Effects Induced by Gamma Irradiation on Free-Volumes, Mechanical, and Thermal Properties of Flame- and Non Flame-Retardant Polyvinylchloride

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ABSTRACT: Flame-retardant polyvinylchloride (FRPVC), typically used in cable insulation and jacketing construction for multi-purpose reactor (MPR) at Atomic Energy Authority of Egypt, as well as carbon-black FRPVC (CB-FRPVC) and nonflame-retardant PVC and CB-PVC materials produced by Egyptian Electrical Cable Company (EECC), have been irradiated up to 160 KGy, at room temperature with a ^{60}Co gamma source. Free-volumes and thermal stability of irradiated and nonirradiated PVC samples have been examined using positron annihilation Lifetime Spectroscopy (PALS) and thermogravimetric analysis (TGA). In addition, the mechanical properties: tensile strength and elongation at break were examined. Considerable presence of flame-retardant and carbon black additives in CB-FRPVC sample led to both quenching and inhibition of Ps formation. The mechanical and thermal characterization showed that irradiation of PVC samples up to 80 KGy effectively induced cross-linking to maxima. Higher doses then after results in degradation and thus a decrease in mechanical strength. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 199–206, 2009

Key words: polyvinylchloride; free volume; positron annihilation lifetime; thermogravemetric; mechanical properties

INTRODUCTION

An extremely important factor in the selection of insulation and jacketing materials is the flammability and good mechanical strength. Polyvinylchloride (PVC) is an important material in cable insulation and jacketing, because it is considered itself as nonflammable due to the presence of chlorine in its structure.[1] The flame-retardancy of PVC can be improved by incorporating flame-retardant chemical elements as additives or as reactive which may significantly influence mechanical, thermal and electrical properties.[2,3]

Radiation cross-linking of wire and cable insulation was first introduced by Ray Chem Corp., USA. in 1957.[4] A unique advantage of this process is the capability of introducing a cross-linked structure to polymers at low temperatures. PVC substances exhibit a wide polymeric variety of radiation effects. These are manifested as changes in appearance, chemical and physical states.[5,6]

A detailed information about chemical and thermal degradation of polyvinylchloride (PVC) based materials is necessary in the assessment of eco-toxicological risk during accidental burning and/or recycling of building materials, cables and other postconsumer products based on PVC. A number of articles[7–9] were published to determine the thermal stability of polymer materials and mechanism of their thermal degradation. The volatile products of heating were detected to assess their risk during burning. The methods of thermal analysis DTA, TG and EGA were the most frequently used in investigation the thermal degradation processes.[3,10]

In the last few decades, a lot of effort has been made to quantify the free volume of polymers.[11] Free volume cavities or voids are open spaces resulting from the chain folding and molecular arrangements of chains. Positron annihilation lifetime spectroscopy (PALS), can determine directly the average free volume size and their relative number density.[12,13] When positrons emitted from ^{22}Na radioisotope enter into a polymer, they interact with surrounding molecules through elastic collision processes and may combine with an electron of the medium and annihilate as a free positron or form a bound state called positronium (Ps). The Ps exists either as a *para*-positronium (*p*-Ps, singlet spin state)

or as *ortho*-positronium (*o*-Ps, triplet spin state). Because *o*-Ps preferentially localizes in the free volume holes of polymer systems, their lifetime and intensity values (τ_3 and I_3) are sensitive to the properties of the matter in which they annihilate.[14,15] Furthermore, the effect of gamma irradiation on PVC has been investigated.[16–18]

The aim of this study is to recognize the changes induced by gamma irradiation on the mechanical, thermal and microscopic structure of flame and non-flame-retardant PVC insulation and jacketing samples using PALS technique.

EXPERIMENTAL DETAILS

Materials

Four samples have been studied: a nonflame-retardant PVC, a non flame-retardant PVC (CB-PVC) containing carbon black additive, a flame-retardant (CB-FRPVC), containing flame retardant and carbon black additives (42%). These three samples obtained from the Egyptian Electrical Cable Company, Cairo, Egypt, a flame-retardant PVC (FRPVC-reactor), used as cable jacketing of the reactor electrical boardroom at the Egyptian MPR, obtained from the Argentinean company (INVAP). The four samples used were in the shape of sheets of about 2 mm thick and density ~ 1.4 g/cm^3.

