric oxygen leading to formation of hydroperoxides after hydrogen abstraction

from the neighbouring ethylene molecules; (2) dehydrofluorination after C–C scission to form unsaturated structure and (3) dehydrofluorination and the subsequent formation of crosslinking structure by reaction with the adjacent macromolecular radical. Accordingly, the plausible mechanism given in Fig. 3 can be proposed. The extent of each of these reactions is going to affect the structure of the irradiated ETFE films leading to changes in their thermal, mechanical properties. FTIR results reported in this work are in a good agreement with FTIR and XPS analysis reported in literature for gamma irradiated ETFE (Zhong et al., 1993).

3.2. DSC analysis

In order to support FTIR results and to determine the variation in the thermal properties and the structural-induced changes in ETFE films, DSC measurements were conducted and the obtained thermograms were further analysed to calculate the degree of crystallinity. Fig. 4 shows typical melting thermograms of ETFE films exposed to various irradiation doses obtained from the first heating run. For instance, the melting temperature (T_m) shows a remarkable shift towards lower values compared to the unirradiated ETFE film as the

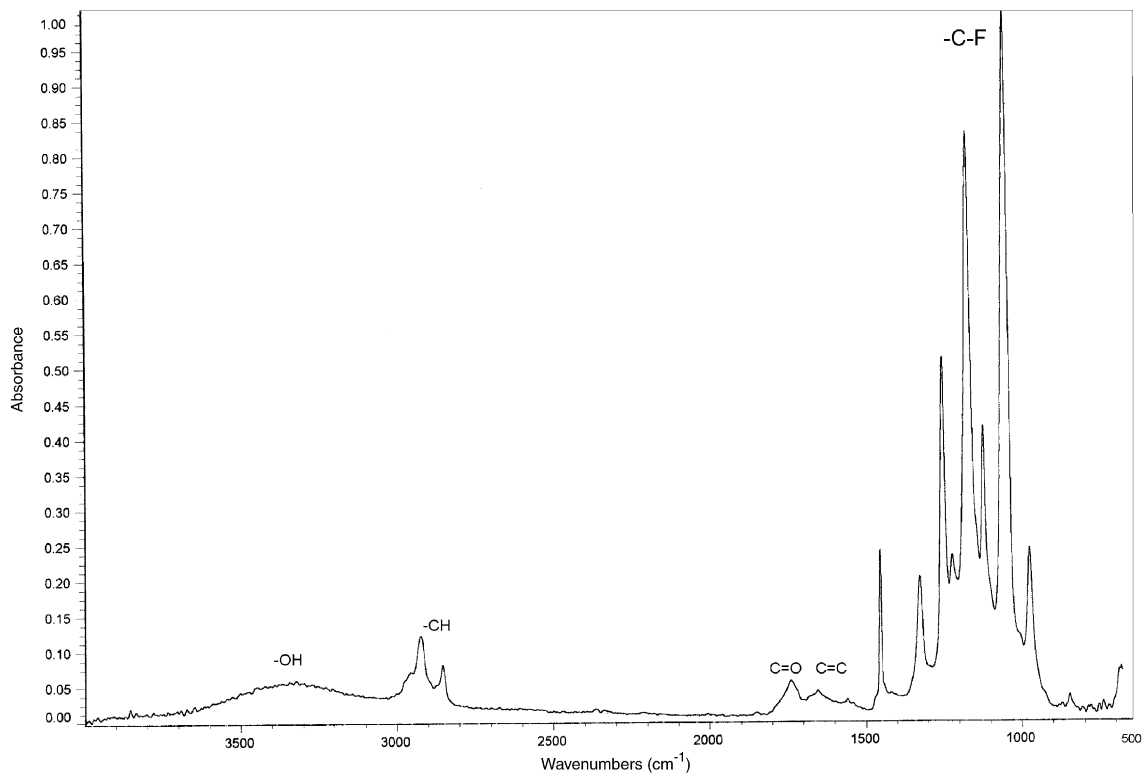


Fig. 2. Typical FTIR spectrum of ETFE film irradiated at 1200 kGy.

