The Effect of Some Fluoropolymers' Structures on Their Response to UV Irradiation

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ABSTRACT: The response of three commercial fluoropolymer films, untreated and γ-irradiated poly(vinyl fluoride)(PVF), poly(vinylidene fluoride)(PVDF), and poly(ethylene-*co*-tetrafluoroethylene)(ETFE), to ultraviolet (UV) irradiation was studied. The changes in tensile properties, thermal behavior, and chemical structure were investigated. The UV resistance of the PVF film is the lowest, and that of ETFE is the highest among the studied films. The biaxially oriented PVF films undergo massive chain scission under the UV irradiation. The chain scission process in both oriented PVF and PVDF films, although at different levels, is accompanied by increased solubility, increased upper glass transition temperatures, and decreased elevated temperature shrinkage. The UV exposure at 50°C, above the polymers' T_g has annealing effects, mainly reflected by a shift to higher temperatures of their upper glass transition. PVF films are unaffected by a low-dose ionizing radiation. However, the γ-irradiated films show reduction of their UV resistance. PVDF films undergo both chain scission and crosslinking by γ radiation, and the addition of UV exposure mainly causes further chain scission. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1471–1481, 1998

Key words: fluoropolymer; gamma irradiation; ultraviolet irradiation; property; structure

INTRODUCTION

The interaction between polymers and irradiation energy of various wavelengths has been of great interest for quite some time. Of special interest has been the polymers' resistance to ultraviolet (UV) irradiation, on one hand, and the utilization of UV or γ irradiation to alter the polymers' performance through chemical and physical structural changes on the other hand. The response of polymers to various radiation sources depends on such parameters as the polymer chemical and physical structure, the radiation wavelength, in-tensity and duration, temperature, and environment. The main two processes induced by radiation are chain crosslinking and chain scission (degradation), the ratio of which determines the resulting polymer structure and properties.

The UV resistance of fluoropolymers mainly depends on the fluorine atoms content and their specific location along the polymer backbone. The UV resistance of essentially three fluoropolymers, namely, poly(vinyl fluoride) (PVF), poly(vinylidene fluoride) (PVDF), and poly(tetrafluoroethylene)(PTFE), was reported. Long-term UV irradiation of PVF and PVDF results in some adverse changes in the visible light transparency and changes in ductility and strength; the level of change was found to depend on the irradiation environment.[1–3] The level of the mechanical prop-

erties deterioration of PTFE was reported to depend strongly on the UV wavelength and the environment as well.[4,5]

The effect of ionizing irradiation, expressed as a ratio of chain scission to crosslinking events, in fluoropolymers was reported to depend strongly on their chemical structure and hydrogen content in the chain backbone.[6-8] The presence of hydrogen atoms may cause formation of unsaturated bonds, which then participate in intermolecular crosslinking, while other structural groups may create radicals of different structures, mobility, and stability. Polymers such as PTFE and poly-(tetrafluoroethylene-co-hexafluoropropylene) (FEP), containing no hydrogen atoms, mainly undergo chain scission. However, polymers such as PVF, PVDF, polytrifluoroethylene (PTrFE), and poly(ethylene-co-tetrafluoroethylene) (ETFE) undergo both chain scission and crosslinking; chain scission increases with an increase in the fluorine atoms content.[8-11] The ratio of chain scission to crosslinking events is higher when the irradiation environment includes oxygen, compared to vacuum.[12] The polymer chain scission causes a crystallinity increase, even at room temperature.[8,13] As far as the mechanical properties are concerned, both the tensile strength and ductility decrease at levels depending on the irradiation dose and the specific polymer studied.[10,14] Komaki[12] reported on the effects of sequential γ and UV irradiation of PVDF. Accordingly, the UV spectra of the PVDF samples suggested that γ irradiation resulted in the formation of conjugated double bonds while the following UV irradiation decreased their amounts. Furthermore, the exposure to UV irradiation, up to 160 h, of low-γ-dose-irradiated PVDF samples did not cause significant changes of the PVDF mechanical properties, while in high-γ-dose-irradiated samples, the UV exposure resulted in a dramatic decrease of the PVDF ultimate elongation, turning the ductile polymer into a brittle material.

The present article reports on the effect of γ and/or UV irradiation on some structure–property relationships of the following selected fluoropolymers: PVF, PVDF, and ETFE. The purpose of the present work is to shed more light on the effects of chain structure on the irradiation-induced changes.

EXPERIMENTAL

The three fluoropolymer films presently investigated included (1) biaxially oriented poly(vinyl fluoride)(Tedlar) from DuPont, Wilmington, DE, (CH_2—CHF); (2) unidirectionally oriented poly-(vinylidene fluoride) (Kynar) from Pennwalt, Bombay, India (CH_2—CF_2); and (3) poly(ethylene-co-tetrafluoroethylene) (Tefzel) from DuPont, Wilmington, DE, (CH_2—CH_2—CF_2—CF_2).

One series of films was exposed to UV irradiation in air at 50°C, using a QUV weatherometer, Q-Panel Comp., equipped with Uvb lamps (313–550 nm). The films were exposed for up to 2400 h, and samples were retrieved every 200 h. Another series of films was γ-irradiated (1–25 Mrad) in air, at a dose rate of 0.15 Mrad/h, using a ^{60}Co source. Some of these irradiated films were further exposed to the UV irradiation for 300 h.

The tensile properties of 10×1.5 cm^2 film strips were measured using an Instron-1126 machine, at a drawing rate of 0.5 cm/min. Thermal analysis of the films was performed using a Mettler TA 3000 DSC at a heating rate of 10°C/min. For the calculation of the degree of crystallinity, crystalline heats of fusion of 104.7 and 162.9 J/g for PVDF and PVF, respectively, were used (that of ETFE is presently unavailable). Infrared (IR) spectra of the various films were obtained using a Perkin–Elmer 157G Grating IR spectrometer. UV spectra were obtained using a Pye–Unicam Sp8-250 ultraviolet–visible (UV–vis) spectrophotometer.

