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Influence of silica fillers during the electron irradiations of DGEBA/TETA epoxy resins, part I: Study of the chemical modification on model compounds

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Abstract

The study of the chemical modifications of model compounds of the diglycidyl ether of bisphenol A/triethylene tetramine (DGEBA/TETA) epoxy resins under electron irradiation is described. The reaction of butylamine and *N*,*N*′-diethylethylene diamine with DGEBA afforded model compounds of the DGEBA/TETA structure. Nanometric silica was used as filler for these model compounds. ^{1}H and ^{13}C NMR analyses allowed identification of the chemical structures before and after irradiation. C–O and C–N scissions were observed with the formation of phenolic and methyl-ketone ends and of primary and secondary amines. For the model compounds containing the 1,2-diaminoethylene structure, the scission of the C–N bond is followed by the formation of an enamine end. The mechanisms of the different bond scissions are proposed. The presence of the nanometric silica fillers allows the protection of some C–N bonds. The reaction of the chemical species formed by electron irradiation with the reactive functions at the silica surface is proposed to explain the chemical modifications observed on the irradiated filled model compounds.

Keywords: Silica filled epoxy resins; Electron irradiations; Structural investigation; ^{1}H and ^{13}C NMR analyses

1. Introduction

The ageing of polymers is a visible phenomenon on usual plastic and composite materials. Its effects result in some aspect modifications and induce alterations in the mechanical properties (yellowing, darkening, embrittlement,...). The ageing is generally increased when the material is exposed to ionising radiation. Use of polymeric materials in high radiation fields involves a good knowledge of their irradiation-induced ageing for a better use in medium and long term and to prevent risks. For such applications, ethylene–propylene–diene monomer (EPDM) and epoxy/amine networks are widely used for their high performance (mechanical properties). Various studies have been carried out on the effect of irradiation on polymers [1–5]. Recently, the COMOR network (COmportement des Materiaux Organiques sous Rayonnement/Behaviour of Organic Materials under Radiation), managed by the CEA (French Atomic Energy Commission) and the CNRS (French National Centre for Scientific Research), has initiated studies on the effect of irradiation on the ageing of different polymers like EPDM [6–8] and epoxy resins [9–15]. In all cases, pure polymers have been studied as models of the commercial materials. The present work is devoted to the study of the influence of silica fillers on the electron irradiation ageing of epoxy resins. Because of its wide use in industrial applications and especially in nuclear environment, the diglycidyl ether of bisphenol A/triethylene tetramine (DGEBA/TETA) resin was chosen. The modelling method has already been used to study the crosslinking kinetics of thermoset polymers [16–19] by HPLC and liquid NMR, and particularly for epoxy resins [20,21]. The aim of this work was to study the chemical behaviour of electron irradiated DGEBA/butylamine and DGEBA/*N*,*N*′-diethylethylene diamine (DGEBA/

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DEDA) model compounds of the DGEBA/TETA epoxy resin. ^{1}H and ^{13}C NMR analyses allowed us to observe the chemical modifications induced by the presence of nanometric silica fillers. The chemical reactions occurring during the irradiations with and without nanometric fillers are detailed.

2. Experimental

2.1. Materials

The prepolymer was the diglycidyl ether of bisphenol A (DGEBA, supplied by Vantico under the reference LY 556). Its epoxy index is 5.4 equiv/kg and its average molecular weight is 370 g/mol ($n = 0.103$). For the model compounds, the amines were butylamine and *N*,*N*′-diethylethylene diamine (DEDA). The coupling agent was glycidyloxypropyltrimethoxysilane (supplied by Degussa under the name Glymo®). The chemical structures of the reactants are presented in Fig. 1.

The nanometric silica used to fill the chemical models was the Aerosil® 200 (supplied by Degussa under the name Aerosil® 200) with an estimated specific surface of 214 m^2/g and an average diameter of particles from 10 to 20 nm.

To obtain the silica filled models, the silica was first dried at 120 °C under vacuum during 12 h and dispersed in a small quantity of methylene chloride. The suspension was mixed with DGEBA for 1 h and the methylene chloride was removed under vacuum. The mixture was then dried under vacuum at 40 °C. Reactivity study of the DGEBA with the nanometric silica was performed using a three-step temperature cure of the epoxy resin: 25 °C for 12 h, a raise of 1 °C/min to 130 °C and a plateau at 130 °C during 5 h. The nanometric silica was then removed from the mixture by filtration. The syntheses of the model compounds were performed in a Teflon® mould at 25 °C for 12 h after mixing. Five grams (13.5 mmol) of DGEBA were mixed with 0.99 g (13.5 mmol) of butylamine or 1.51 g (13 mmol) of DEDA. For the grafting of the glycidyloxypropyltrimethoxysilane on the nanometric silica a suspension of Aerosil® 200 (1 g) and Glymo® (0.6 g, 2.54 mmol) in dry toluene was refluxed for 15 h in a dry Teflon® flask.