irradiation dose increases from 100 to 1200 kGy. This can be clearly seen from the relationship between the T_m and the irradiation dose shown in Fig. 5. It is known that the temperature range of melting represents the crystallite sizes and higher T_m results from larger crystallite sizes or greater perfection and vice versa. Therefore, the results of melting behaviour indicate that irradiation has a strong effect on the crystalline region of ETFE copolymer and the overall impact is in a form of size reduction of the crystallinities caused by main chain scission and/or formation of defects.

Further, to elucidate the melting behaviour as well as the effect of irradiation on the copolymer structure and correlate that with the various competitive reactions taking place in irradiated samples, the changes in heat of melting (ΔH_m) and the degree of crystallinity are correlated with the irradiation dose as shown in Fig. 6. Both the ΔH_m and the degree of crystallinity initially increase up to a dose of 100 kGy beyond which they steadily decrease until reaching their minimum values at 1200 kGy. This behaviour can be explained based on the fact that ETFE is semi-crystalline copolymer. That is, there are crystalline regions, which are impeded in the amorphous matrix. This means that the location of radiation-induced changes in any of these discriminated regions is going to play a significant role in affecting the structural properties of the ETFE films. At low

irradiation doses, main scission reaction starts to take place causing an increase in molecular mobility and allowing some of the broken polymer chains to recrystallise and others in the amorphous region to crystallise during the irradiation process. This is consistent with the fact that irradiation temperature is greater than of the glass transition temperature of ETFE copolymer which leads to existence of sufficient molecular mobility for broken chains to reorganise and recrystallise. Consequently, a mutual increase in the heat of melting and the degree of crystallinity takes place at a dose of 100 kGy. This increase might be also prompted by the possibility of having high concentration of the oxygenated species (peroxides and hydroperoxides), which can change the density of region where they are formed and modify the interaction between chain segments in a way that reduces the deformation in crystalline structure caused by irradiation.

Further increase in the irradiation dose causes an increase in the chain scission accompanied by a reduction in the number and the length of chains suitable for recrystallisation due to the formation of unsaturated structure after the elimination of HF in the broken chains. Therefore, the crystallisation in the amorphous region is inhibited by the growing of crosslinking effect. This eventually leads to rapid decrease in the heat of melting and the degree of

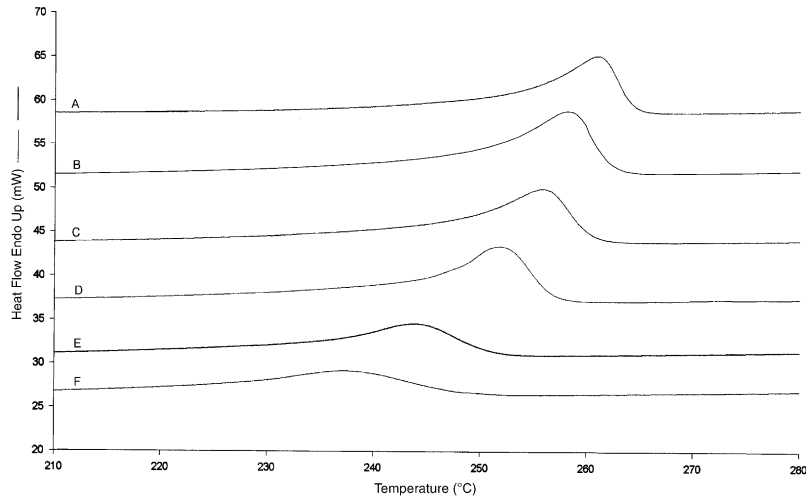


Fig. 4. Typical melting thermograms of (A) unirradiated ETFE film and ETFE films irradiated at various doses: (B) 100 kGy; (C) 200 kGy; (D) 400 kGy; (E) 800 kGy; (F) 1200 kGy.

