Using COC as Pharmaceutical or Cosmetic Storage Material. II. Effect of Electron Beam Radio-Sterilization

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ABSTRACT: This study was performed on cycloolefin materials. These polymers are more and more used in the cosmetic and pharmaceutical fields. Samples were subjected to an electron beam radio-sterilization. Different irradiation doses ranging from 25 to 150 kGy were used to study the irradiation effect on the structure and properties of the material. In this study, we were mainly interested in additive degradation, and in the modification of polymer thermomechanical properties, as elasticity, glass transition temperature, and swelling ability. Although the modification of the polymer chains was important, effect on thermomechanical properties was quite weak. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1829–1839, 2008

Key words: cycloolefins; ageing; electron beam irradiation; antioxidants

INTRODUCTION

During the last few years, radio-sterilization has been extensively used to sterilize medical devices and pharmaceutical packaging. Ionizing radiations provide indeed an interesting alternative to autoclaving or dry heat sterilization that can damage materials and lead to problematic losses of shape and mechanical properties. Gamma radiation is one of the most commonly used methods, but electron beam technology, which is able to deliver high doses in a short time (several tens of kGy per second) competes with this traditional ionizing technology that delivers tens of kGy per hours. Both methods are known to produce free radicals, by breaking the molecular chain bonds of polymeric materials. The free radicals are able to bond with other molecules in their immediate vicinity. This can lead to crosslinking, to unsaturations in the polymer chains and grafting of oxidation groups as peroxide, alcohol, and carbonyl functions.[1–3] Oxidation, crosslinking, and scission can severely affect the mechanical properties. A crosslinked polymer is generally stronger but less ductile whereas shorter chains have worse thermomechanical properties with a greater sensitivity to creeping.

Moreover these scissions are responsible for the formation of radiolysis products of low molecular weight. A lot of volatile products have been detected after radio-sterilization, such as alcohols, carboxylic acids, ketones, aldehydes, and alkanes.[4] These degradation products are firstly trapped in the polymer but they can further migrate. Migration of these potential toxic species is an important safety problem in the field of pharmaceutical or cosmetic packaging and should be thus quantified.

It should be noticed that these modifications strongly depend on the polymer structure, the dose, the irradiation atmosphere, and on the amount of antioxidants added to the polymer. Moreover degradation process will continue after irradiation. This is due to the trapped free radicals that will be able to react even when the sterilization has been performed since a long time.[5]

In this study, we studied the behavior of cycloolefine polymers under irradiation. These thermoplastic and amorphous polymers are more and more used in the cosmetic and pharmaceutical packaging but are quite new compared with other well-studied packaging polymers such as PP or PE. We showed how these polymers and their antioxidants were degraded with the irradiation dose. We studied the potential migrants generated by irradiation, the influence of antioxidant concentration on the polymer degradation, and the poststerilization ageing process. At least, we estimated the consequences of the polymer degradation on the thermomechanical properties of the material. A dose of 25 kGy, which is commonly used for sterilization, was chosen as the lowest dose in our study.

EXPERIMENTAL

Polymer

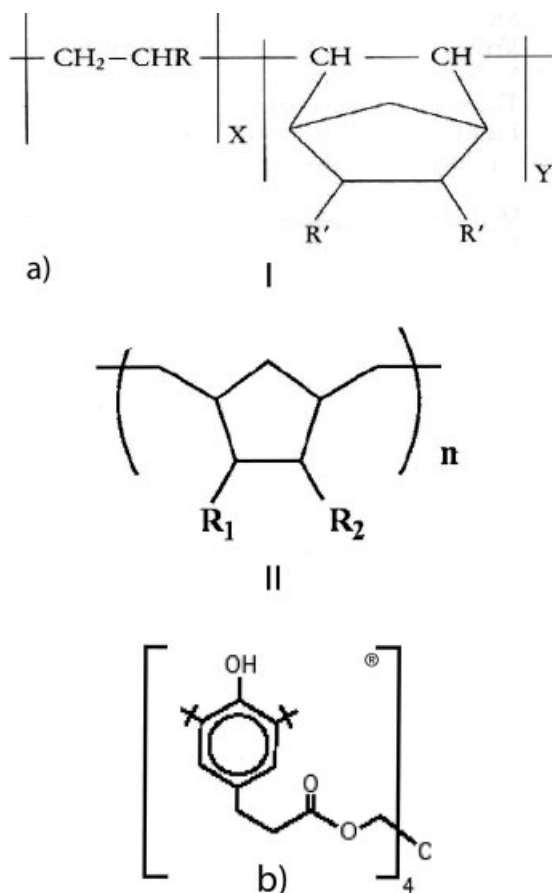We mainly used a cycloolefin copolymer (COC) called TOPAS 8007® [Fig. 1(a)] supplied by Ticona.

Figure 1 (a) Formula of TOPAS® (I) and ZEONOR® (II) cycloolefins (b) Formula of Irganox 1010®.

It was used as granules, or as plates 1 or 3.25 mm thick. This polymer is an ethylene and norbornene based copolymer. To compare the effect of irradiation with another cycloolefin having a different antioxidant content, we used a cycloolefin polymer produced by Zeon company (granules), called ZEONOR 750R®. It was obtained by ring opening polymerization of norbornene. This polymer has a T_g of 70.5°C, which is comparable with the T_g of TOPAS® 8007 (78.5°C). Moreover, to see the influence of T_g on the oxidation in the postirradiation ageing, another ethylene/norbornene copolymer of higher T_g (135°C)

was used (TOPAS 6013® from Ticona) for oxidation study by FTIR. Table I sum up the samples used and analysis done on them.

Sample irradiation

Samples were irradiated by an electron beam produced by a high power generator (10 MeV) from a 10 kW power accelerator (Ionisos, Fr.). Samples were exposed to three different irradiation doses: 25, 75, and 150 kGy. They were packed under ambient conditions in glass bottles.