2.2. Irradiation conditions

Samples were irradiated by electron beam (2.5 MeV, 250 kGy/h) under helium (1.1 atm) at 20 °C with a Van De Graaff electron accelerator in the Laboratory of Irradiated Solids (LSI) of the Ecole Polytechnique of Palaiseau. The chosen doses were 2, 5 and 10 MGy. After irradiation, samples were kept under vacuum at −30 °C.

2.3. Techniques

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC400 Fourier transform spectrometer at 400.13 and 100.62 MHz, respectively. Chemical shifts are reported in ppm down-field from tetramethylsilane (TMS) used as an internal reference. Multiplicities are defined as singlet (s), doublet (d), triplet (t), quadruplet (q), and multiplet (m).

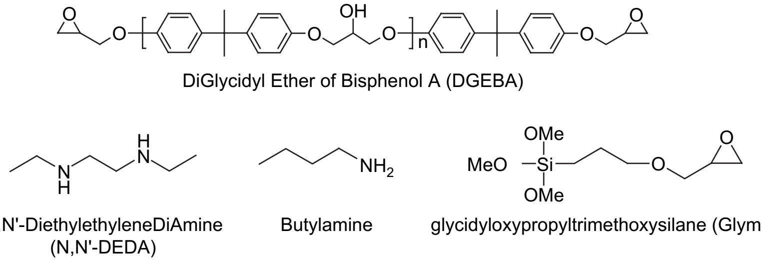
The particle size of the silica particles was measured with a Coulter LS 230 laser analyser. The specific surface was measured with a Coulter SA 3100. MET pictures were obtained with a JEOL transmission electronic microscope functioning at 220 kV. A small quantity of product was dispersed in ethanol under ultrasound during 10 min to limit particle agglomerates. One drop of this suspension was deposited on a copper covered carbon grid. The observations were carried out after ethanol evaporation.

3. Results and discussion

3.1. Influence of the nanometric silica fillers on the chemical structure of the model compounds

3.1.1. Reactivity of the DGEBA with the silica

The DGEBA was mixed with untreated or treated nanometric silica and the mixture was submitted to the temperature programme used for the cure of the epoxy resin. In order to follow the chemical changes of the DGEBA, ^{1}H and ^{13}C NMR analyses were performed on the DGEBA before mixing with nanometric silica and after cure and filtration. Before mixing, the characteristic signals of the diols end-chains and of the hydroxypropyl ether units are observed. On the ^{13}C NMR spectrum of the filtered solution of DGEBA after cure, these signals disappeared (Fig. 2). When the DGEBA was submitted to the same temperature programme without nanometric silica, these signals were still present. The disappearance of these signals is due to the presence of the nanometric silica in the mixture during the thermal treatment. The silica surface is characterised by two distinct functions [22–25]: silanol groups (Si—OH) and siloxane groups (Si—O—Si). During cure, interactions between reactive functions of the polymer and silanol functions at the surface of the silica may occur. The presence of hydroxy functions on the polymer chain can



DiGlycidyl Ether of Bisphenol A (DGEBA)

N,N'-DiethylethyleneDiAmine (N,N'-DEDA)

Butylamine

glycidyloxypropyltrimethoxysilane (Glymo)

Fig. 1. Chemical structures of reagents.

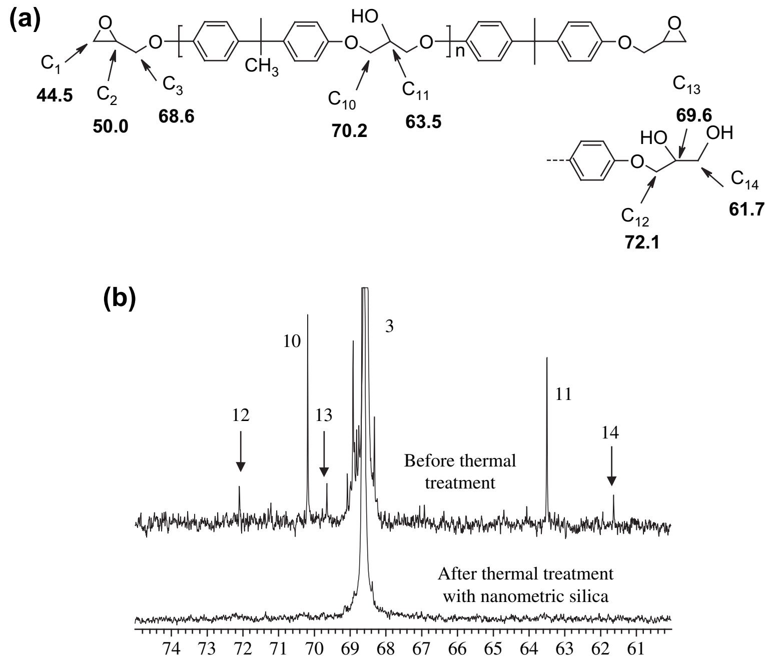


Fig. 2. (a) Formula and (b) expansion of the ^{13}C NMR spectrum of DGEBA before and after thermal treatment with the nanometric silica fillers.

favour its adsorption or its fixation by hydrogen bonds at the surface of a silica particle. This retention explains the absence of characteristic signals in the NMR spectrum of the filtered solution of DGEBA after cure.

