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Influence of electron irradiation on the mobility and on the mechanical properties of DGEBA/TETA epoxy resins

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Abstract

The thermomechanical properties of DGEBA/TETA resins are analysed as a function of the irradiation dose. Irradiation by electrons results in a decrease of the glass transition temperature and the elastic modulus in the rubbery region. The Arrhenius diagrams obtained for the various doses show that the cooperative mobility associated with the α relaxation becomes faster after the irradiation. More local mobility corresponding to the β and γ relaxations is also modified, but in a lesser extent. These results can be interpreted invoking a destruction of the crosslinks within the resin. The effects of irradiation on the stress–strain curves are also discussed and are shown to be connected with both the physical aging kinetics and the spatial heterogeneity of the crosslink density in the resin.

Keywords: Epoxy resin; Mechanical behaviour; Electron irradiation

1. Introduction

Epoxy resins are widely used in industrial applications such as adhesives and matrices for composite materials. These materials are especially used in the coating of nuclear waste and, in particular, parts of structures in reactor environments. They are selected for their high performances (lightness, mechanical properties) achieved through the synthesis and the processing. Since these applications involve high radiation fields, the knowledge of radiation induced aging of the resin is needed. A description of the relationship between the molecular architecture and the degree of radiation induced alteration is expected. Changes in the properties of polymeric materials caused by ionising radiation have been mainly ascribed to chemical reactions like chain scission and/or formation of crosslinks. For example, it has been reported in epoxy resins that further curing is produced by irradiation of γ rays and electrons. Numerous papers have been devoted to this subject, especially in the case of epoxy–amine networks [1–3].

In this work, we study the diglycidyl ether of bisphenol A/triethylene tetramine (DGEBA/TETA) model epoxy (Fig. 1). The chemical evolution of the material under irradiation has been studied with infrared spectroscopy and ^{13}C NMR measurements [4]. This study has evidenced the formation of unsaturated bonds on the amine skeleton and chain scissions located on the quaternary carbon atom of DGEBA. There is still a gap between the identification of the defects at the level of the network and the observed effect on the thermomechanical behaviour. The aim of this work is to correlate the nature of the defects created during irradiation and these macroscopic properties. We have thus performed high-resolution low frequency mechanical spectroscopy measurements in the small deformation range, which yields the characterisation of the principal (α) and the secondary relaxations (β, γ, …). We first describe the DGEBA/TETA system and the effect of a post-curing thermal treatment. Then we detail the thermomechanical properties of the irradiated materials and their evolution with time and when they are submitted to a thermal treatment. We have also studied the response of the irradiated material in the high deformation range by means of compression tests. We show evidence that the irradiation process accelerates the molecular mobility and decreases the glass transition as a result of chain scissions. This higher molecular mobility results, in turn, in: (i) a faster crosslinking process after irradiation; and (ii) a faster physical aging (structural relaxation), even at room temperature. Therefore, this paper reports how irradiation treatment and physical aging combine. Moreover, we show evidence that the irradiation process increases the heterogeneity of crosslink density inside the resin.

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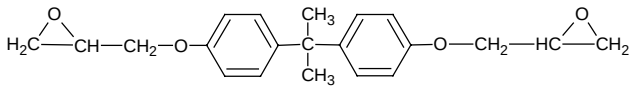
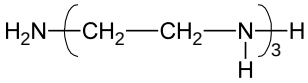


Diglycidyl Ether of Bisphénol A
(DGEBA)



TriEthylene TetrAmine
(TETA)

Fig. 1. Chemical structures of the epoxide monomer and of the hardener.

2. Experimental

2.1. Materials

DGEBA was used as the epoxide monomer, and TETA was used as the curing agent. The chemical structures of the epoxide monomer and the hardener are shown in Fig. 1. The DGEBA epoxide monomer is a CIBA product (Ref. LY 556). Its epoxy index (number of epoxy moiety per kilogram of DGEBA) varies between 5.2 and 5.45 equiv/kg and its average molar mass between 367 and 385 g/mol. TETA was also purchased from CIBA (Ref. HY 956). Curing of DGEBA/TETA mixture was performed in two steps after degassing at 60°C for 10 min under vacuum: the molten mixtures of the epoxide monomer and TETA were kept at 80°C for 1 h and subsequently at 140°C for 1 h. To obtain the best reticulation rate, the materials were mixed in the stoichiometric ratio $m_{DGEBA}/m_{TETA} \approx 10/1.3$. The mixtures were cast into an aluminium mould.

2.2. Irradiation conditions

Specimens were irradiated in dry air at 20°C by a 1.5 MeV electron beam from a Van de Graaf electron accelerator (DRFMC/SP2M, CEA Grenoble). The samples are placed in a cell with a titanium window transparent to the electrons. The dose rate was evaluated to be 250 kGy/h and the total doses chosen were 2 and 5 MGy, as in Ref. [4].

2.3. Techniques

2.3.1. Calorimetric and dynamic mechanical spectroscopy measurements

Specimens for mechanical testing were machined to the required dimensions from cast plaques by cutting them with a circular saw. The DSC measurements of the unirradiated and irradiated epoxy resins were performed on a TA Instruments calorimeter from the ambient temperature to 200°C, with a rate of 10°C/min.

The low frequency dynamic mechanical measurements were performed on a torsion pendulum set-up built in our laboratory [5]. The dynamic shear modulus, $G = G' + iG''$ and the loss factor $\tan\delta = G''/G'$ was recorded in the temperature range from −150 to 400°C and in the frequency range from 10^{-4} to 1 Hz. The measurements were performed with a heating rate of 1.5°C/min. The samples used are parallelepipedic with dimensions of $50 \times 5 \times 2$ mm^3. Isochronous (fixed frequencies) as well as isothermal (fixed temperature) measurements were carried out. The temperatures T_α, T_β and T_γ were defined as the temperatures corresponding to the maximum of G'' at 1 Hz. Elastic modulus in the rubber-like region was evaluated as the minimum value of storage modulus beyond the glass transition region.