Sample preparation and storage

For additive analyses, polymeric granules were used. The 1 mm thick plates were used to perform IR analysis and the 3.25 mm thick plates for mechanical measurements. Swelling ratio analyses were performed by thermogravimetric analysis (TGA) on granules. For mechanical measurements the samples were plane-parallel: the sections S ($S = hl$) and the lengths L were similar for all the samples ($L = 44.9 \pm 0.1$ mm, $l = 5.93 \pm 0.05$ mm, and $h = 3.25 \pm 0.01$ mm). l was set to different values for some samples to prove there was no effect of the sample width on the result obtained ($4 < l < 6$ mm).

Prior to differential scanning calorimetry (DSC) analysis, samples were heated 10 min in the crucible at 160°C to give to all of them the same initial thermomechanical history and to assure a good contact between crucible and sample.

Irradiated samples were stored in the fridge (5°C) to reduce the poststerilization ageing effects. Poststerilization ageing was specifically studied by storing some of the samples in glass vials at 83°C during several weeks.

Additive extraction

To identify and quantify the additives in the polymer and their eventual degradation products, we used a dissolution/precipitation process. Amount of 3 g of polymer were dissolved at reflux in 50 mL of

TABLE I
Summing-up of the Polymer Samples Used and of the Analysis Done on Them

Polymer Commercial Name	Shape	T_g (°C)	Done Analysis
TOPAS 8007	Granules	78.5	Study of antioxidant and of its degradation products (extraction +HPLC), DSC, SEC, dissolution tests, soxhlet, swelling tests (ATG), oxidation (FTIR)
	Plates 1 mm thick		Oxidation, aging (FTIR)
	Plates 3.25 mm thick		Mechanical tests
TOPAS 6013	Plates 1 mm thick	135	Aging (FTIR)
ZEONOR 750R	Granules	70.5	Study of antioxidant in polymer (extraction + HPLC), SEC, DSC, oxidation (FTIR), dissolution tests

toluene (HPLC grade Carlo Erba) at around 70°C under stirring. After complete dissolution, the polymer was precipitated by slowly adding 50 mL of methanol under stirring. For the TOPAS 8007® 150 kGy irradiated sample, the polymer was only partly soluble. Polymer was then removed from the additive solution by filtration on a paper filter and the precipitate was carefully rinsed with methanol. Solutions containing potentially additives, oligomers, and degradation products were then evaporated by rotavapor at 60°C (under vacuum).

Additive analysis

Before injection in the HPLC system, the dry residue containing additives, oligomers, and degradation products was dissolved in a mixture of 0.5 mL of tetrahydrofuran (HPLC grade Prolabo) and 0.5 mL of acetonitrile (HPLC grade Prolabo). Solution was filtered on a 0.45 μm Teflon filter.

We used an RP-HPLC method, which was previously developed in the laboratory to analyze additives in pharmaceutical polymers. This method used three mobile phases composed by a mixture of one up to five solvents (methanol, acetonitrile, tetrahydrofuran, water and ethyl acetate all HPLC grade), and a gradient elution that consisted on linear gradients from one mobile phase to another. The apparatus used was constituted of a gradient pump Spectrum System P4000 (TSP) (flow rate of 1 mL/min), of an automatic injector AS 3000 Spectro System (TSP), and of an UV detector Spectro System 1000 (TSP); the detection wavelength was of 280 nm. The column was a LiChrocart 250-4 RP select B (5 microns) Lichrosphere (Interchim). The injection volume was of 20 μL. Acquisition was done using the Chromquest software (TSP, version 3.0). Identification of the additives in the extracted solutions was performed by comparing their retention times with those of pharmaceutical additive standards (Irganox® from Ciba and BHT from Sigma). Quantification was carried out by establishing a calibration plot with prepared solutions of known concentrations in additives.

Soxhlet extraction

Soxhlet extraction was used to calculate the insoluble ratio of polymer chains with toluene as solvent. The soxhlet extraction duration was of 24 h. Samples and cellulose thimbles were weighed before extraction and after extraction (they were previously dried). The mass of polymer after extraction correspond to the insoluble part of the polymer (crosslinked chains).

FTIR

The spectrometer apparatus was a Perkin–Elmer Spectrum 2000. It was used in the ATR (attenuated total reflection) mode with a diamond crystal (golden gate–Specac) and in transmission mode. To express band intensity we used the height of the band. The wavelength range was from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1} during 16 scans.

Differential scanning calorimetry

DSC analysis was performed on a TA instrument Q1000 in a modulated mode. The modulation parameters were the following: the amplitude was of ±1°C, the period was of 60 s and the heating rate was of 3°C/min under nitrogen blanketing. The temperature ranged between 40°C and 160°C. Hermetical aluminum pans (20 μL) were used.

Thermogravimetric analysis

TGA was used to study polymer swelling by a given solvent. The apparatus was a Perkin–Elmer TGA7. The temperature ranged between 35°C and 470°C. It was used under nitrogen blanketing, and the analysis was stopped just before the polymer's degradation temperature was reached. The scanning heating rate was of 20°C/min.

Mechanical tests

Mechanical tests were done with plane-parallel samples using a micro-press prototype developed by Digipharm and our laboratory.[6] The Young's modulus and the yield stress (maximal stress) were obtained using a three point single beam test. The experimental procedure and the evaluation of mechanical properties were described in details in previous work.[7] The parallelepipes were placed on two cylindrical supports and stressed using a 2 mm flat punch pushing on a cylindrical stainless steel beam at constant velocity 0.200 mm min^{-1}. The forces applied versus the beam deflexion were recorded. The material was flexed till the sample broke or till the deflexion reached 5 mm. Six samples were tested for each irradiation dose. The Young's modulus E was obtained from the slope of the linear part of the loading curve and calculated using the following equation:

$$E = \frac{F\,p^3}{4\,d\,h^3\,l}$$

where F is the load applied, p the distance between the two supports (p = 34.12 mm), d is the central deflexion and h, l are the thickness and the width of the sample, respectively.

