# Influence of silica fillers during the electron irradiation of DGEBA/TETA epoxy resins, part II: Study of the thermomechanical properties

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## Abstract

This work describes the influence of silica fillers on the thermomechanical properties of diglycidyl ether of bisphenol A/triethylenetetramine (DGEBA/TETA) epoxy resins during ageing under electron beam irradiation. Whatever be the silica filler (pure micrometric ground and spherical silicas, nanometric silicas and coupling agent treated silicas), the glass transition temperature of the epoxy resins decreases with increasing irradiation dose, meaning that the main effect of the irradiation is chain scission. No influence of the silica fillers has been detected from the changes in the glass transition temperature with the increase in the irradiation dose. The disappearance of the cooperativity of the $\gamma$ relaxation, the decrease of the $\alpha$ relaxation and the decrease of the elastic modulus at the rubbery plateau observed by dynamic mechanical analyses involve a decrease in the crosslink density of the epoxy resins. The occurrence of chemical reactions between the epoxy resin and the silica surface at high irradiation doses has been shown. Moreover, we show evidence that chemical reactions between the epoxy resin and the silica surface occur at high irradiation dose.
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*Keywords:* Silica filled epoxy resins; Electron irradiation; Network degradation; Thermomechanical behaviour

## 1. Introduction

The increasing use of polymers in radiation environments involves a good knowledge of their irradiation induced ageing to predict the evolution of properties and to improve safety. 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 developed great activity on the study of the irradiation effect on the ageing of different kinds of polymers like ethylene—propylene—diene monomer (EPDM) [1—3] and epoxy resins [4—9] selected for their high performances. These previous works were carried out

on pure polymers as model compounds of commercial resins. However, formulations of commercial polymers are complex, with additives like pigments, plasticizers and fillers. The aim of the present work is to study the influence of the silica fillers on the ageing of epoxy resins under electron beam irradiation. In the first part of this work [10], the chemical modifications of model compounds under the irradiation are described and the influence of the silica fillers is shown. The formation of primary and secondary amines, phenolic, methyl—ketone and enamine ends was observed. The protective effect of the nanometric silica fillers and the chemical reactions of the reactive functions formed during the irradiation with the reactive species on the silica surface were demonstrated. In this paper, the evolution of the thermomechanical properties of silica filled epoxy resins is described. Micrometric and nanometric silica particles have been used as fillers in the diglycidyl ether of bisphenol A/triethylenetetramine (DGEBA/TETA) epoxy resins. We first describe the influence of the silica fillers on

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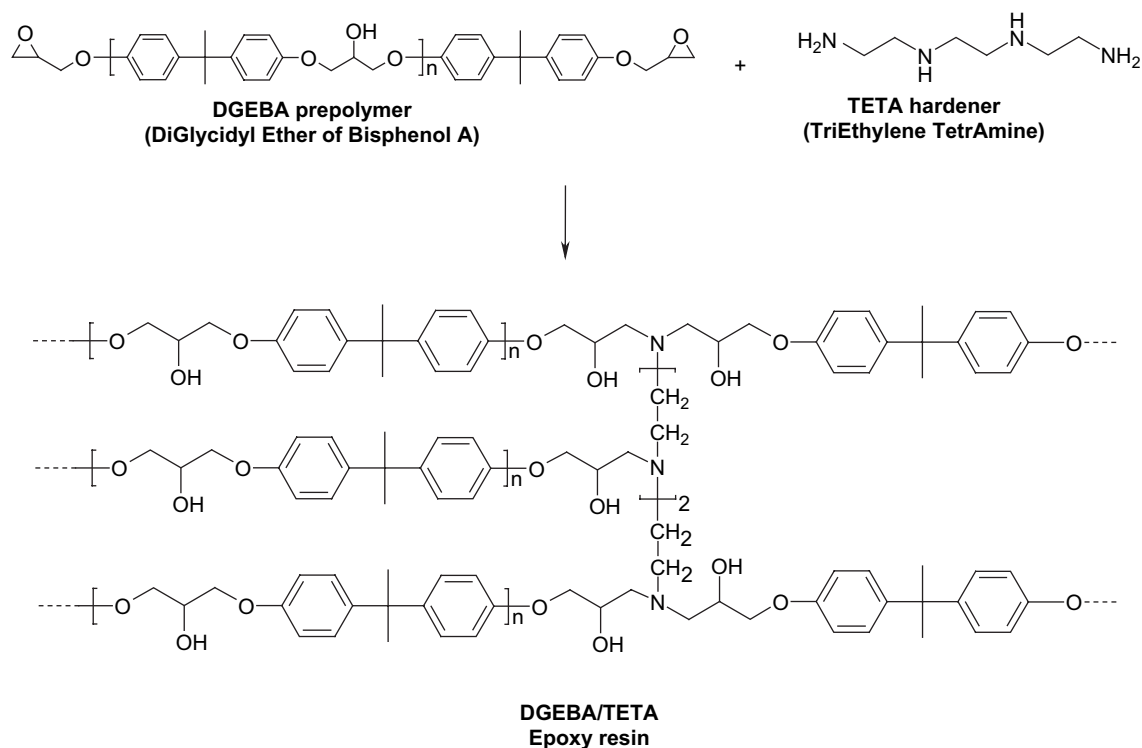
Fig. 1. Chemical structure of the prepolymer, the hardener and the epoxy resin.