2.3.2. Compression tests

The uniaxial compression tests were carried out on an INSTRON machine at 25°C, on cylindrical samples with a diameter of 5 mm and height of 10 mm. The crosshead speed was at 4.8×10^{-3} s^{-1}.

3. Results and discussion

3.1. Reference state and effect of a post-curing treatment

3.1.1. Calorimetric measurements

We have studied the thermal stability of the epoxy resins before further characterisations in order to be able to isolate the effects specifically related to the irradiation process. The DSC thermograms obtained after a thermal treatment at 145°C (for 1 min), and successive heating scans up to 140°C displayed shifts of the glass transition. The material still evolves after the initial cure treatment (140°C, 1 h), which did not allow the maximum conversion to be obtained. Thus, in order to determine the time necessary to achieve an acceptable stability of the resin, we have studied the evolution of the storage modulus with time under helium atmosphere for a frequency of 1 Hz at 140°C. Above 140°C, the resin quickly degrades. As shown in Fig. 2, after a 160 h thermal treatment the modulus still increases and it is apparent that the network formation reaction is slow, but not complete. Nevertheless, the highly crosslinked resin obtained after this post-curing treatment was considered as the reference state. Fig. 3 presents the evolution of the heat capacity of the unirradiated DGEBA/TETA resin after the former thermal treatment. The glass transition temperature, T_g, as determined from the inflexion point, and the heat capacity increment before the irradiation have been estimated to be 115°C and 0.3 J/kg, respectively.

3.1.2. Molecular mobility and dynamic mechanical spectrometry results

The evolution of the loss factor, $\tan\delta$, and of the storage modulus, G', measured on the DGEBA/TETA resins between 123 K (−150°C) and 423 K (150°C) and for a frequency of 1 Hz are shown in Fig. 4a and b before and

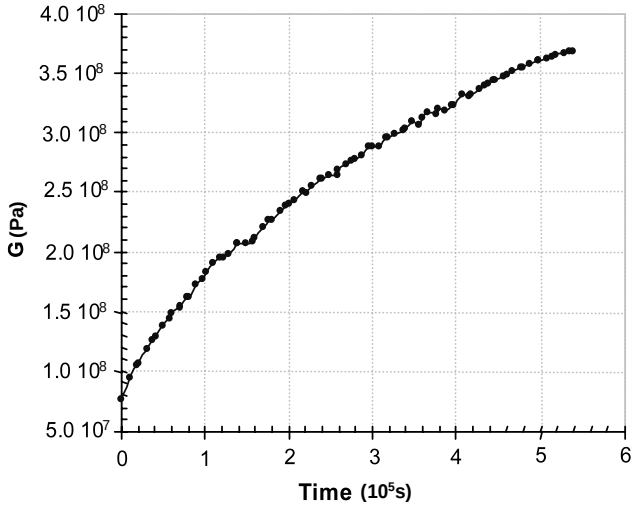


Fig. 2. Evolution of the modulus G during a thermal treatment at 140°C in the DGEBA/TETA resin.

after the former thermal post-curing treatment. In both cases, the loss factor tan δ displays a maximum and G' decreases sharply in the glass transition temperature range and then approaches a constant value (rubbery plateau). This main relaxation phenomenon, denoted α, is due to generalised and cooperative diffusive movements of repeat units. Two secondary relaxations peaks are also observed, similar to some already observed on similar resins [1–3]. These relaxations are named γ and β relaxations from low to high temperature, respectively. The corresponding characteristic temperatures T_α, T_β, T_γ at 1 Hz have been estimated to be 420 K (147°C), 301 K (28°C) and 223 K (−50°C), respectively, after the post-curing treatment. The γ relaxation was associated to local movements (Table 2) of the chains between the reticulation points, especially to crankshaft type motions of the glycidyl units [6–8]. The β relaxation would be the result of chains movements further

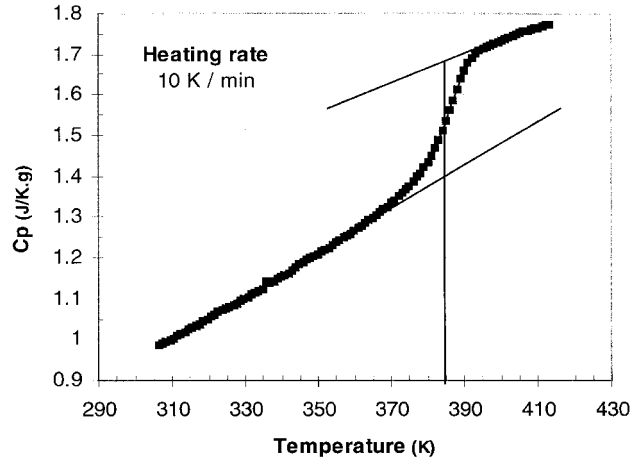


Fig. 3. Evolution of the heat capacity C_p of the unirradiated DGEBA/TETA resin.