The relative concentrations of Cl, Ca, Pb, and Sb in the PVC materials were analyzed by X-ray fluorescence and listed in Table I. The CB-FRPVC material was examined previously,[19] and its structure was confirmed by organic analysis results using Schoniger's flask. The results in weight percentage are 42.5% for carbon, 5.3% for hydrogen with accuracy amounts to 0.2%.

Gamma irradiation treatment

The samples were gamma irradiated, in air, at room temperature and in ambient humidity. ^{60}Co is used as a gamma source (Gamma cell 4000 A) with activity of 9100 Ci. The absorbed doses were 40, 80,120, and 160 kGy at a dose rate of ~ 5 KGy/h at the National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt.

Positron annihilation lifetime measurements

Positron annihilation lifetime measurements were performed by using a convential fast-fast coincidence system in air at room temperature. A 20 µCi ^{22}Na positron source was deposited on a Kapton foil of 0.3 mm thickness and sandwiched between two similar pieces of each sample. The gamma rays with energies of 1.27 MeV,emitted from a β-decay of ^{22}Na

TABLE I
Relative Concentrations of Cl, Ca, Pb, and Sb in PVC Samples

Sample	Chlorine (Cl) %	Calcium (Ca) %	Lead (Pb) %	Antimony (Sb) %
PVC	1.85	1.16	4.57	0.00
CB-PVC	1.84	0.71	13.89	2.45
CB-FRPVC	857.01	273.36	169.15	113.17
FRPVC-reactor	927	114.98	77.29	52.03

source and those of 0.511 MeV, emitted from positron annihilation in a sample were measured by the start and stop counters respectively. Each spectrum has counts of about million and a time resolution of 230 ps full width at half maximum (FWHM). The average lifetime of spectra were analyzed through finite term lifetime analysis using PATFIT program.[20] The acquired lifetime spectra were resolved into three lifetime components τ_1, τ_2, and τ_3 with intensities I_1, I_2, and I_3, respectively. The shortest lifetime component (τ_1, I_1) is attributed to the annihilation of *p*-Ps, which is characterized by $\tau_1 = 0.125$ ns. The intermediate lifetime component, τ_2 with intensity I_2, is usually considered to be mainly due to annihilation of positrons with the free electrons at the polymer matrix- additive interface. The longest-lived component τ_3 with intensity I_3 is due to pick-off annihilation of the *o*-Ps localized in the free volume holes present mainly in the amorphous regions of the polymer matrix.[21]

According to the free volume model[22,23] for positronium formation, the longest lived component of the positron lifetime spectra, τ_3 and the correspondent *o*-Ps intensity, I_3 may be correlated with the mean radius and the relative number of the free volume cavity in the polymer material, respectively. According to this model, τ_3 should increase with increasing volume of the voids, and I_3 should increase with increasing number of the voids. In the free volume model, the *o*-Ps is confined in the spherical potential well and the lifetime of this species τ_3 is directly related to the free volume radius (R). Assuming that the annihilation rate of the *o*-Ps inside the electron layer of width ΔR at the internal surface of V_f is 2 ns^{-1}, the size of the V_f can be estimated through the following equation:

$$(\tau_3)^{-1} = 2\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]\text{ns}^{-1}, \quad (1)$$