Second, the maximal load applied F_{max} was measured and used to calculate the yield stress (σ_y) using this equation:

$$\sigma_y = \frac{3\,F_{max}\,p}{2\,h^2\,l}$$

Size exclusion chromatography

Size exclusion chromatography (SEC) analysis was performed at 60°C in toluene on a PL laboratory PL-GPC 220: two detectors were used, a RI detector and a viscosimeter. The solvent flow was of 1 mL/min. The polymer concentration was around 6 mg/mL. About 200 μL were injected onto two PL laboratory Mixed B 10 μm columns (300 × 7.5 mm), which span a wide range of molecular weight (500–10,000,000 g/mol). TCB was used as a flow-rate marker and narrow polystyrene standards were injected to quantify the molecular weight. The following molecular weights were used:

$$M_n = \frac{\Sigma N_i M_i}{\Sigma N_i}, \ M_w = \frac{\Sigma N_i M_i^2}{\Sigma M_i N_i}, \ \text{and} \ M_z = \frac{\Sigma N_i M_i^3}{\Sigma N_i M_i^2}$$

where N_i is the number of chains having a molar mass M_i

RESULTS AND DISCUSSION

Degradation of the antioxidant

Amount of extractable antioxidant

The phenolic antioxidant found in the polymers was Irganox 1010[R] [Fig. 1(b)]. The extracted amount was around 1470 ppm in TOPAS 8007[R] but much higher in ZEONOR[R] (3500 ppm). As the irradiation dose increased, both cycloolefins showed a significant decrease in the extractable level of their antioxidants (Fig. 2). For the lower doses, the amount of degraded Irganox 1010[R] was quite the same for the both polymers (around 1000 ppm after a 25 kGy irradiation). It is well known that sterically hindered phenols such as Irganox 1010[R] gradually degrade with the increase of the irradiation dose, but this degradation leads to two processes that do not have
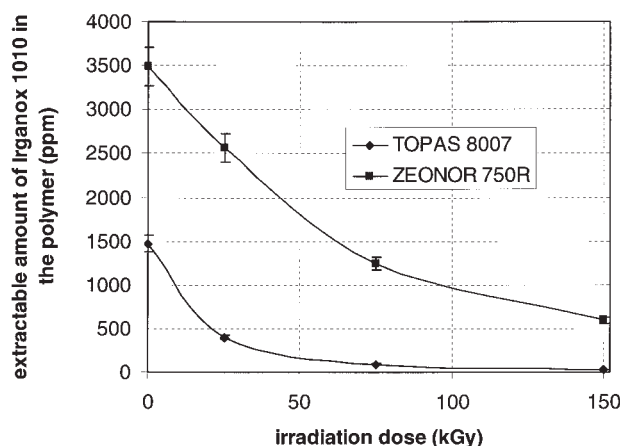

Figure 2 Evolution of the extractable amount of Irganox 1010[R] in TOPAS 8007[R] and ZEONOR 750R[R] with the beta irradiation dose (n = 5).

the same consequences. The degraded molecules may be to some extent covalently bound to the polymer chains[8] whereas a part of the antioxidant gives rise to some free and mobile degradation products.

Study of the extractable degradation products of antioxidant

Studying the free degradation products is an important deal because these molecules, of lower mass than the primary antioxidant, may then migrate more easily from the polymer into the pharmaceutical or cosmetic formulation and may induce toxicity. For Irganox 1010[R], the degradation products had been studied by Bourges and Allen.[9–11] Bourges found four main degradation products after irradiation and postirradiation reactions: a phenol, a quinone,[9] a quinone methide, and a hydroxylbenzaldehyde.[11] Allen[10] was able to detect 56 different components in a 50 kGy electron beam irradiated polypropylene sample, but most of them were in very low concentration and could not be identified by mass spectroscopy.

To study these potential migrants, we followed for TOPAS 8007[R] the evolution of extractable degradation products by HPLC analysis. In our case, we must remind that:

- some of the degradation products might result from a postageing process promoted by the extraction process: during extraction, the irradiated polymer was heated at 60–70°C in organic solvent during around 45 min.
- as the detector was an UV one set at a wavelength of 280 nm, only the degradation products absorbing in this area and thus containing aromatic cycles could be detected. No degradation products of the single polymer might be detected unless they had recombined with aromatic fragments of the additive (Irganox 1010[R] contains four phenolic groups).

Chromatograms of the extracts corresponding to irradiated and nonirradiated polymers were compared. On the chromatogram of the extract corresponding to the nonirradiated sample, there was a major peak assigned to Irganox 1010[R] and three little peaks (labeled 1, 2, 3 on Fig. 3) corresponding to synthesis residues of Irganox 1010[R]. All these peaks decreased with irradiation dose and had almost totally disappeared for the 150 kGy dose. In counterpart, some new chromatographic peaks appeared.

For a 25 kGy dose, there was a dozen of new peaks at short retention times t_r (t_r < 30 min or A zone). In our RP-HPLC system, the smaller retention times correspond to the more polar and to the smaller molecules. The peaks located in A zone were
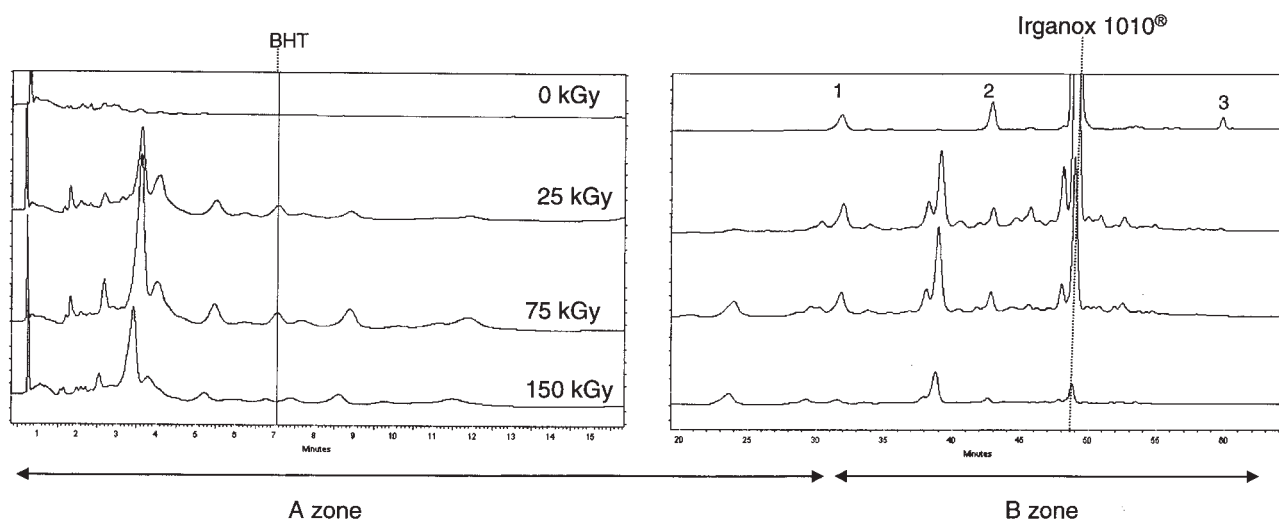
Figure 3 HPLC chromatograms of the TOPAS 8007® extractables for nonirradiated sample and 25, 75, and 150 kGy irradiated samples. The detection was performed by an UV detector at a wavelength of 280 nm.