3.1.2. The DGEBA/butylamine model compound

The DGEBA was mixed with untreated or treated nanometric silica and butylamine. The reaction was performed at 25 °C for 12 h. The attack of the primary amine function

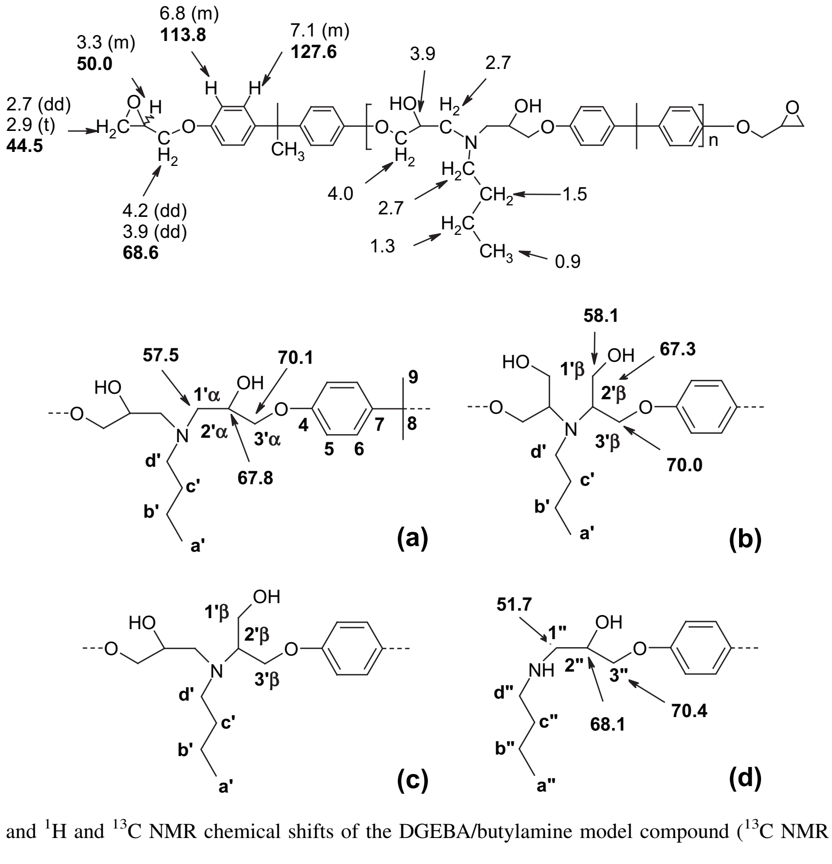


Fig. 3. Chemical structures and ^1H and ^{13}C NMR chemical shifts of the DGEBA/butylamine model compound (^{13}C NMR chemical shifts in bold).

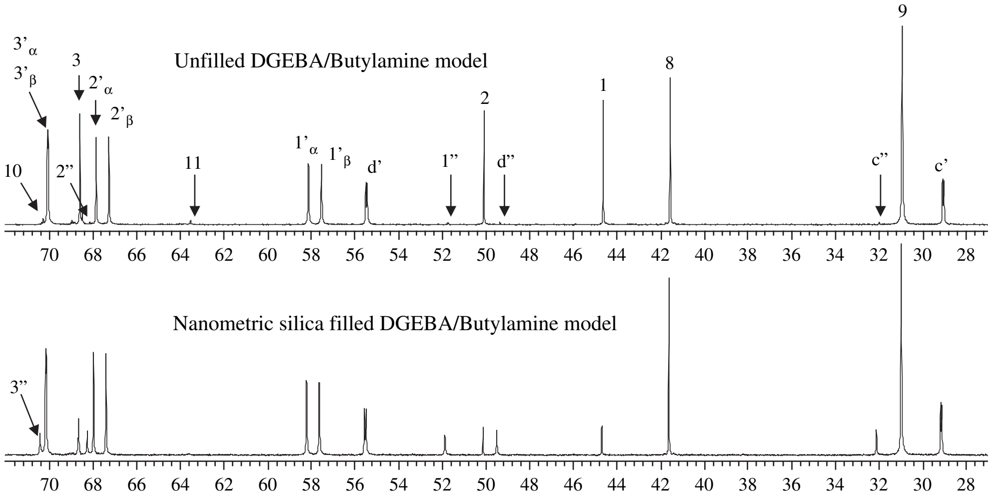


Fig. 4. Comparison of ^{13}C NMR spectrum of unfilled and pure nanometric silica filled DGEBA/butylamine model compounds (expansion from 27 to 72 ppm).

can be achieved on the less or on the most substituted carbon of one or two epoxy rings. Four kinds of structures can be detected and are presented in Fig. 3 with their corresponding ^{1}H and ^{13}C NMR chemical shifts. The butylamine mono-substituted structure (d) corresponds to an intermediate stage. The consumption of the epoxy rings was estimated by the ^{1}H NMR analysis to 70%.