Gel content in the irradiated PVDF films was determined using N,N,-dimethylacetamide (DMA) at 160°C. Samples, 0.3–0.5 g, encased in stainless steel screeds, lined with a filter paper, were immersed in the boiling solvent for 48 h, washed with the boiling solvent, dried in vacuum at 110°C for 24 h, and weighed. The gel content in the irradiated PVF films was determined, using N-dimethylformamide (DMF). The change in shrinkage of the irradiated-oriented PVF and PVDF films was determined by measuring the area change of 3×3 cm^2 samples after 3 h of heating in an air oven at a temperature 10°C below the polymer melting temperature.

RESULTS AND DISCUSSION

Exposure to UV Irradiation

The difference among the UV resistances of the three fluoropolymers, as reflected by their tensile properties, is depicted in Figure 1. The ultimate elongation of the PVF film decreases from 120 to 80%, after 800 h of exposure to the UV irradiation.
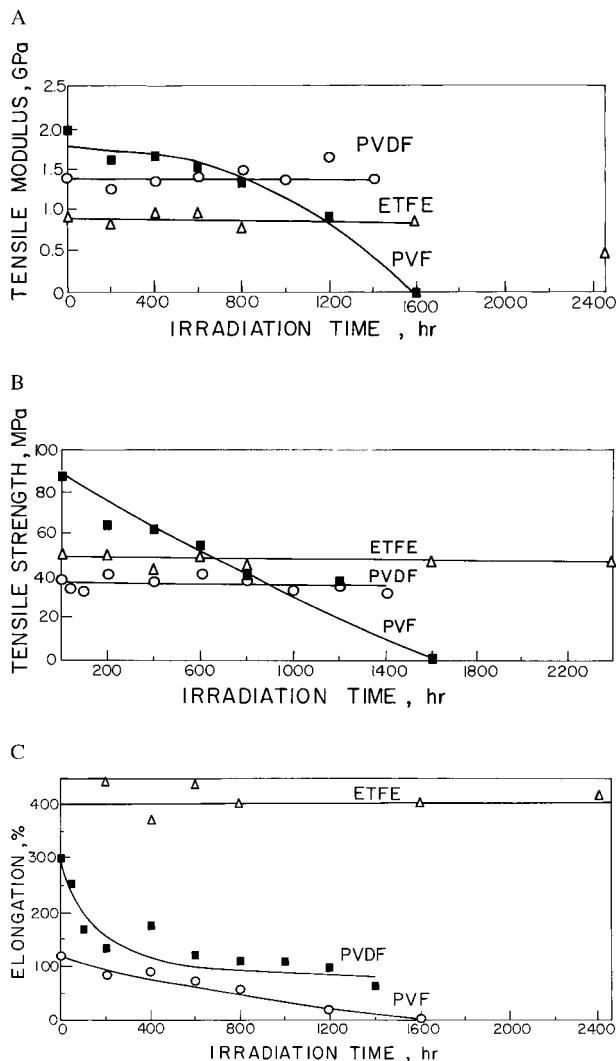
A

B

C

Figure 1 The effect of UV irradiation on the tensile properties of PVF, PVDF, and ETFE films: (A) Tensile modulus; (B) tensile strength; (C) elongation.

Further irradiation results in a larger drop in ductility, reaching practically zero elongation after 1600 h of exposure. The elongation of PVDF decreases from 300 to 120% by exposure up to 200 h; longer exposures do not seem to further affect the film's ductility. Interestingly, the elongation of ETFE is practically unaffected by the UV exposure, up to 2400 h. At the same time, the tensile strength of the PVF films gradually deteriorates with the UV exposure time, while that of the PVDF and ETFE films maintain their original values. Similarly, the elastic modulus of the PVF film decreases with exposure time, while those of the other two fluoropolymers remain practically unchanged.

To determine the effect of the UV irradiation

on the PVF chains, its extraction in boiling DMF[15,16] was attempted. Only 10 wt % of the original film was soluble; however, the insoluble fraction gradually and drastically decreased with the UV exposure duration, down to approximately 10 wt % after 1600 h (see Fig. 2). Thus, the solubility increase with exposure time different from the behavior of crosslinking-type polymers, is a result of the increasing net chain scission events. The solubility level of the PVDF films in boiling DMA was not affected by the UV exposure; hence, all films were fully soluble. The large changes observed in the PVDF films ductility and the maintained full solubility indicate that, largely, only chain scission events, rather than crosslinking, take place upon the UV irradiation. The predominance of chain scission is strongly supported by the elevated temperature shrinkage of both the PVF and PVDF oriented films. As depicted in Figure 3, the shrinkage of both polymers gradually decreases with the exposure time. As was previously reported for oriented PVC films,[17] the strained tie molecules in the oriented films were the first to be affected by the UV energy. Hence, since stretched tie molecules cause heat shrinkage, their scission reduces shrinkage at a level proportional to the amount of chain scission events.