thus characteristic of small molecules. Among theses peaks, one might correspond to BHT (butylhydroxytoluene) (retention time at 7 min same as the standard). A great number of other peaks corresponding to larger degradation products (with 1–4 phenolic cycles in their structure or containing polymer chains fragments in their structure) were detected in the B zone (30 min $< t_r$) even at retention times greater than that of Irganox 1010®.

For the 75 kGy dose, a significant decrease of the peaks characteristic of larger degradation products (B zone) was observed. On the contrary, the peaks located at shorter retention times (A zone) increased in intensity. This suggested that there was a further degradation of the longer degradation molecules by cleavage, to form smaller degradation products.

For the 150 kGy dose, there were almost no more large degradation product left (there were only few peaks located in the B zone and of very small intensity), and even the intensity of peaks located in the A zone decreased: for example, the peak assigned to BHT disappeared. For such high doses the degradation products might be smaller and thus more volatile: they might have disappeared before HPLC analysis was done, because of the heat produced during the irradiation or the extraction process. For such doses there might be also a bigger covalent binding of degradation products on the polymer chains.

This HPLC study on Irganox 1010® degradation in TOPAS 8007® had shown that the degradation products of Irganox were further degraded by increasing the irradiation dose. This had two major consequences:

- the 25 kGy dose generated higher number of extractable degradation products than 75 or 150

kGy, that is to say a higher number of potential migrants.
- degradation products might be degraded instead of antioxidant as dose was increased. It might partly contribute to the slowdown of Irganox consumption as irradiation dose was increased (Fig. 2).

Degradation of polymer chains

Chemical crosslinking of the chains

To point out the chemical crosslinking of the chains, dissolution tests were performed on irradiated samples. ZEONOR 750R® was perfectly soluble in hot toluene even for 150 kGy doses. In the case of TOPAS 8007®, the polymer was soluble for 25 and 75 kGy doses but the 150 kGy irradiated sample was only partially soluble. Three different Soxhlet extractions were done on 150 kGy sample to quantify the amount of insoluble polymer. An insoluble ratio of $65 \pm 9\%$ ($n = 3$) was calculated. This ratio corresponds to the ratio of chemically crosslinked chains in the polymer.

Scissions and branching of the chains (SEC analysis)

Zeonor 750R® and TOPAS 8007® had molecular weights in the same range. M_n of Zeonor® is 30,000 $\pm$ 500 g/mol ($I_p = 2$) and M_n of TOPAS 8007® is 49,000 $\pm$ 700 g/mol ($I_p = 2$).

For ZEONOR 750R® chain modifications induced by irradiation were quite low due to the high antioxidant concentration in the initial polymer: M_n was almost constant with the dose [Fig. 4(a)] and M_w
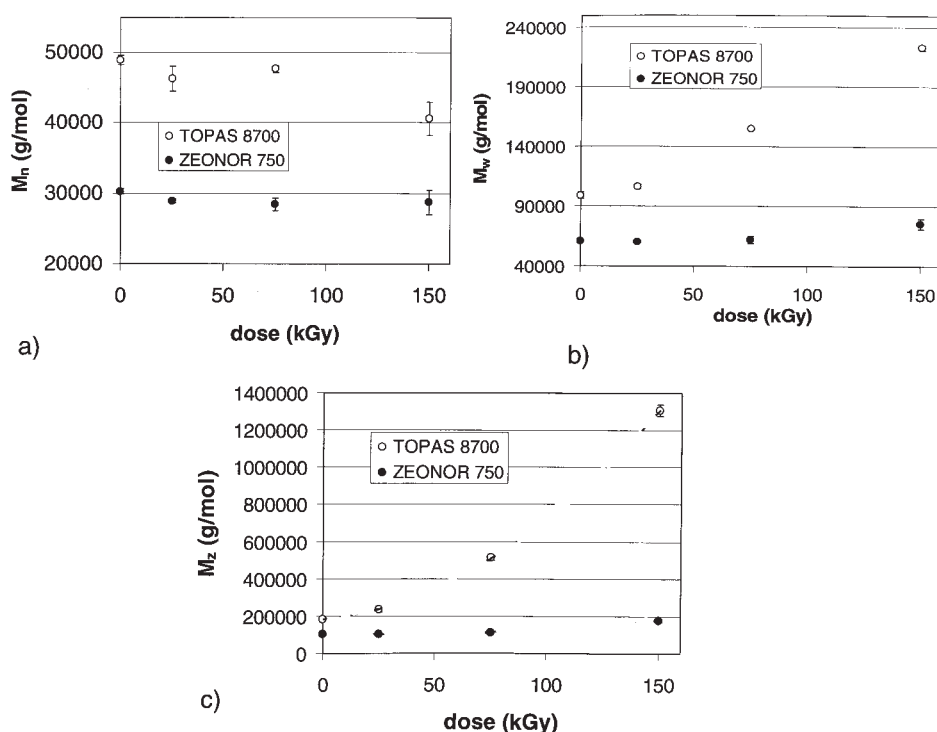
Figure 4 Evolution of molecular weights M_n (a) M_w (b) and M_z (c) ($n = 4$).

[Fig. 4(b)] and M_z [Fig. 4(c)] were hardly increased and mostly only for the higher irradiation dose. The molecular weight increases after a 150 kGy irradiation dose were around +22% for M_w and +77% for M_z. These results showed there were branching but not significant scissions of the polymer chains. As a consequence the polydispersity index remained quite low ($I_p = 2.6$ for 150 kGy samples).