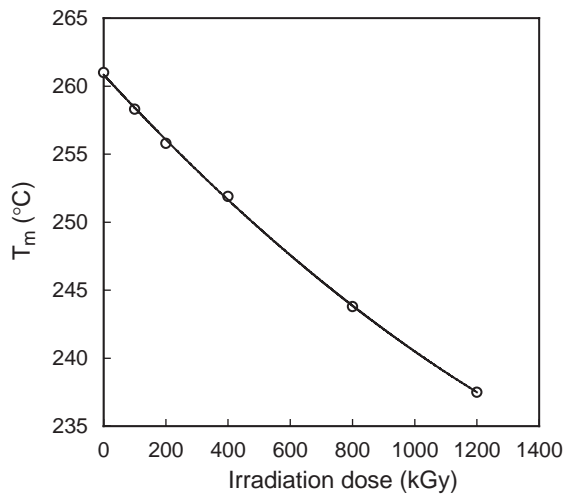


Fig. 5. The relationship between the melting temperature (T_m) and the irradiation dose.

Fig. 8, which shows the variation of the T_c and the heat of crystallisation with the irradiation dose. This can be attributed to the formation of crosslinks, which disrupt the packing of the chains and restrict the mobility of macroradicals, which can not undergo recombination and thereby inhibiting crystallisation upon cooling. Similar behaviour has been reported for gamma irradiated ETFE (Rosenberg et al., 1992) and also for PVDF films irradiated by electron beam at doses equal to those used in the present study (Nasef et al., 2002). It can be concluded the radiation-induced crosslinking is playing a very significant role in

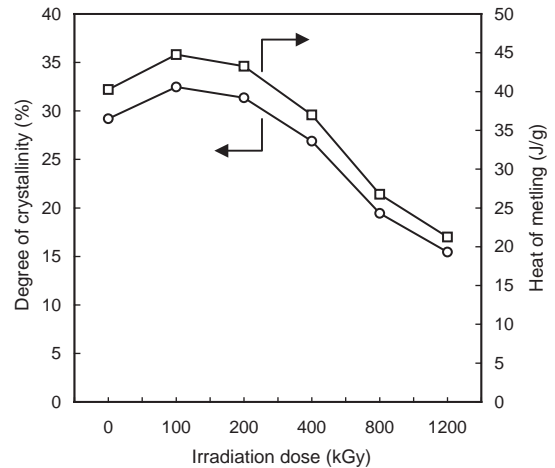


Fig. 6. Variation of the heat of melting at the degree of crystallinity with the irradiation dose.

affecting the thermal properties of irradiated ETFE films.

3.3. Mechanical properties

The effect of irradiation dose on mechanical properties such as tensile strength and elongation (%) at break of the ETFE films is given in Figs. 9 and 10, respectively. As can be seen in Fig. 9, the tensile strength increases at the dose of 100 kGy then decrease gradually with the further increase in the dose until 800 kGy, beyond which it levels off. This can be explained