and $V_f = 4\pi R^3/3$; R is the radius of voids in which the *o*-Ps survives and $\Delta R = R_0 - R = 0.1656$ nm is the width of the electron layer of the *o*-Ps annihilated by pick-off process.[21] The fractional free volume (%) is expressed as an empirically fitted equation[24] as:
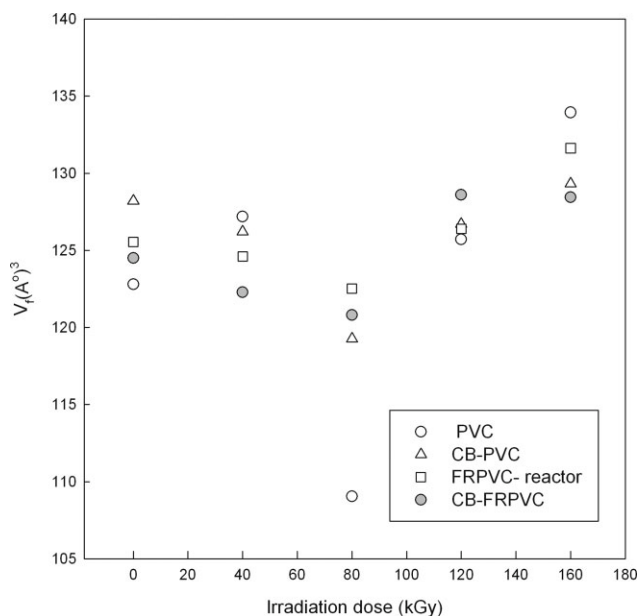
Figure 1 Average free volume size, V_f as a function of gamma irradiation doses for PVC samples.

$$f = AV_f I_3 \qquad (2)$$

where V_f (in Å^3) is the volume of free-volume holes calculated by using the spherical radius (R) of Eq. (1) from τ_3 in ns, I_3 in % is its intensity, and A is empirically determined to be in the range from 0.001 to 0.002 for common polymers.

Mechanical measurements

Tensile properties of the films were measured by using HOUNS FILD testing machine, England, connected to a personal computer. The ISO 37-1977 (E) and ISO 34-1975 (E) standards were followed to measure tensile strength and elongation.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using Shimadzu system, Type TGA-50, in nitrogen atmosphere 20 mL/min in the temperature range from ambient to 600°C at a heating rate of 20°C/min. Both peak maxima and temperature for wt loss were measured to characterize the thermal stability of the PVC samples.

RESULTS AND DISCUSSION

Effect of fillers and stabilizers on PVC

PVC itself may be considered flame retardant, because of the presence of chlorine in its structure, but when more flame retardants, fillers, and stabilizers, are added, the flammability can be more depressed. From the elemental analysis of CB-FRPVC sample and X-ray fluorescence results for all PVC samples (Table I), it is obvious that the investigated FRPVC-reactor and CB-FRPVC samples contain relatively larger amounts of additives compared with the nonflame-retardant samples. There are two flame-retardant additives, chlorine (Cl) and antimony (Sb) in the form of antimony oxide (Sb_2O_3). The Cl percentage may be present as an additive and in the constitution of the polymer itself.[1] Providing good mechanical and electrical properties. With a remarkable resistance to outside influence as Cl atoms increase attraction between chains of the polymer due to the C—Cl dipolar.[19] Sb_2O_3 is an important synergist when combined with a halogenated flame retardant, by extending the time that the halogen can be effective.[25] A stabilizer such as Pb is added to PVC samples as an acid scavenger, forming PbO, to inhibit acid generation by the decomposition of FRPVC materials. The acid must be stabilized or bound in the cable system to prevent corrosion of the conductor and to prevent further degradation of the polymer. It is well known that PVC material free from Pb degrades at 160°C. Addition of Pb stabilizer shifts degradation temperature up to 210°C.[19] Calcium in the form of calcium carbonate ($CaCO_3$) is added to PVC as filler, which gives a smooth surface and cost reduction. However, because of its spherical partial geometry, it does not significantly reinforce the compound and because of its high alkalinity, it can interfere with halogenated flame retardants. The addition of CB as a filler introduces an additional physical and chemical crosslinking to PVC, serving as an obstacle against the segmental motion. It is used for reinforcement against UV resistance as it absorbs UV radiation and inhibits decomposition of the polymer by sunlight.[25]