For TOPAS 8007®, SEC analysis was done on the soluble fraction. The evolution of the molecular weight (Fig. 4) was greater than for ZEONOR: M_w and M_z began to increase after a 25 kGy dose (+8 and +28%, respectively) and the increase of these masses became much more pronounced as the dose increased (+56 and +180%, respectively, for 75 kGy samples and +125% and +615% for 150 kGy samples). Branching occurred and was particularly important at high irradiation dose. There were also chain scissions as proved by the small M_n decrease (−5.5% for 25 kGy to −17% for 150 kGy).

Weight calculations were in agreement with chromatogram shapes (Fig. 5). For ZEONOR 750R®, only a significant peak broadening was observed at shorter elution times for the 150 kGy samples proving the existence of branching. For TOPAS, chromatograms showed that there were new weight distributions because of chain branching: marked shoulders appeared at shorter elution times for the 75 and 150 kGy samples, what explained the high polydispersity index found for the 150 kGy sample ($I_p = 6$).

It is interesting to notice that, in both cases (ZEONOR and TOPAS), below a given level of antioxidant, degradations of the polymer chains became significant and competed with degradation of the antioxidant.

Chemical functions characteristic of polymer oxidation (FTIR)

Just after irradiation, no extensive modification of the cycloolefin spectra (TOPAS and ZEONOR) was observed on ATR spectra [Fig. 6(a)]. In the 3400–3700 cm^{-1} range, corresponding to hydroxide and hydroperoxide absorption wavelengths, no difference was observed. Only a slight alteration was observed around 1700 cm^{-1} for TOPAS®, and was confirmed by FTIR measurement in transmission mode on thick samples [Fig. 6(b)]. In this frequency range, bands characteristic of C=O functions (1714 cm^{-1}) grew with the irradiation dose [Fig. 6(b)]. It proved that some of the free radicals in the polymer chains had reacted with oxygen.

Postirradiation ageing (FTIR)

Ageing of irradiated TOPAS® with time was studied. This process was due to the existence of trapped radicals in the polymer. Even for low temperature storage (5°C), reactions between radicals and oxygen were already observed (Fig. 7). The presence of new carbonyl functions was a proof of further chain reac-
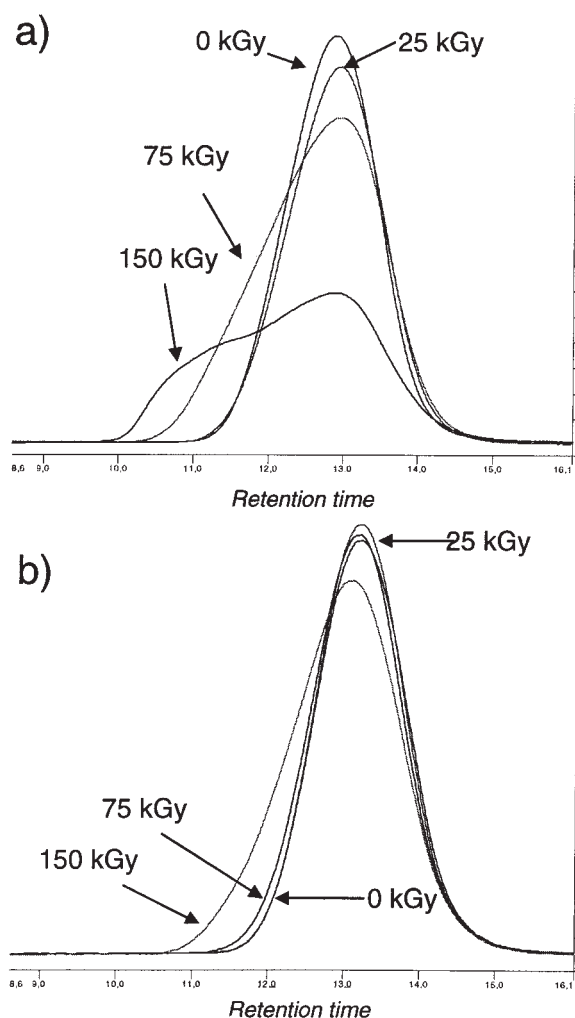
Figure 5 SEC chromatograms (a) TOPAS 8007® (b) ZEO-NOR 750R®.

tion: after a storage of 6 months in fridge, the C=O band absorbance (1714 cm^{-1}) increased from a factor of 1.2 for the less irradiated polymers to a factor of 1.7 for the most irradiated samples. The number of trapped radicals generated by irradiation increased with the irradiation dose.

To study long time ageing, an accelerated ageing was done by storing the polymers several weeks at 83°C. Two TOPAS® samples having different T_g (78.5 and 134°C) were studied, to put into evidence the impact of the polymer chain mobility on the kinetic of the ageing. Chain mobility might have an effect on the diffusion speed of oxygen. After 2 months of storage slight modifications were observed in the 3400–3600 cm^{-1} zone. Bands grew at 3530, 3550, and 3620 cm^{-1} that can be associated to OH and OOH grafting. This OH and OOH grafting was enhanced by the irradiation dose (Fig. 8). For both TOPAS® a sharp increase of the C=O band intensity was moreover observed. For TOPAS 8007®, for which the chain motion at 83°C was higher

(storage temperature is above the polymer T_g), we observed a fast recombination of the radicals with oxygen (Fig. 9): in the first storage days (<4 days) a great part of the trapped radicals had reacted. The kinetic was slower for TOPAS 6013®, in which the chain mobility was more restricted (storage temperature was 50°C below T_g). In the first 24 h, the kinetic was 1.5–3 times slower, but for longer times (2 months), the oxidation ratio became however greater than in the TOPAS 8007®.

Evolution of thermomechanical properties of the polymer

Modification of thermal properties

A calorimetric study was done to put into evidence modifications in the thermal transitions. Both TOPAS 8007® and ZEONOR 750R® polymers had a glass transition on the reversing signal and an enthalpic relaxation on the nonreversing signal (Fig. 10). The glass transition temperature was around 78.5 for TOPAS® and around 70.5 for ZEONOR®. The relaxation occurred at 69°C for TOPAS 8007 (1.55 J/g) and at 64.5°C for ZEONOR® (1.15 J/g).

