

Influence of gamma irradiation on the chemical and physical properties of DGEDDS / PDA and DGEDDS / MDA epoxy resins

N. Rami^{1,*}, H. Meghraoui¹, R. Ziraoui¹, T. El khoukhi², M. Mouhib³, A. El Harfi¹

1 Laboratory of Macromolecular and Organic Chemistry, Faculty of Science, University Ibn Tofail, BP 133, 14000 Kenitra, Morocco

2 Unit Radiological Monitoring of the Environment, National Center for Energy Sciences and Nuclear Techniques (CNESTEN), BP 1382 RP 10001 Rabat, Morocco

3 Station of ionization Boukhalef, INRA, Regional Centre, Tangier, Morocco

Received in 03 Oct 2010, Revised 02 Dec 2010, Accepted 13 Dec 2010.

* Corresponding author: email: najima_rami@yahoo.fr; Tel : +212 6 60 50 24 28

Abstract:

In this work we studied the effects of exposure to gamma radiation on two type epoxy resins: diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether 4,4'-dihydroxydiphenyl sulfone (DGEDDS) crosslinked with methylenedianiline (MDA) and 1,2-phenylenediamine (PDA). These resins were synthesized by condensing mass of the diol with epichlorohydrin in a basic medium. IRTF spectrometry and ¹H NMR was used to identify their structures before crosslinking. Then we followed the aging ATG by X microanalysis also allowed us to highlight the phenomenon of oxidation of the surface observed by SEM photos. Knowledge of the glass transition temperature and the starting temperature of degradation indicates a correlation between thermal stability and structure. The improvement of thermal properties could be a key issue to ensure structural stability of a matrix and therefore a better resistance to radiation.

Key words: Epoxy resin, gamma irradiation, TGA, SEM

1. Introduction

The study of the effects of radiation on materials based on polymers arises with the construction of the first nuclear power plant. In particular, the thermosetting matrix composites have been introduced gradually in the industry. Studies show these polymers generally highly aromatic, good performance under severe conditions [1]. They are widely used in the coating of nuclear waste and in the assembly or replacement of some structural parts. They are light weight materials that have excellent mechanical properties [2].

In this context, we proposed to realize total synthesis of two epoxies: diglycidyl ether of bisphenol A (DGEBA), which we used as a model and diglycidyl ether 4,4'-dihydroxydiphenyl sulfone (DGEDDS) structure similar to that of DGEBA.

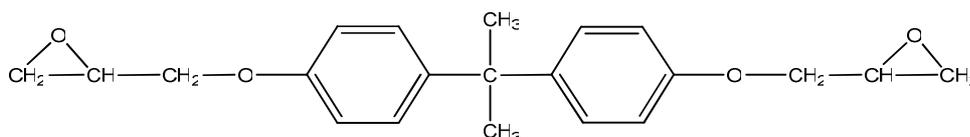
The overall objective of this work is to increase knowledge of degradation mechanisms and to be able to better predict the effects of radiation on such materials.

2. Materials

Our materials synthesized, were multifunctional epoxy resins and crosslinked with aromatic diamine hardeners. The method used for this synthesis is the glycidylation via condensation of epichlorohydrin molecules containing at least two hydrogens type mobile diacid, diamine, and polyphenols [3]. The products we have synthesized were the diglycidyl ether of bisphenol A and diglycidyl ether of 4,4'-dihydroxy diphenyl sulfone respectively called DGEBA and DGEDDS later in the article.

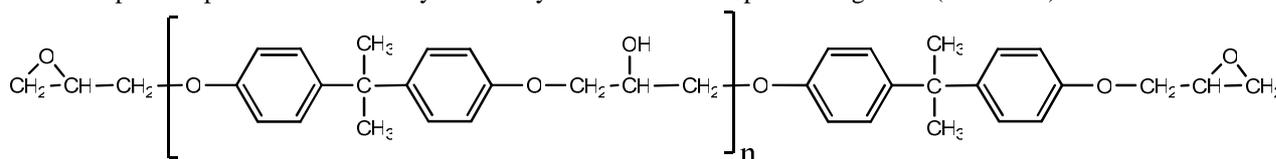
2.1. Synthesis of DGEBA

Diglycidyl ether of bisphenol A resin was obtained by condensation of epichlorohydrin (2,3 Epoxy Chloro Propane 1) and bisphenol A (4,4 bis-isopropylidene). (Scheme 1)



Scheme 1. Chemical structure of DGEBA.