the evolution of the glass transition temperature and of the relaxation temperatures with the irradiation doses by Differential Scanning Calorimetry (DSC) and dynamic mechanical analyses (DMA). The influence of the silica fillers on the evolution of the crosslink density of the epoxy resin with increasing irradiation dose is then studied.

## 2. Experimental

### 2.1. Materials

The epoxy resin was obtained by the curing of the diglycidyl ether of bisphenol A (DGEBA) prepolymer (supplied by Vantico under the reference LY 556) with the triethylenetetramine (TETA) hardener (supplied by Vantico under the reference HY 951). The DGEBA epoxy index is 5.4 equiv/kg and its average molecular weight is 370 g/mol. The chemical structures of the reagents and of the obtained epoxy resins are shown in Fig. 1. The epoxy resins were prepared according to the supplier's specifications. To 40 g of DGEBA, a quantity $x$ of silica was mixed in the expected amount: 11.3 g for a 20% mixture and 30 g for a 40% mixture. After a first degassing under vacuum, 5.2 g of TETA were added. The mixture was then degassed under vacuum, poured into a steel mould, and submitted to a three-step temperature programme: 25 °C for 12 h, a raise of 1 °C/min to 130 °C and a plateau at 130 °C for 5 h. This temperature programme allows us to achieve a slow and complete cure and to obtain a thermally stable epoxy resin without degradation.

Different kinds of silica with different geometries were used and divided into two groups: (a) micrometric silicas and (b) nanometric silicas (supplied by Degussa under the name Aerosil® 200). In the first group, three kinds of micrometric silicas were used: (i) a spherical silica (supplied by Rhodia under the name Rhodia Marbles, called here *spherical silica*), (ii) a pure ground silica (supplied by Sifraco under the name Millisil C10®, called *pure micrometric silica*) and (iii) a coupling agent treated ground silica (supplied by Qwartz-werke under the name Silbond® W12EST, called *treated micrometric silica*). The specific surface and the average particle sizes of those silicas are presented in Table 1 and Fig. 2. A coupling agent treated nanometric silica was obtained by grafting the glycidyloxypropyltrimethoxysilane (supplied by Degussa under the name Glymo®) on the particles surface: 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.

The Scanning Electron Microscopy (SEM) views of micrometric silica fillers show the differences in geometry

Table 1
Specific surface and granulometry of silica particles

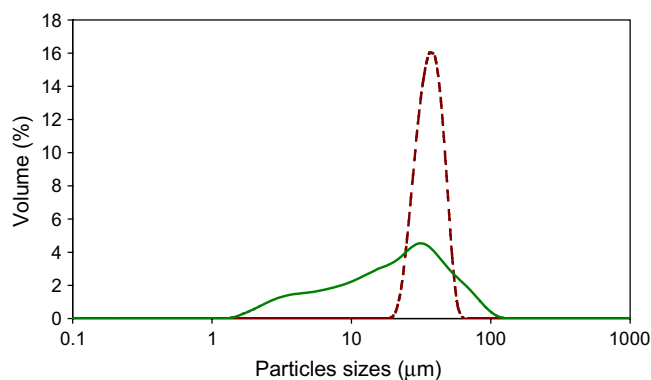|  | Specific surface (m²/g) | Granulometry of the particles (μm) |
|---|---|---|
| Spherical silica | 0.05 | 30–50 |
| Pure ground silica | 0.92 | 10–60 |
| Treated ground silica | 0.80 | 10–60 |
| Nanometric silica | 214 | $10^{-2}$–$2.10^{-2}$ |

Fig. 2. Comparison of the spherical (- -) and micrometric (—) silicas particle size distributions.

and size dispersity between the spherical and ground silicas (Fig. 3).

## 2.2. Irradiation conditions

Irradiation was made by Electron Beam (2.5 MeV, 250 kGy/h) under helium (1.1 atm) at 20 °C with a Van De Graaff electron accelerator at 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

Dynamic mechanical analyses (DMA) were carried out with a single cantilever DMA 2980 TA Instrument apparatus. The measurements were performed at a 1 Hz frequency, a 20 μm amplitude and a heating rate of 1.5 °C/min from −95 °C to 170 °C. The glass transition temperatures of the unirradiated and irradiated epoxy resins were measured by Differential Scanning Calorimetry (DSC) with a Perkin Elmer DSC 7 apparatus from 30 °C to 160 °C with a rate of 10 °C/min. The particle size of the silica particles was measured with

a Coulter LS 230 laser analyser. Specific surfaces were measured with a Coulter SA 3100. SEM images were obtained with a Hitachi 2300 scanning electron microscope.

