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Degradation of epoxy resins under high energy electron beam irradiation: Radio-oxidation

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Abstract

The degradation of two epoxy systems exposed to electron beam irradiation in oxygen atmosphere has been studied and compared to our previous results obtained under helium atmosphere. A multi-scale approach to the degradation has been carried out using a variety of analytical methods including solid state NMR spectroscopy, 2D-WISE experiments, SEC measurements and infrared spectroscopy associated with chemical derivatisation treatments. It is shown that the degradation of both polymers is governed by radiolytic processes which involve chain scissions. The formation of oxidation products, mainly carboxylic acid chain ends, was shown at the surface of the irradiated film. Oxidative degradation is limited to the first 20 μm of the film due to the low oxygen diffusion coefficient in epoxy polymers combined with the high dose rates of irradiation.

Keywords: Electron beam irradiation; Epoxy polymer; NMR; Infrared spectroscopy; Radio-oxidation

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1. Introduction

Due to their high performance, epoxy polymers are commonly used materials either pure or as matrix elements for many applications in the nuclear industry. In such environments high energy radiation causes irreversible chemical modifications of polymer chains leading to material ageing. Understanding chemical degradation mechanisms is a key for a comprehensive approach to lifetime prediction of materials in use and for the development of new resistant polymer formulations. Our investigations were focused on the DGEBA/TETA epoxy system obtained from diglycidyl ether of bisphenol-A, a prepolymer chosen because of its high industrial importance, and triethylene tetramine as a hardener. We first studied a linear phenoxy polymer, poly(2-hydroxyether of bisphenol-A) called PKHJ® and denoted as PR for phenoxy resin hereafter. In addition to its industrial interest, this linear polymer, thermoplastic and soluble in many solvents, provided an interesting model compound mimicking the epoxy part of the more complex 3D DGEBA/TETA network. The radiodegradation phenomena under electron beam in an inert atmosphere (pure radiolysis processes) were first studied and published in another paper [1]. Pure radiolysis conditions exist in some confined configurations or when the materials are exposed to high dose rates of irradiation, for example in accident conditions. But in most industrial nuclear applications polymer materials are exposed to relatively low doses in air atmosphere. In such a case, oxygen can potentially represent as an important acceleration factor of degradation. Primary radicals produced through the radiolysis may react with molecular oxygen forming secondary radicals which amplify the propagation processes and lead to new oxidation products. But in epoxy materials oxidation reactions are reported to be generally limited to the material skin due to a very low oxygen diffusion coefficient [2,3].

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The study of the degradation of epoxy/amine systems under high energy radiation has been the focus of several published works [4–14]. While a few of them concerned the determination of structural changes [1,14–19] almost nothing was reported about the specific effect of oxygen on the chemical degradation. Park et al. [7] studied the radio-oxidation of a TGMDA/DDS system irradiated under electron beam and observed two separated absorption bands at 1720 and 1660 cm^{-1} by IR spectroscopy. The former was attributed to the formation of a ketone or a carboxylic acid and the second to an amide or an aromatic ketone. Observing similar modifications for samples irradiated under nitrogen atmosphere they concluded that the minute amount of oxygen dissolved into the matrix had an important role. Conversely Celina et al. [20] described the role of oxygen as unnoticeable because of low diffusion coefficient. Debré et al. [19] did not observe significant changes on DMA (dynamic mechanical analysis) measurements and IR spectra of a DGEBA/DDS (diaminodiphenyl sulfone) system gamma irradiated up to 2 MGy, demonstrating the confinement of oxidation products to the surface.

In this work we investigated the radio-oxidation degradation mechanisms of PR and DGEBA/TETA epoxy systems. Both materials were exposed to electron beam irradiation under oxygen atmosphere in the same conditions as those used for radiolysis experiments under helium [1]. The identification and spatial location of specific oxidation processes were made using a panel of methods of characterisation at different scales by comparing results obtained in oxidant and non-oxidant irradiation conditions.

2. Experimental

2.1. Materials and methods

Phenoxy resin granules with grade PKHJ® were obtained from Imchemrez Chemicals Corporation (PKHJ® acronym stands for Phenoxy Ketone Hydroxy, the J letter corresponds to an arbitrary scale of viscosity from Union Carbide Corporation, first manufacturer of PKHJ®). Prepolymer DGEBA LY556 and hardener TETA HY951 were purchased from Vantico (formerly Ciba Specialty Chemicals). Granules and pieces were