The final product produced industrially is actually a bifunctional diepoxide oligomer: (Scheme 2)



Scheme 2. Chemical structure of DGEBA produced industrially

The index (n) is a function of polycondensation epichlorohydrin / Bisphenol A and the viscosity of the prepolymer depends on the value of this index:

- For $n < 1$ is a liquid at room temperature and its viscosity increases automatically when n is close to 1
- For $n > 1$, is a solid that must be melted or dissolved to be used.

The DGEBA resin that we use in our work is synthesized in our laboratory according to the protocol described in the patents by P. Castan [1]. Its index of epoxy (number of epoxy groups of DGEBA / kg) is between 5.2 and 5.45 eq / kg, which corresponds to an index polycondensation n between 0.1 and 0.14. Its number average molecular weight varies between 367 and 385 g / mol.

Experimental Protocol

In a three-necked, fitted with a condenser and a dropping funnel, is placed 2 g of bisphenol A ($8.76 \cdot 10^{-3}$ mol) and 4,86 g of epichlorohydrin ($2.63 \cdot 10^{-2}$ mol). After dissolution of bisphenol A, the mixture is heated at 100°C for 3 hours with magnetic stirring. Then 5,5g of soda (50% wt) is cooled to 60 °C using a dropping funnel, and stirred for 40 minutes. We add water and extract the organic phase with chloroform, dried over Na_2SO_4 and evaporated under vacuum. At the end we obtained 2.1g of viscous whitish (yield equals to 70%).

2.1.1 Nuclear magnetic resonance (NMR) of the DGEBA

The ^1H NMR of the product obtained shows the presence of different types of protons, so the CH_2 protons give a multiplet centered epoxy to 2.8 ppm, CH epoxies proton resonates as a multiplet centered at 3.3 ppm, and OCH_2 protons appear as a split doublet centered at 4.1 ppm. As for the proton carried by the aromatic rings, they resonate as a classical AB system between 7 and 7.3 ppm.

Also in Table 1, we compared the Heights of Integration (HI) of different types of epoxy protons, and this, by referring to the height equal to 1 integration proton CH. (Table 1)

Type proton	HI theoretical	HI experimental
CH_2 epoxy	2	2.1
CH epoxide	1	1
OCH_2	2	1.9

Table 1: ^1H NMR absorption bands of the resin DGEBA

We note that the heights of fully integrating experimental verify the report 2/1/2 expected.

In addition we compared the heights of integration of the protons and aromatic epoxy. If we consider IR as the Report Integration epoxy protons to those of aromatic protons, we define IR theoretical and experimental IR, then:

IR theory: 1.25

Experimental IR: 1.12

2.1.2 Infrared Spectroscopy Fourier Transform (FTIR) of the DGEBA

The allocations made on this resin (Fig.1) are grouped in Table 2.