Thermal analysis of the UV exposed films was performed by first heating to a temperature 30°C above melting (first run), cooling at a constant rate, and reheating (second run). The DSC first-run thermogram of all PVF samples shows both a glass transition and a melting endotherm, while in the second run, the T_g is not observable. The T_g, observed in the first run, considered as the upper glass transition,[18] gradually and signifi-
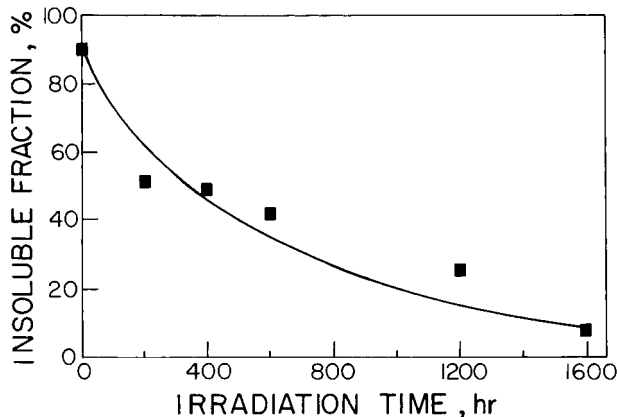

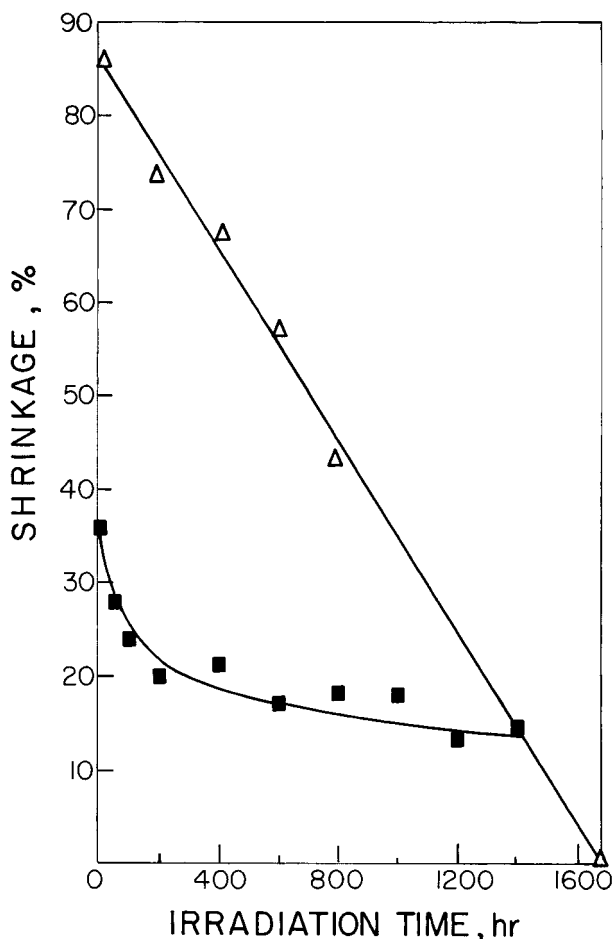**Figure 2** The DMA insoluble fraction in UV-irradiated PVF films as a function of irradiation time.

Figure 3 The shrinkage of UV-irradiated PVF and PVDF films as a function of irradiation time.

cantly increases with exposure time (Fig. 4). This T_g shift to higher values is probably due to annealing during the UV exposure at 50°C and the formation of oxygenated groups (the formation of the latter, increasing with exposure time, was proven by IR spectroscopy in the wavelength range of $1600-1800\ cm^{-1}$). The PVF films melting temperature measured in the first and second runs are quite similar, though the second run T_m is systematically somewhat higher than the first-run T_m. Both melting temperatures gradually decrease from 192 to 187°C, with UV exposure time up to 1600 h probably due to chain scission and oxidation. Simultaneously, the degree of crystallinity only slightly decreases with the exposure time. It should be mentioned that the second-run crystallinity of all PVF films, independent of the exposure time, is about 7% lower than that measured in the first run (20 and 27%, respectively, for the untreated film). Since there is only a slight effect

of the UV irradiation on the degree of crystallinity, and since the difference in the crystallinity between the two runs is quite constant, this difference mainly reflects the preferred orientation in the original films, which is lost upon melting, and some thermal history effects.

Interestingly, the DMF soluble fraction of the UV-exposed PVF, a fraction increasing with exposure time (see Fig. 2), exhibits lower T_m and crystallinity than the corresponding irradiated samples before extraction. Hence, the soluble fraction, although of a lower molecular weight, has, upon cooling from the melt, a less-ordered crystalline phase, probably due to chain branching and introduction of carbonyl groups during UV exposure in air.

The DSC thermograms of the PVDF films exhibit a second-order transition at 58°C, shifted to higher temperatures with UV exposure (Fig. 5), and a melting endotherm. Both melting temperature and degree of crystallinity of the first and second runs were only slightly affected by the UV exposure, up to 1400 h. The second-run melting endotherm for all the studied PVDF films is always sharper than the first run one, due to the different crystallization processes in the original and the recrystallized films.

Different from the T_m behavior, the lower temperature transition is significantly affected by the weatherometer exposure environment. This transition, so-called T'_β, has been assigned to PVDF molecular segments in the amorphous phase, anchored in both ends, namely, tie molecules and folds.[19-21] To ascertain the origin of the significant T'_β increase, from 58 to 75°C, after 1000 h of
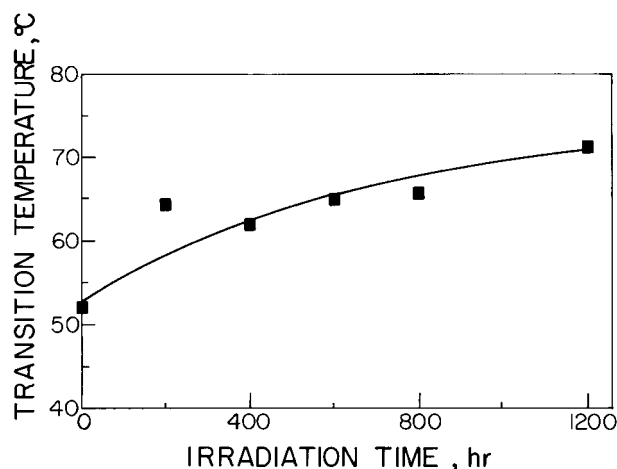

Figure 4 The upper T_g (first DSC run) of UV-irradiated PVF films as a function of irradiation time.