Positron annihilation results

Figures 1 and 2 show the discrete average values of free volume hole size (V_f) and its fraction (f) against dose for four PVC samples. It can be seen that gamma irradiation causes a continuous decrease in V_f up to 80 KGy. Meanwhile, Figure 2 reveals that by increasing gamma irradiation doses f decreases in both CB-PVC and FRPVC-reactor up to 80 KGy while it shifts to a higher dose value of 120 KGy in CB-FRPVC. However, for the PVC sample, an increase in V_f and f can be observed with gamma irradiation by 40 KGy, and then they show a rapid decrease by gamma irradiation of 80 KGy. It can be seen that there is an inflection point for PVC, CB-PVC, and FRPVC-reactor samples at 80 KGy, which shifts to 120 KGy in CB-FRPVC sample, then the values of V_f and f increase. Nevertheless the increase is much faster in PVC sample than in the other three
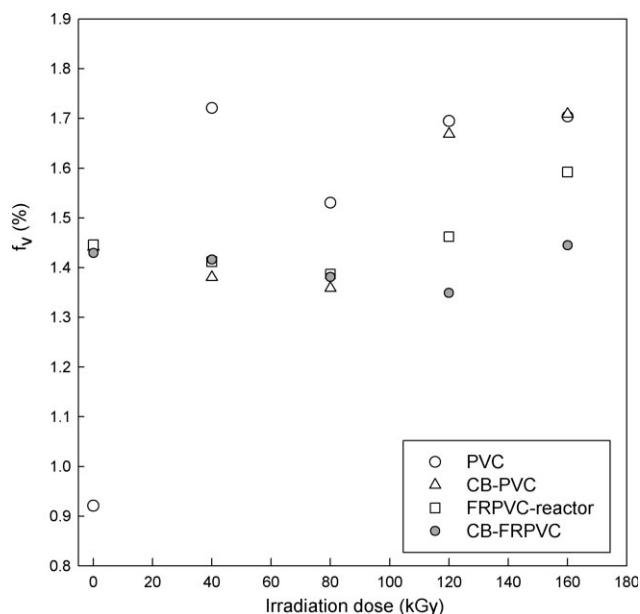
Figure 2 Free volume fraction $f_v\%$ as a function of gamma irradiation doses for PVC samples.

samples. The shift of inflection point of free volume fraction f to 120 KGy for CB-FRPVC can be ascribed to the fact that this sample contain carbon black and high amount of flame-retardant additives such as Cl and Sb, as listed in Table I, leading to both quenching and inhibition of Ps formation.[10]

For PVC sample, which is free from flame-retardant and carbon black additives, the low irradiation dose of 40 KGy can induce the formation of cross-links in the polymer.[26] Eventually forming a three dimensional network. As a result, the o-Ps size and its probability formation increases leading to an increase in V_f and f. Irradiation of PVC sample by more than 40 KGy results in formation of holes of smaller size where Ps annihilates. Thus, shorter free volume size and smaller fraction can be noticed as shown in the figures.

The decrease in free volume size (V_f) up to 80 KGy dose in CB-PVC, FRPVC-reactor and CB-FRPVC samples indicates that gamma irradiation causes contraction to the molecular sized free volumes. The size decrease might be attributed to the collapse of free volume because of chain scission or the formation of intermolecular double bonds and/ or intermolecular cross-link through the recombination of PVC radicals.[18] The production of free radicals by irradiation increases the electron density which decreases the o-Ps lifetime leading to a decrease in V_f. On the other hand, the slight decrease in free volume fraction f, which is a measure of the relative number concentration of free cavity sites in the samples, is due to the formation of conjugation bonds through degradation of PVC.

The observed increase in V_f and f after 80 KGy dose in all samples indicates that some of the larger free volume appeared where o-Ps can be trapped. It might cause the increase in average of free volume. This result shows that the increase in the number of chain ends accompanied by the successive chain cleavage predominates over the formation of conjugated double bonds. It is reported that,[27] irradiation by 160 KGy dose applied to PVC sample inducing the formation of reactive species namely tertiary and allylic chlorines.

Mechanical properties results

The mechanical properties are depending not only on the sample formulation, but also on the irradiation dose. Figure 3 shows the variation in the tensile strength of PVC samples at different gamma irradiation doses up to 160 KGy.