In order to determine the chemical structure modifications involved by the presence of the nanometric silica, the ^{13}C NMR spectra of the unfilled DGEBA/butylamine model compounds were compared to those of the pure nanometric silica filled model compound. On the pure nanometric silica filled model compound spectrum (Fig. 4), the signals of the remaining glycidyl carbons (C_1, C_2 and C_3) are less intense compared to the signals of the mono-substituted amine structure carbons ($C_{c''}$, $C_{d''}$, $C_{1''}$, $C_{2''}$ and $C_{3''}$) which are more intense. A similar observation was made in the case of the treated nanometric silica filled model compound. In the presence of the nanometric silica, the reactivity of the primary amine to form a secondary amine structure is improved. Hydrogen bonds with oxygenated functions on the surface of the silica may improve the nucleophilic character of the primary amine function and so improve the reaction with the epoxy rings. The predominance of the secondary amine structures shows a weakening of their reactivity on the epoxy rings. Steric hindrance and weaker mobility of the chain of the DGEBA may explain this result.

For the treated nanometric silica filled DGEBA/butylamine model compound, the NH functions of the amine can react with the epoxy ends of the coupling agent grafted on the silica surface. However, the number of epoxy ends of the coupling agent in the mixture is very small. Their influence on the stoichiometry of the reaction is not detectable by the NMR analysis. The epoxy ring consumption was estimated with the ^{1}H NMR spectrum as 70% for the unfilled model compound, 85% for the pure nanometric silica filled model compound

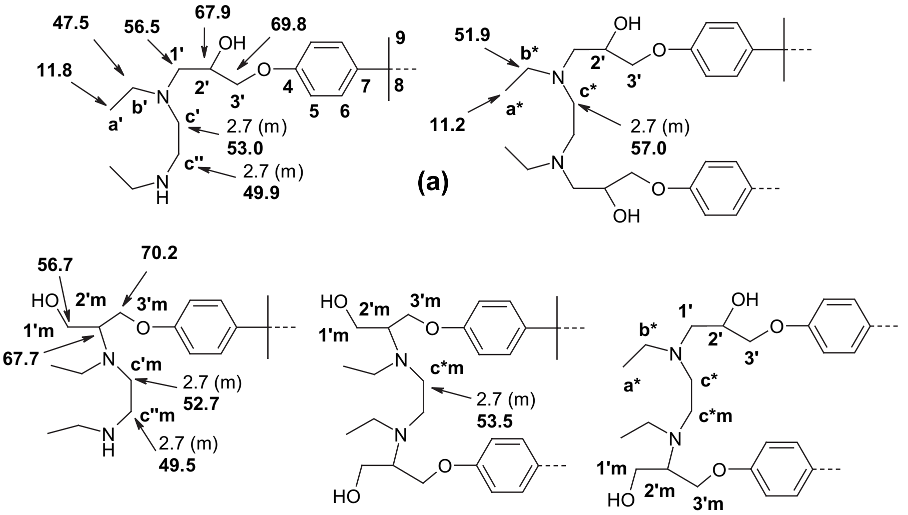


Fig. 5. (a) Major, (b) minor and (c) combined chemical structures of the DGEBA/DEDA model compound (^{13}C NMR chemical shifts in bold).

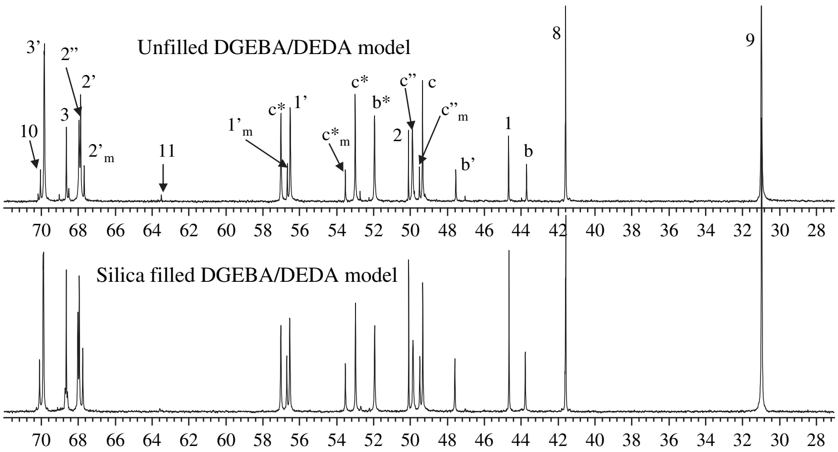


Fig. 6. Comparison of ^{13}C NMR spectrum of unfilled and pure nanometric silica filled DGEBA/DEDA models (expansion from 27 to 72 ppm).

and 81% for the treated nanometric silica filled model compound.