Table I   The Effect of Annealing of PVDE Films on Their T'_β Value

Annealing Temperature (°C)	Transition Temperature T'_β (°C)		
	Unradiated	UV-Irradiated (600 h)	UV-Irradiated (1400 h)
Unannealed	58	74	75
42	60	62	69
75	86	86	86
96	101	102	102
125	129	129	129
140	138	137	137

exposure, some PVDF films, original and irradiated, were heat-treated at various temperatures for 300 h. As seen in Table I, T'_β continuously increases with the annealing temperature; however, the values are practically identical for the three types of films (original and those UV-irradiated for 600 and for 1400 h). Thus, the shift in the T'_β values is caused mainly by the annealing rather than by the irradiation, in the weatherometer. This relaxation transition, typical to highly crystalline polymers, corresponds to the releasing of segmental mobility within the T_g to T_m temperature interval. The transition temperature is determined by the length and conformational state of the sections of molecules between lamellar crystallites.[22–24] The annealing leads to the thickening of crystallites at the expense of folded chains and tie molecules, resulting in their straightening and straining. Due to this process, the segmental mobility of these molecular elements becomes more hindered, and the corresponding transition temperature increases. The differences in the increasing T'_β temperature of the 42°C annealed films and the decreasing T'_β temperature upon annealing the irradiated films (see Table I) reflect the UV irradiation effect. The latter causes scission of tie chains and decreases the crystallites' limiting action on the amorphous segmental motion. Moreover, since strained chains are more susceptible to scission by radiation, the annealing process, described above, adds to the radiation damage. More chain scission occurs during the UV exposure step, causing decreasing film ductility and heat shrinkability (see Fig. 3). The foregoing analysis is generally also applicable to the UV effect on the PVF film. It should be mentioned here, however, that both the T_m and degree of crystallinity of ETFE were practically unaffected by the imposed UV irradiation (>313 nm).

Analysis of the UV exposure results show that there is a clear difference in the behavior of the three fluoropolymers. PVF seems to undergo large changes, ETFE is highly resistant, and PVDF exhibits an intermediate case. All three polymers consist of C—C, C—H, and C—F bonds, which, as being recalled in Table II, are prone to break upon exposure to UV irradiation. It is interesting to analyze what in the structure of the various fluoropolymers causes their different interactions with the UV light.

The C—F bond is too strong to be affected by the UV irradiation. The C—C bond is the weakest among the three relevant bonds. However, the fluorine atoms along the chain backbone presumably stabilize the C—C bond, increasing its resistance to the UV irradiation, an effect applicable to both ETFE and particularly to PVDF, in which half of the C atoms are directly bound to two F
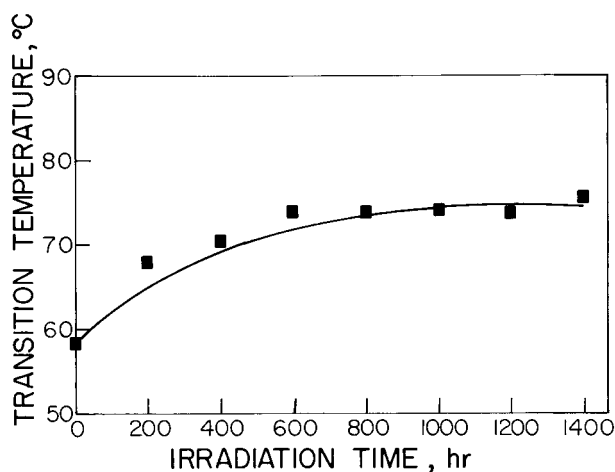

Figure 5   The T'_β (first DSC run) of UV-irradiated PVDF films as a function of irradiation time.

Table II Energy of Radiation in the UV Range and Some Typical Chemical Bond Strength Values

Radiation Wavelength (nm)	Energy (kcal/einstein)	Bond Type	Bond Energy (kcal/mol)
290	100	C—F	119
300	95	C—H	85–100
350	81	C—C	75–80
400	71	C—O	75–80

atoms. The PVDF films are, however, preferentially oriented, containing strained tie molecules in an amount increasing with exposure time, as discussed above. These high-energy PVDF chain segments are more sensitive to the UV irradiation and get scissioned in spite of the F atoms stabilization effect. The profuse chain scission in the PVF films is contributed to both the preferred orientation, as in the PVDF films, and its chemical structure, containing a vinyl fluorine. According to Makuuchi et al.,[17] UV irradiation results in a stable —CF* radical, which reacts with the air oxygen to form carbonyl and/or carboxyl groups through the C—C bond cleavage. This mechanism cannot be applied to PVDF since an unstable —CH* radical will be formed.[17]

Exposure to Sequential γ and UV Irradiation

To study the effect of chemical structural changes by ionizing irradiation on the UV resistance, films of two fluoropolymers, PVF and PVDF, were first γ-irradiated at doses up to 25 Mrad and then exposed to UV irradiation for 300 h.

PVF

The tensile properties of the PVF films are practically unaffected by the ionizing irradiation (up to 10 Mrad), as depicted in Figure 6. However, UV radiation, for just 300 h, of these films results in a gradually decreasing ultimate elongation with the γ irradiation dose down to practically zero for the 10 Mrad dose film [Fig. 6(A)]. The tensile strength of the irradiated, by both γ and UV, gradually decreases with irradiation dose [Fig. 6(B)]. The tensile modulus is practically unaffected by the γ irradiation, whereas the addition of UV irradiation is insignificant up to 5 Mrad films and deteriorating for the 10 Mrad films [Fig. 6(C)]. This behavior probably stems from a sequence of events. The low-dose ionizing irradia-

tion causes some chain scission[8,10] associated with the formation of double bonds along the PVF chain, as shown below, through the evolution of HF molecules. These events do not significantly affect the tensile properties; however, the following UV exposure in air causes the formation of carbonyl groups, as shown below, accompanied by chain scission. The number of these events increases with the ionizing irradiation dose, resulting in a gradual increasing films brittleness and lower strength, as seen in Figure 6.