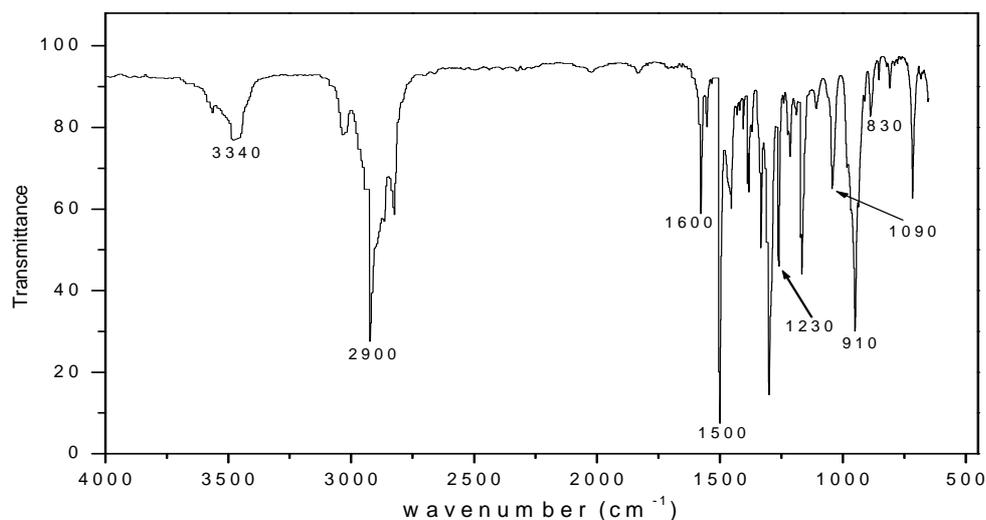


Fig.1: FTIR of DGEBA

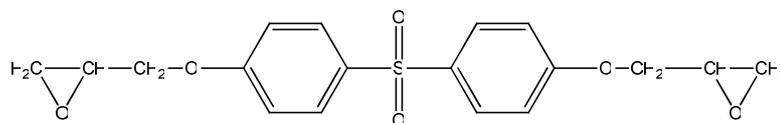
Band ν (cm ⁻¹)	Functions
3340	Residual OH
2900; 1500; 1450	Methylene CH
3040, 1600, 760	Para substituted aromatic ring
1230	Aromatic OC (Ar-O)
1030; 1090; 1180	CO alcohols and ethers
910; 830	Epoxy

Table 2: Infrared absorption bands of DGEBA resin

According to results of NMR and FTIR analysis, we notice the presence of synthesized product (DGEBA) and a residue of bisphenol-A did not react during condensation.

2.2. Synthesis of DGEDDS

It is an epoxy resin DGEBA counterpart, based on 4,4'-giving dihydroxydiphenylsulfone by condensation with epichlorohydrin resin diglycidyl ether of 4,4'-dihydroxydiphenylsulfone [i].(Scheme 3)



Scheme 3. Chemical structure of DGEDDS.

Experimental Protocol

In a three-necked, fitted with a condenser and a dropping funnel, is placed 2.5 g of 4,4'-dihydroxydiphenylsulfone (10⁻² mol) and 8.25 g of soda (10% wt). The mixture is heated to 60 ° C for 10 minutes with magnetic stirring, then we added 4.32 g of epichlorohydrin. The temperature reached to 100 ° C in 20 minutes and remains constant about 3 hours [5].

Then the liquid becomes more viscous and heterogeneous, after cooling, carefully separating the aqueous phase and wash the organic phase several times with portions of water. After separation by chloroform and drying with sodium sulfate, discard the rest of epichlorohydrin using a rotary evaporator.

At the end we obtain a brown viscous resin in 89% yield.

2.2.1 Nuclear Magnetic Resonance (NMR) of DGEDDS

The NMR ¹H 300MHz resin in CDCl₃ shows the presence of aromatic protons between 7.2 and 7.9 ppm on the one hand, and secondly the sign on the proton motive epoxy, made by the epichlorohydrin, and the protons of-CH₂ of

epoxy ring resonates at 2.9 ppm, protons of-CH₂ in the alpha position of oxygen at 4.3 ppm and the H proton gives a multiplet cycle 3.8 ppm.

We have the HI protons and aromatic epoxy, then:

IR theory: 1.25

Experimental IR: 1.09

The gap between theoretical IR and experimental IR showed that the addition of epichlorohydrin was not complete. This is probably due to the existence of sulfonyl groups which relocates the oxygen doublets and stiffens the molecule.

2.2.2 Infrared Spectroscopy Fourier Transform (FTIR) of DGEDDS

The infrared spectrum (Figure 4) shows the different groups of the molecule 4,4' dihydroxydiphenylsulfone, its functions are grouped in Table 3.