3.1.3. The DGEBA/DEDA model compound

N,*N*′-Diethylethylene diamine was reacted with DGEBA with and without nanometric silica fillers with the conditions described on the experimental part. The ^{13}C NMR analysis allowed us to detect major and minor structures: the former were obtained by the attack of the amines on the less substituted carbon of the epoxy rings and the latter were obtained by the attack of the amines on the most substituted carbon. Moreover, both amine functions of the DEDA do not necessarily react. The chemical structures and the corresponding ^{1}H and ^{13}C NMR chemical shifts are presented in Fig. 5. The consumption of the epoxy rings was estimated with the ^{1}H NMR spectrum to 86%.

In order to determine the modifications of the chemical structure due to the presence of nanometric silica fillers, the ^{13}C NMR spectrum of the unfilled DGEBA/DEDA model compound was compared to the one of the pure nanometric silica filled model compound (Fig. 6). In the filled model compound spectrum, the signals of the remaining glycidyl extremities carbons (C_1, C_2 and C_3) are more intense meaning that more epoxy rings did not react in the filled model compound. As for the DGEBA/butylamine model compound, the reaction of the secondary amines of the DEDA on the epoxy rings is weakened in the presence of nanometric silica fillers. The epoxy rings consumption was estimated with the ^{1}H NMR spectrum to 71% for the pure nanometric silica filled model compound and to 74% for the treated nanometric silica filled model compound.

3.2. Influence of the irradiations on the chemical structure of the model compounds

3.2.1. Influence of the irradiations on the DGEBA chemical structure

After the electron beam irradiation, the DGEBA was analysed by NMR. On the irradiated DGEBA ^{1}H and ^{13}C NMR spectra, various new signals were detected simultaneously. On the ^{1}H NMR analysis, the appearance of new aromatic signals with increasing intensity according to increasing irradiation dose was detected (Fig. 7). The appearance of those signals is explained by the homolytic scission of the C—O bond in the α position of the aromatic nucleus leading to the formation of a phenolic extremity and of an enol—ketone extremity (Fig. 8). By quantitative ^{13}C NMR analysis, the

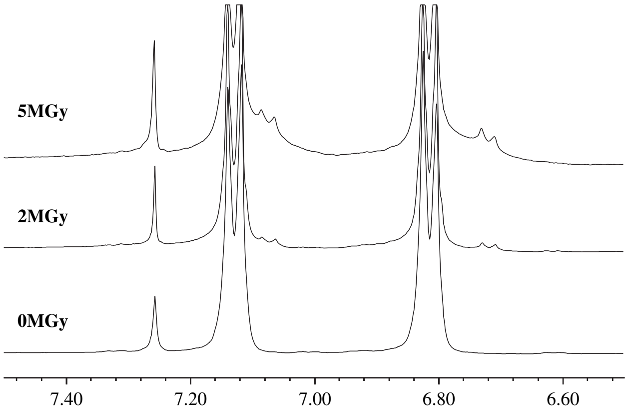


Fig. 7. Evolution of the ^{1}H NMR spectra of nanometric silica filled DGEBA in function of irradiation dose (expansion from 6.5 to 7.5 ppm).

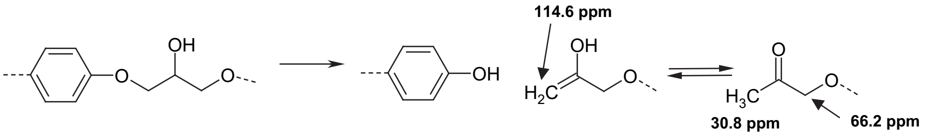


Fig. 8. Homolytic scission and proposed rearrangement mechanism.

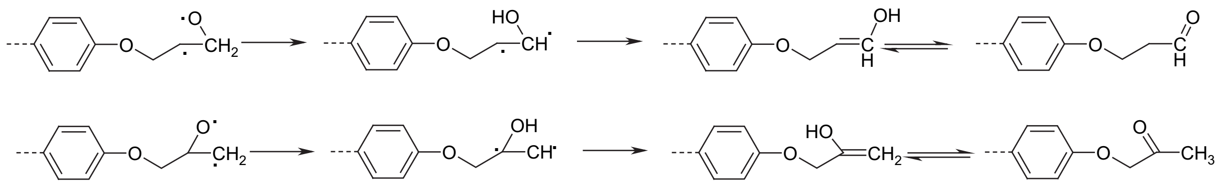


Fig. 9. Rearrangement mechanisms proposed for the opening of epoxy ring by irradiations.

radio-chemical yield of formation of phenolic extremities was estimated as 1.48×10^{-7} mol/J.