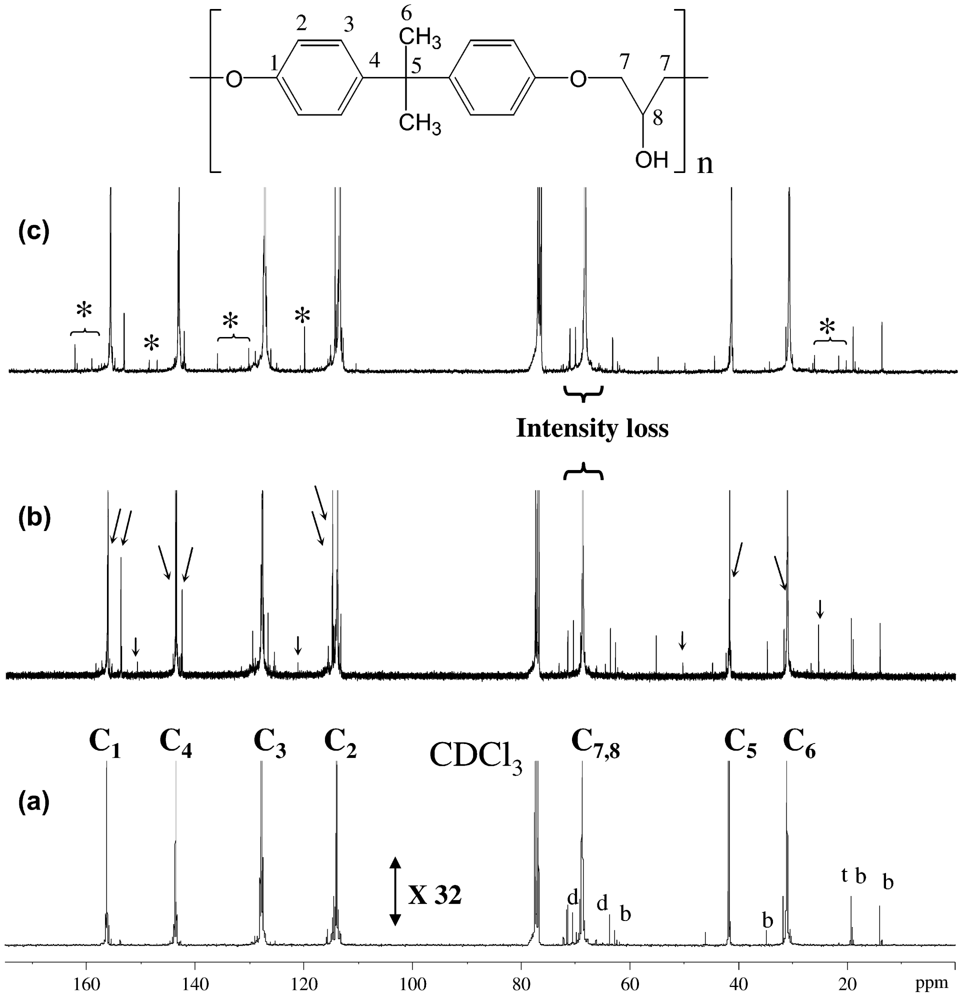


Fig. 1. ^{13}C spectra of polymer film in $CDCl_3$: (a) initial PR film, (b) irradiated at 10 MGy under helium; (c) irradiated at 5 MGy under oxygen. The intense ageing peaks corresponding to the radiolysis process (formation of phenolic chain end) and lower anaerobic peaks are indicated by arrows. The symbol '*' corresponds to other weak signals which result from radio-oxidation processes. The symbols (b), (t) and (d) stand for butanol, toluene (the main impurities) and diol chain ends.

Table 1
^1H and ^{13}C chemical shifts assigned to oxidation products

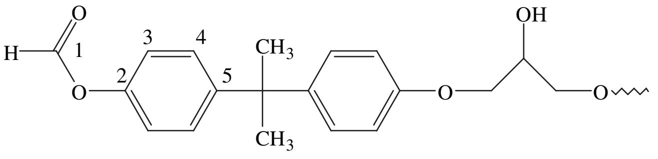
	^{13}C	^1H
O–C=O	162.8, 162.4, 159.7 (*162.4*)	
Aromatic	149.2, 147.7, 136.6, 130.8, 120.5 (*160.3*, *151.9*, *129.8*, *118.6*)	(*7.1*, *7.0*)
CH_3 acetate	26.5, 22.0, 20.5	2.06
H formate		8.3, 8.0, 7.9 (*7.9*)

In parentheses are indicated the chemical shifts calculated with ACD predictor program for the proposed phenyl formate structure (Scheme 1).

used for DSC. Conversely thin films of roughly 100 μm thick [1] and powder samples (obtained by crushing the materials at liquid nitrogen temperature) were prepared for IR and NMR. Irradiations were carried out in the same conditions as in our previous work but in an atmosphere of oxygen. Seven doses in the range 0.05–5 MGy were applied to PR samples and a single dose of 5 MGy in the case of DGEBA/TETA.