In the case of ZEONOR®, no modification of the transition temperature was observed: glass transition and enthalpic relaxation temperatures were constant with the irradiation dose [Fig. 11(a)]; in the case of TOPAS® the differences between irradiated and nonirradiated samples were weak: a decrease of both transition temperatures was observed with the irradiation dose. This modification was small but reproducible (−1.5°C for 150 kGy sample).

It is well known that the glass transition temperature depends on the structure of the polymer. Firstly, chains ends introduce a supplementary free volume that let the T_g decrease. As a consequence T_g is a function of the chain length. Fox[12] proposed a relationship between this temperature (T_{gn}) and the number average chain length X_n

$$T_{gn} = T_{g0} - k/X_n$$

where T_{g0} is the asymptotic value of T_g as molecular weight increases; k is a constant for a given polymer.

Secondly, the crosslinking of the chain may stiffen the polymer and increase its T_g. T_g increase is dependant on the crosslink density X as shown by the Gibbs Di Marzio relationship:[13]

$$T_g = T_{gi}/(1 - k'X)$$

where T_{gi} is the T_g of the noncrosslinked polymer and k' a constant for the polymer.

In some particular cases a T_g decrease may be observed for crosslinked samples[14] because of a kind of spacing effect of the chains. Influence of branching is more complex. Big bulky pendant groups can
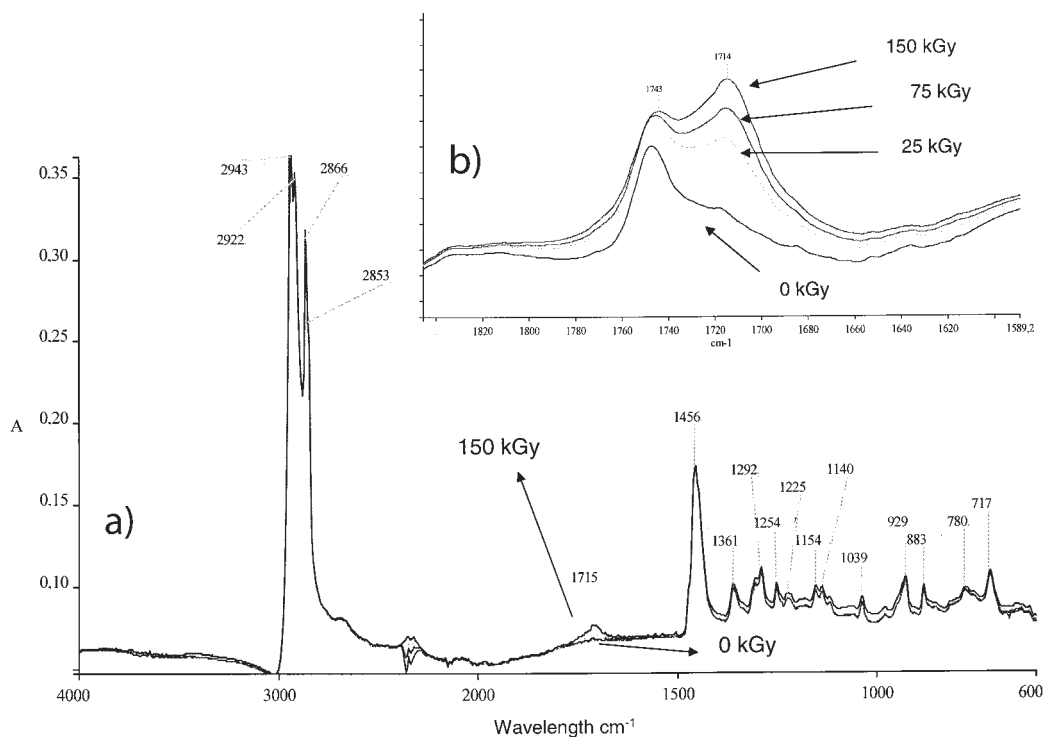
Figure 6 (a) FTIR-ATR spectra of the nonirradiated sample and of the 25, 75, and 150 kGy irradiated TOPAS 8007® samples. (b) Same analysis done by transmission on 1 mm slabs.

lower the T_g by limiting chain packing and creating free volume.[15,16] But depending on density of branching and length of branched chains, there may be an increase in chain interaction and entanglement density that restrict chain mobility.[17–19]

For our samples, the temperature lowering might be linked to the increase of free volume (scission + branching). For the 150 kGy sample, even if most of the chains were chemically crosslinked (65% found by soxhlet extraction), the crosslinked density was certainly so weak that it did not restrict the chain mobility.

The evolution of enthalpic relaxation was also studied [Fig. 11(b)]. This relaxation is characteristic of polymer ageing. Ageing resulted from the evolution of the metastable glassy state towards a true equilibrium state. It strongly depended on the sample thermal history. The more the polymer had moved from a metastable state towards a true equilibrium state, the greater the relaxation enthalpy was. Generally, if the sample was heated above T_g, rapidly cooled and immediately analyzed by DSC, this relaxation disappeared: chains had no time to move nor to reorganize themselves in a more stable state. But, depending on the cooling rate and on chain mobility, a small relaxation might be however observed.

To give all the samples the same thermal history, they were heated 10 min at 160°C, and cooled in the same conditions before DSC analysis. A weak increase of the enthalpy of relaxation was observed

after irradiation [Fig. 11(b)]. Chain reorganization kinetic was a bit faster for irradiated samples.