During the electron beam irradiation, a decrease of the intensity of the epoxy rings signals of the DGEBA was observed in ^{1}H NMR. The radio-chemical yield of the loss of epoxy ring was estimated to be 2.41×10^{-7} mol/J. Epoxy rings are more sensitive to electron beam irradiation than C—O bonds in the α position of the aromatic nucleus. The suggested mechanisms to explain the disappearance of epoxy rings are presented in Fig. 9. The opening of the epoxy rings allows the formation of aldehyde and ketone ends.

3.2.2. Influence of the irradiations on the DGEBA/butylamine and the DGEBA/DEDA chemical structures

After the electron beam irradiation, the DGEBA/butylamine and the DGEBA/DEDA model compounds were analysed by NMR. On the DGEBA/butylamine model compound, the ^{13}C NMR signals of the C—N bonds formed by the reaction of the butylamine on the DGEBA disappeared during irradiation (Fig. 10). In addition to the scissions of the C—O bonds in the α position of the aromatic nucleus, the main effects of the irradiation on this model compound are the scissions of the C—N bonds. For the DGEBA/butylamine model compound, the C—O and C—N irradiation sensitive bonds are presented in Fig. 11.

The suggested mechanisms start by a C—N scission occuring either on the oligomer chain or on the dangling butylamine group (Fig. 12). The secondary amine structure obtained by the C—N scission on the dangling butylamine group is an intermediate state which undergoes other chain scissions during the irradiation and which is not detected in the unfilled model compound.

On the DGEBA/DEDA model compound, the main effects of the electron beam irradiation are also C—O and C—N bond scissions. The chemical bonds likely to be broken by the irradiation and the proposed mechanisms are presented in Fig. 13. In the case of the *a* and *a'* scissions of the C—O bond on the α position of the aromatic ring, a phenolic and a methyl-ketone end are formed. In the case of the *b* and *b'* scissions of the C—N covalent bond obtained by the epoxy ring opening, a secondary amine and a methyl-ketone

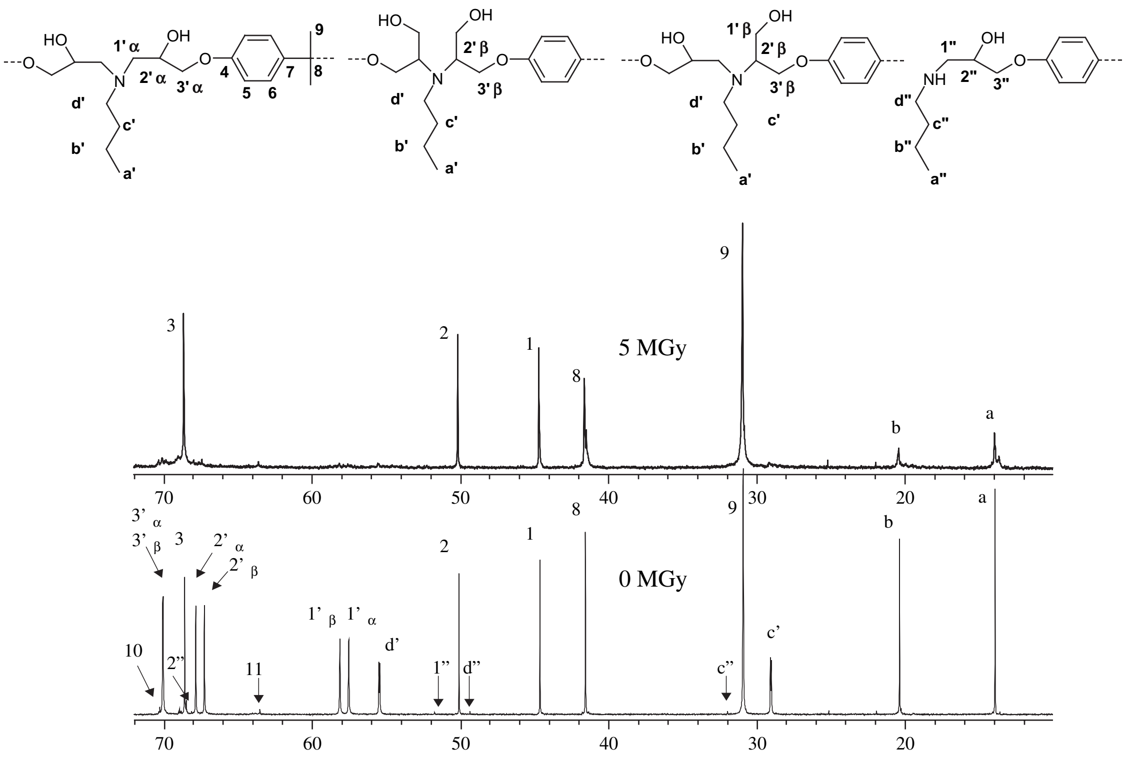


Fig. 10. Expansion from 10 to 72 ppm of the ^{13}C NMR spectrum of the unirradiated and 5 MGy irradiated DGEBA/butylamine model.