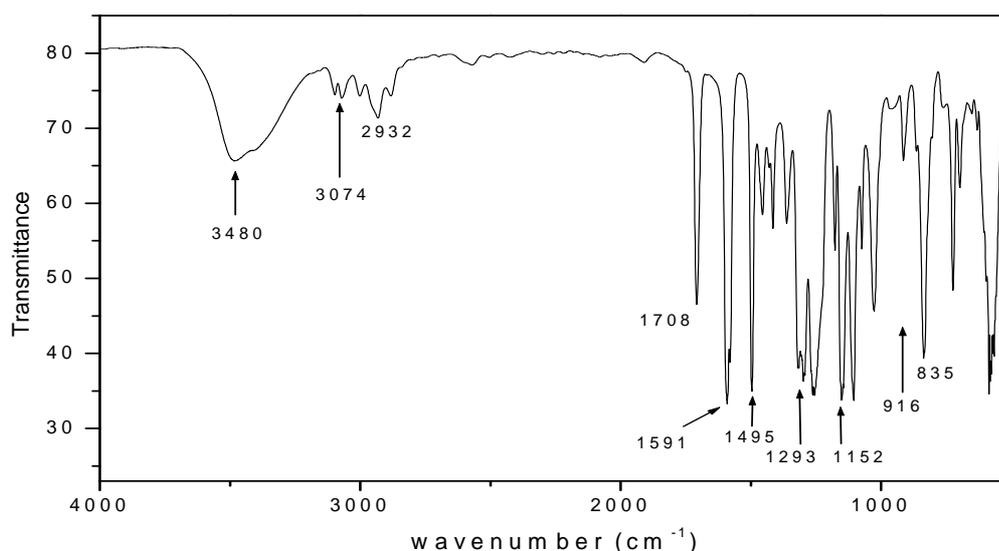


Fig.2: FTIR spectrum of DGEDDS

Table 3: Infrared absorption bands of the resin DGEDDS

Band ν (cm ⁻¹)	Functions
3480	Residual OH
2932	Methylene CH
1591, 1415, 1495, 726	Para substituted aromatic ring
3074 1708	Aromatic CH
1293, 585	R-SO ₂ -R
1258, 1104, 1028	CO-Ar
916, 835	Epoxy

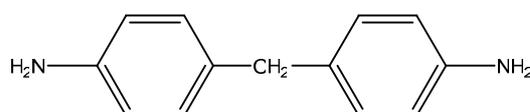
Thus, all analysis NMR ¹H and FTIR confirm the structure of the synthesized product.

2.3. Hardening

During crosslinking, thermosetting resins become insoluble and infusible by exothermic chemical reactions (polyaddition reaction irreversible) between the epoxy prepolymer and the hardener. The resulting material is an infinite three-dimensional network. Most formulations require a supply of heat to crosslink [ii,iii].

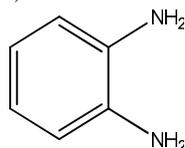
Thus, our crosslinking are performed by two primary diamine curing whose chemical formulas are as follows: (Schemes 4, 5)

- The methylene dianiline (MDA)



Scheme 4. Chemical structure of methylene dianiline.

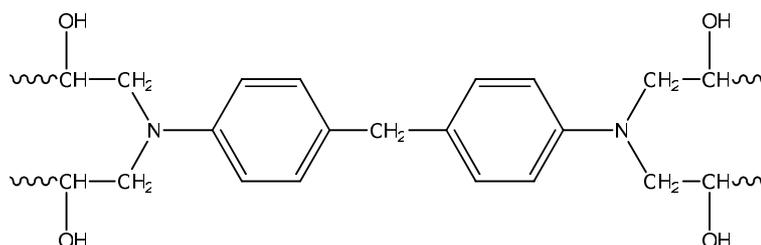
- The 1,2-phenylene diamine (PDA)



Scheme 5. Chemical structure of 1,2-phenylene diamine.

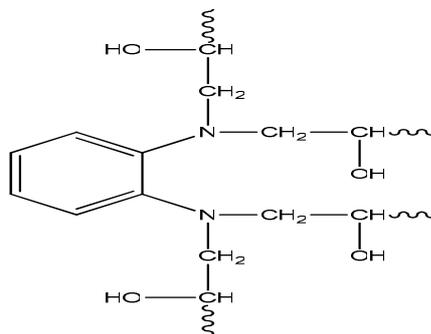
These hardeners are each equal to four features, which means that during the crosslinking reaction with a bifunctional resin, for example, their two amine groups react with four epoxide functional theory when they are in stoichiometric proportion. The final product is, in both cases a three-dimensional chemical network bridged by the following respective forms: (Schemes 6,7)

- 2.3.1 With the MDA.