## 3. Results and discussion

### 3.1. Effects of the irradiation on the glass transition temperature

The change in the glass transition temperature of each epoxy resin formulation with increasing dose is presented in Fig. 4. For the unirradiated epoxy resins, the glass transition temperatures are quite close from one resin formulation to another and equal to $119 \pm 1$ °C. The glass transition temperature is not significantly modified by the presence of the silica fillers. For all the filled epoxy resins, a decrease in the glass transition temperature with the increase in the irradiation doses was observed. This observation confirms that one of the main effects of the irradiation on the unfilled and silica filled epoxy resins is chain scission leading to the increase in chain mobility in accordance with previous works on unfilled epoxy resins [5,7]. A similar decrease has been observed for different filled resins (Fig. 4a), for different quantities (Fig. 4b), on treated and untreated silicas (Fig. 4c) and for different particles sizes (Fig. 4d). These results mean that the influence of the silica fillers on the irradiation effect on the epoxy resin is not revealed by the measurement of the glass transition temperature by DSC.

The crosslink density ($n$) has been estimated from the glass transition temperatures using the Di Marzio law:

$$Tg = \frac{Tgl}{(1 - KFn)}$$

where Tgl is the glass transition temperature of a hypothetical linear copolymer containing all the structural units of the network except crosslinks, $K$ is a universal constant, and $F$ is the average molecular weight per rotatable bond of network chains. Here $F = 18.92$ g/mol, $Tgl = 323$ K and $K = 3$ according to
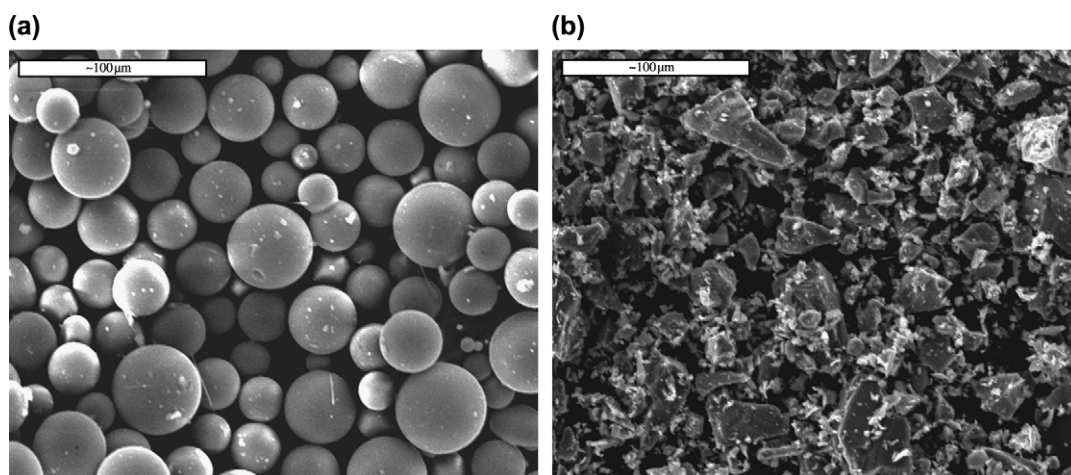