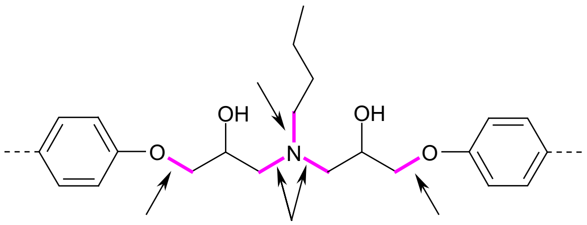


Fig. 11. Irradiations sensitive covalent bonds of DGEBA/butylamine model compound.

end are formed. In the case of the *c* and *c'* scissions of the C–N bond on the ethylene group of the DEDA, the structure obtained is a secondary amine. In the case of the *d* and *d'* scissions of the C–N bond on the 1,2-diaminoethylene structure, a secondary amine and an enamine end are formed. In this latter case, the obtained structure is typical of the DGEBA/DEDA model compound and explains the appearance of a new ^{13}C NMR signal at 92.4 ppm. The ^{13}C NMR signal at 93.1 ppm corresponds to a secondary enamine formed by the combination of the *d* and *c'* scissions (Fig. 14). These results permit us to confirm the hypothesis proposed by Longieras et al. [14].

3.2.3. Influence of the silica fillers on the irradiation effects of the chemical model compounds

After the electron beam irradiation, the ^{1}H and ^{13}C NMR spectra of the unfilled model compounds were compared to those of the nanometric silica filled models. The quantitative effects of the irradiation were estimated in terms of radiochemical yields.

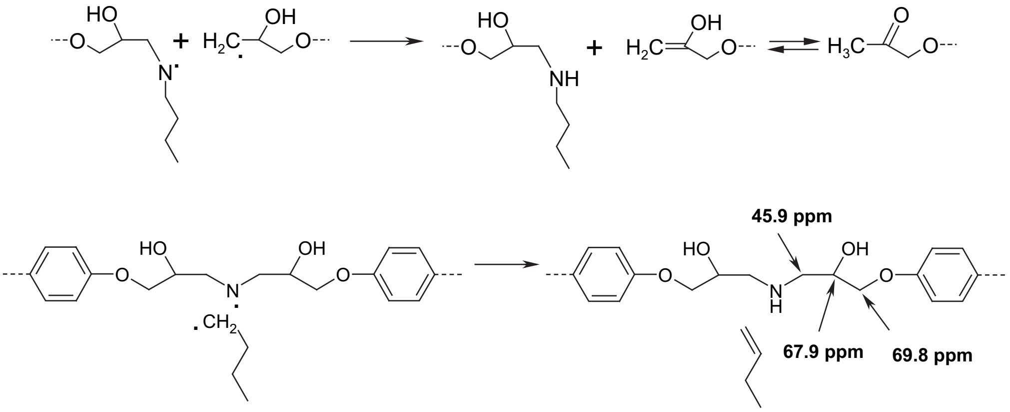


Fig. 12. Homolytic scissions and suggested mechanisms for the DGEBA/butylamine model compound.

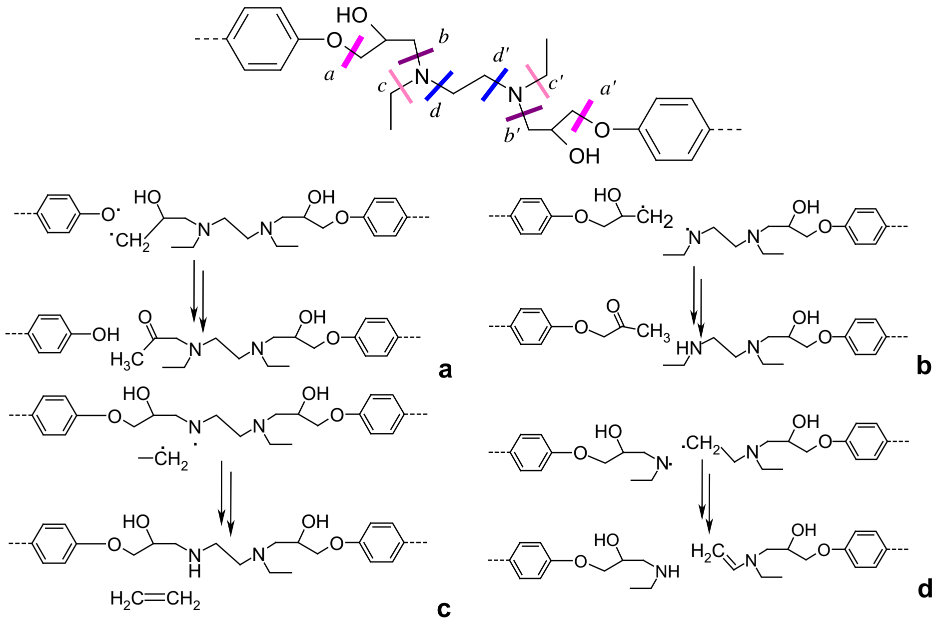


Fig. 13. C–O and C–N bonds likely to be broken and created species by irradiations.