Infrared spectroscopy measurements were carried out on thin films. IR spectra in the transmission mode were recorded on a Nicolet FTIR 760 spectrophotometer (number of scans: 32, resolution: 4 cm^{-1}). This apparatus is equipped with a Nicplan microscope allowing micro-FTIR measurements (number of scans: 512, resolution: 4 cm^{-1}). Surface analysis was carried out by using a Nicolet 5-SXC IRTF equipped with a Thunderdome ATR (number of scans: 128, resolution: 4 cm^{-1}). The Thunderdome is a single reflection ATR accessory with a germanium crystal. The analysed depth is wavelength dependent and is between 0.5 and 3.3 μm (3600–600 cm^{-1}). Coupling the IR analysis with chemical derivatisation treatments allowed *in situ* identification of the carbonylated degradation products [21]. Irradiated films were exposed to NH_3 (Ucar) gas at room temperature in all-Teflon reactors. NH_3 reacts with carboxylic acids, formates, and esters and converts them into carboxylate, formamide and amides, respectively. NH_3 is unreactive with ketones and aldehydes.

NMR experiments in $CDCl_3$ solution were carried out at room temperature on a Bruker Avance 400 MHz spectrometer using a standard QNP probe (5 mm diameter tubes). High resolution ^{13}C solid state NMR spectra were acquired with a standard X-H CP/MAS probe for 4 mm external diameter rotors using a magic angle spinning rotation frequency $\nu_r = 15$ kHz and a cross polarization period of 2 ms. A linear ramp (40–100%) on the ^{13}C channel was introduced during the cross polarization period in order to avoid Hartman–Hahn mismatch during polarization transfer. Homonuclear $^1H-^1H$ dipolar spectra were measured as cross sections in 2D WISE (wide-line separation experiment) using experimental parameters $\nu_r = 7$ kHz and $t_{CP} = 100$ μs and ^{13}C TPPM decoupling during the t_1 period [1].



Scheme 1. Chemical structure of phenyl formate chain end.

For a complete description of materials, preparation protocols, the different analytical methods and experimental conditions we used, the characterisation of initial materials and reference state, the reader can also refer Ref. [1].

3. Results and discussion

3.1. Structural modifications and macroscopic evolution of the phenoxy resin

The ^{13}C NMR spectrum in $CDCl_3$ of a PR film irradiated in the presence of oxygen strongly resembles the spectrum of the same sample irradiated in helium atmosphere (Fig. 1). Firstly, the same structural changes with almost equal proportions were observed as compared to reference sample: (i) eight new intense lines and a net loss of hydroxypropylidene moiety intensity previously attributed to the main chain scission radiolysis mechanism producing phenolic chain ends and acetone; (ii) smaller peaks attributed to minor modifications. Secondly, additional weak peaks were visible in the specific regions of ester/acid (close to 160 ppm), methyl and aromatic carbons. These signals could be easily identified because a selective increase (by a factor of 2) of their intensity could be observed when the ^{13}C measurement was carried out on an irradiated powder sample. The observed ^{13}C and ^1H chemical shifts (^1H spectrum not shown) gathered in Table 1 were assigned to acetate and formate groups. A phenyl formate chain end could be proposed on the basis of calculated spectra with ACD predictor program (Scheme 1). It is worth noticing that peroxides and hydroperoxides which are typical chemical species of oxidation were not detected here.

As under helium atmosphere, a gradual decrease of the glass transition temperature T_g and the molecular weight measured by SEC (steric exclusion chromatography) were observed in the course of irradiation under oxygen atmosphere. Almost equal variations were reached at 5 MGy: T_g decreased by about 15 °C and M_n and M_w were reduced by factors of 4.5 and 3, respectively (as compared to factors 4.2 and 2.7 found under helium). These results suggested that (i) chain scission

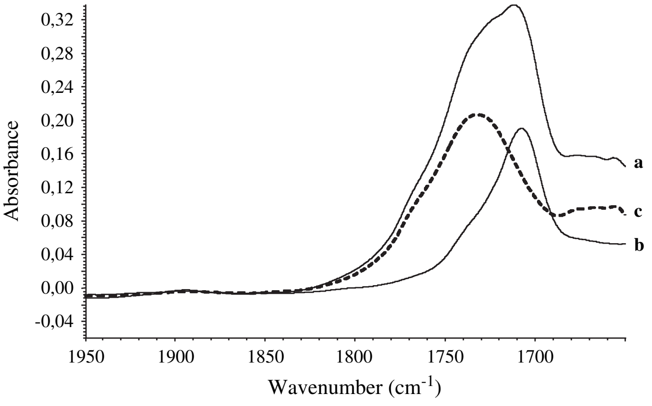


Fig. 2. Subtracted IR spectra (irradiated – reference) of PR films (irradiated at 5 MGy – initial) for irradiations under oxygen (a) and helium (b); (c) difference (a) – (b).