Scheme 6. Reaction with MDA

- 2.3.2. With the BDA.



Scheme 7. Reaction with BDA

2.4. Implementation of samples

The mixture of epoxy and hardener before the crosslinking is carried out according to the protocol adopted by S. Fetouaki and al [iv], methylene dianiline (MDA) and 1,2-phenylene diamine (PDA), which crystallized at room temperature are placed in an oven at 120 ° C (a temperature above its melting temperature) while the resin is heated to 60 ° C. When rendered, each hardener is mixed with the resin with stoichiometric ratios to a single fluid phase, then being at 70 ° C. The samples thus prepared were sealed in test tubes and underwent a curing cycle of 12 hours at 70 ° C, followed by a second curing cycle of 1 hour at 140 ° C.

Finally, the samples were cut in the form of pellets of diameter 10 mm and thickness of 1mm whose faces are perfectly parallel.

2.5. Campaign radiation

The samples were irradiated at room temperature and in air by the action of an ionizing radiation Gamma in the National Center of Energy, Nuclear Science and Technology (CNESTEN) Morocco. We used as a radioactive source Cobalt Gamma radiation transmitter. The total doses of radiation that campaign are about 20 and 500 kGy.

3. Experimental methods

3.1. Thermo-Gravimetric Analysis (TGA)

To conduct a study on the degradation and thermal stability, we have used the technique of Thermo-Gravimetric Analysis (TGA) in dynamic (nonisothermal). The principle of this technique is to continuously monitor the change in

mass of a sample function of temperature. The TGA measures the mass changes accompanying structural changes during heat treatment such as decomposition or oxidation. These curves can better appreciate the changes in mass [3].

The instrument used for this study is to type Rheometric Scientific STA 1500. The sample is placed in a platinum basket suspended from a balance beam, is located in a room with controlled temperature and speed of temperature rise under constant flow of synthetic air or inert gas (N₂). The balance scale is provided by an electromagnetic compensation system. The change in mass, given by rebalancing the system is recorded as a function of the temperature rise.

Analyses are performed on samples of about 10mg. The accuracy in temperature measurement is ± 0.2 ° C in the temperature range 20 to 700 ° C with a rate of rise in temperature (15 ° C / min) under a flow of inert gas (N₂).

3.2. Scanning electron microscopy (SEM)

The scanning electron microscope was used to produce photographic images. The observations were made on a microscope JEOL JSM-5500.

Samples with a mass of 10mg are coated with a carbon deposit to avoid the effects of surface charge. A beam of electrons accelerated through a fixed potential (15kV, in our case) which excites the surface of the sample.

3.3. X-ray microanalysis

The electron probe microanalysis and X-ray emission, or X microanalysis is a method of quantifying the precise chemical composition. The apparatus used is type-EDAX FALCON coupled with SEM.

4. Results and discussion

4.1. Study of thermo-degradation

Our objective is to understand the influence of radiation on the evolution of physico-chemical and thermal behavior of systems DGEBA / MDA, DGEBA / PDA, DGEDDS / MDA, DGEDDS / PDA.

In the Thermogravimetric analysis ATG, we followed changes in mass of the samples studied as a function of temperature before and after irradiation.

Pyrolysis of these samples was carried out under a stream of nitrogen with a flow rate of 5ml / s, the heating rate is 15 ° C / min.

4.1.1. Thermal behavior of the DGEBA crosslinked with the MDA and PDA

The diagrams obtained show the thermal properties of systems DGEBA / MDA and DBEBA / PDA before and after irradiation with total doses 20 and 500 kGy are shown in Figures 6 and 7.