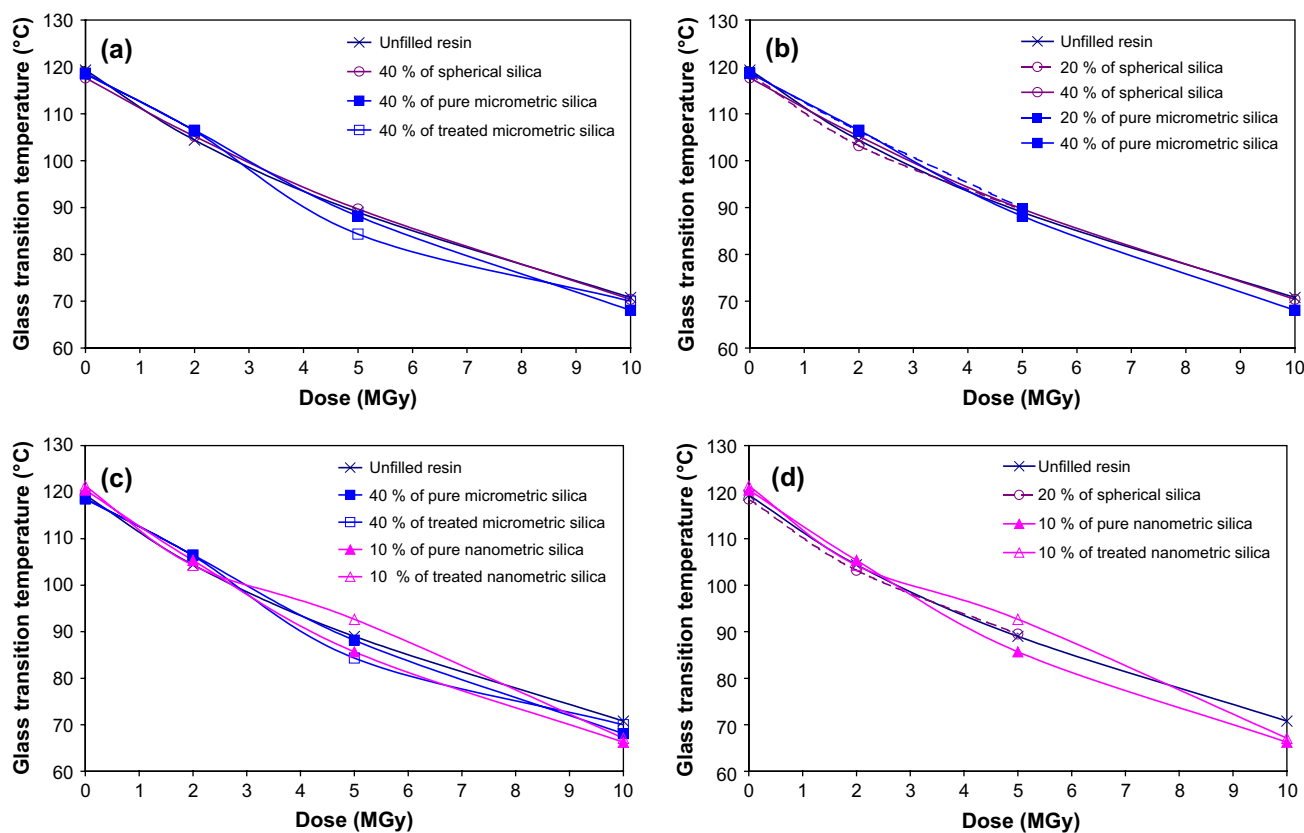Fig. 3. SEM images of (a) spherical and (b) ground silicas.

Fig. 4. Evolution of the glass transition temperature of the filled and unfilled epoxy resins with (a) the silica nature, (b) the silica quantity, (c) the chemical treatment, and (d) the silica particle size.

Bellenger et al. [11]. No significant changes in the crosslink densities estimated by this method were detected for the filled and unfilled resins (Table 2). As the degradation of the polymer network and the increasing probability to have a chain scission on a dangling chain are not taken into account in the Di Marzio law [6], dynamic mechanical analyses were performed for more accurate estimation of crosslink densities.

### 3.2. Study by dynamic mechanical analysis

The evolution of $E'$, $E''$ and $\tan \delta$ has been studied by dynamic mechanical analyses. An example of DMA thermograms is presented in Fig. 5.

For all the studied epoxy resins, the same kind of phenomena could be observed with the irradiation dose increase: (i) for the high temperatures, a decrease in the elastic modulus at the rubbery plateau ($E'$, Table 3), (ii) a decrease in the $\alpha$ relaxation temperature (T$\alpha$, Table 4), and (iii) a decrease in the $\gamma$ relaxation temperature corresponding to the local motions at low temperatures (T$\gamma$, Table 5).

### 3.2.1. Effects of irradiation on the elastic modulus at the rubbery plateau

While increasing irradiation doses to 5 MGy, a decrease in the elastic modulus at the rubbery plateau has been observed for the unfilled and silica filled epoxy resins, whatever be the filler (Fig. 6).

For each irradiation dose, the ratio of the elastic modulus at the rubbery plateau of each filled epoxy resin to the one of the unfilled epoxy resin, $E'c_{\text{filled resin}}/E'c_{\text{unfilled resin}}$, allowed us to show the evolution of the $E'c$ modulus due to the fillers. From the evolution of these ratios, some further information could be obtained on the evolution of the crosslink density of the filled epoxy resins against the one of the unfilled epoxy resin.

On the unirradiated epoxy resins (Fig. 7), a raise in the modulus ratio was observed with the increase in the amount of filler and of the specific surface. As is well known, the reinforcement effect of the silica fillers is improved when