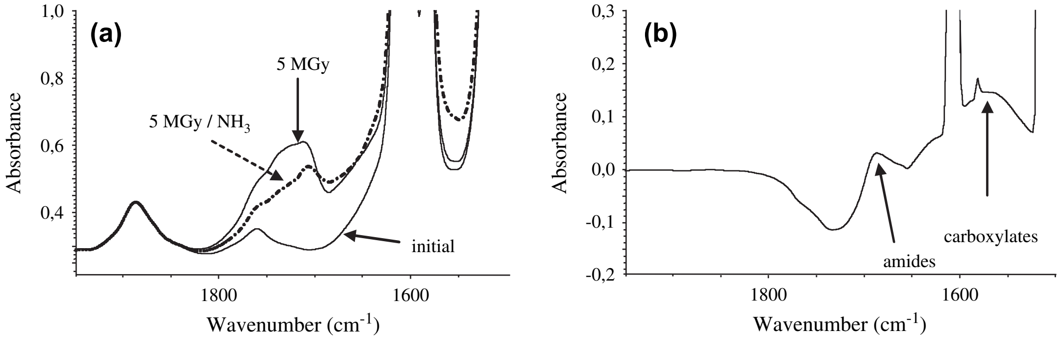


Fig. 3. (a) IR spectra of PR film irradiated at 5 MGy obtained before and after a chemical treatment with ammonia and of initial sample; (b) subtracted IR spectrum (after – before chemical treatment).

degradation governs the modifications of polymer properties whatever the atmosphere is, (ii) radio-oxidation processes, if any, are certainly confined to a thin layer at the polymer surface. This is a consequence of the combined effect of the relatively high dose rate and the low oxygen permeability in our materials.

The comparison of the IR spectra of films irradiated, respectively, under helium and oxygen showed the occurrence of oxidative reactions in the second experimental conditions. The IR spectra of both films reported in Fig. 2 show the formation of an IR band at 1708 cm^{-1}. This band is assigned to ketone structures, including mainly acetone and the chain ketone previously identified as radiolysis products [1]. It is accompanied by a shoulder centred at 1725 cm^{-1} only observed on the IR spectra of the sample irradiated in oxygen and attributed to oxidative species.

The chemical derivation reaction with NH_3 gas coupled to IR spectroscopy was used to identify the nature of carbonyl groups formed. The spectrum obtained after 20 min of treatment is shown in Fig. 3 and compared to the spectrum of irradiated and non-irradiated sample. A loss of absorbance in the carbonyl region was obvious, revealing the presence of carboxylic acid, formate or ester structures. This was confirmed by the growth of the derivative species at 1560 cm^{-1} (carboxylate) and 1680 cm^{-1} (amide), respectively. An absorbance at 1739 cm^{-1} converted into an absorbance at 1690 cm^{-1} after NH_3 treatment had already been observed in PR photo-oxidised films [3]. Among possible attributions a formate chain end was proposed equivalent to the structure given above and compatible with present NMR results. After the chemical treatment the IR spectrum conserved a residual absorption band at 1708 cm^{-1} which corresponds to unreactive ketones. It is worth noticing that the chemical treatment of ammonia with a polymer film irradiated under helium does not produce any modification of the IR spectrum in the carbonyl region.

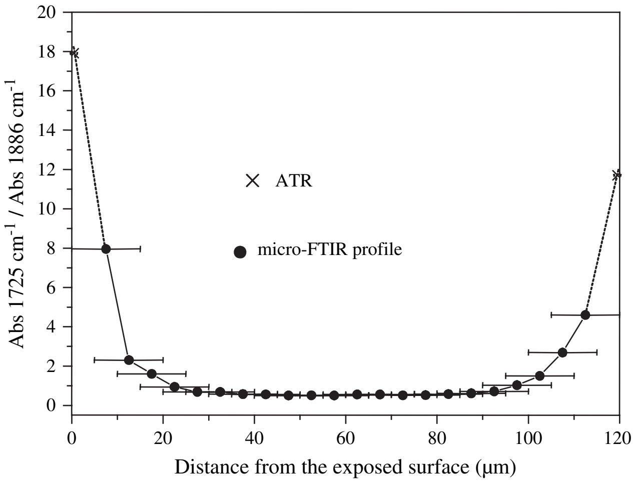


Fig. 4. Oxidation profile of PR film irradiated at 5 MGy: (vertical scale) ratio between absorbance at 1725 and 1886 cm^{-1} measured by spectrophotometry (●) and ATR measurements (×); (horizontal scale) distance from the irradiated surface of the polymer film.

