Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Polymer 44 (2003) 4889–4897

polymer
www.elsevier.com/locate/polymer

Ageing of EPDM elastomers exposed to γ-radiation studied by ^{1}H broadband and ^{13}C high-resolution solid-state NMR

P. Palmas[a,*], R. Colsenet[b], L. Lemarié[a], M. Sebban[a]

[a] *CEA (Commissariat à l'Energie Atomique) Le Ripault BP 16 37260 Monts, France*
[b] *Cemagref 17 av. De Cucillé 35044 Rennes cedex, France*

Received 3 February 2003; received in revised form 17 April 2003; accepted 30 May 2003

Abstract

Ageing of EPDM synthetic elastomers exposed to γ-irradiation has been investigated using solid-state NMR Spectroscopy. Both ^{13}C high-resolution and ^{1}H wideline measurements were carried out to evaluate chemical degradation including oxidation products formation, chain scission and crosslinking phenomena. Highly specific structures were tentatively proposed as a result of careful examination of ^{13}C chemical shifts. The importance of diene monomer, the stabilising effect of curing process and the addition of antioxidants were evaluated on the basis of several polymer compositions.

Keywords: Elastomer; γ Radiation; Solid-state NMR

1. Introduction

As far as warranty of safety and reliability of nuclear power stations is concerned, understanding of degradation mechanisms and lifetime prediction of materials exposed to high energy radiations (γ, α or β) are relevant problems which must be solved. One important class of compounds exposed to such ambiance are polymer-based assemblies which experience relatively low radiation doses for a long period of time. This concerns Ethylene Propylene Diene Monomer (EPDM) elastomers based formulations which are used especially for cable insulation and joints.

Polymer exposed to high-energy radiation experience chemical degradation which may induce a drastic performance loss of material properties. This results from statistical interaction of energetic particles with polymer atoms which produces organic radicals. Then, depending on molecular mobility and chemical structure, these thermodynamically non-stable species degenerate more or less rapidly throw different chemical reactions involving the polymer itself, oxygen or other radicals. Generally, the chemical processes can yield at the same time chain scissions, crosslinking reactions and different oxidation states. Understanding these different degradation mechanisms and related kinetics is an essential step in predicting lifetime of in service compounds and simultaneously selecting correct polymer formulation for future materials. Such investigations have been undertaken only very recently in the field of radio-degradation of EPDM materials [1–3].

Chemical information about radio-degradation mechanisms is available from spectroscopic methods aimed at identifying new species and measuring their concentration. Solid-state NMR has shown its efficiency in characterizing insoluble polymer materials and detecting low level of degradation (in the range of 1 carbon/1000) especially in vulcanised elastomers [4]. In this field, this non-destructive bulk analysis technique appears as an interesting alternative to the more conventional approach based on Infrared spectroscopy coupled to chemical derivation method [1]. Another approach to access high-resolution chemical information was recently proposed by Alam et al. [5,6] to study the oxidative degradation of polyisoprene. The method is based on ^{17}O NMR measurements of a polymer which has been aged in the presence of isotopically enriched oxygen gas. Basically, the method has the advantage of being very specific because only oxidized species are detected without background signal due to unaffected polymer. The main drawback resides in the strong line broadening which results from efficient ^{17}O (spin 5/2)

---

[*] Corresponding author. Fax: +33-2-47-34-51-48.
E-mail address: palmas@ripault.cea.fr (P. Palmas).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00476-2

quadrupolar relaxation and can lead to dramatic loss of spectral resolution. It has been shown that the problem can be circumvented by increasing the temperature of NMR experiment up to 125 °C in trichlorobenzene. However, at such temperatures, one can expect occurrence of undesired chemical modifications which alter the representativity of the measurements. Especially hydroperoxides are known to decompose above 100 °C to produce alkoxy radicals. As a consequence, although attractive, the method is expected to be totally inefficient in studying insoluble polymers in which the ^{17}O linewidth becomes too large. This concerns pure polymers and certainly even swollen materials.

Another approach offered by solid-state NMR is the possibility to access local molecular dynamics within a wide range motion frequency scale. The sensitivity and efficiency of this approach in detecting small modifications occurring in elastomers EPDM during thermal ageing have been demonstrated [4]. An alternative way to enhance polymer mobility consists in swelling the sample with a deuterated solvent [7]. This approach incontestably powerful in the case of pure polymer gels must be utilized with caution when applied to complex industrial formulations which contain additives like fillers and antioxidants.

In a previous work [4], we demonstrated the availability of a structural and dynamic approach based on ^{1}H broadband and ^{13}C high-resolution solid-state NMR spectroscopy for studying curing and thermal ageing of EPDM elastomers. The aim of the present paper is to investigate γ radiation induced degradation of this material using the same methodology. The importance of diene monomer, the effect of crosslinking curing process with dicumyl peroxide, and the efficiency of antioxidants are evaluated in the basis of several chemical formulations. In the first part, we examine in details our observations about chemical degradation as well as the evolution of concentrations as a function of radiation doses. The second part focuses on molecular mobility information measurements based on wideline ^{1}H T_2 relaxation and 2D ^{1}H–^{13}C high-resolution wideline separation sequences.