The UV spectra, after subtracting the original film spectrum, and IR spectra of the irradiated PVF films are depicted in Figure 7. In the UV range, the absorbance at 226 and 274 nm are assigned to diene and triene (conjugated double bonds), respectively. The absorbance intensity at these two wavelengths significantly increases with the γ dose and, subsequently, practically disappear upon the UV exposure [Fig. 7(A)]. In addition, the IR spectra in the 1500–1900 cm^{-1} range of the PVF films [Fig. 7(B)] are sensitive to the sequence of radiations. The absorbance peaks at 1600, 1725, and 1850 cm^{-1} are assigned to —C=C—, —C=O, and —CF=O bonds, respectively. As seen in Figure 7(B), the ionizing irradiation results in an increase in the content of carbonyl and double bonds, while the addition of UV exposure causes a decrease in the double bond absorbance intensity. The addition of UV exposure results in an increase in the three absorbance peaks and the appearance of a peak at 1750 cm^{-1}, assigned to the —CF—C=O group. Hence, conjugated double bonds are formed mainly during the ionizing radiation and the addition of UV exposure mainly causes chain scission, accompanied by the formation of carbonyl groups. The results of these processes, due to irradiation, are also reflected by the DMF insoluble fraction data. This fraction in the PVF film decreases with the γ dose, from 90 down to 15% in the 0–25 Mrad
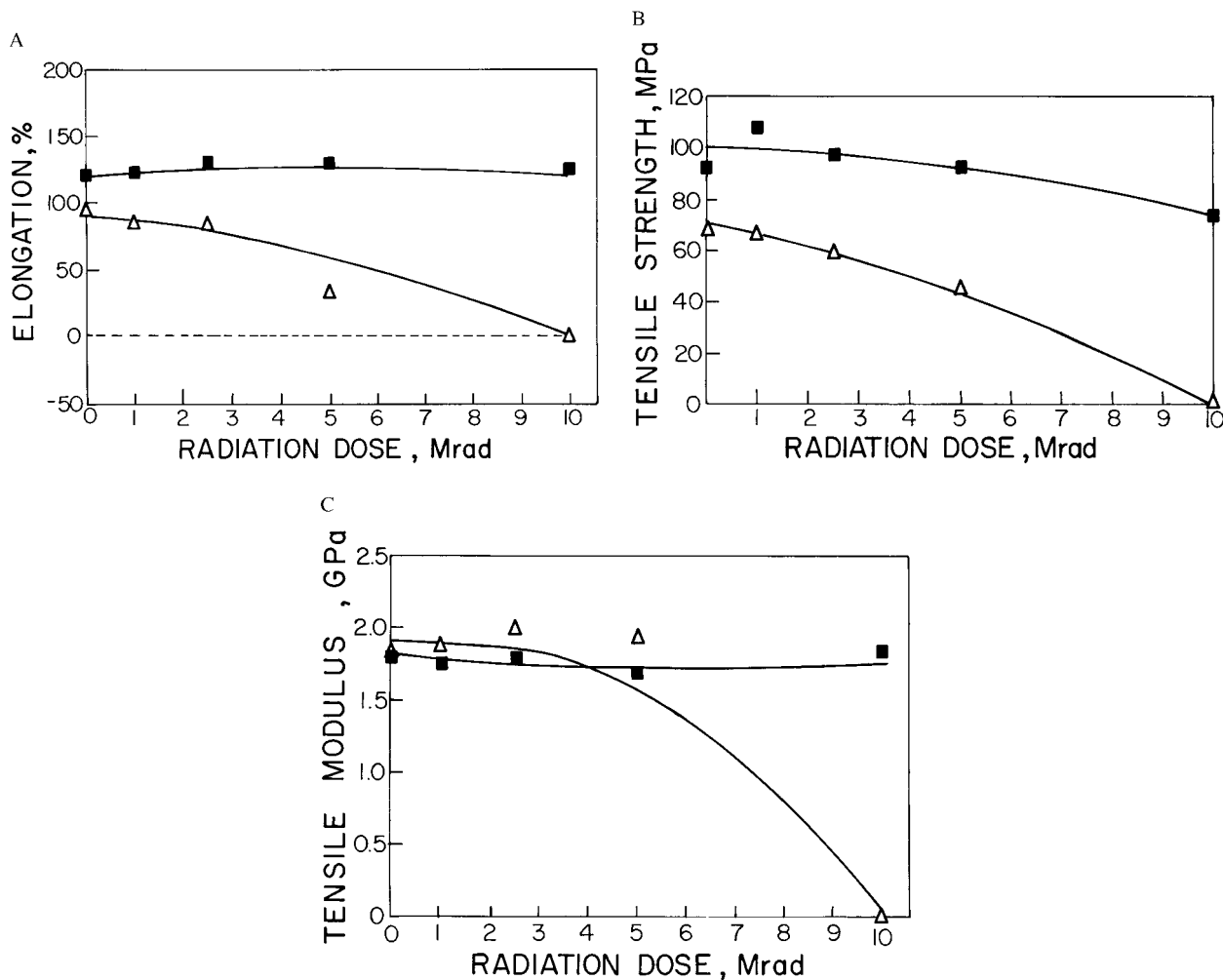
Figure 6 The effect of γ' (■) and γ + 300 h UV (△) irradiation on the tensile properties of PVF films as a function of γ irradiation dose. (A) Elongation; (B) tensile strength; (C) tensile modulus.

range. The addition of UV exposure decreases further the insoluble fraction, from 55 down to 0% in the same dose range (not shown). The increasing solubility may be a result of both molecular scission and increasing polarity due to the introduction of an increasing number of carbonyl groups, further supporting the above-suggested sequence of radiation effects.