Table 2
Crosslink densities ($n$) of epoxy resins submitted to irradiation estimated by Di Marzio law

| Fillers | $n_{0 \text{ MGy}}$ (mmol/g) | $n_{2 \text{ MGy}}$ (mmol/g) | $n_{5 \text{ MGy}}$ (mmol/g) | $n_{10 \text{ MGy}}$ (mmol/g) |
|---|---|---|---|---|
| Unfilled resin | 3.11 | 2.54 | 1.90 | 1.07 |
| 20% of spherical silica | 3.08 | 2.49 | 1.92 | |
| 40% of spherical silica | 3.05 | 2.57 | 1.93 | 1.05 |
| 20% of pure micrometric silica | 3.09 | 2.62 | 1.93 | |
| 40% of pure micrometric silica | 3.09 | 2.62 | 1.86 | 0.93 |
| 20% of treated micrometric silica | 3.17 | 2.56 | 1.94 | |
| 40% of treated micrometric silica | 3.08 | 2.62 | 1.69 | 1.03 |
| 10% pure nanometric silica | 3.15 | 2.58 | 1.75 | 0.84 |
| 10% treated nanometric silica | 3.19 | 2.53 | 2.06 | 0.89 |
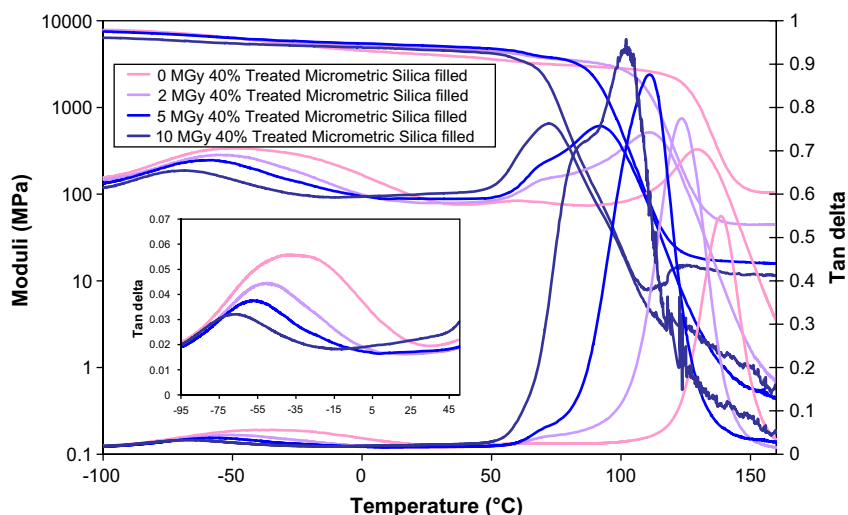
Fig. 5. Thermograms of the treated micrometric silica filled epoxy resins unirradiated and irradiated to 2 MGy, 5 MGy, and 10 MGy.

the contact surface between the fillers and the epoxy resin is increased. Moreover, the chemical treatment of the silica fillers involving a decrease in the amount of hydroxyl functions at the silica surface leads to a decrease in the modulus ratio meaning a lower reinforcement effect.

For the 20% spherical silica filled epoxy resin (Fig. 8), the ratio stays constant with the increase in the irradiation dose. The reinforcement effect of the spherical silica fillers and the interactions of the particles with the epoxy resin remain constant. For the 20% pure and treated micrometric silica filled epoxy resins, the ratio increases with increasing dose meaning that the reinforcement rises. The increasing interactions of the micrometric silica particles with the epoxy resin balance the decrease in the intrinsic properties of the epoxy resin.

For 40% of silica filler, the reinforcement effect and the interactions of the silica particles with the epoxy resin increase with increasing irradiation dose except for the 40% pure micrometric silica filled epoxy resin at the 5 MGy dose (Fig. 9). With a 40% amount of pure micrometric silica fillers, the interactions with the silica surface during cure involve a less complete network than the one of the unfilled epoxy

resin and consequently a lower resistance to the irradiation. This result is in agreement with previous works on model compounds where it was observed that the presence of nanometric silica fillers leads to less branched structures [10]. For the high irradiation doses, the decrease in the intrinsic properties of the epoxy resin is not compensated by the reinforcement effect of the pure micrometric silica fillers. In the case of the 40% spherical silica filled epoxy resin with a lower contact surface, the crosslinking reaction was not so disturbed and the irradiation effects on the epoxy resin intrinsic properties are balanced by the reinforcement effect of the silica fillers.

For the 10% pure and treated nanometric silica filled epoxy resins, the ratio decreases for a low irradiation dose of 2 MGy and then raises for a 5 MGy irradiation dose (Fig. 10). The reinforcement effect of the nanometric silica fillers is stronger than for the other fillers at high irradiation doses. The more important contact surface of the nanometric silica permits the increase in the interactions of the silica particles with the epoxy resin. This fact involves a weaker crosslinking, leading to a less dense network. At low doses, bonds cleavage on the weak network prevails. The reinforcement effect of the