2. Experimental part

2.1. Sample preparation

Two series of samples were prepared with two different polymers EPDMa (NORDEL 2722) and EPDMb (NORDEL IP 3725) both provided by Dupont. Each series consists of four samples denoted as EPDMa1-4 and EPDMb1-4. First, an uncrosslinked elastomer denoted as EPDM1 was studied. Second, an elastomer mixed with 3 phr (parts per hundred rubber) of dicumyl peroxide crosslinking agent was cured under uniaxial pressure $P = 3.2 \times 10^5$ Pa at temperature $T = 180$ °C to prepare a crosslinked elastomer (denoted as EPDM2). Finally, EPDM3 and EPDM4 consist of crosslinked samples containing 1 phr of Vulcanox 4010 Na (primary amine based antioxidant provided by CIBA) and 0.1 phr of Irganox 1035 (primary phenol based antioxidant provided by Bäyer), respectively. The concentrations used correspond to standard values recommended by the manufacturers. The synthetic elastomer of the first series (EPDMa1-4) is an ethylene propylene 1,4 hexadiene monomer copolymer with mass ratios $z = 75.3$, 18.6 and 6.1%, respectively. The elastomer of the second series (EPDMb1-4) is an ethylene propylene ethylidene norbornene (ENB) monomer copolymer mass ratios $z = 70.4$, 27.7 and 1.9%, respectively. The mass ratios were determined from high-resolution solid-state NMR measurements [4]. Sample sheets with a thickness of 1 mm were irradiated with a ^{60}Co source at a dose rate of 1 kGy/h. The irradiation was performed at 20 °C under pure oxygen flow providing samples with cumulated doses ranging from 50 to 450 kGy. Under these conditions, the oxidation is expected to be almost uniform in the material.

2.2. Methods

^{13}C High-resolution solid-state NMR experiments were carried out using an AVANCE Bruker 400 MHz spectrometer with standard broadband X-H CP/MAS probe (7 mm external diameter rotors). ^{1}H wideline measurements were performed using an AVANCE Bruker 300 MHz spectrometer with selective solenoid probe (5 mm diameter tubes). All experiments were performed at room temperature.

^{13}C high-resolution solid-state NMR spectra were recorded from a single pulse experiment using standard magic angle sample spinning (MAS) speed $\nu_r = 7$ kHz and high-power ^{1}H decoupling during acquisition. Before Fourier transform, exponential multiplication was applied to experimental free induction decays. Because non-unique linewidth was observed in the spectrum, multiplications with several line broadenings were used instead of a single one to obtain the best signal/noise ratio for all the lines of interest. A first line broadening LB = 80 was applied for the examination of the 212–170 ppm region, a second one LB = 30 for the 82–70 ppm region and no window function was applied for the 14 ppm line. After Fourier transform and global baseline correction, total spectrum integration was assigned to 1000 carbons as a reference. Then local baseline corrections in the three different regions were carried out and the individual lines integrated.

^{1}H T_2 relaxation of the whole polymer system was measured using Hahn echo sequence. As described in Ref. [4], relaxation curves were satisfactorily fitted assuming two components : a rapid gaussian decay and a slow exponential decay which account for regions containing rigid polymer fragments and highly mobile polymer fragments, respectively. The fitting procedure then yields the relaxation time of rigid component T_{2r}, the relaxation time of mobile component T_{2m} and the mobile phase ratio x.

Proton heteronuclear dipolar spectra arising from residual dipolar local fields due to the ^{13}C-bonded protons were measured using 2D WISE experiment. As pointed out in Ref. [4], two different experiments were carried out to investigate the dynamics of the semi-crystalline polymer system: two sets of parameters ($T_{CP} = 2$ ms, $\nu_r = 800$ Hz) and ($T_{CP} = 200$ μs, $\nu_r = 4$ kHz) were used to sample the protons located in soft and rigid domains, respectively. These experiments are referred to as 'soft WISE' and 'rigid WISE' experiments hereafter. Quadrature detection during the evolution period was achieved using TPPI phase cycling. This procedure allows acquisition of dipolar spectra not affected by chemical shift distortions, although these effects are relatively weak for the present system which exhibits a proton chemical shift dispersion small compared to residual dipolar interactions.

Additional details about all these experiments can be found in Ref. [4].