To determine the distribution of oxidation species through the sample in the direction of irradiation (the oxidation profile) two different approaches were used. The first method is based on the classical depth-profiling analysis using micro-FTIR spectroscopy. The experimental procedure consisted first in slicing a 100 µm thin layer of an oxidised polymer sample with a microtome in a plane perpendicular to the irradiation axis. To facilitate this operation, the polymer film (120 µm thick) irradiated at 5 MGy was first embedded in an inclusion resin. The IR spectra of narrow areas (20 µm in width) were then acquired by shifting the position of 5 µm increments.

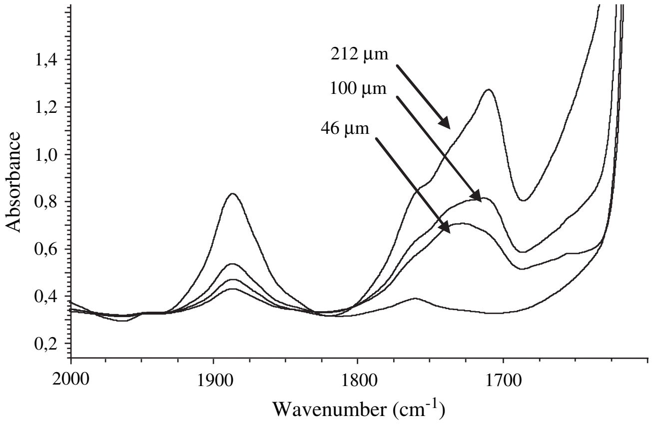


Fig. 5. Transmission IR spectra of PR films of different thicknesses irradiated at 5 MGy.

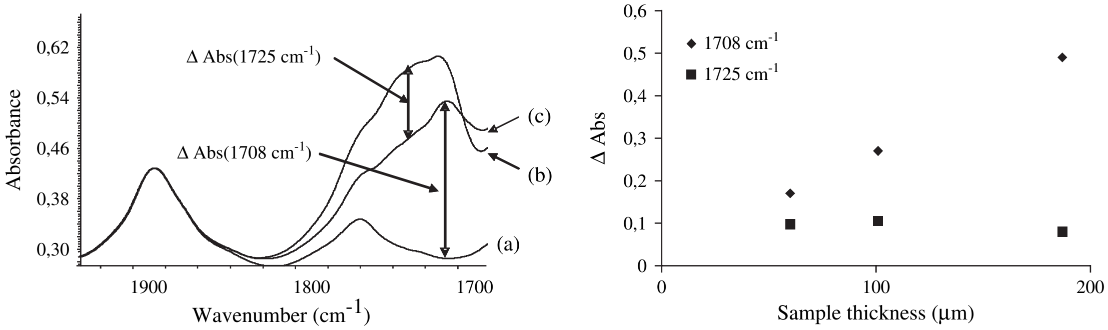


Fig. 6. (Left) Transmission spectra of (a) non-irradiated sample, (b) irradiated sample at 5 MGy and (c) same sample after a chemical treatment with NH_3. ΔAbs(1725 cm^{-1}) corresponds to the decrease of absorbance at 1725 cm^{-1} provoked by chemical treatment; ΔAbs(1708 cm^{-1}) the variation of absorbance between treated irradiated sample and reference sample. (Right) Graph of variations of these two quantities as a function of the thickness of the film.

The absorbance at 1724 cm^{-1} (scaled according to an internal reference at 1886 cm^{-1} whose intensity is invariant throughout degradation) of the analysed zone was then plotted as a function of the distance from the edge of the sample. The resulting graph was further completed by incorporating one point at both sides obtained from ATR measurements as this method probes about the first micron near the surface. As shown in Fig. 4, a highly heterogeneous distribution of oxidation species was obtained indicating that oxidation processes are confined to a thin layer of about 20 µm at both sides of the film. The superficial oxidation was further confirmed by a second approach using standard IR measurements of polymer films with three different thicknesses (46, 100 and 212 µm) and irradiation at 5 MGy. By comparing the spectra it is obvious that a different evolution relative to thickness governed the absorbance at 1725 and at 1708 cm^{-1} (Fig. 5), respectively, assigned to oxidative species and to ketonic radiolysis products. As direct quantification of the two types of species was not possible due to partial convolution in this region, the reaction with ammonia was applied to derive selectively carboxylic acids, esters and formate groups (Fig. 6). Two quantities were then calculated: ΔAbs (1725 cm^{-1}) the decrease of absorbance at 1725 cm^{-1} produced by chemical treatment which is proportional to the amount of oxidation species; ΔAbs(1708 cm^{-1}) the absorbance variation at 1708 cm^{-1} between irradiated sample after chemical treatment and reference