The effects of ionizing radiation cause cross-linking and degradation in polymers.[5] The cross-linking results in increasing mechanical properties up to a level where the degradation causes a decrease in mechanical properties. It is clear from Figure 3 that the tensile strength of the PVC samples increases with the irradiation dose indicating that cross-linking is the predominant process up to a dose of 80 KGy; however beyond that dose the degradation dominates over the cross-linking process leading to a decrease in tensile strength for all samples.

Moreover, the additions of carbon black CB to PVC introduces an additional physical and chemical cross-linking and inhibit decomposition of the
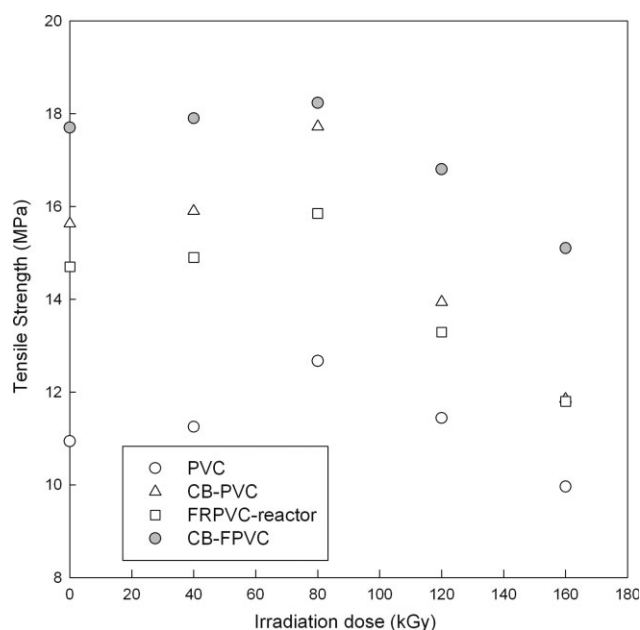

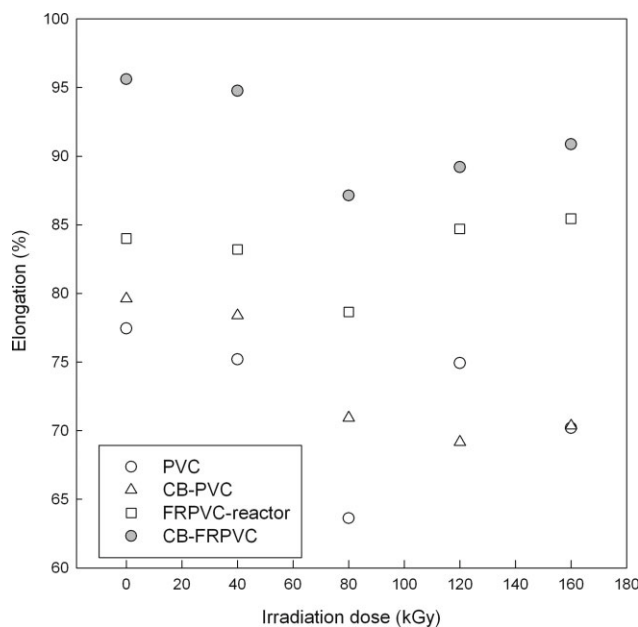**Figure 3** Tensile strength behavior of PVC samples at different irradiation doses.

Figure 4 Elongation behavior at break of PVC samples at different irradiation doses.

polymer.[25] The increase in cross-link density of the PVC samples by addition of CB is due to the presence of active cross-linking sites in the PVC samples, which continued to form cross-linking. As a result, CB-PVC and CB-FRPVC samples, show higher values of tensile strength than the other samples.