Table 3
Evolution of the elastic modulus at the rubbery plateau ($E'$) of the unfilled and silica filled epoxy resins

| Fillers | $E'_{0\ MGy}$ (MPa) | $E'_{2\ MGy}$ (MPa) | $E'_{5\ MGy}$ (MPa) | $E'_{10\ MGy}$ (MPa) |
|---|---|---|---|---|
| Unfilled resin | 39.4 | 15.9 | 5.1 | 1.4 |
| 20% of spherical silica | 52.6 | 21.1 | 7.0 | |
| 40% of spherical silica | 79.3 | 29.8 | 14.1 | |
| 20% of pure micrometric silica | 65.6 | 28.3 | 10.6 | |
| 40% of pure micrometric silica | 118.6 | 49.0 | 14.5 | 3.6 |
| 20% of treated micrometric silica | 62.4 | 25.9 | 9.7 | |
| 40% of treated micrometric silica | 103.3 | 44.5 | 15.8 | 4.8 |
| 10% pure nanometric silica | 69.5 | 30.2 | 13.4 | 5.6 |
| 10% treated nanometric silica | 73.4 | 26.2 | 14.5 | 7.0 |

Table 4
Evolution of the α relaxation temperature (Tα) of the unfilled and silica filled epoxy resins measured by the tan δ curves

| Fillers | $T\alpha_{0\ MGy}$ (°C) | $T\alpha_{2\ MGy}$ (°C) | $T\alpha_{5\ MGy}$ (°C) |
|---|---|---|---|
| Unfilled resin | 136.5 | 121.4 | 111.6 |
| 20% of spherical silica | 140.6 | 120.1 | 106.2 |
| 40% of spherical silica | 142.2 | 121.0 | 112.3 |
| 20% of pure micrometric silica | 137.4 | 125.6 | 109.9 |
| 40% of pure micrometric silica | 138.2 | 122.7 | 108.6 |
| 20% of treated micrometric silica | 140.8 | 121.9 | 110.8 |
| 40% of treated micrometric silica | 138.6 | 123.6 | 111.4 |
| 10% pure nanometric silica | 138.2 | 117.5 | 107.7 |
| 10% treated nanometric silica | 139.1 | 123.2 | 116.8 |

Table 5
Evolution of the γ relaxation temperature (Tγ) of the unfilled and silica filled epoxy resins measured by the tan δ curves

| Fillers | $T\gamma_{0\ MGy}$ (°C) | $T\gamma_{2\ MGy}$ (°C) | $T\gamma_{5\ MGy}$ (°C) | $T\gamma_{10\ MGy}$ (°C) |
|---|---|---|---|---|
| Unfilled resin | −39.9 | −51.9 | −59.4 | −66.5 |
| 20% of spherical silica | −35.0 | −52.5 | −60.3 | |
| 40% of spherical silica | −33.9 | −53.9 | −59.9 | |
| 20% of pure micrometric silica | −35.5 | −48.6 | −59.0 | |
| 40% of pure micrometric silica | −33.3 | −50.1 | −55.8 | −67.5 |
| 20% of treated micrometric silica | −36.9 | −50.8 | −56.4 | |
| 40% of treated micrometric silica | −36.4 | −50.3 | −57.5 | −65.4 |
| 10% pure nanometric silica | −41.4 | −58.2 | −61.4 | −65.6 |
| 10% treated nanometric silica | −46.3 | −58.7 | −61.4 | −65.6 |

nanometric silica fillers can then be improved as the irradiation dose increases by the previously quoted chemical reactions [10] between the reactive species arising from the radiative cleavage of the resin bonds and those present on the silica surface.

### 3.2.2. Effects of irradiation on the α and γ relaxations

With the irradiation doses increase, a shift to lower temperatures of the α and γ relaxation maxima has been observed.

The γ relaxation has been studied by Heux et al. [12] and was divided into two parts: (i) the inferior part at low temperatures corresponds to the oxypropylether chain motion and (ii) the superior part at highest temperatures corresponds to the co-operative character of the relaxation. The decrease in the γ relaxation temperature with increasing dose is accompanied by a decrease in the tan δ signal intensity and can be described as the disappearance of the superior part of the relaxation. This phenomenon corresponds to a decrease in the cooperative character of the relaxation explained by the decrease in the crosslink density of the epoxy resin. The decreasing of the γ relaxation intensity is explained by the progressive disappearance of the implied chains in the relaxation.

The evolution of the α relaxation temperatures determined from the E″ curves is presented in Fig. 11.

The α relaxation temperature of the pure and treated micrometric silica filled resins decreases less quickly than the other
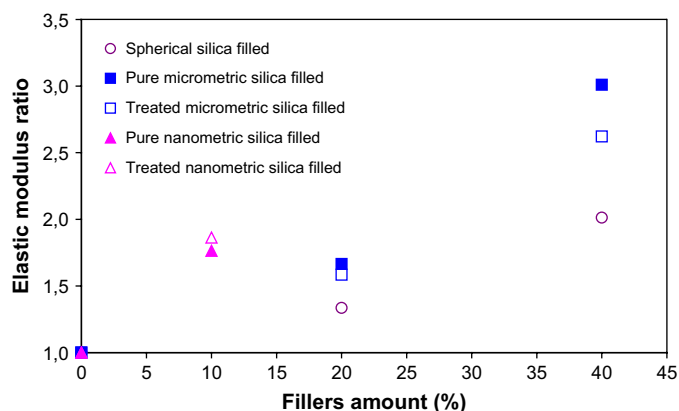