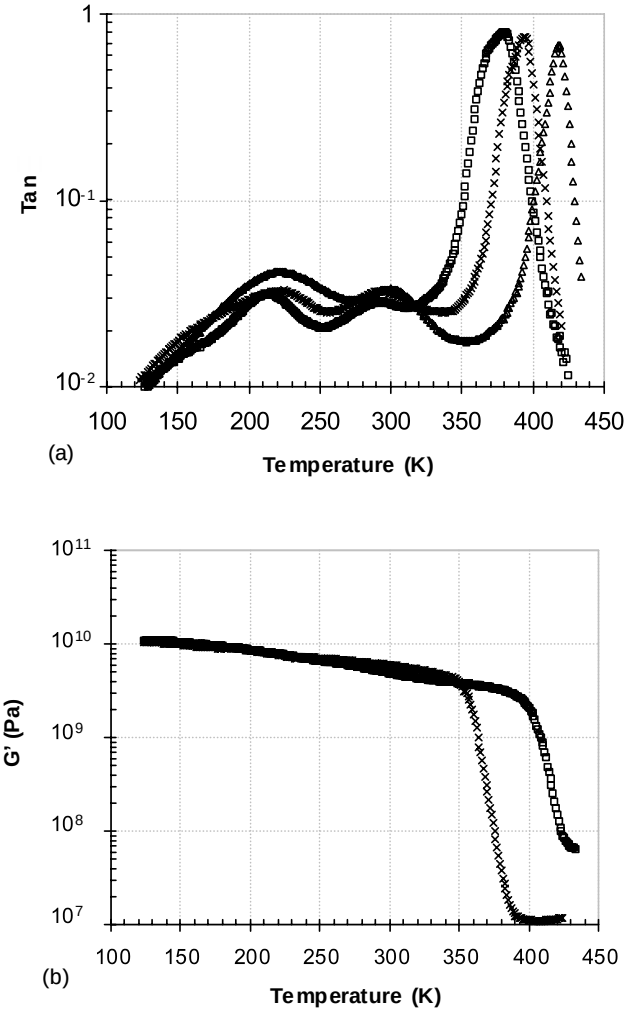


Fig. 4. (a) Isochronous spectrum of tan δ measured at 1 Hz for the unirradiated DGEBA/TETA system, before (×) and after (:) the post-curing treatment. (b) Isochronous spectrum of G measured at 1 Hz for the unirradiated DGEBA/TETA system, before (×) and after (:) the post-curing treatment.

restricted by crosslinking points in strongly crosslinked areas produced by an heterogeneous reticulation reaction [1–3].

As shown in Fig. 4b, the post-curing treatment effect is to increase the temperatures T_α, and T_β. T_α is much increased, T_β is less shifted and T_γ is not affected. The sharp decrease of G' at the glass transition relaxation is also shifted towards higher temperatures and the rubbery plateau modulus is increased. The slight increase of G' on the rubbery plateau observed before the post-curing treatment vanishes in the ultimately cured material. As a result, it is very apparent that the crosslinking reaction is thus enhanced by this curing treatment.

In order to study the temperature dependence of the relaxation time associated with the α relaxation in the unirradiated resin after the post-curing treatment, we have performed isothermal measurements around the glass transition temperature, starting from the highest temperature,

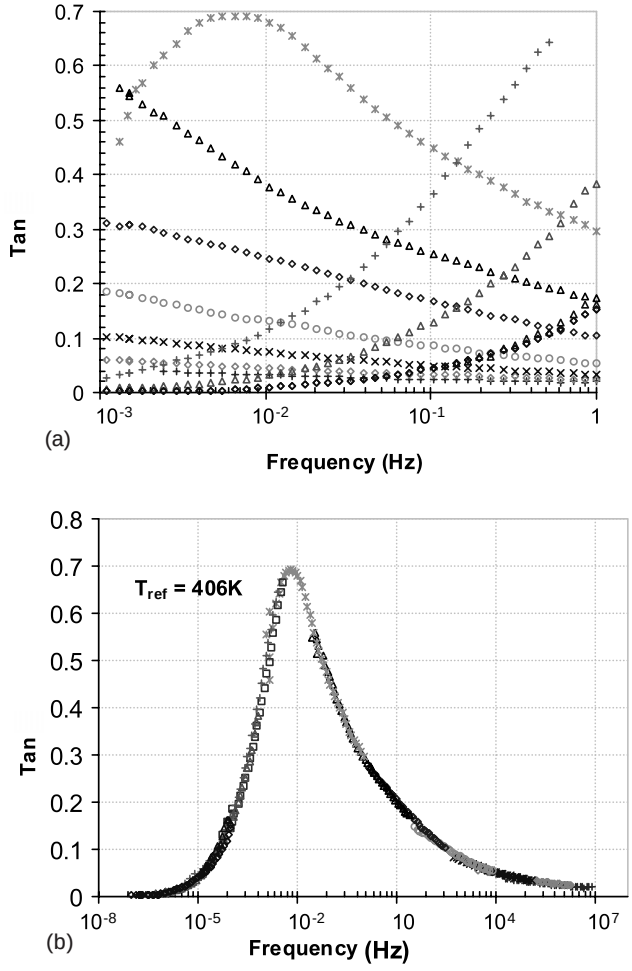


Fig. 5. Evolution of tan δ at various temperatures (a) and master curve (b) of tan δ for the DGEBA/TETA system. T = (+) 382 K; (◇) 384 K; (×) 390 K; (○) 394 K; (◇) 398 K; (△) 402 K; (✳) 406 K; (+) 414; (+) 418 K; (◇) 422 K; (▲) 426 K.