High energy irradiation of polymers creates free radicals by the scission of the weakest bonds. These new entities react with each other or with molecular oxygen if the exposure environment contains it. In addition, applied additives produce free radicals on irradiation. These radicals might react with polymer radicals to enhance cross-linking and chain scission in polymer matrix with an increase in irradiation dose. The enhanced cross-linking density may not necessarily increase the tensile properties of the polymer, because of the radiation induced scission of long polymer backbone chain and the brittleness character of the polymer induced at higher cross-linking density. As a result, irradiation doses more than 80 KGy decay the mechanical strength causing a decrease in tensile strength as shown in the figure.

Elongation at break of the samples depends upon the nature of the polymer and on the degree of cross-link, which restricts the movement of the polymer chain against the applied force. Figure 4 shows the variation of elongation at break, as a function of irradiation dose for unirradiated and irradiated PVC samples with different additives. It can be seen that elongation at break values decreases with a semi linear manner up to irradiation dose of 80 kGy, after which it increases slightly in CB-FRPVC and FRPVC-reactor, whereas it is almost constant in CB-

PVC and fluctuates in PVC sample up to 160 KGy. The slight increase of elongation at break in CB-FRPVC and FRPVC-reactor samples may be due to the presence of Ca as filler, which gives a smooth surface and delays the brightness character for the two samples.[19]

From the above results, it is concluded that the exposure to a total dose of 80 KGy confers satisfactorily mechanical parameters to PVC samples. Nevertheless, after gamma irradiation at 80 Kg, PVC samples lost the mechanical strength.

Thermogravimetric analysis

Thermogravimetric analysis was performed to investigate the effect of gamma irradiation on the thermal stability of the different PVC samples. The thermal stability behavior of the unirradiated PVC samples is displayed in Figures 5–9 show TGA thermograms of PVC irradiated samples within the temperature range 20–600°C. The data of thermograms, and the evaluation of temperature for 10, 25, and 50% weights, as well as the residual weight percentage at 600°C for unirradiated and irradiated PVC samples are summarized in Table II.

As shown in the figures the Thermogravimetric (TG) curves of the thermal degradation of PVC samples can be divided into two stages: the first stage is mainly due to the emission of hydrogen chloride. At this stage all the samples lost weight by about 40–60%. The thermal decomposition in the second stage is mainly due to the cyclization of conjugated polymer including cross-linking.[28] In general, the TG curves show many similarities between the PVC, CB-PVC, FRPVC-reactor, and CB-FRPVC samples. The char residue is high and increases by 28, 32, 24, and 38% respectively.

From the thermal stability behavior of the unirradiated PVC samples as shown in Figure 5, it can be seen that for a temperature up to ~ 280°C, the residual weight for PVC sample is lower than that of CB-PVC, FRPVC-reactor and CB-FRPVC indicating that the incorporated additives provide thermal stability to the copolymer matrix especially in the case of CB-FRPVC which contains high amount of flame retardant and carbon black.

In addition, it can be seen from the data given in Table II that unirradiated samples of PVC as well as CB-PVC, FRPVC-reactor and CB-FRPVC demos treated 10% weight loss at acquired 239, 246, 247, and 257°C whereas for the same samples with an irradiation dose of 40 kGy, the same weight loss was observed at 229, 252, 246, and 254°C, respectively. This shows that the addition of additives to unirradiated blend does not seem to exert any detrimental influence on the thermal stability.

TABLE II
Data Derived From TGA Thermogram of Gamma Irradiated Different PVC Samples

PVC sample	Irradiation doses (kGy)	Decomposition temperature (°C)			Residual weight % at 600(°C)
		TWL$_{10\%}$	TWL$_{25\%}$	TWL$_{50\%}$	
PVC	0	239	276	320	28.5
	40	229	264	310	24.8
	80	241	279	348	25.8
	120	233	268	313	25.3
	160	226	262	303	24.3
CB-PVC	0	247	280	317	32.3
	40	252	287	338	35.7
	80	244	284	325	35
	120	246	286	329	35.3
	160	207	271	306	24.9
FRPVC-reactor	0	247	281	314	24.9
	40	246	280	309	25.2
	80	245	279	313	28.5
	120	244	281	311	28.2
	160	243	278	306	27.6
CB-FRPVC	0	257	289	437	38.4
	40	245	279	313	32.3
	80	232	274	307	32
	120	238	278	319	36.3
	160	246	286	479	42.5

TWL 10%, TWL 25%, TWL 50% are the temperatures in °C at which occurs the 10, 25, and 50% weight losses, respectively.