Fig. 7. Evolution of the ratio of the elastic modulus at the rubbery plateau of the each filled epoxy resins by one of the unfilled epoxy resin versus fillers amount, before irradiation.

ones. The predominance of mechanical coupling between resin and fillers on the measure of the α relaxation temperature is displayed. For the unfilled epoxy resin, the spherical and nanometric silica filled epoxy resins, the decrease in the α relaxation is important for the low irradiation doses and less important for the higher irradiation doses. On the spherical silica filled epoxy resins, the measure of the α relaxation is not influenced by the reinforcement effect of the silica and the evolution of its α relaxation temperature is quite similar to the one of the unfilled epoxy resin. The high weakness of the network of the nanometric silica filled epoxy resins towards irradiation is revealed by the important decrease in the α relaxation temperature for the low irradiation doses [10]. It was also shown that the reactive chemical species formed during the irradiation as hydroxyl functions can react with the reactive function of the silica surface as silanol and siloxane [10]. For the high irradiation doses, these reactions between the reactive species created into the resin and those present in the silica surface can compensate the effect of the irradiation on the α relaxation temperature.



Fig. 6. Evolution of the elastic modulus with the irradiation dose.
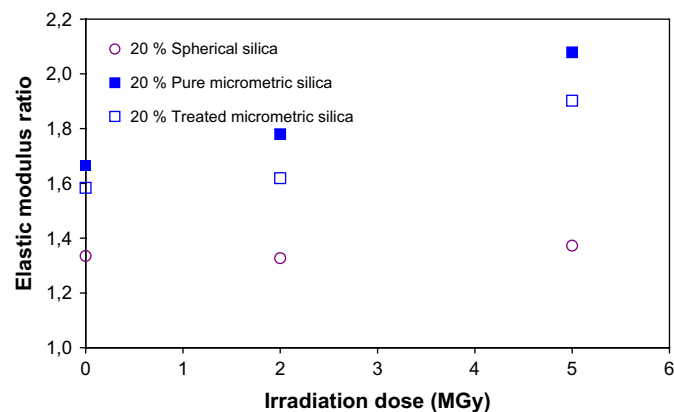


Fig. 8. Influence of the irradiation on the evolution of the ratio of the elastic modulus at the rubbery plateau of the each 20% filled epoxy resins by one of the unfilled epoxy resin.
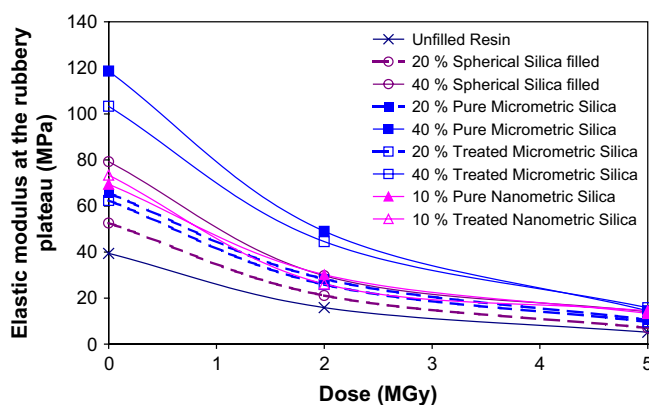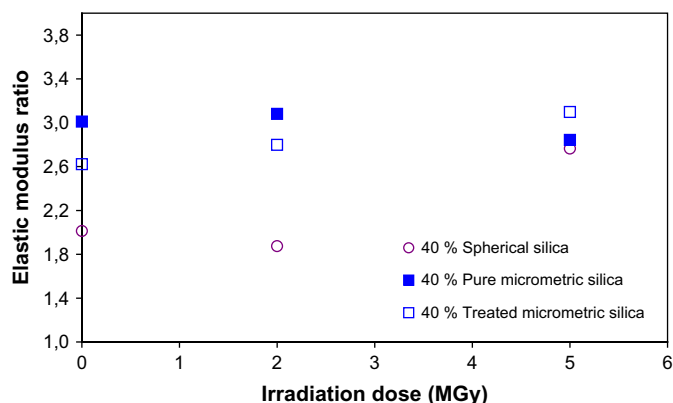
Fig. 9. Influence of the irradiation on the evolution of the ratio of the elastic modulus at the rubbery plateau of the each 40% filled epoxy resins by one of the unfilled epoxy resin.



Fig. 11. Evolution of the $\alpha$ relaxation temperature with the irradiation dose for the filled and unfilled epoxy resins.