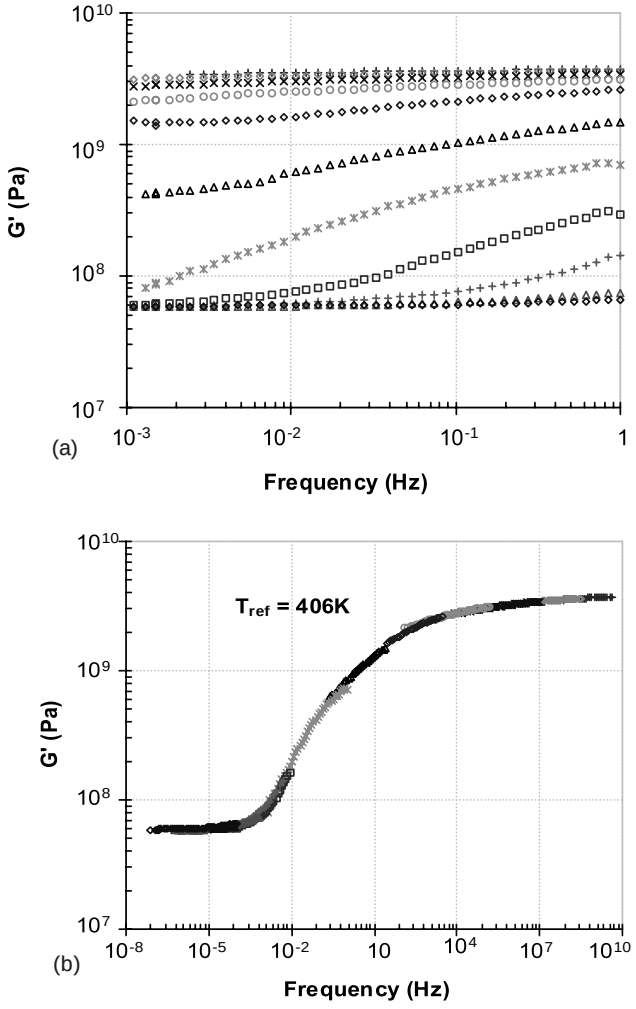


Fig. 6. Evolution of G' at various temperatures (a) and master curve (b) of G' for the DGEBA/TETA system. Same legend as for Fig. 5.

426 K (153°C), and decreasing by steps of 4°C. Figs. 5a and 6a show the isothermal data obtained for tan δ and G' for temperatures ranging from 426 K (153°C) to 382 K (109°C), and for frequencies varying from 10^{-3} to 1 Hz. Figs. 5b and 6b present the master curve obtained for tan δ and G', for a reference temperature of 406 K (133°C) by means of the time–temperature superposition principle. With the assumption that the maximum of G'' corresponds to $\omega_0 \tau_m = 1$, we have determined the temperature dependence of the relaxation time τ_α (Fig. 7) related to the α relaxation. From the measurements of tan δ, G' and G'' between 123 K (−150°C) and 423 K (150°C) at three different frequencies (1, 0.1 and 0.01 Hz), we have also determined the temperature dependence of the relaxation

Table 1
Glass transition temperature of irradiated and unirradiated samples

	T_{g1} (°C)	T_{g2} (°C)	T_{g4} (°C)	ΔC_p (J/kg)	ΔT_{C_p} (K)
DGEBA/TETA system unirradiated	109	115	120	0.35	18
DGEBA/TETA system irradiated with 2 MGy	73	81	87	0.45	25
DGEBA/TETA system irradiated with 5 MGy	60	68	78	0.56	26

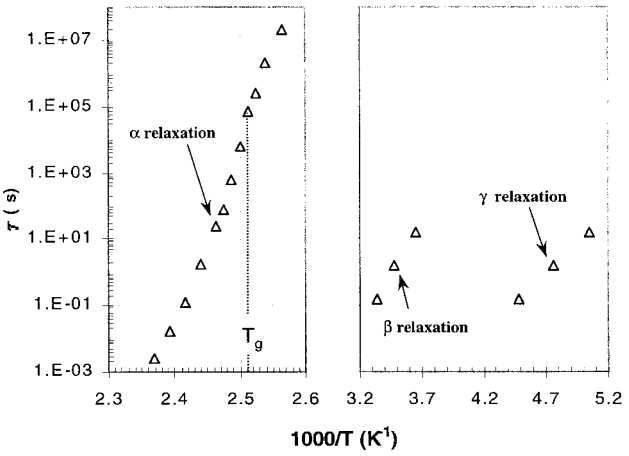


Fig. 7. Relaxation diagram for the unirradiated DGEBA/TETA system. For clarity, two different scales have been used.

times τ_β and τ_γ related to β and γ relaxations. The relaxation diagram of Fig. 7 summarises these results. β and γ processes can be described by an Arrhenius law, $\tau_i = \tau_{0i} \exp(E_{ai}/RT)$ with i = β or γ. The values of the preexponential factors and activation energies are given in Table 1. The high activation energy, $E_{a\beta}$, and the low value of the preexponential factor $\tau_{0\beta}$ suggest that the β relaxation is due to cooperative movements. Moreover, for the γ relaxation, the activation energy, $E_{a\gamma} =$ 65 kJ/mol, and the preexponential factor, $\tau_{0\gamma} = 10^{-17}$ s, indicate that the movements associated with the γ relaxation are simpler, but with a certain degree of cooperativity. For a comparison, the relaxation time τ_α can also be fitted by an Arrhenius law whose activation energy can be estimated in the glassy state and in the vicinity of T_g to $E_{a\alpha} = 560$ kJ/mol, indicative, as expected to a cooperative process.