From Figures 6–9 it can be concluded that: in the region of TWL 0–10% and TWL 10–25%, thermally initiated homolysis of the groups causes the scission of the PVC chains and this chain scission is associated with weight loss. In the region of TWL 10–60%, maximum decomposition of blends takes place. This may be attributed to enhanced cross-linking of the matrix in presence of additive that causes further increase in the cross-link density of the matrix.

From the above results, there is a correlation between the volume of nanoholes as measured by PALS and decomposition behavior determined by TGA. The higher mean volume of the cavity, the higher decomposition permeability. CB-FRPVC
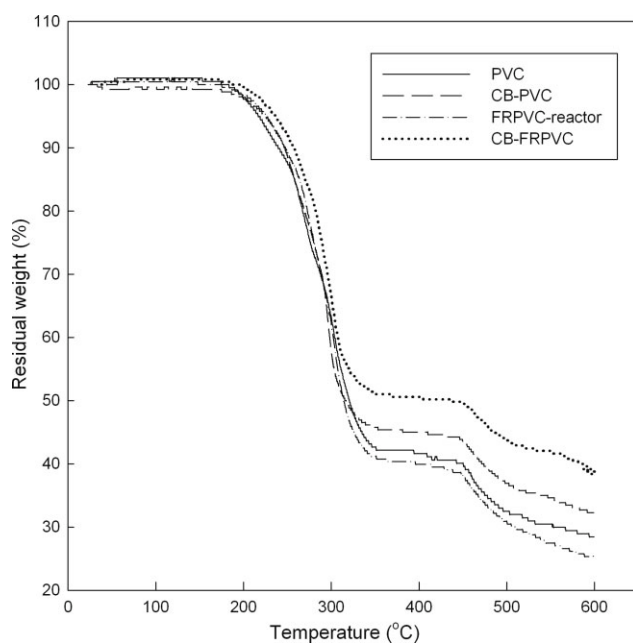

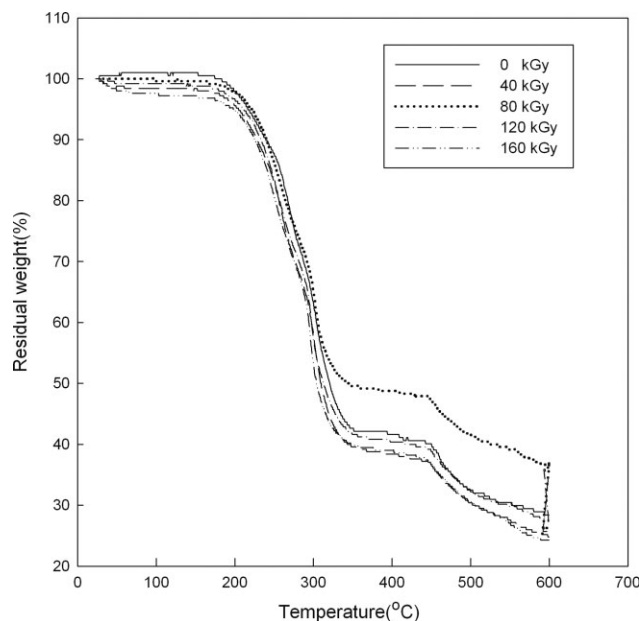**Figure 5** TGA curves of unirradiated different PVC samples.