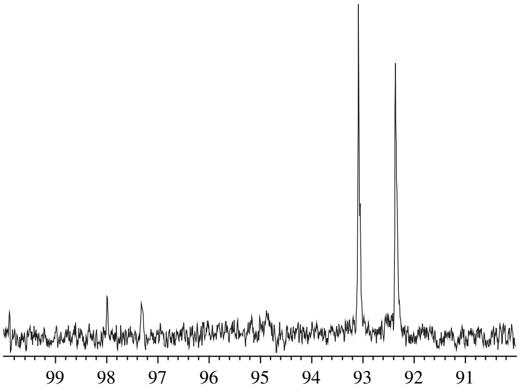


Fig. 14. ^{13}C NMR signals due to the *d* rupture.

In the case of the DGEBA/butylamine model compound, the radio-chemical yields of the C–O bond scission in the α position of the aromatic nucleus estimated by the ^{1}H NMR analysis are not significantly different (DMSO: 3.26×10^{-7} mol/J, 3.38×10^{-7} mol/J and 3.61×10^{-7} mol/J, respectively, for the unfilled model compound, the pure nanometric silica filled model compound and the treated nanometric silica filled model compound). On the pure and on the treated nanometric silica filled model compounds, the secondary amine structure presented in Fig. 12 has been detected meaning that not all the C–N bonds have been broken during the irradiation (characteristic carbons at 69.8, 67.9 and 45.9 ppm). These amine structures are protected from the irradiation by the screening effect of the nanometric silica fillers.

In the case of the DGEBA/DEDA model compounds, the radio-chemical yields were estimated for the *a* and *d* scissions (Table 1). In those both bond scissions, the radio-chemical yields are lowered in the presence of nanometric silica fillers. The screening effect due to the nanometric silica fillers reduces the number of bond scissions.

By quantitative ^{13}C NMR, the intensity of the phenolic end signal was compared to the one of the methyl-ketone end (Table 2). The ratios of the signals' integrations are lower for the pure and treated nanometric silica filled model compounds. In the presence of pure and treated nanometric silica, the number of phenolic ends detected is reduced. Interactions or covalent bonds can be achieved between the reactive functions formed by the electron beam irradiations on the model compound and the reactive functions on the silica particles' surface. The reactive functions created by the irradiations on the model compound are hydroxyl and amine functions. Hydroxyl, amine functions and epoxy rings from the raw materials are also residual. The reactive functions on the silica particles surface are silanol and siloxane. On nanometric silica filled polysiloxane, the increase of the crosslink density due to electron beam irradiations had already been observed by Stevenson et al. [26]. During the irradiation, covalent bonds were created between the polymer chains and the silica particles' surface. Chemical reactions between amine and silanol at the quartz surface improved in presence of alcohol had been observed by Vidyadhar et al. [27]. In our case, formation of covalent bonds and crosslinking on epoxy resin model compounds by nanometric silica particles has been shown by NMR analyses.

Table 1
Radio-chemical yields of the *a* and *b* scissions for the DGEBA/DEDA model compound

DGEBA/DEDA model compound	*a* Scission	*d* Scission
Unfilled	2.11×10^{-7}	1.34×10^{-7}
Pure nanometric silica filled	1.55×10^{-7}	5.34×10^{-8}
Treated nanometric silica filled	1.72×10^{-7}	9.29×10^{-8}

Radio-chemical yield (mol/J) = number of scission per gram of model compound (mol/g)/energy of irradiation per gram of model compound (J/g).

Table 2
Integrations ratios of the characteristic signal of the phenolic extremity and of the methyl-ketone

	$\text{Int}_{\text{phenolic ext}}/\text{Int}_{\text{methyl-ketone ext}}$
Unfilled DGEBA/DEDA	0.24
Pure nanometric silica filled DGEBA/DEDA	0.15
Treated nanometric silica filled DGEBA/DEDA	0.19

4. Conclusion

Influence of nanometric silica fillers on the chemical structure of the unirradiated and irradiated DGEBA/TETA epoxy resins was revealed by the study on model compounds. On the unirradiated model compounds, in the presence of nanometric silica fillers, it has been proved that the reactivity of the secondary amine is reduced during the reaction leading to a less branched structure. On the irradiated model compounds, ^{1}H and ^{13}C NMR analyses allowed us to show the formation of primary and secondary amines, phenolic, and methyl-ketone ends by C–O and C–N bond cleavage under the irradiations. The formation of enamine ends was shown on the model compounds containing 1,2-diaminoethylene structures. Moreover, the protective effect of the nanometric silica fillers was also revealed by less bond cleavage under the irradiations on filled model compounds compared to unfilled model compounds. Chemical reactions of the reactive functions formed by the cleavage under the irradiations on the model compounds with the reactive species present on the silica surface have been demonstrated by quantitative ^{13}C NMR.

Acknowledgments

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