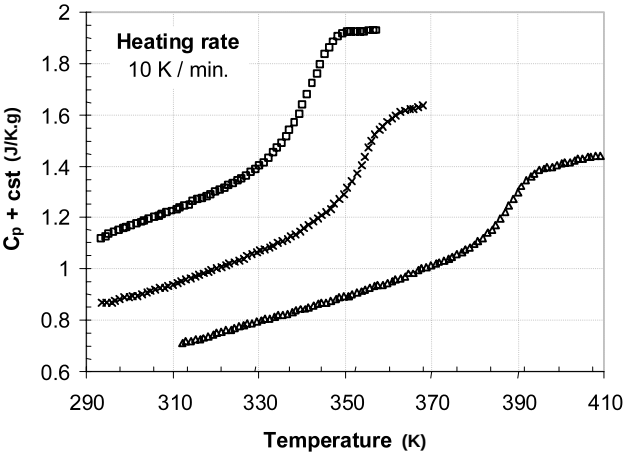
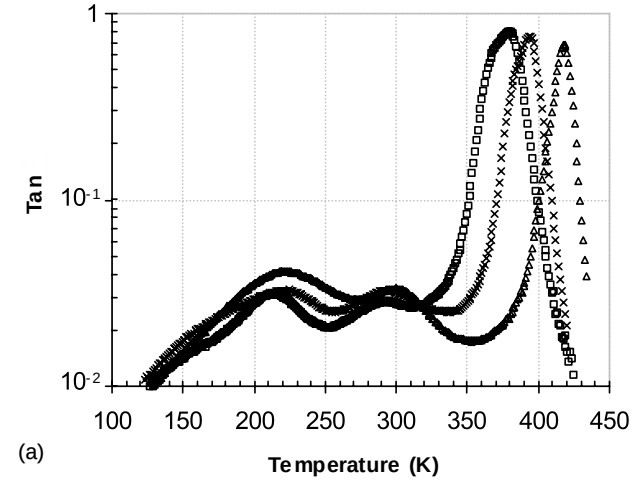


Fig. 8. Heat capacity C_p of the unirradiated and irradiated DGEBA/TETA system: unirradiated resin (:); resin irradiated with 2 MGy (×); resin irradiated with 5 MGy (△).



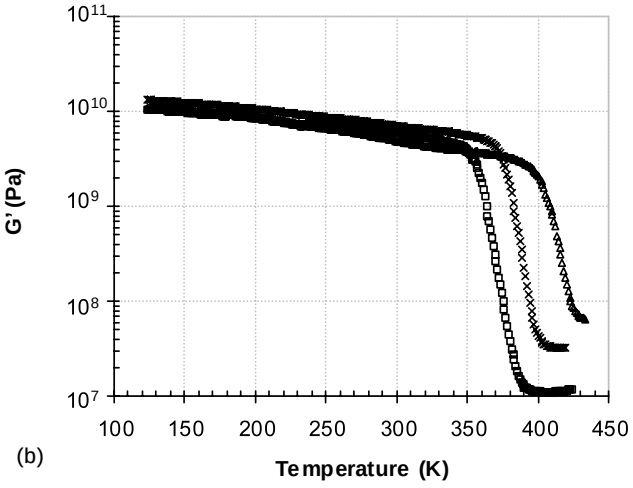


Fig. 9. (a) Evolution of tan δ on the DGEBA/TETA system for various doses: unirradiated (△); irradiated with 2 MGy (×); irradiated with 5 MGy (:). (b) Evolution of G' on the DGEBA/TETA system for various doses: unirradiated (△); irradiated with 2 MGy (×); irradiated with 5 MGy (:).

3.2. Influence of irradiation on the mechanical properties

3.2.1. Irradiated epoxy resins without post-irradiation thermal treatment

We have measured by DSC the heat capacity C_p of the irradiated samples after maintaining them for one month at −30°C (Fig. 8) in order to prevent any physical aging at room temperature. The glass transition temperatures obtained are given in Table 1. The main effect of the irradiation process is to decrease the glass transition temperature, as a result of chain scissions. Such a decrease has already been observed in similar epoxy resins [1–3]. Moreover, the increase with the irradiation dose of the temperature interval, ΔT, related to the ΔC_p increment in the glass transition region (Table 1) can be attributed to structural heterogeneities of the network and to a resulting distribution of glass transition relaxation.

We have also studied by dynamic mechanical spectroscopy the evolution of tan δ and G' with the irradiation

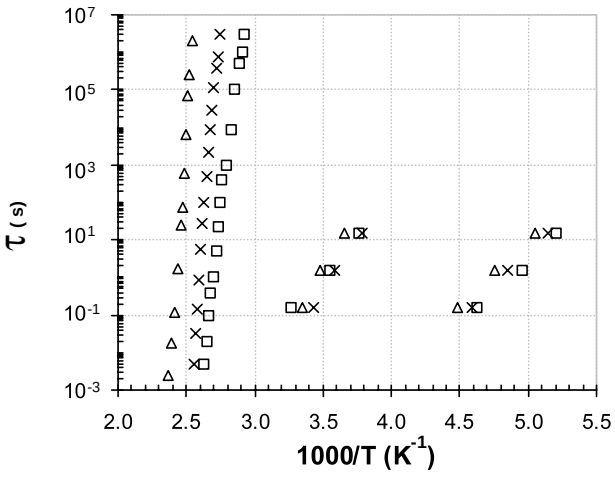


Fig. 10. Relaxation diagram of the unirradiated DGEBA/TETA system (△) and of the resin irradiated with 2 MGy (×) and 5 MGy (:).