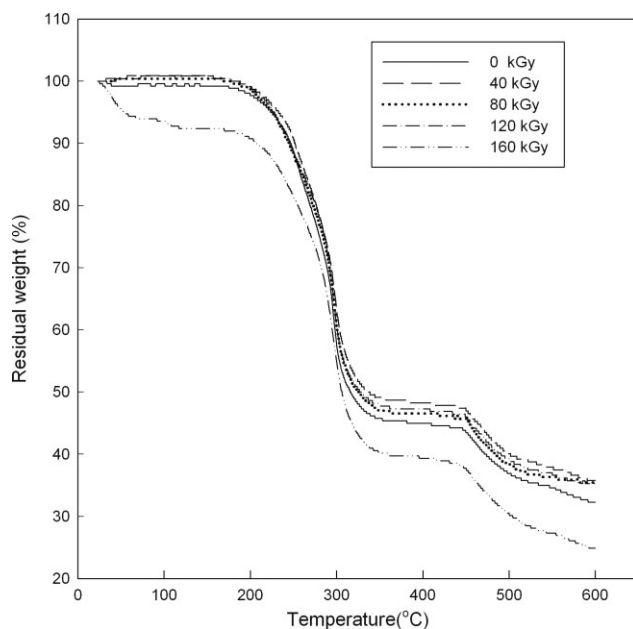**Figure 6** TGA thermograms of PVC before and after gamma irradiation (40, 80, 120, and 160 KGy).

Figure 7 TGA thermograms of CB-PVC before and after gamma irradiation (40, 80, 120, and 160 kGy).

Figure 9 TGA thermograms of CB-FRPVC before and after gamma irradiation (40, 80, 120, and 160 kGy).

sample possesses the smallest average volume of nanoholes and this explains its lower decomposition at high doses, whereas PVC sample shows the highest value of nanohole mean volume and this agrees with its maximum decomposition at high doses. In addition, The PALS results correlate with mechanical properties, where the irradiation dose above 80 KGy is too high inducing the formation of reactive species and an increase in free volume size leading to trapping Ps. On the other hand, higher irradiation than
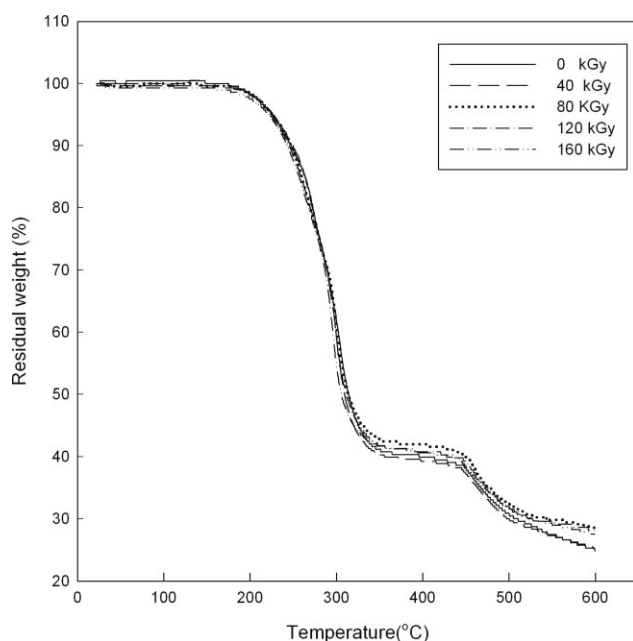
80 KGy exerts damaging effects that induced scission of long polymer backbone chain and brittleness character of the polymer at higher cross-linking density. The presented results show that changes and damaging effects of radiation on PVC samples are small up to 80 KGy in most instances.

CONCLUSIONS

The results indicate that the implemented radiation doses affect the characteristics of PVC samples at structural levels as studied by PALS which can be correlated with the macroscopic mechanical properties and with TGA measurements. From the results of PALS, the different V and f values before and after irradiation indicate that free volume size in the investigated samples changes. Also, the large amount of flame retardant and carbon black additives in CB-FRPVC sample leads to both quenching and inhibition of Ps formation which results in shifting degradation to higher values than that of the other samples. The results of TGA and mechanical measurements showed that cross-linking is predominant up to a dose of 80 KGy and the samples exhibit satisfactory mechanical properties. However beyond that dose the degradation dominates and the PVC sample lost its mechanical strength.

Figure 8 TGA thermograms of FRPVC-reactor before and after gamma irradiation (40, 80, 120, and 160 kGy).

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