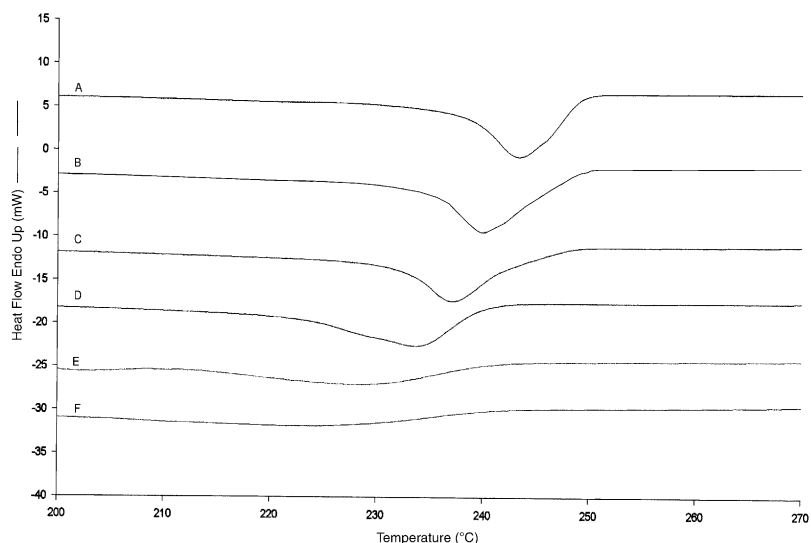


Fig. 7. Typical cooling thermograms of (A) unirradiated ETFE film and ETFE films irradiated at various doses: (B) 100 kGy; (C) 200 kGy; (D) 400 kGy; (E) 800 kGy; (F) 1200 kGy.

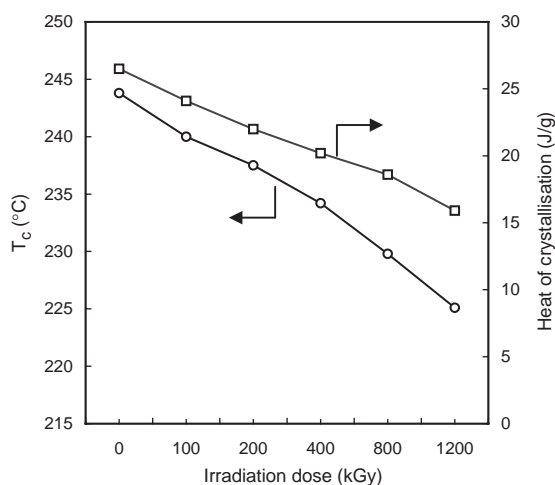


Fig. 8. Variation of crystallisation temperature (T_c) and heat of crystallisation with the irradiation dose.

based on the fact that mechanical properties of irradiated films reflect the structural changes taking place during the irradiation. Therefore, the initial increase in the tensile strength is associated with corresponding increase in the degree crystallinity and the subsequent continuous decrease is also due to the decrease in degree of crystallinity that mostly stemmed from the increase in the chain scission reaction. However, the tendency of tensile strength to level off above 800 kGy is due to the dominance of crosslinking and the marginalisation of unsaturation and hydroperoxidation effects.

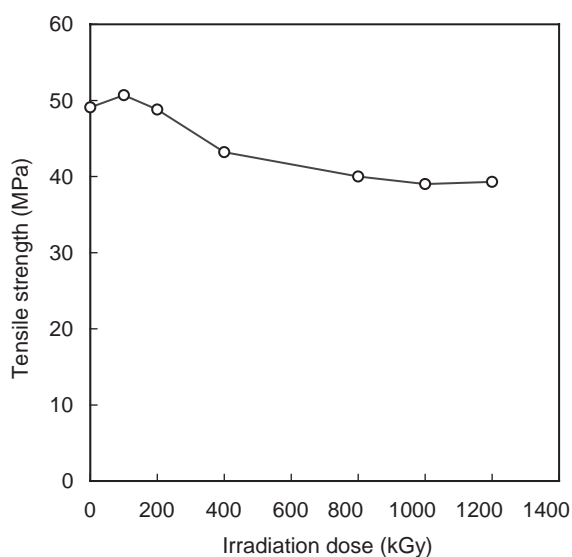


Fig. 9. The effect of irradiation dose on the tensile strength of ETFE films.