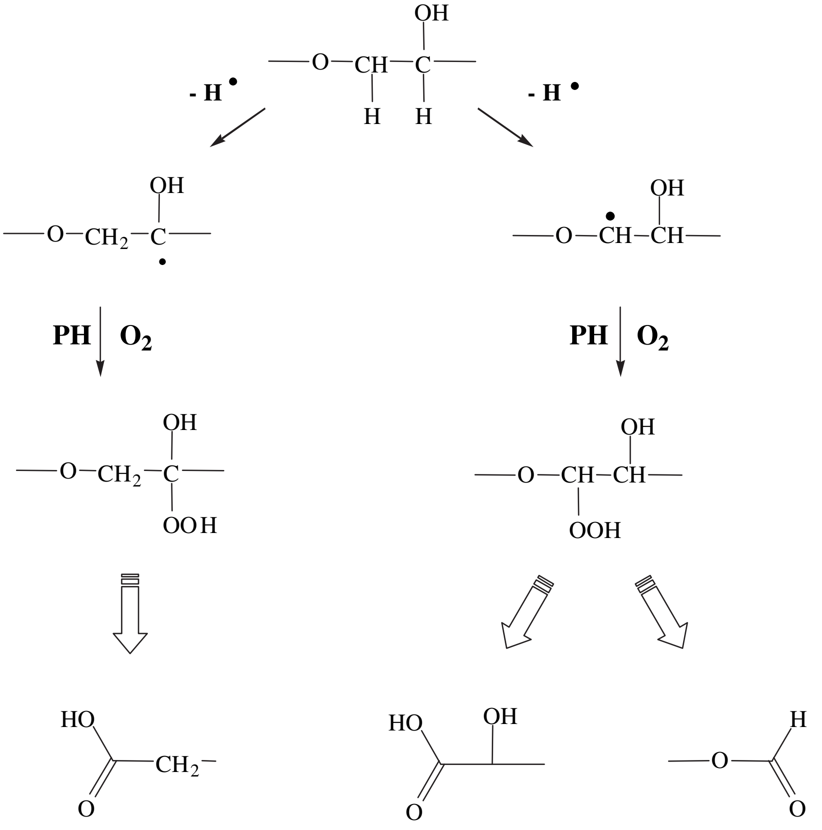


Fig. 7. Proposed simplified mechanism accounting for the formation of carboxylic acids and formate chain ends.

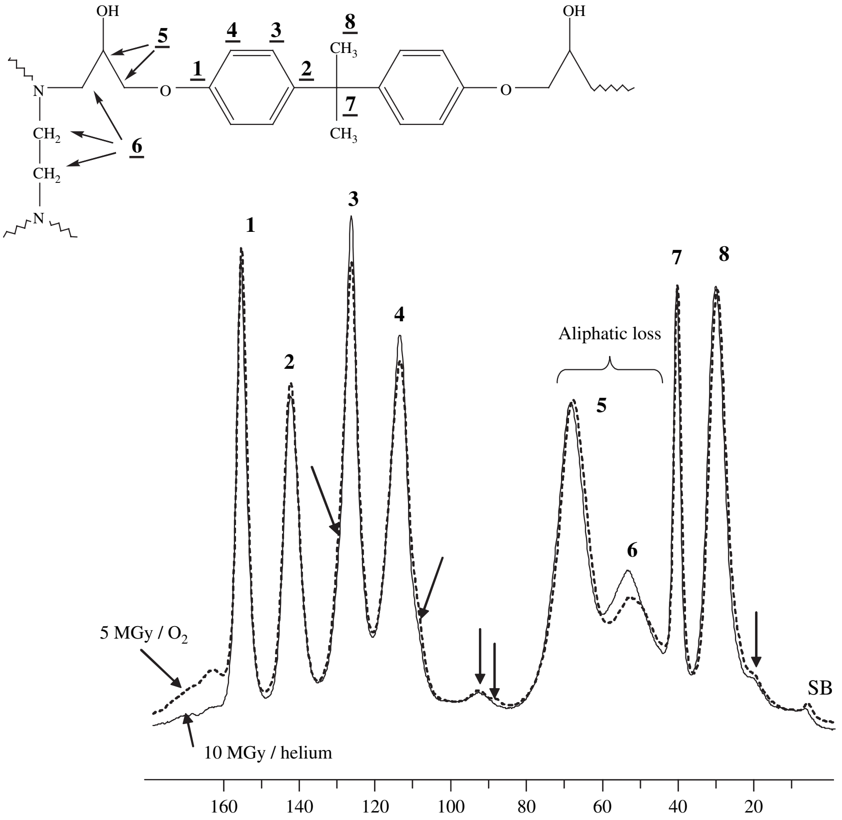


Fig. 8. ^{13}C CP/MAS solid state NMR spectra of DGEBA/TETA powder irradiated at 10 MGy under helium and 5 MGy under oxygen. Degradation peaks are indicated by arrows and SB stands for spinning sidebands.