The thermal behavior of the PVF films also reflects the radiation effects. The degree of crystallinity (Fig. 8) of the PVF film (first run) is practically unaffected by the γ irradiation, while the second-run crystallinity is significantly lower than the first-run crystallinity and gradually decreases with the γ radiation dose. Since γ irradiation takes place at ambient temperature, the resulting radiation effects do not cause changes in

the crystallinity, as found for the first run. However, recrystallization from the melt of the irradiated polymer reflects the observed changes in crystallinity caused by the chemical processes induced by the radiation. The gradual decrease already in the first-run crystallinity of the γ- and UV-irradiated films (Fig. 8) is actually caused by the UV exposure temperature (50°C). The direct effect of the addition of UV exposure on the first-run crystallinity cannot therefore be evaluated herein. However, Figure 8 shows that the second-run crystallinity is further decreased by the addition of UV exposure. The rather large difference between the first- and second-run crystallinity of the original PVF film should be noted, which is mainly a result of the original film preferred biaxial orientation, which relaxes upon the first-run
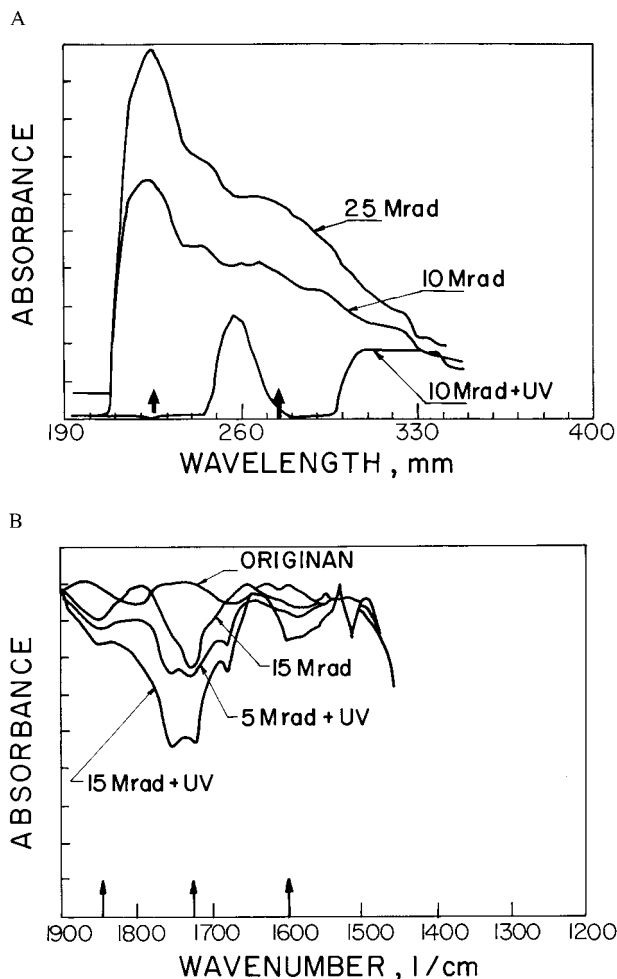
A

B

Figure 7 The UV (A) and IR (B) spectra of γ and γ + 300 h UV-irradiated PVF films.

Figure 8 The degree of crystallinity of γ and γ + 300 h UV-irradiated PVF films as a function of the γ irradiation dose: first run ($\square$, $\blacksquare$) and second run ($\triangle$, $\blacktriangle$).

age. The formation of both carbonyl groups (mainly in the presence of oxygen) and crosslinking (mainly in the absence of oxygen) leads, upon the annealing at the UV exposure temperature, to the observed shift in the upper T_g. It should be mentioned that no direct evidence for the crosslinking event was presently found.

PVDF

The response of the PVDF films to the sequential combination of ionizing and UV irradiation is quite different from that of the PVF films. The ultimate elongation decreases with increasing the γ dose (Fig. 10), much steeper than as a result

melting. The melting temperature (not shown) of the γ-irradiated films gradually decreases, from 194 to approximately 186°C, with the increasing radiation dose up to 25 Mrad; there is no significant difference between the first- and second-run T_m, excluding the maximal dose. The addition of UV exposure causes further melting temperature decrease down to 175°C for the 25 Mrad film. The changes in crystallinity and T_m resulting from the radiation treatments further support the suggested chemical processes associated with the irradiation. Interestingly, the upper T_g is only slightly affected by the ionizing radiation. However, its indirect effect on this transition is noticed after the addition of UV exposure (Fig. 9). As suggested above, the ionizing radiation mainly results in the formation of double bonds, whereas the subsequent UV exposure causes their cleav-
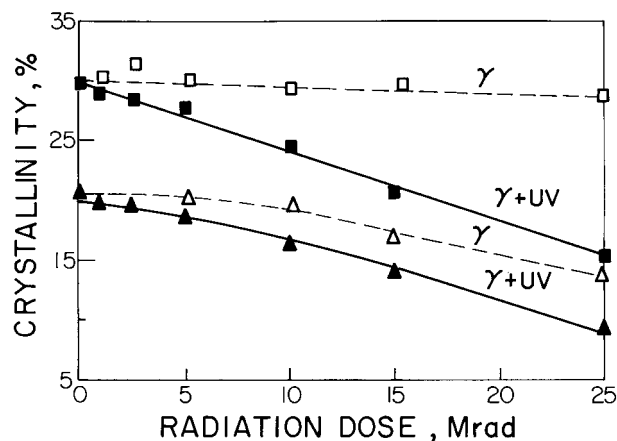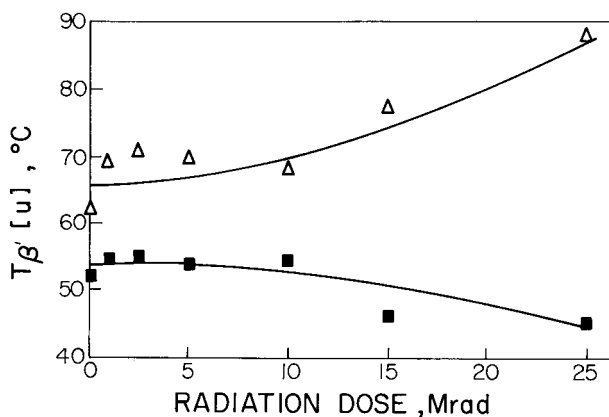