Fig. 10 clearly shows that the elongation per cent at break decreases gradually with the increase in the irradiation dose. This can also be attributed to the effect of crosslinking, which imposes a restriction on the movement of the chains in the irradiated ETFE films and such effect grows with the increase in the irradiation dose until it eventually leads to the formation of a network structure in films. These results suggest that the degree of crosslinking is a function of irradiation dose, i.e. the higher the irradiation dose, the higher the

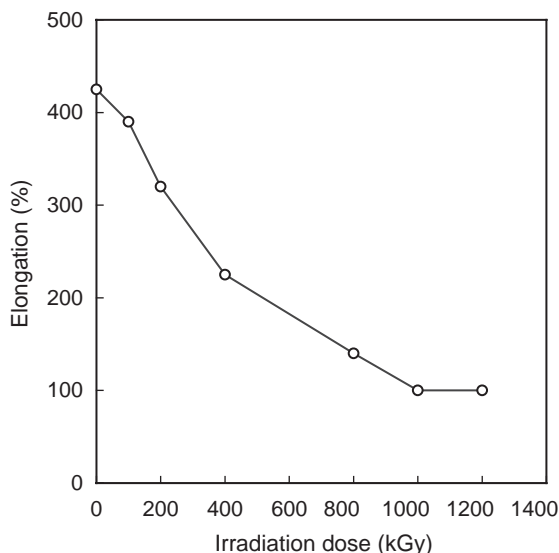


Fig. 10. The effect of irradiation dose on the elongation (%) at break of ETFE films.

degree of crosslinking. These results are in good agreement with those reported for electron and gamma irradiated ETFE under argon atmosphere and at various temperatures in the range of 77–543 K (Oshima et al., 1997).

It is noteworthy to mention that the properties of ETFE polymer vary depending on the tetrafluoroethylene/ethylene ratio, the degree of alteration and the type as well as the content of the termonomer (additive). Therefore, one would expect the recorded properties (T_m , T_c , ΔH_m , degree of crystallinity, tensile strength and elongation % at break) for the ETFE films used in this work to be affected by such factors. Particularly, the additives mostly comprising of a termonomer and/or filler which are normally added in favour of better film processibility and physical properties would alter the properties of the ETFE films. Nevertheless, the data are in good agreement with the published data for this polymer.

4. Conclusions

The electron irradiation-induced changes in the properties of ETFE films were studied. The irradiated ETFE films were found to undergo several changes in their chemical structure due to main chain scission, HF elimination followed by unsaturation as well as crosslinking and hydroperoxidation.

The increase in irradiation dose was found to down shifts the melting temperature, which is a sign of crystalline defects caused by chain scission and cross-

linking. The heat and temperature of crystallisation decreased rapidly with the dose increase indicating that thermal crystallisation process was inhibited by crosslinking.

The degree of crystallinity and the heat of melting of were found to initially rise up to 100 kGy beyond which they decrease steadily with further dose increase indicating transfer of chains from amorphous to crystalline region due to chain scission. That is confirmed by the strong dependence of the tensile strength on the irradiation dose. The variation of the elongation per cent to lower values with the dose increase confirms the formation of predominant of crosslinking structure in ETFE films.