## 4. Conclusions

In this work, thermomechanical properties of different silica filled epoxy resins have been studied as a function of the irradiation dose. For all the silica filled epoxy resins, the irradiation exposure results in a decrease in the glass transition temperature which is attributed to chain scissions. No influence of the silica fillers was revealed. Further investigations have been carried out by DMA. The elastic modulus at the rubbery plateau and $\alpha$ and $\gamma$ relaxation temperatures decrease with increasing irradiation dose. The improvement of the reinforcement effect of the fillers with the increase in the contact surface between the silica particles and the epoxy resin by hydrogen bonds was confirmed before irradiation. Two phenomena have been displayed: (i) high proportions of filler lead to weak crosslinking during cure, involving a weak network and (ii) chemical reactions between the new functions formed by the bond scission under irradiation and the silica surface lead to a reinforcement effect which increases with the increase in the 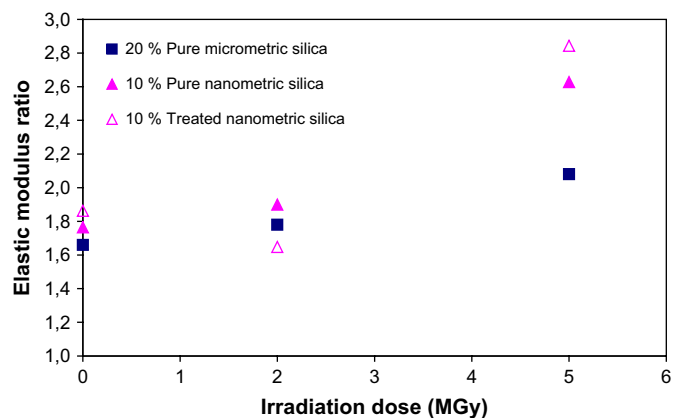irradiation dose, and with the increase in the contact surface. The shift of the $\gamma$ relaxation temperature corresponds to the disappearance of the superior part of the relaxation meaning a decrease in the cooperative character of the relaxation and a decrease in the number of implied chains in the relaxation. The decrease in the $\alpha$ relaxation temperature confirms the phenomenon of chain scissions and the increase in the interactions with high contact surface silica fillers.

## Acknowledgments

Fig. 10. Influence of the irradiation on the evolution of the ratio of the elastic modulus at the rubbery plateau of the each filled epoxy resins by one of the unfilled epoxy resin.
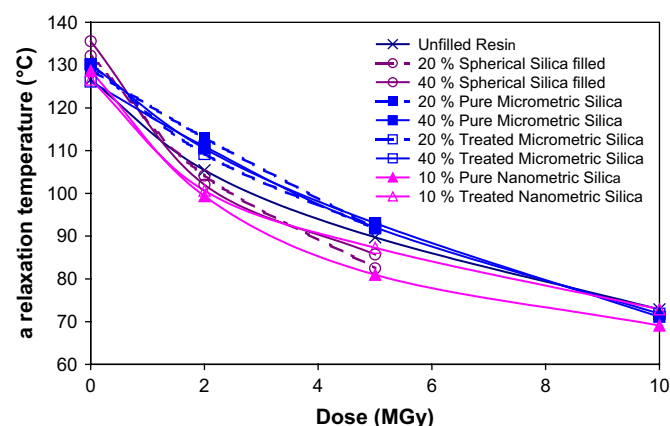
## References

[1] Rivaton A, Cambon S, Gardette JL. J Polym Sci Part A Polym Chem 2004;42(5):1239–48.
[2] Rivaton A, Cambon S, Gardette JL. Nucl Instrum Methods Phys Res Sect B 2005;227(3):343–68.
[3] Celette N, Stevenson I, Davenas J, David L, Vigier G. Nucl Instrum Methods Phys Res Sect B 2001;185:305.
[4] Ngono Y, Marechal Y. J Polym Sci Part B Polym Phys 2001;39(11):1129–36.
[5] Vignoud L, David L, Sixou B, Vigier G. Polymer 2001;42(10):4657–65.
[6] Devanne T, Bry A, Audouin L, Verdu J. Polymer 2005;46(1):229–36.
[7] Devanne T, Bry A, Raguin N, Sebban M, Palmas P, Audouin L, et al. Polymer 2005;46(1):237–41.
[8] Longieras N. Thesis Université Blaise Pascal. Clermont-Ferrand; 2004.
[9] Davenas J, Stevenson I, Celette N, Cambon S, Gardette JL, Rivaton A, et al. Nucl Instrum Methods Phys Res Sect B 2002;191:653–61.
[10] Benard F, Campistron I, Laguerre A, Laval F. Polym Deg Stab, in press. doi:10.1016/j.polymdegradstab.2006.01.022.
[11] Bellenger V, Morel E, Verdu J. J Polym Sci Part B Polym Phys 1987;25(6):1219–34.
[12] Heux L, Halary JL, Lauprêtre F, Monnerie L. Polymer 1997;38(8): 1767–78.