Table 1
Chemical shift assignment for non-irradiated reference samples. All ^{13}C chemical shifts were referenced according to isolated CH_2 signal at 30 ppm. α, β and γ notations have their usual meaning indicating the backbone carbon position relative to carbon branching. The branching nature is specified using the subscripts 'p' for propylene, 'h' for hexadiene and 'e' for ethylidene norbornene

Chemical shift (ppm)	Assignment
149.2	2-Phenyl 2-propanol
146.1	Ethylidene norbornene unsaturation
129.7–125.3	Hexadiene unsaturation
127.8–126.1–124.3	2-Phenyl 2-propanol
110.5	Ethylidene norbornene unsaturation
71.6	2-Phenyl 2-propanol
45	$(CH_2\alpha\alpha)_p$–$(CH_3)CH$–$\mathit{CH_2}$–$CH(CH_3)$–
37.2	$(CH_2\alpha)_p$, CH from hexadiene
34.4	–CH_2–$CH(CH_2R)$–$\mathit{CH_2}$–, $(CH_2\alpha)_h$
32.7	CH from propylene
30	Isolated CH_2, $(CH_2\gamma,\delta)_p$
27.3	$(CH_2\beta)_{p,h,e}$
24.5	$(CH_2\beta\beta)_p$–$(CH_3)CH$–CH_2–$\mathit{CH_2}$–CH_2–$CH(CH_3)$–
22.8	CH_2 nearby CH_3 chain end
20.3	–$(CH_3)CH$–CH_2–$CH(CH_3)$–
19.7	CH_3 from propylene
17.9	CH_3 from hexadiene (*trans* isomer)
15	CH_3 chain end ($n_{CH_2} < 5$)
14.2	CH_3 chain end
13.8	CH_3 from ethylidene norbornene
12.8	CH_3 from hexadiene (*cis* isomer)

3. Results and discussion

3.1. Chemical shift assignments and proposed mechanisms

^{13}C NMR spectra of samples EPDMa2 and EPDMb2 (cured ethylene propylene hexadiene/ethylidene norbornene elastomers) non-irradiated and irradiated at 450 kGy are shown in Fig. 1. The main spectral assignments of reference samples were carried out on the basis of published results obtained for polymer in solution [8–10], in the swollen state [10] or in the solid-state [11]. All chemical shifts together with corresponding chemical substructure are gathered in Table 1. Concerning the EPDMa series, the present results (Fig. 1(d)) show that only the first unsaturation of hexadiene is involved during the polymerisation reaction leading to an α-methyl dangling unsaturation in the polymer. The detection of methyl signal at 12.8 and 18 ppm is an indication for the presence of both *cis*- and *trans*-isomers. Concerning the EPDMb2 series (Fig. 1(b)), the lines at 146 and 111 ppm indicate that only the unsaturation from the cycle of ENB is involved during the polymerisation reaction. Extra signals (see Fig. 1 and Table 1) were assigned to 2-phenyl 2-propanol indicating that this compound is the main degradation product of dicumyl peroxide agent used for the curing process of polymer. New features are clearly evidenced in the spectra of irradiated samples (Fig. 1(a) and (c)): first, additional lines in the regions of carbonyl, acid/ester, alcohol/ether, peroxide, epoxide and methyl groups are clearly evidenced. Second, a strong decrease of unsaturations (due to diene moiety) is observed. And finally a small increase of methyl chain end signal can be seen for the EPDMa series (Fig. 1(c)). NMR chemical shifts of new oxidation species were tentatively assigned to specific substructures of the polymer using experimental data of related compounds from published results [9,12], Aldrich catalogue as well as calculated spectra from ACD predictor commercial program. These proposed structures were deduced only from chemical shift information and must be seen as the more probable solutions compatible with the present experimental observations. We discuss below these assignments which are all gathered in Table 2. Looking at the broad line in the region 211–196 ppm, at least five maximums at 211.2, 207.5, 205.5, 203.5 and 196.5 ppm can be pointed. The first one certainly corresponds to main chain ketones. The second chemical shift is compatible with α-methyl ketone or α,β-unsaturated ketone, the latter being less probable because an extra line due to the unsaturation would appear at 140 ppm (not detected here) 205.5 and 203.5 ppm chemical shifts are assigned to aldehyde functions. The smallest line at 196.5 can be assigned to α,β-unsaturated aldehyde but is also compatible with methyl, phenyl ketone which is another possible dicumyl peroxide degradation product. The second region of interest in the range (180–162 ppm) concerns carboxylic carbons. The main signal between 176.5 and 173 ppm is characteristic of γ-lactone or ester compounds. No additional spectral information may be used to make a choice between both possibilities: in one hand, the ester function would produce two extra lines at 64 and 51 ppm which are not clearly detected here. Probable reasons of non-detection of these signals are weak intensity, broadening and overlap with the main signal of the carbon spectrum. In the other hand the methine carbon of the γ-lactone if any expected at 81 ppm certainly overlaps with