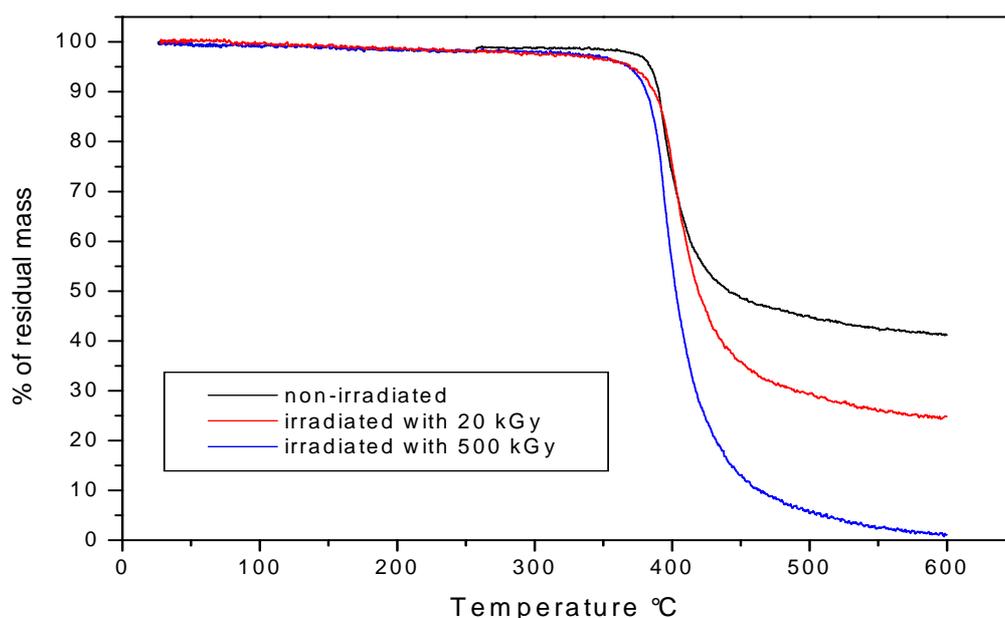


Fig.3: Evolution of the mass measured by TGA, resin DGEBA / MDA non-irradiated and irradiated respectively with 20 and 500 kGy

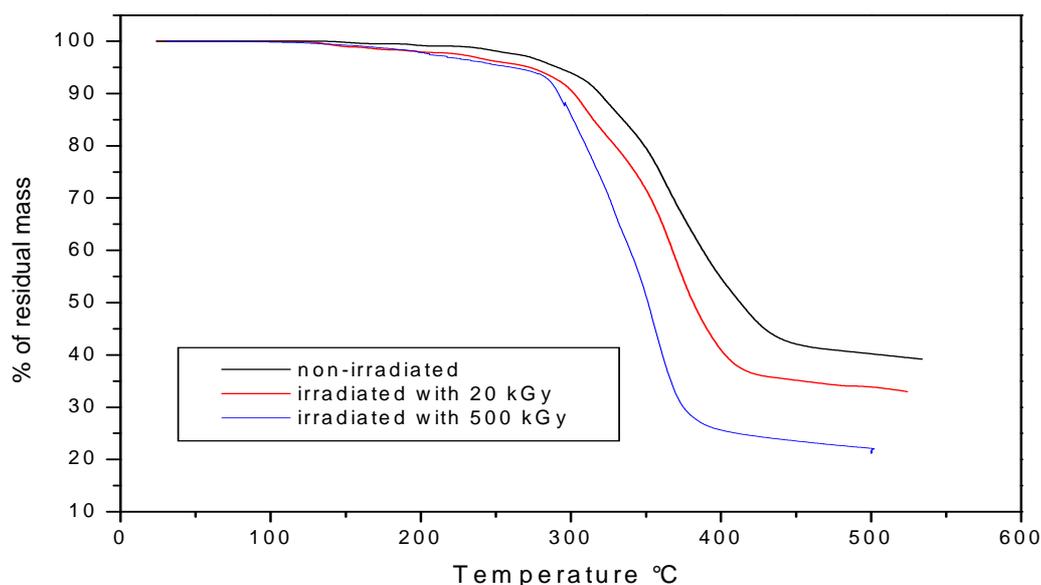


Fig.4: Evolution of the mass measured by TGA, resin DGEBA / PDA unirradiated and irradiated respectively with 20 and 500 kGy

These curves show an aspect of decreasing percentage of mass remaining as a function of temperature.