Swelling behavior

We observed the effect of chain degradation on the swelling behavior of polymer granules in alcohol. For TOPAS® 8007 a measurement was made after 75 days of storage at 83°C ($T > T_g$: rubber state) in octanol (Fig. 12). Swelling ratios were measured with TGA by quantifying the mass loss due to the evaporation of octanol. The swelling was firstly enhanced by irradiation, and then irradiation seemed to inhibit the sorption (Fig. 12). After 7 months of storage,
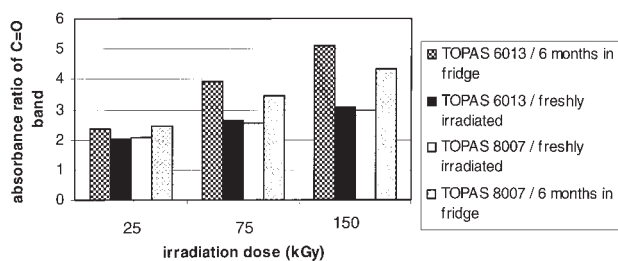

Figure 7 Comparison of the 1714 cm^{-1} C=O band relative absorbance for the freshly irradiated samples and samples stored 6 months in fridge. (1) 25 kGy dose, (2) 75 kGy, and (3) 150 kGy. Samples were analyzed by transmission. Relative absorbance was defined as the ratio of the C=O band absorbance observed divided by the C=O band absorbance for the unaged and nonirradiated sample.
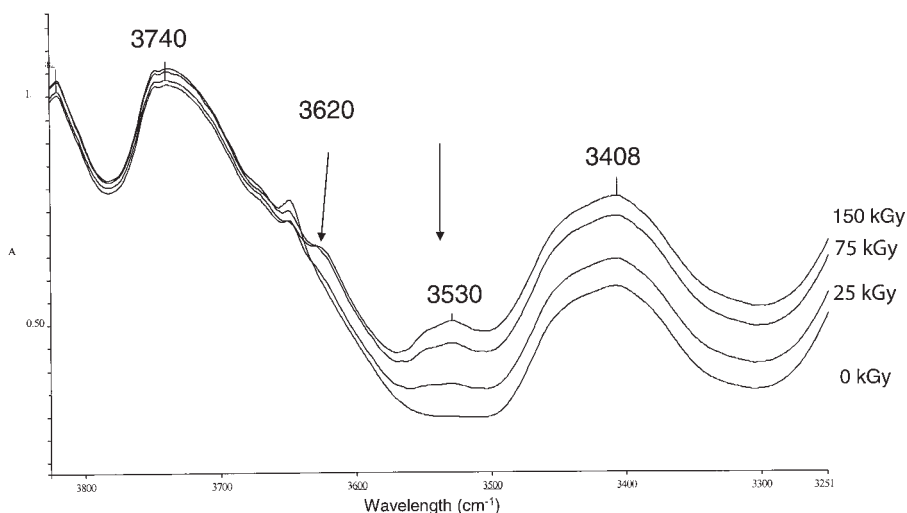
Figure 8 Comparison between the FTIR spectra of the irradiated and nonirradiated samples in the 3700–3400 cm^{-1} range after 2 months of storage at 83°C (TOPAS 8007®).

polymer that was irradiated at 25 kGy was no more in a granular shape and was partly dissolved in octanol. For higher doses, samples were still in the shape of swelled granules.

It is known that in a rubber state ($T > T_g$), an increase in the density of crosslinks (physical crosslink due to entanglement and chemical crosslink) might rise the elastic modulus of polymer and thus decrease its swelling ability (elastic contribution of the crosslinked chains might inhibit the sorption). At 25 kGy the shorter chains generated by scission might favor swelling, because shorter chains are less able to form entanglements. For higher doses, scissions still occurred, but are balanced by important chain branching resulting in an important mass increase, that can favor entanglements. Moreover for the 150 kGy sample, there was even a chemical

crosslinking that allowed to have lower swelling ratio than for the nonirradiated sample.

Mechanical tests

The Young's modulus was found by three points bending. Mechanical tests were done at ambient temperature (polymer in the glassy state). For TOPAS 8007 modulus was the same as the Young's modulus given by Ticona (2.6 GPa). There was no hysteresis as sample was unloaded and both the load–unload cycles were the same. Young's modulus and yield stress were not affected by the variation of the sample width named l ($4 < l < 6$ mm).

Some weak variations of the Young's modulus [Fig. 13(a)] and of the yield stress [Fig. 13(b)] were observed after irradiation. Firstly a lowering was observed for the 25 kGy samples (−5% for modulus and −8.5% for yield stress). Then, the yield stress increased for doses ≥75 kGy. For Young's modulus, the increase observed was in the experimental error.
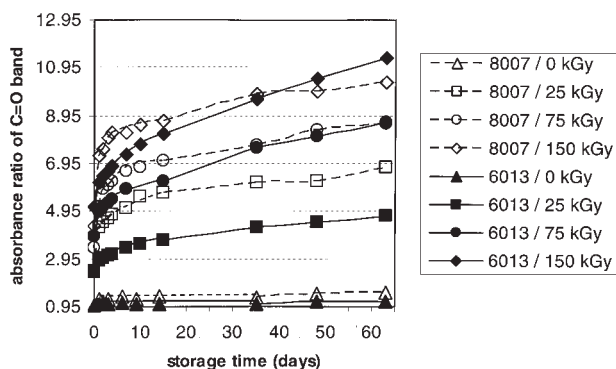

Figure 9 Evolution of the C=O band at 1714 cm^{-1} with the poststerilization ageing treatment (storage at 83°C) for the different irradiated samples. Samples were analyzed by transmission. Relative absorbance was defined as the ratio of the C=O band absorbance observed divided by the C=O band absorbance for the nonaged and nonirradiated sample.
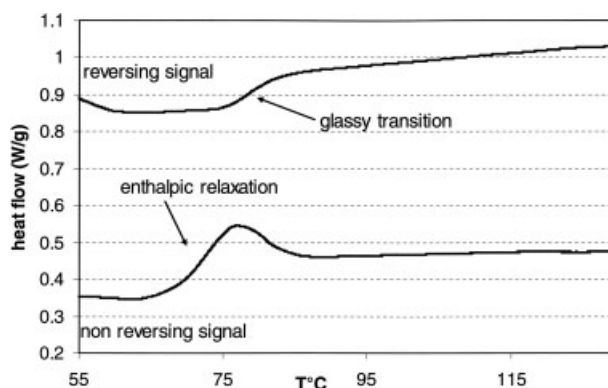