dose. These results are presented in Fig. 9a and b. The changes induced by the irradiation process on the dynamic mechanical properties are again in good agreement with DSC results. The α relaxation temperature is shifted to lower temperatures as the irradiation dose increases but the secondary relaxations are less affected. The analysis of the shape of the α relaxation can provide additional information about the structure of the crosslinked networks [9,10]. The broadening of the α relaxation peak observed in Fig. 9a is attributed to an heterogeneity of the resin or to a reverse crosslinking phenomenon during the experiment [9,10]. The decrease of the real modulus related to α relaxation appears also for a lower temperature and the elastic modulus in the rubbery region, G'_c, decreases with the irradiation dose. It is known in highly crosslinked materials that the glass transition temperature and the modulus at the rubbery plateau are related to the crosslink density [11]. The crosslink density ν was deduced by means of the commonly used expression

$$G'_c \approx \nu RT \quad (1)$$

where R is the gas constant, T the absolute temperature, ν the crosslink density. By using Eq. (1), the crosslink densities obtained are 3.1×10^{-2} mol/cm^3 for the unirradiated material and 4.8×10^{-3} mol/cm^3 for the resin irradiated with 5 MGy indicating that massive chain scission takes place during irradiation. Several works have studied resins showing similar behaviour against dose [1–3]. This decrease of the number of crosslinks is coincident with the lowering of the glass transition temperature, T_g. This effect may be the result of chain breaks taking place especially on the quaternary carbon atom of the DGEBA, as it has been shown in Refs. [1–3].

In order to study the changes in the molecular motions induced by the irradiation treatment, we have obtained the relaxation diagrams of the DGEBA/TETA systems irradiated with 2 and 5 MGy in a similar way as for the unirradiated resin. The results obtained are displayed in Fig. 10. In order to limit the structural evolution of the irradiated material, measurements are performed for frequencies varying from 10^{-2} to 1 Hz, every 2° (from 392 to 356 K). For each studied material, we carried out a temperature scan test at three frequencies under the same conditions as for the characterisation of the reference DGEBA/TETA system. Again, we calculated the activation energies and the preexponential factor τ_0 for the two distinct irradiation doses. Table 2 summarises the values obtained for the irradiated materials. The effects of the irradiation treatment are opposite to the one observed during the post-curing treatment. The main α relaxation displays a marked evolution. This relaxation is strongly cooperative. The irradiation probably creates scissions and decreases this cooperativity. The secondary relaxation times can be regarded as scarcely altered. The γ relaxation, which is the most local one, is the least affected. It seems not very dependent on the reticulation rate (as we observed during the post-curing treatment). To conclude, the main consequence of the irradiation process is chain scission. The unsaturated bonds created on the amine skeleton, as observed in Ref. [4], is a less significant effect.

3.2.2. Effect of a post-irradiation thermal treatment

As displayed in Fig. 11, we have also measured the heat

Table 2
Preexponential factors and activation energies related to α, β and γ relaxations in the unirradiated and irradiated samples

	Unirradiated DGEBA/TETA resin	DGEBA/TETA resin irradiated with 2 MGy	DGEBA/TETA resin irradiated with 5 MGy
T_g (°C)	113	81	68
T_α (°C)	147	122	107
$E_{a\alpha}$ (kJ/mol)	560	480	400
τ_α (s)	5×10^{-70}	7×10^{-66}	10^{-57}
$E_{a\beta}$ (kJ/mol)	120	104	74
τ_β (s)	3×10^{-23}	77×10^{-21}	9×10^{-15}
$E_{a\gamma}$ (kJ/mol)	65	64	64
τ_γ (s)	2×10^{-17}	10^{-17}	2×10^{-17}

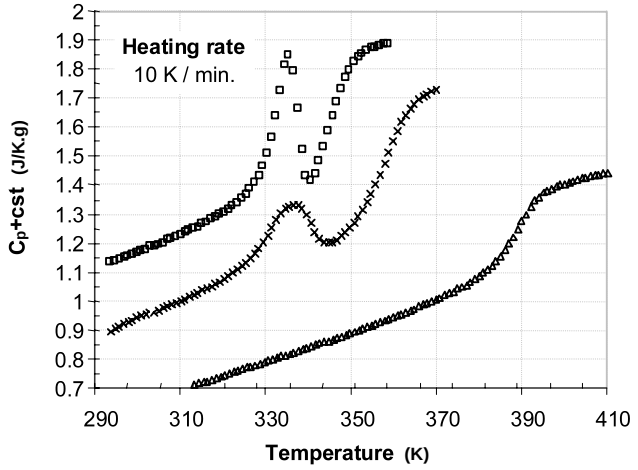


Fig. 11. Heat capacity C_p of the unirradiated and irradiated DGEBA/TETA system: unirradiated and aged 3 months at ambient temperature (:); irradiated with 2 MGy and aged 3 months at ambient temperature (×); irradiated with 5 MGy and aged 3 months at ambient temperature (△).

capacity of the irradiated samples and of the unirradiated resin after a thermal treatment at 293 K under vacuum during 3 months. The reference state DGEBA/TETA system is not sensible to physical aging at ambient temperature. On the contrary, the irradiated and aged samples exhibit peaks referred to as pre-peaks as they occur at a temperature noticeably lower than T_g. The glass transition temperature of these resins is closer to the room temperature, and such an aging treatment at ambient temperature has a significant effect. In order to confirm that a pre-peak would be observed in the healthy resin at a higher aging temperature, we have also carried out an isothermal aging treatment at temperature $T_v = 65°C$ during 3 h on the unirradiated material. The ratio T_v/T_g is chosen to be constant, i.e. $T_v/T_g = 338/386$ evaluated for the unirradiated material. As a consequence, an aging temperature of 65°C for the reference resin is the same as the one occurring for the specimen irradiated with 5 MGy ($T_g = 68°C$) and aged at 20°C. Before this treatment, we have erased any aging induced structural modification that occurred at room temperature with a thermal treatment at 10 K/min till $T_g + 5°C$, followed by a temperature descent at 20 K/min. The results obtained from DSC are presented in Fig. 12. Such a thermal treatment does not affect the reticulation rate. One observes a pre-peak of C_p near 95°C (368 K) in the unirradiated material (Fig. 12a). If one maintains the unirradiated material seven days at 65°C, the peak becomes stronger. For the irradiated materials, the aging peak around 80°C (353 K) is obvious, and appears in the vicinity of T_g (Fig. 12b).One can account for the marked differences in the behaviour of the resins, depending on whether the aging temperature is close or far below T_g, with a physical interpretation of structural relaxation in terms of a large distribution of relaxation times [12–17]. The irradiation process increases the molecular mobility and thus accelerates the aging kinetics.