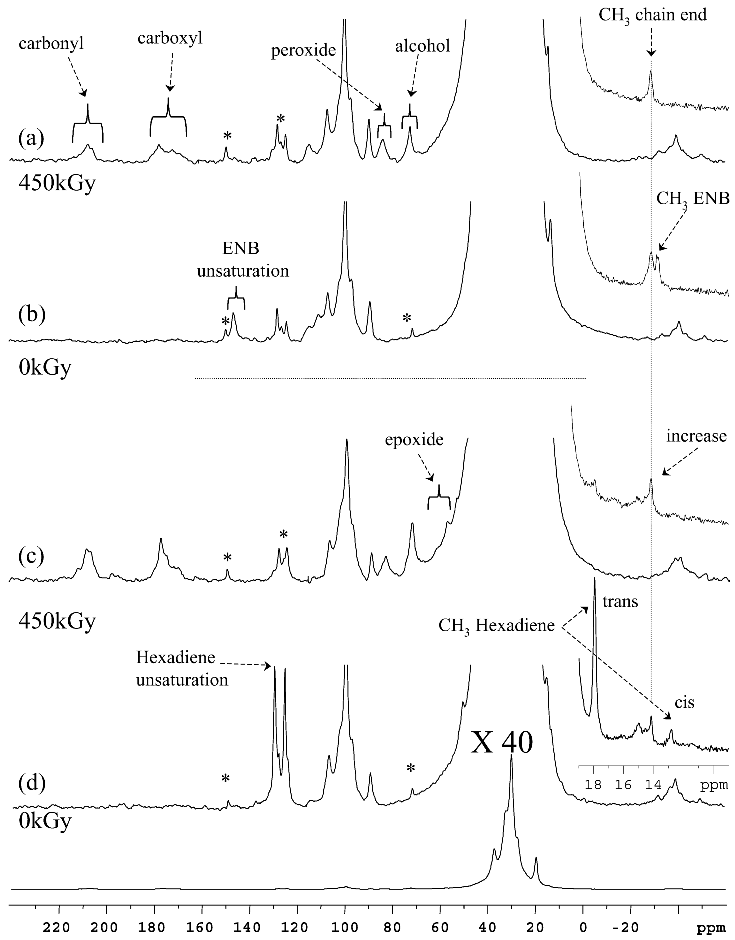


Fig. 1. ^{13}C NMR spectra of EPDMb2 cured ethylene propylene ENB (a,b) and EPDMa2 cured ethylene propylene hexadiene (c,d) non-irradiated and irradiated at 450 kGy. Chemical shifts of 2-phényl 2-propanol, a dicumyl peroxide degradation product, are marked by an Asterisk.

the secondary and tertiary hydroperoxides signal occurring at the same chemical shift (see below). Two additional broad absorptions are observed, one centred at 179.5 ppm and the second one in the 171.5–162 ppm domain. 179.5 ppm is a characteristic chemical shift of carboxylic acid. The second shoulder could result from α,β or β,γ-unsaturated acid or ester. The peak centred at 82.8 ppm is characteristic of secondary and tertiary peroxide or hydroperoxide, primary hydroperoxide being excluded. As stated before, a contribution from γ-lactone is also expected at this chemical shift. In the same way only tertiary and secondary forms are observed in the alcohol region. Two small extra signals are observed at 57.7 and 53.3 only for the EPDMa series which contain hexadiene as diene. These chemical shifts are characteristic of epoxy carbon [13] probably at α or β position of a branched methyl. Epoxy formation can result from the reaction of peroxide radical with unsaturation [1,13]. The absence of epoxide function for EPDMb series can be explained by the lowest level of diene unsaturation of reference sample or the steric constraints existing in ENB and not in hexadiene.

3.2. Intensity evolution as a function of radiation dose

For the first series, ^{13}C high-resolution spectra were recorded at intermediate doses of irradiation. Fig. 2 shows the concentration evolution (expressed in carbon/1000 carbons) as a function of radiation doses of unsaturations, oxidation products and methyl chain end as measured from line integration in the carbon spectrum of EPDMa2. The