sample which is proportional to the quantity of ketones produced by radiolysis. The resulting graph of these two variations of absorbance vs the thickness of the three samples reveals the invariance of ΔAbs(1725 cm^{-1}). This is a proof of the existence of a limited zone of oxidation which is independent of the thickness of the irradiated sample. In contrast, the residual absorption ΔAbs(1708 cm^{-1}) is proportional to the thickness showing that the radiolytic degradation is homogeneous in the sample for at least 200 μm. Note that similar results were obtained at doses of 3 and 1 MGy (not shown).

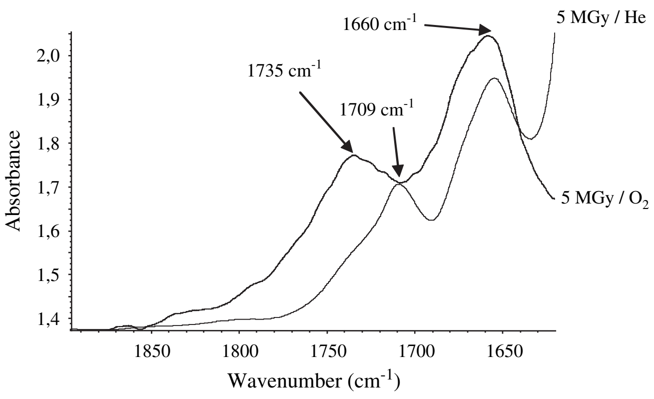


Fig. 9. Subtracted IR spectra (irradiated – reference) of DGEBA/TETA films (irradiated at 5 MGy – initial) for irradiations under helium (transmission mode) and under oxygen (ATR mode was used due to enhance fragility of the film).

As a conclusion, a simplified mechanism accounting for the formation of carboxylic acids and formate chain end at the surface of radio-oxidised films can be proposed. Depending on the site of hydrogen abstraction by radicals formed in the radiolytic process, two mechanisms accounting for the formation of the oxidative species can be envisaged (Fig. 7).

3.2. Structural modifications and macroscopic evolution of the DGEBA/TETA network

As shown in the PR system the radio-degradation in the presence of oxygen is strongly heterogeneous in the conditions of irradiation we used. Thus oxidation reactions are mainly located at the surface of the polymer, the sample volume being essentially affected only by radiolysis phenomena. As a focus of the present study was to show the occurrence of oxidative degradation reactions, we characterised a single powder sample irradiated at a dose of 5 MGy. The ^{13}C CP/MAS solid state NMR spectrum is shown in Fig. 8 together with the spectrum of sample irradiated at 10 MGy under helium. The comparison of both spectra unambiguously reveals the formation of the main radiolysis products (previously identified as a vinyl amine [1] and, only in aerobic conditions, the growth of a large and intense signal in the region 165–180 ppm characteristic of carboxylic acids, esters and amides). This modification is accompanied by a loss of methylene amine signal at 55 ppm which is slightly higher in the presence of oxygen than under

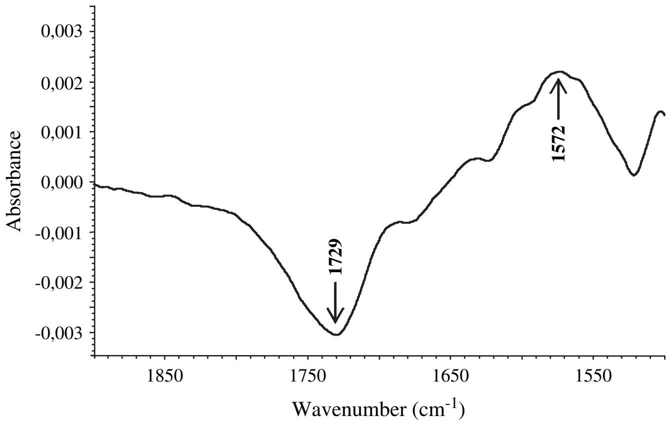


Fig. 10. Subtracted IR spectrum (after – before chemical treatment with NH_3) of a DGEBA/TETA film irradiated at 5 MGy under oxygen atmosphere.

helium. In Fig. 9 is presented the ATR infrared spectrum of DGEBA/TETA irradiated at 5 MGy under oxygen compared with the transmission infrared spectrum of the same sample irradiated under helium. It is evident that radio-oxidation results in the formation of a carbonyl band centred at 1735 cm^{-1}. NH_3 treatment carried out on irradiated films caused an important decrease of the absorption at 1735 cm^{-1} and the development of a carboxylate band at 1572 cm^{-1} suggesting the presence of carboxylic acids as the main oxidation product (Fig. 10). On the basis of our previous results the unreactive absorption detected in both cases at 1660 cm^{-1} is assigned to unsaturation of amide, mostly resulting from pure radiolytic processes [1]. The absence of this band in the case of PR sample indicates that this product resulted from the degradation of the amine part of the polymer (Fig. 11). A loss of absorbance of methylene amine at 2820 cm^{-1} was also noticed. The formation of amide, ester and carboxylic acid functions had also been observed by Ngono [22] on the DGEBA/TETA modified system.