Figure 9 The upper T_g of γ ($\blacksquare$) and γ + 300 h UV-($\triangle$) irradiated PVF films as a function of the γ irradiation dose.

Figure 10 The ultimate elongation of γ and $\gamma + 300$ h UV-irradiated PVF films as a function of γ irradiation dose.

Figure 12 The T'_β (first DSC run) of γ and $\gamma + 300$ h UV-irradiated PVDF films as a function of the γ irradiation dose.

of just UV irradiation (Fig. 1). The addition of UV exposure causes further elongation decrease, down to practically zero for the 10 Mrad film. These changes in ductility are accompanied by minor changes in the films' ultimate strength and tensile modulus (not shown). This behavior may stem from either chain scission, crosslinking, or both.[8,10] In an attempt to ascertain the main events taking place during the radiation, affecting the mechanical behavior, solvent extraction experiments were undertaken. Irradiated films were extracted in boiling DMA and the resulting gel values are depicted in Figure 11. Practically no gel was formed in the low dose range, up to 5-Mrad irradiated films, including after their expo-
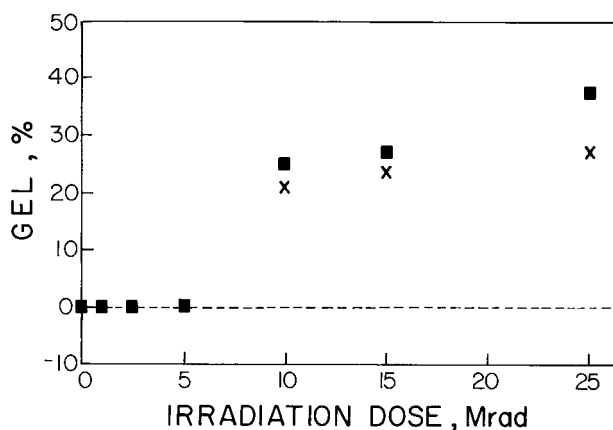

Figure 11 The gel content in γ and $\gamma + 300$ h UV-irradiated PVDF films as a function of γ irradiation dose.
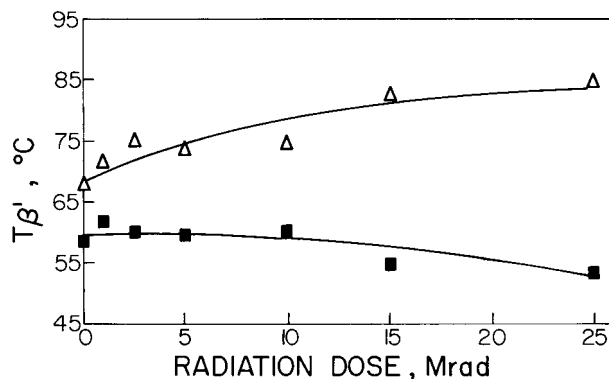
sure to UV. However, the higher dose films, γ and $\gamma + $ UV, contain a significant amount of gel, up to 38% in the 25-Mrad irradiated film, which decreases somewhat upon the addition of UV exposure. Hence, crosslinking has indeed occurred by the γ irradiation. The absence of gel in the lower dose films indicates that significant crosslinking did not occur; however, some grafting is possible. Analysis of the sol–gel results, using the Charlesby and Pinner equation,[25] yields an estimated ratio of scission to crosslinking events of 6 : 5. Thus, whereas the ionizing radiation results in both chain scission and crosslinking, the addition of UV exposure results mainly in some chain scission.

Further support for the above analysis was obtained by spectroscopy studies. The UV spectra, in the range of 190–330 nm, and the IR spectra, in the range of 1600–1900 cm^{-1}, of the PVDF films (not shown) show that the ionizing radiation results in conjugated double bonds, increasing with irradiation dose. The addition of UV exposure causes the opening of these bonds, resulting in (in the presence of oxygen) chain scission and carbonyl groups formation.

The PVDF crystallinity and melting temperature results for the irradiated PVDF films are not presented; their variation with radiation are not significant to add further information to the present discussion. Of interest is the behavior of the T'_β transition temperature (Fig. 12). The ionizing radiation, up to 10 Mrad, does not affect the T'_β value, while higher doses cause a slight shift to lower temperatures. However, the addition of UV exposure causes an upward shift, increasing with the γ dose. The 300-h UV exposure of the 25-Mrad

irradiated film causes T'_β to increase from 55 to 85°C. As mentioned above, this transition is shifted to higher temperatures due to the annealing effect during the UV exposure. However, the maximal value observed for the just-UV-exposed samples is 75°C after 1400 h of UV exposure (see Fig. 5). Since, in the present series of experiments (Fig. 12), the films were exposed to UV for just 300 h (the corresponding T'_β value for the just-UV-exposed film is approximately 70°C), the high T'_β value, 85°C, indicates that the UV exposure, following γ radiation, does affect this transition; just UV exposure, as shown above, does not affect this transition temperature. This behavior may reflect crosslinking events, rather than only chain scission events, occurring by the UV exposure, of chains containing double bonds, introduced by the earlier ionizing radiation, in agreement with the spectroscopy results. Since the crosslink density is expected to be rather low, based on the extraction experiments and literature reports,[11,15,26] the net effect of crosslinking and scission events on crystallinity and melting temperature is not large, as mentioned above.