Figure 10 Modulated DSC thermogram for the TOPAS 8007® sample (nonirradiated).
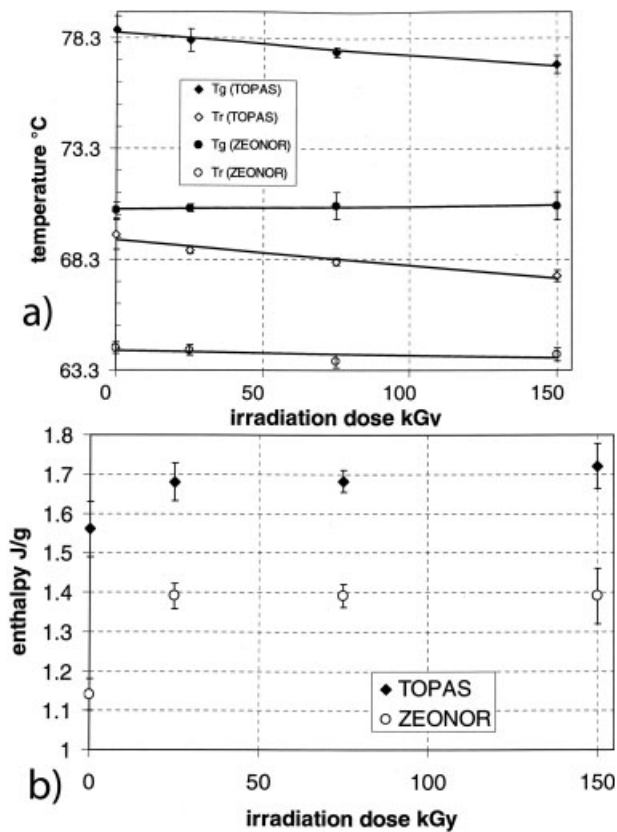
Figure 11 (a) Evolution of the glass transition temperature and enthalpic relaxation temperature with irradiation dose for TOPAS 8007® and ZEONOR 750R®. (b) Evolution of the enthalpy relaxation with irradiation dose for TOPAS 8007® and ZEONOR 750R® ($n = 4$).

By seeing the curve shape, we concluded there was a minimum for mechanical properties located between 0 and 75 kGy. This minimum occurred in the same irradiation range as the maximum observed for polymer swelling. In the glassy state, the Young's modulus is generally less affected by the density of crosslinks than in the rubber state. This might explain the low variations observed for
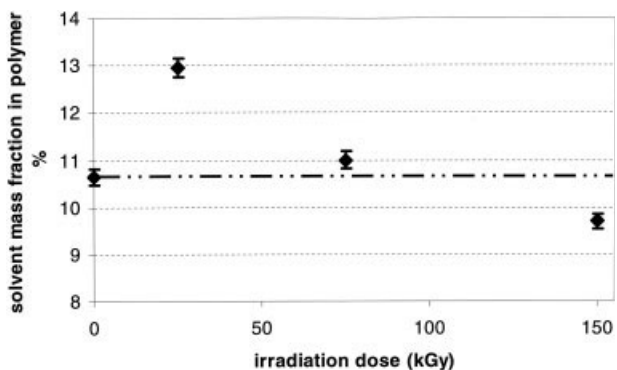

Figure 12 Solvent mass fraction in polymer measured by TGA analysis. Evolution with the irradiation dose for the TOPAS 8007® stored 75 days at 83°C in octanol ($n = 3$).
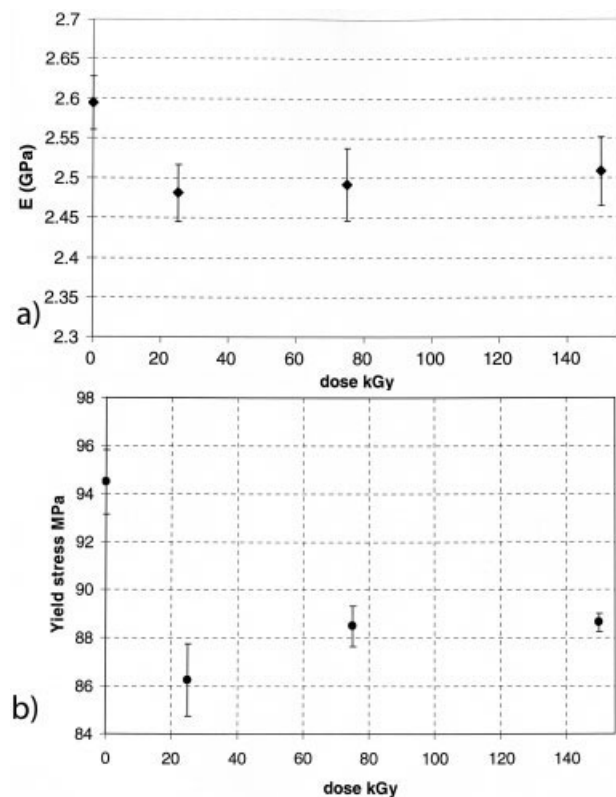
Figure 13 (a) Evolution of the Young's modulus with the irradiation dose for TOPAS 8007® samples. (b) Evolution of the yield stress with the irradiation dose for TOPAS 8007® samples ($n = 6$).

the Young's modulus. However crosslink density might influence failure process in the glassy state: sufficiently high density may inhibit failure induced by crazing phenomena.[20]

CONCLUSIONS

The dose commonly recommended for sterilization of packaging is 25 kGy, but we have seen that, in the case of a COC (TOPAS 8007) containing around 1500 ppm of Irganox 1010 as antioxidant, this dose generated the higher number of degradation products, that is to say the higher number of potential migrants. Moreover for the 25 kGy irradiation, swelling ability was greater and mechanical properties were worse. This was linked to further decomposition of degradation products and to important branching and crosslinking that occurred at higher doses. But the consequences of irradiation on the polymer's thermomechanical properties were quite weak, even if the chains were strongly modified by irradiation. Decrease of T_g with the irradiation dose was extremely weak. Mechanical properties firstly decreased slightly because of chain scissions that were in a second time counterbalanced by branching and crosslinking of the chains.

Initial amount of antioxidant added to the polymer was a very important point. A great amount of antioxidant will protect the chains from damages due to irradiation, but, below a given level of antioxidant, polymer chains will be damaged. Choosing the best compromise for irradiation dose is not obvious: if high doses might be more advantageous to limit the number of potential migrants and the loss of mechanical properties, they will on the other hand consume a great part of the antioxidant initially added to polymer to prevent from long term oxidation and to increase its lifetime.

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