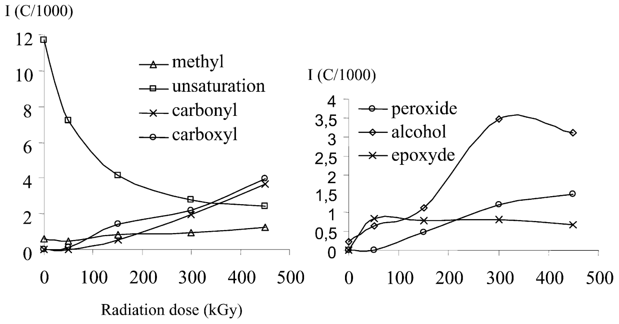
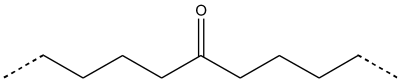
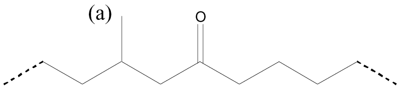
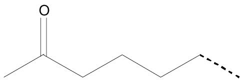
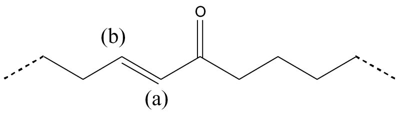
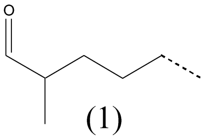
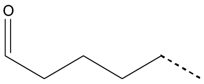
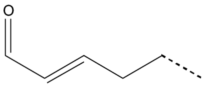
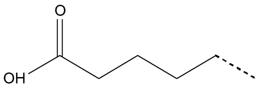
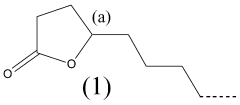
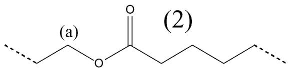
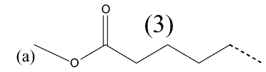
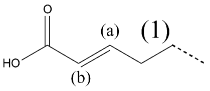
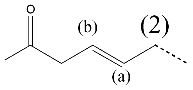
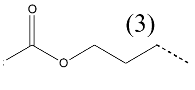
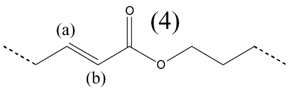
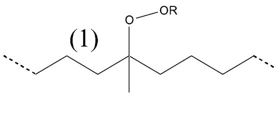
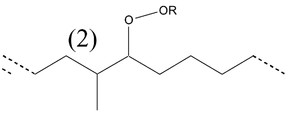
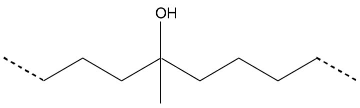


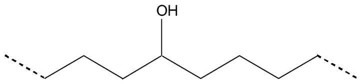
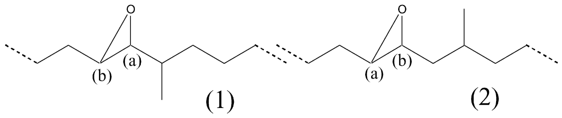
Fig. 2. Concentration evolution of different chemical species as a function of radiation dose as measured from line integration in the carbon spectrum of EPDM2a. Experimental error was estimated to 0.2 C/1000.

Table 2
Chemical shift assignments of oxidation products detected on irradiated samples. (First column): experimental chemical shift (in order to make more accurate comparisons between calculated and experimental chemical shifts, all ^{13}C chemical shifts were rescaled according to the calculated value 29.5 ppm of isolated CH_2 signal); (second column): chemical shifts calculated from ACD; (third column): chemical shifts of similar structures extracted from Aldrich spectrum catalogue; (fourth column): more probable proposed structure compatible with chemical shifts. The main chemical shift indicated corresponds to the carbon bonded to oxygen with a double bond if any (carbonyl and carboxyl groups) or with a single bond (peroxide, alcohol, epoxide). In italic are indicated additional specific carbon chemical shifts of the structure extracted from Aldrich catalogue or calculated spectra

Exp.	Calc.	Aldrich	Formula
211.2	211.6	211	
	211.5	211.5; *20.9*$^{(a)}$	
207.5	207.9	209	
	206.5; *134*$^{(a)}$; *141*$^{(b)}$		
205.5, 203.5	204.5 (1), 202.4 (2)	205, 202.2	 (1)  (2)
196.5	194	196	
179.5	180.1	180	
176.5–173.5	177.3; *80.3*$^{(a)}$, 173.9; *64.1*$^{(a)}$, 174.1; *51.3*$^{(a)}$	177.5; 81 (1), 176; 64 (2), 176; 51.5 (3)	 (1)  (2)  (3)
171.5–162	171.5; *149.7*$^{(a)}$, *124*$^{(b)}$ (1), 170.6; *134.2*$^{(a)}$, *130.2*$^{(b)}$ (2), 170.8 (3), 166.2; *149*$^{(a)}$, *121*$^{(b)}$ (4)	174; 152; 121 (1)	 (1)  (2)  (3)  (4)
82.8	with R = H, 87.3 (1), 80.1 (2), with R = $C_{quaternary}$, 87.6 (1), 80.7 (2)		 (1)  (2)
73.5	71.7	73	

(continued on next page)

Table 2 (*continued*)

Exp.	Calc.	Aldrich	Formula
71.7	71.8	72	
57.7; 53.3	61$^{(a)}$; 53.1$^{(b)}$ (1), 56.5$^{(a)}$; 53.1$^{(b)}$ (2)		