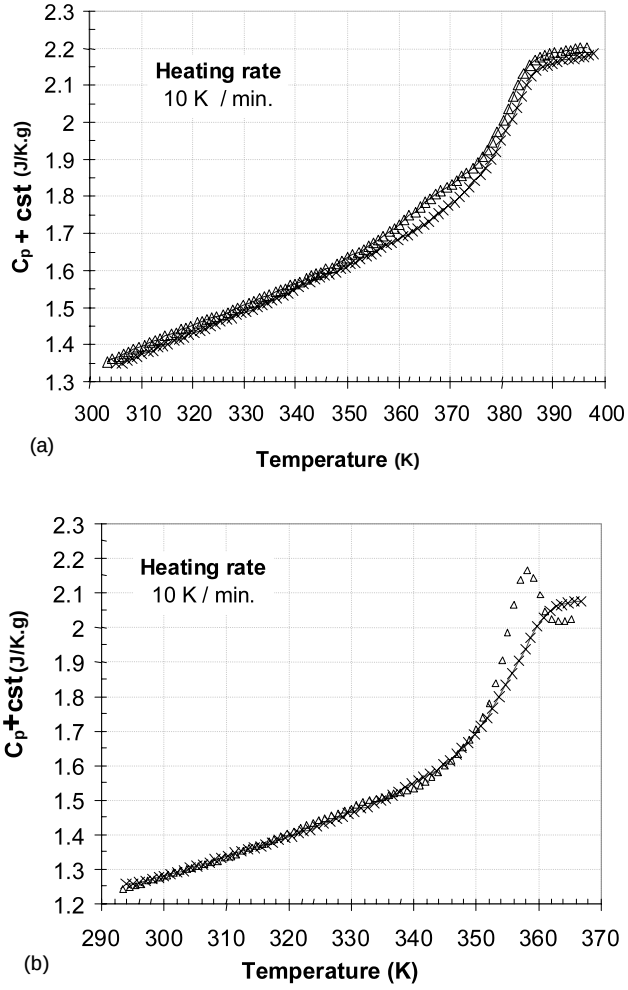


Fig. 12. (a) Heat capacity C_p of the unirradiated DGEBA/TETA resin without any aging thermal treatment (+), after a 3 h thermal treatment at 65°C (△), (b) Heat capacity C_p of the DGEBA/TETA resin irradiated with 2 MGy, after a 3 h thermal treatment at 65°C (△), irradiated with 2 MGy and without any aging thermal treatment (×).

3.2.3. Influence of irradiation on the mechanical properties in the high deformation range

The aim of the compression tests is to study the influence of the irradiation dose, on the plastic flow. As shown in Fig. 13, the evolution of the stress–strain curve obtained for unirradiated resins for a deformation rate of $4.8 \times 10^{-3}\ s^{-1}$ corresponds well to that observed in the case of amorphous polymers and shows three domains. For small deformations, one observes a linear dependence of the stress–strain (elastic deformation). When the rate of deformation reaches 9%, the stress reaches a maximum, at the yield stress, and is denoted by σ_y. We observe a domain of nearly constant stress (plastic flow stress σ_p), which leads to plastic strain hardening. This phenomenon is well apparent above 15% of deformation. The stress–strain curves obtained at ambient temperature on the irradiated samples without any post-irradiation thermal treatment are also displayed in Fig. 13. In the elastic range, the slope of the

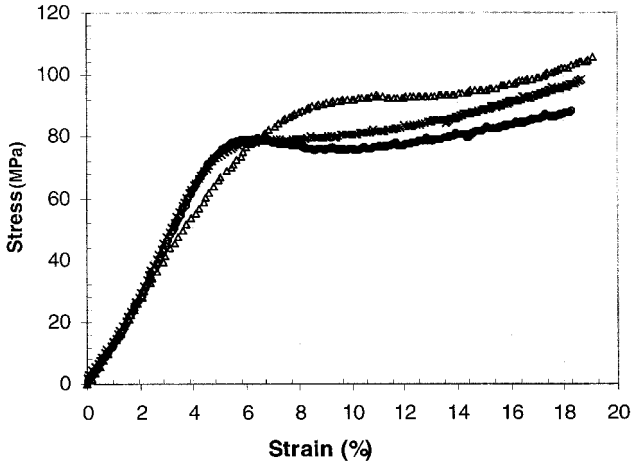


Fig. 13. Stress–strain curves of unirradiated DGEBA/TETA system non-aged (△), resin irradiated with 2 MGy without any thermal treatment (×), and resin irradiated with 5 MGy without any thermal treatment (○).

stress–strain curve is similar in the irradiated samples but the threshold stress σ_y decreases and is reached for lower strains.

In order to determine which aspects of the large deformation behaviour of the irradiated sample are related to the shift of the glass transition temperature T_g, and which can be ascribed to the irradiation process, we have displayed in the same diagram, compression tests carried out at different temperatures, T (Fig. 14). For a constant ratio T/T_g, in the high strain range, the behaviours of the irradiated and unirradiated resins are very close. Therefore, the differences observed in the plastic flow behaviour, can largely be accounted for by a variation of T_g.