References

- Adem, E., Richards, J., Burillo, G., Avolas-Borja, M., 1999. Changes in poly(vinylidene fluoride) by electron irradiation. *Radiat. Phys. Chem.* 54, 637.
- Anderson, R.F., Punderson, E.I., 1979. Poly(tetrafluoroethylene) and related plastics. In: Banks, R.E. (Ed.), *Organo-fluorine Chemical and their Industrial Applications*. Society of Chemical Industry, Ellis Howard Ltd, London.
- Brack, H.-P., Buhner, G.H., Bonorand, L., Scherer, G.G., 2000. Grafting of pre-irradiated poly(ethylene-*alt*-tetrafluoroethylene) film with styrene: influence of base polymer film properties and processing parameters. *J. Mater. Chem.* 10, 1795; Gal'Pein, Y.L., Tsvankin, D.Y., 1976. *Vysolomol. Soedin. Ser. A* 18: 2691 (Translated in *Polym. Sci. USSR* 1977; 19: 3073).
- Carlson, D.P., Schmiegel, W., 1988. Fluoropolymers, organic. In: Gerhartz, W. (Ed.), *Ullmann's Encyclopedia of Industrial Chemistry*. VCH, Weinheim, pp. 393–429.
- Feiring, A.E., 1989. Recent developments in fluoropolymer chemistry. In: Saegusa, T., Abe, A. (Eds.), *Frontiers of Macromolecular Science*. Blackwell Scientific Publications, Oxford.
- Fischer, D., Lappan, U., Hopfe, I., Eichhorn, K.-J., Lunkwitz, K., 1998. FTIR spectroscopy on electron irradiated polytetrafluoroethylene. *Polymer* 39, 573.
- Forsythe, J.S., Hill, D.J.T., 2000. The radiation chemistry of fluoropolymers. *Prog. Polym. Sci.* 25, 101.
- Forsythe, J.S., Hill, D.G.T., Logothetis, A.L., Seguchi, T., Whittaker, A.K., 1997a. Thermal and mechanical properties of radiation induced crosslinking of poly(tetrafluoroethylene-co-perfluoro methyl vinyl ether). *Radiat. Phys. Chem.* 30, 8101.
- Forsythe, J.S., Hill, D.G.T., Logothetis, A.L., Seguchi, T., Whittaker, A.K., 1997b. An NMR study of the radiation induced crosslinking of poly(tetrafluoroethylene-co-perfluoro methyl vinyl ether). *Macromolecules* 30, 8101.
- Iwasaki, M., Toriyama, K., 1967. Photoinduced and thermal radical conversions in gamma-irradiated copolymers of polytetrafluoroethylene-hexafluoropropylene as studied by electron spin resonance. *J. Chem. Phys.* 47, 559.

- Iwasaki, M., Toriyama, K., Sawaki, T., Inoue, M., 1967. Electrons spin resonance of gamma irradiated polytetrafluoroethylene-hexafluoropropylene copolymers. *J. Chem. Phys.* 47, 554.
- Lappan, U., Häußler, L., Pompe, Lunkwitz, K., 1997. Thermal stability of electron beam-irradiated polytetrafluoroethylene. *J. Appl. Polym. Sci.* 66, 2287.
- Lyons, B.J., 1995. Radiation crosslinking of fluoropolymers—a review. *Radiat. Phys. Chem.* 45, 159.
- Mark, H.F., Bikales, N.M., Overberger, C.G., Menges, C., 1988. *Encyclopedia of Polymer Science and Engineering*, Vol. 16. Wiley, New York, pp. 614–641.
- Nasef, M.M., Saidi, H., Dahlan, K.M., 2002. Investigation of electron irradiation induced-changes in poly(vinylidene fluoride) films. *Polym. Degrad. Stab.* 72, 85.
- Oshima, A., Tabata, Y., Kudoh, H., Seguchi, T., 1995. Radiation induced crosslinking of polytetrafluoroethylene. *Radiat. Phys. Chem.* 45, 269.
- Oshima, A., Ikeda, S., Seguchi, T., Tabata, Y., 1997. Temperature effect on radiation induced reactions in ethylene and tetrafluoroethylene copolymer (ETFE). *Radiat. Phys. Chem.* 50, 519–522.
- Rosenberg, Y., Siegmann, A., Narkis, M., Shkolink, S., 1992. Low dose gamma-irradiation of some fluoropolymers: effect of polymer chemical structure. *J. App. Polym. Sci.* 45, 783.
- Tanaka, R., Yotsumoto, K., Mizuhashi, K., Tamura, N., 1984. *Manual on CTA film dosimeter*. JAERI-Memo 6948.
- Zhong, X., Yu, L., Sun, J., Zhang, Y., 1993. XPS studies on radiation-induced structural changes in copolymer of tetrafluoroethylene and ethylene. *J. Appl. Polym. Sci.* 47, 21.