most important feature is the strong and rapid decrease of unsaturation of diene moiety. This evolution is effective at the lowest doses: about 5 C/1000 are lost at 50 kGy and 10 C/1000 at 300 kGy leading to a plateau value of 2 C/1000. Half of this value is due to 2-phenyl 2-propanol alcohol carbon (see below); the other half is assignable to additional unsaturations probably produced during irradiation. At the same time gradual increase of oxidation products is observed reaching different levels: 1.5 C/1000 for peroxides/hydroperoxides, 3.7 for carbonyl groups (ketones, aldehydes) and 4 for carboxylic groups (acids, esters, lactones). A slightly different behaviour is observed for alcohol concentration which passes through a maximum value of 3.5 at 300 kGy and then slowly decreases. The non-zero value (0.21 C/1000) of alcohol concentration on reference sample is due to 2-phenyl 2-propanol carbon at 71.6 ppm. The same contribution is seen for EPDMa4, EPDMb2 and EPDMb3 as shown in Table 3. The concentration of this compound which is present in reference samples is constant during irradiation as revealed by the quaternary aromatic carbon transition at 149.2 ppm. An interesting feature observed for all samples is the existence of an induction period corresponding to a dose of 50 kGy during which no concentration evolution of oxidation products is detected. A completely different behaviour is observed for epoxide functions for which a maximum concentration of 1 C/1000 is immediately reached at 50 kGy and then remains constant for higher doses. Alternatively, a small but significant increase ($<$ 1 C/1000) of methyl chain end is measured revealing main chain scission processes during ageing. The same effect was observed in Ethylene Propylene rubber γ irradiated in vacuum [10,11].

3.3. Comparisons between formulations

The concentration evolution of species for different formulations irradiated at 450 kGy is shown in Table 3. These values correspond to the difference integration between irradiated sample and reference sample. It is first interesting to compare EPDMa and EPDMb series which contain 6% of hexadiene and 2% of Ethylidene norbornene, respectively. An examination of the results obtained from EPDM1 and EPDM2 (crosslinked and uncrosslinked sample) evidences stronger ageing effects for the EPDMa series: (i) a higher level of oxidation product concentration is measured, especially for carbonyl, carboxyl and to a lesser extent alcohol functions; an exception is provided by EPDMb1 in which a peroxide concentration higher than in EPDMa1 is detected; (ii) a non-zero epoxide function concentration value is detected only in EPDMa series; (iii) a small increase of methyl chain end is observed only in EPDMa series. Such different behaviours toward ageing of EPDMa and EPDMb compositions can be correlated to the initial residual diene unsaturation present in non-irradiated sample. Actually, the concentration level of these unsaturations is substantially high and different for both compositions. A similar situation is observed both for uncured (EPDMa1, EPDMb1) and cured samples (EPDMa2, EPDMb2) because only a small part of unsaturations is

Table 3
Difference integration between sample irradiated at 450 kGy and reference sample calculated for the different formulations. For EPDMb series, the unsaturated carbon concentration was calculated by multiplying by two the line integration of aromatic quaternary carbon at 146.2 ppm. EPDMa2 at 0 kGy instead of EPDMa4 was used as the reference sample to calculate EPDMa4 concentrations in this table. 'nd' stands for non-detected. A non-zero value (about 0.2 C/1000) for alcohol concentration on reference sample is due to 2-phenyl 2-propanol a dicumyl peroxide degradation product present in EPDM2-4

	Carbonyl	Carboxyl	Hexadiene unsaturation	ENB unsaturation	Peroxide	Alcohol	Epoxide	Methyl chain end
EPDMa1	3.49	3.58	−11.66		2.13	3.02	0.93	0.62
EPDMa2	3.64	3.95	−9.29		1.48	2.89	0.67	0.66
EPDMa4	nd	nd	0.78		nd	0.38		0.28
EPDMb1	2.05	2.56		−4.2	3.22	2.66	nd	−0.13
EPDMb2	1.92	2.46		−3.82	1.3	1.72	nd	−0.26
EPDMb3	1.83	1.99		−3.62	1.62	0.74	nd	−0.31

really consumed by dicumyl peroxide during the curing process (see Table 3 and Ref. [4]). Hence, we propose that the presence of residual unsaturation is responsible for a strong acceleration of oxidation reactions occurring in the polymer sample exposed to γ-radiations. The residual unsaturation level is thus a crucial parameter which should be controlled during curing process of such elastomers when used to the production of high energy resistant materials.

Another interesting feature is the evaluation of crosslinking effect on ageing by comparing cured and uncured samples. Present results show that, whereas, no significant differences are observed for carbonyl and carboxyl groups, substantial higher level of peroxide, alcohol and epoxide concentration are measured on uncrosslinked samples. This beneficial effect of curing which is especially stronger for EPDMb series is not assignable to different initial residual unsaturation concentration existing in both samples because this difference is small. It could be related to macromolecular effect on chemical kinetics due to changes of crosslink density: chain steric constraints and motion, oxygen and polymer chain diffusion rates. The efficiency of antioxidants were evaluated in the basis of EPDMa4 and EPDMb3 formulations containing 0.1% Irganox and 1% Vulcanox, respectively. Oxidation products detected in EPDMb3 were found to be substantially less concentrated than those obtained from EPDMb2 (without antioxidant), but the stabilizing effect is small. On the other side, no oxidation product was detected at all in EPDMa4 indicating a total stability of such formulation exposed to γ-ray irradiation doses below 450 kGy.