CONCLUSIONS

The response of three commercial fluoropolymer films, of different chemical structures, to ionizing and/or UV irradiation, as reflected by their tensile properties, thermal behavior, and chemical changes, was investigated. The main conclusions drawn are as follows:

1. Films of PVF, PVDF, and ETFE respectively, exhibit, increasing UV resistance. PVF undergoes a quite severe degradation, ETFE doesn't show any significant alterations, and PVDF exhibits an intermediate response.

2. The UV exposure taking place at about 50°C, above the polymers' T_g, has annealing effects evidenced by a significant shift, increasing to higher temperatures with annealing time, of the characteristic polymers' upper glass transition. This annealing effect at a temperature of about 50°C is of interest, not just in the accelerated UV tests but also in practice.

3. The biaxially oriented PVF films undergo, upon exposure to UV, massive chain scission mainly by two mechanisms, as follows: Scission of strained tie molecules, strained due to the original preferred orientation and, in addition, due to the annealing effects; and formation of radicals, stabilized by the fluorine atoms, by the abstraction of hydrogen atoms in the vinyl position, followed by further hydrogen abstraction, which, in the presence of oxygen, causes chain scission and carbonyl groups formation.

4. The chain scission process in both oriented PVF and PVDF films, although at different levels, is accompanied by the formation of oxygen-containing groups, increased solubility, increased upper glass transition temperatures, and reduced heat shrinkage. Films of preferred orientation are less resistant to irradiation due to the strained chain segments, which increase in number with the films' degree of orientation.

5. PVF films seem to be unaffected by low-dose ionizing irradiation. However, the γ radiation decreases the films' UV resistance. The changes occurring by the γ irradiation, though not easily observed, play an important role in the subsequent accelerated degradation upon UV exposure.

6. PVDF films undergo both chain scission and crosslinking during ionizing irradiation. The subsequent UV exposure results mainly in further chain scission.

7. The shift of the PVDF T'_β to higher temperatures by γ + UV irradiation is larger than the shift due to just UV exposure; the latter mainly reflects annealing effects, while the former is due mainly to the chain crosslinking events during the initial exposure to the ionizing irradiation.

REFERENCES

1. M. J. Berry and H. W. Dursch, *Am. Chem. Soc. Symp. Ser.,* **220,** 99 (1983).
2. M. J. Berry and H. W. Dursch, *Solar Energ. Mater.,* **3,** 247 (1980).
3. E. Anagnostow, *Sci. Tech. Aerospace Rep.,* **17,** 3 (1965).
4. C. V. Stephenson, B. C. Moses, and W. S. Wilcox, *J. Polym. Sci.,* **55,** 451 (1961).
5. C. V. Stephenson and W. S. Wilcox, *J. Polym. Sci., Part A,* **1,** 2741 (1963).
6. *Encyclopedia of Chemical Technology,* Vol. 11, McGraw-Hill, New York, 1960. p. 24.
7. *Encyclopedia of Chemical Technology,* Vol. 11, McGraw-Hill, New York, 1960. p. 42.

8. Y. Rosenberg, A. Siegmann, and M. Narkis, *J. Appl. Polym. Sci.,* **43,** 535 (1991).

9. S. Straus and L. A. Wall, *SPE Trans.,* **4,** 61 (1964).

10. R. Timmerman and W. Greyson, *J. Appl. Polym. Sci.,* **6,** 456 (1962).

11. Y. Komaki and K. Ohtsu, *Nucl. Tracks,* **11,** 151 (1986).

12. Y. Komaki, *Radiat. Phys. Chem.,* **27,** 399 (1986).

13. K. D. Pae, S. K. Bahteja and J. R. Gilbert, *J. Polym. Sci., Polym. Phys.,* **25,** 717 (1987).

14. G. D. Sands and G. F. Pezdirtz, *Proceedings of the 150th National Meeting of the American Chemical Society,* American Chemical Society, Washington, DC, 1965.

15. Y. Rosenberg, M.Sc. thesis, Technion–Israel Institute of Technology, 1989.

16. *Encyclopedia of Chemical Technology,* Vol. 11, McGraw-Hill, New York, 1960. p. 57.

17. K. Makuuchi, M. Ajano and T. Abe, *J. Polym. Sci., Polym. Chem.,* **14,** 617 (1976).

18. *Encyclopedia of Polymer Science and Engineering,* Vol. 17, John Wiley & Sons, New York, 1986. p. 468.

19. C. Leonard, J. L. Halary, L. Monerie and F. Micheron, *Polym. Bull.,* **11,** 195 (1984).

20. R. F. Boyer, *J. Polym. Sci., Polym. Symp.,* **50,** 189 (1975).

21. M. Brierty, V. J. Douglass and T. A. Weber, *J. Polym. Sci., Polym. Phys.,* **14,** 1271 (1976).

22. E. Egorov and V. Zhihenkov, *Vysokomol. Soedin.,* **25,** 693 (1983).

23. V. Berstein, E. Egorov, V. Marichin and L. Myasnikova, *Vysokomol. Soedin.,* **27,** 771 (1985).

24. V. Berstein and E. Egorov, *Differential Scanning Calorimetry of Polymers,* Ellis Horwood, Chichester, 1992. p. 320.

25. A. Charlesby and S. H. Pinner, *Proc. Soc. London,* **249,** 367 (1959).

26. Y. H. Kao and P. J. Phillips, *Polymer,* **27,** 1669 (1986).