The stress–strain curves obtained on the irradiated samples after 3 months of thermal aging at ambient temperature are displayed in Fig. 15a and b. After thermal aging, in the deformation range, one observes a well-defined stress peak on the irradiated materials, even more apparent for the sample irradiated with 5 MGy. This effect can be specifically ascribed to the thermal aging phenomenon [18], which is much stronger in the sample irradiated with 5 MGy as deduced from the calorimetry analysis.

Such effects of thermal aging, stress–strain curves were shown to be concomitant with the development of heterogeneity of deformation, with shear hands: the thermally aged samples show a pronounced stress peak near the yield accompanied with the formation of shear band and then deformation heterogeneity.

Such deformation heterogeneity is suspected in the case of irradiated material before thermal aging in order to explain the differences observed in Fig. 14. The irradiated resin exhibits a marked stress peak and spatial heterogeneity of the crosslink.

Density is believed to result in heterogeneity in the deformation field of the sample. Further direct observation of the deformation mechanisms (and heterogeneity) at the sub-millimetre scale is necessary to confirm this point.

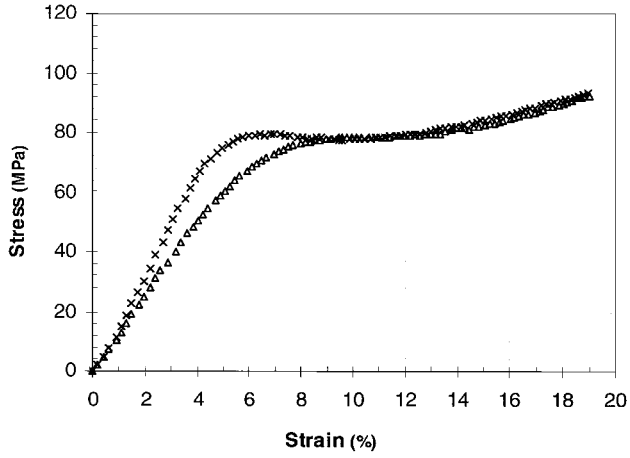


Fig. 14. Stress–strain curves of DGEBA/TETA systems: resin irradiated with 5 MGy, with $T/T_g = 0.8$ (×), resin unirradiated with $T/T_g = 0.8$ (△).

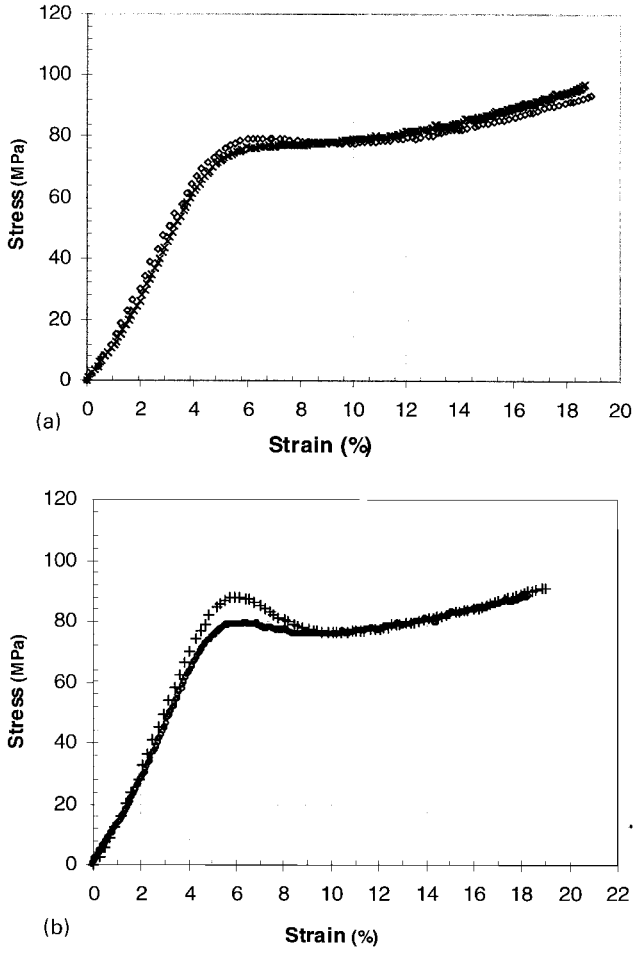


Fig. 15. (a) Stress–strain curves of the DGEBA/TETA resin irradiated with 2 MGy before (×) and after (◇) a 3 months thermal treatment at ambient T. (b) Stress–strain curves of the DGEBA/TETA resin irradiated with 5 MGy before (○) and after (+) a 3 months thermal treatment at ambient T.

4. Conclusions

In this study, the dynamic and mechanical properties of epoxy resins cured with curing agent formed by an aliphatic amine have been analysed as a function of the irradiation dose. A post-curing treatment completes the reticulation process. The irradiation process results in a decrease of the glass transition temperature T_g and of the elastic modulus in the rubbery region. These findings can be attributed to a destruction of the crosslinks or chain scissions within the resin. The relaxation diagrams obtained for the various doses show that the cooperative mobility associated with the α relaxation is also shifted to low temperature with irradiation. On the contrary, more local mobility corresponding to γ relaxation is not affected. The irradiation process decreases the yield strain and this decrease can be accounted for by the increase of the heterogeneity in the resin. Moreover, the thermal aging kinetics is much increased by the irradiation process. As the glass transition temperature T_g is shifted to lower temperatures, the mobility is much increased and the thermal aging phenomena play a significant role in the behaviour at ambient temperature. Irradiation aging and thermal aging act in opposite directions: the irradiation creates structural defects like chain breaks, while thermal aging induces their reaction and enhances the reticulation process. The effect of aging is particularly obvious on the stress–strain curves, where stress peaks are observed. The other changes in the high stress range following the irradiation can be related to the shift of the glass transition temperature T_g.

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