In summary, the radio-oxidation processes occurring in DGEBA/TETA under irradiation led to the formation of different species including mainly carboxylic acid end-groups therefore producing additional chain scission reactions occurring preferentially in the amine moiety previously identified as the most fragile site of the polymer. This was confirmed by the selective increase of mobility affecting methylene amine carbon groups as revealed by 2D-WISE spectroscopy (Fig. 12). The examination of the different cross sections showed a reduction of residual dipolar linewidth of about 16% at 56 ppm (to be compared to 10% in an inert atmosphere at 10 MGy) while no significant changes were noticed for the other chemical shifts.

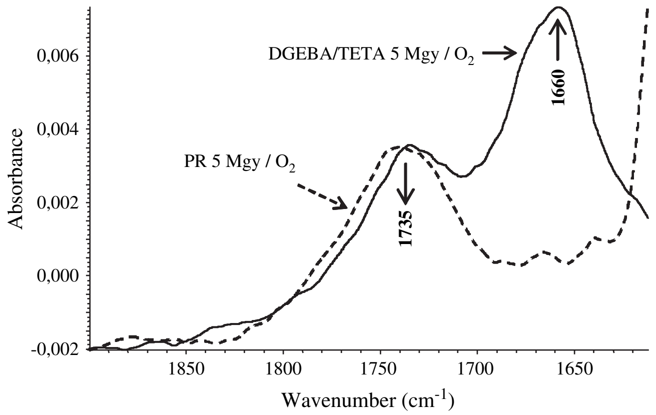


Fig. 11. ATR spectra of PR and DGEBA/TETA irradiated at 5 MGy under oxygen.

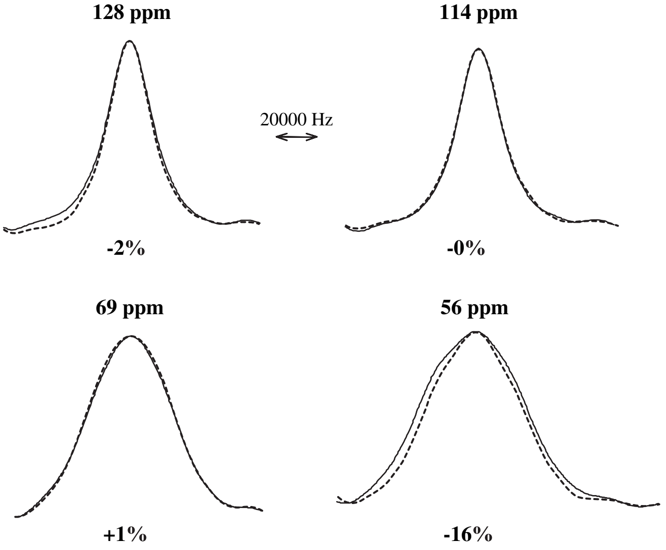


Fig. 12. Dipolar spectra for protonated carbons' chemical shifts extracted from WISE experiment of both DGEBA/TETA reference sample (continuous lines) and irradiated at 5 MGy under oxygen (dotted lines). As described in Ref. [1] we used $TPPM_1$ decoupling during evolution and restricted the Fourier transform to initial t_1 decay (without MAS echos). The difference in line width of both dipolar spectra is indicated in percent on the bottom.

4. Conclusions

Experimental results presented in this article show that the degradation of PR and DGEBA/TETA under high energy electron irradiation in the presence of oxygen principally leads (in our conditions of irradiation) to the same chemical reactions as in pure radiolysis conditions: chain scission reactions occurring at the hydroxypropylidene site leading to the formation of phenolic chain ends and volatile products in PR, and occurring at the amine site in DGEBA/TETA network leading to the formation of a vinyl amine chain end. In addition oxidation processes are shown to be limited to a thin superficial layer of a few microns (<20 μm) and lead in both cases to the formation of carboxylic acid chain ends as the main oxidation product, whose formation involves chain scission. Ester functions and formate chain ends were also identified in the case of PR films. In the case of the DGEBA/TETA network, our result suggests the formation of additional species resulting from the oxidation of the methylene amine part of the hardener, probably amides or other unsaturation.

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