3.4. Ageing effect on molecular mobility

$1/T_2$ evolution as a function of radiation dose is shown in Fig. 3 for different compositions. It is clear from Fig. 3 that a global hardening within the whole proton system occurs during irradiation of EPDM1,2,3 as revealed by an increase of both relaxation rates and a decrease of the mobile phase ratio. The chemical mechanism responsible for the observed hardening of the sample is assigned to crosslinking reactions which reinforce the macromolecular skeleton leading to a strong reduction of the molecular mobility. This chemical process which is dominant under anaerobic environment is accompanied by oxidation products formation and small amount of chain scission reactions, as revealed by ^{13}C high-resolution spectra. It may be noted that the relaxation curves as a function of radiation doses differ from those obtained for the oxidation products (Fig. 2) by the absence of any induction period for weak irradiation doses. This is a consequence of the non-oxygen dependence of crosslinking reactions responsible for the observed material hardening.

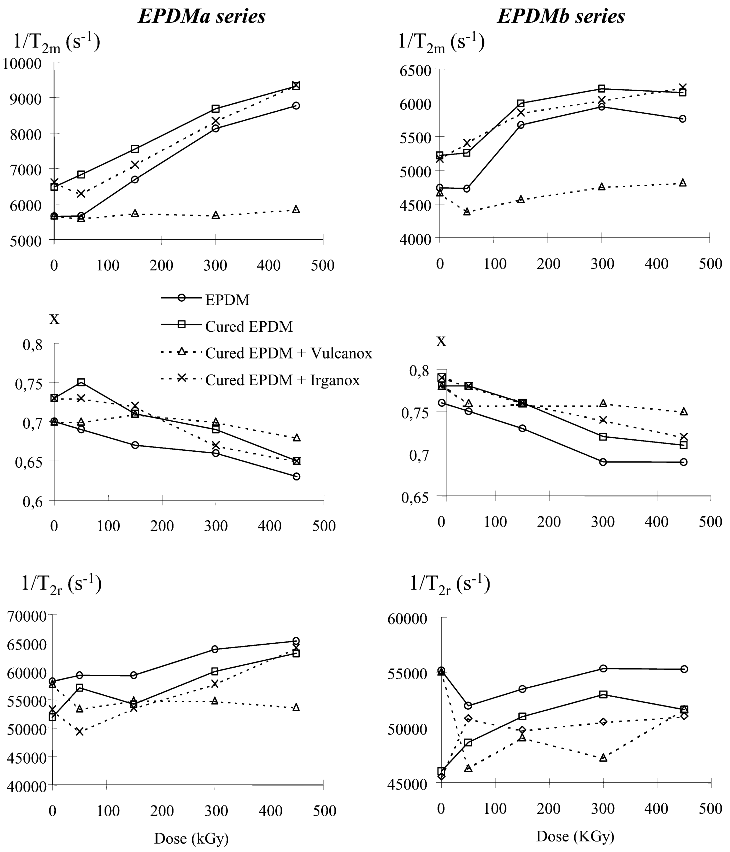


Fig. 3. The course of x the mobile phase ratio, ($1/T_{2m}$) and ($1/T_{2r}$) the relaxation rates in the mobile phase and rigid phase as a function of radiation dose for the different EPDM compositions.

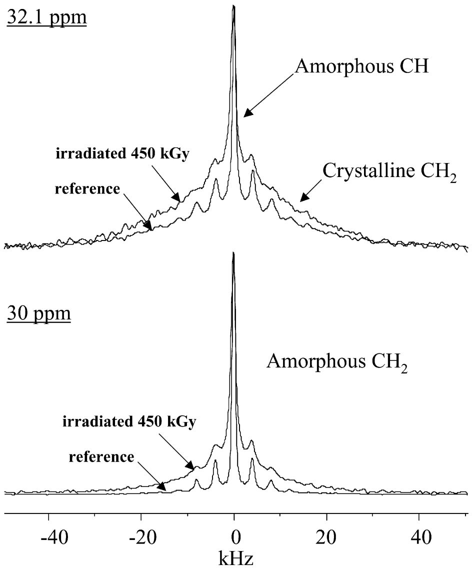


Fig. 4. MAS modulated ^{1}H dipolar spectra from rigid WISE (MAS frequency 4 kHz and contact time 200 μs) 2D map for two different ^{13}C chemical shifts $\delta = 30$ and 32.1 ppm.

As a consequence, the effect of radiation on ageing is detected even at the lowest doses by T_2 measurements.

Comparison between formulations confirms the main conclusions deduced from the analysis of oxidation products from high-resolution ^{13}C spectra: (i) the EPDMb series is more stable than the EPDMa series (especially visible on T_{2m}) as a result of acceleration effect of residual diene unsaturation on ageing; (ii) no significant difference is observed between crosslinked and uncrosslinked samples indicating that the amount of crosslinking and scission reactions which affect the polymer molecular mobility are not influenced by the curing process. This result agrees well with the evolution of oxidation product concentrations from Table 3 if we assume that only the carboxylic function can be responsible for the polymer chain scission [1,13]. Actually, the carboxylic concentration is seen identical for cured and uncured sample although the alcohol and peroxide concentrations are different; (iii) a complete inefficiency of 0.1% Irganox antioxidant and complete efficiency of 1% Vulcanox antioxidant are evidenced from EPDM3b and EPDM4a. Soft WISE and Rigid WISE 2D [4] experiments were carried out to elucidate potential sample heterogeneities which take place during irradiations. Dipolar slices for amorphous $CH_{2\gamma}$ at 30 ppm in one hand and crystalline CH_2, amorphous CH at 32.1 ppm in an other hand extracted from rigid WISE 2D map are shown in Fig. 4. Examination of these spectra shows the formation after irradiation of an homogeneous broad line 20–40 kHz wide, not modulated by sample rotation, which corresponds to a new family of protons experiencing strong dipolar interactions. Comparisons of slices at different chemical shifts in WISE experiments show that the modifications of mobility occur uniformly in the amorphous content and are not dominated by changes affecting crystalline domains.

4. Conclusion

Ageing of EPDM elastomer formulations exposed to γ irradiation has been investigated using solid-state NMR spectroscopy. Both ^{13}C high-resolution and ^{1}H wideline approaches were combined to detect and quantify chemical degradation including oxidation products formation, chain scission and crosslinking reactions at a level as low as 1 C/1000.

The major effect of irradiation observed is a strong hardening of the amorphous polymer phase. This evolution which was detected even at the lowest dose of irradiation is assigned to crosslinking reactions. After an induction period corresponding to 50 kGy dose, oxidation products like carboxylic, carbonyl, alcohol, peroxide and epoxide groups were detected and the corresponding concentrations measured as a function of radiation dose from line integration. A higher level of degradation was measured in samples containing hexadiene as diene. This effect was assigned to a higher level of diene unsaturation present in the initial polymer of the EPDMa series. The effect of curing process on ageing was also evaluated. While a small difference was found resulting in lower alcohol peroxide and epoxide concentrations in cured samples, no difference was noted for carbonyl and carboxylic concentrations. Concerning the antioxidant, no stabilising effect was noted for the composition containing 0.1% Irganox whereas a complete stability of 1% vulcanox composition was observed up to the highest dose of 450 kGy.

Highly specific structures were tentatively proposed as a result of careful examination of ^{13}C chemical shifts. Further examination of these structures in term of chemical mechanisms and kinetics is possible but is beyond the scope of present paper. This will be the subject of a future work including present results as well as those obtained independently by S. Cambon using Infrared spectroscopy coupled to chemical derivation methods [1].

Acknowledgements

This work is part of the COMOR (Comportement des Matériaux Organiques sous Rayonnement) organisation activities inside CEA. We are very grateful to Dr Stéphanie Labayle Camus for improvements of the manuscript.

References

[1] Cambon S. PhD Thesis. Clermont Ferrand, Blaise Pascal University; 2001.

[2] Davenas J, Stevenson I, Celette N, Cambon S, Gardette JL, Rivaton A, Vignoud L. Nucl Instrum Methods Phys Res, Sect B—Beam Interact Mater Atoms 2002;191:653–61.

[3] Celette N, Stevenson I, Davenas J, David L, Vigier G. Nucl Instrum Methods Phys Res, Sect B—Beam Interact Mater Atoms 2001;185: 305–10.

[4] Palmas P, Le Campion L, Bourgeoisat C, Martel L. Polymer 2001;42: 7675. and references therein.

[5] Alam TM, Celina M, Assink RA, Clough RL, Gillen KT. Radiat Phys Chem 2001;60:121–7.

[6] Alam TM, Celina M, Assink RA, Clough RL, Gillen KT, Wheeler DR. Macromolecules 2000;33:1181–90.

[7] Assink RA, Gillen KT, Sanderson B. Polymer 2002;43:1349–55.

[8] Pooter MD, Smith PB, Dohrer KK, Bennett KF, Meadows MD, Smith CG, Schouwenaars HP, Geerards RA. J Appl Polym Sci 1991;42:399.

[9] Heinen W, Ballijns LN, Wittenburg WJA, Winters R, Lugtenburg J, van Duin M. Polymer 1999;40:4353–63.

[10] O'Donnel JH, Whittaker AK. Polymer 1992;33(1):62–7.

[11] O'Donnell JH, Whittaker AK. Br Polym J 1985;17(1):51–5.

[12] Assink RA, Celina M, Dunbar TD, Alam TM, Clough RL, Gillen KT. Macromolecules 2000;33:4023–9.

[13] De Paoli MA. Eur Polym J 1983;19(9):761–8.