Furthermore, we have classified the characteristics of these materials (Table 4), in accordance with conventional standards [v,vi] by:

- T_d: the starting temperature of degradation which corresponds to a loss of 2% by mass.
- T₁₀: temperature in a 10% loss of mass.
- T₅₀: temperature in a 50% loss of mass.
- S_{dr}: the threshold of rapid degradation.
- R₅₀₀ (%) The remaining fraction at 500 ° C.

Table 4: Key features of heat extracted diagrams ATG samples DGEBA / MDA and DGEBA / PDA unirradiated and irradiated respectively with 20 and 500 kGy

Matrix DGEBA / MDA	T _d (° C)	T ₁₀ (° C)	T ₅₀ (° C)	S _{dr} (° C)	R ₅₀₀ (%)
Unirradiated	303	389	437	380	44.62
Irradiated with 20 kGy	278	385	418	371	29.24
Irradiated with 500 kGy	276	379	402	368	5.44
Matrix DGEBA / PDA	T _d (° C)	T ₁₀ (° C)	T ₅₀ (° C)	S _{dr} (° C)	R ₅₀₀ (%)
Unirradiated	241	318	409	311	40.09
Irradiée avec 20 kGy	186	301	376	289	34,05
Irradiée avec 500 kGy	185	290	350	282	22,20

From these results we notice a shift in the onset temperature of degradation (T_d) of 303 °C to 278 °C (20 kGy) and 276 °C (500 kGy) for the MDA, and 241 °C to 186 °C (20 kGy) and 185 °C (500 kGy) for the PDA. Thus the significant effect of irradiation is to shift the T_d to lower temperatures. This could be explained by the partial destruction of crosslinking node, under the effect of irradiation.

It also concluded that the resin DGEBA crosslinked with the MDA has a higher T_d than crosslinked with PDA before and after irradiation, so the system DGEBA / MDA exhibits resistance to thermal degradation compared to the DGEBA / PDA.

4.1.2. DGEDDS Thermal behavior of cross-linked with the MDA and PDA

For DGEDDS crosslinked resin with MDA and PDA, we also followed the evolution of mass as a function of temperature under the same conditions as the DGEBA (Figures 5 and 6).

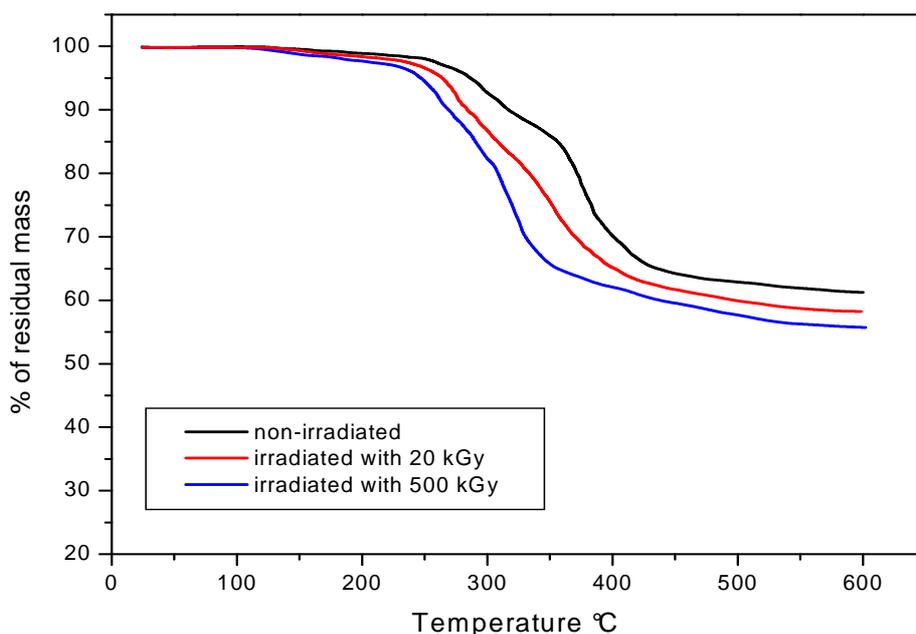


Fig.5: Evolution of the mass measured by TGA, resin DGEDDS / MDA non-irradiated and irradiated respectively with 20 and 500 kGy

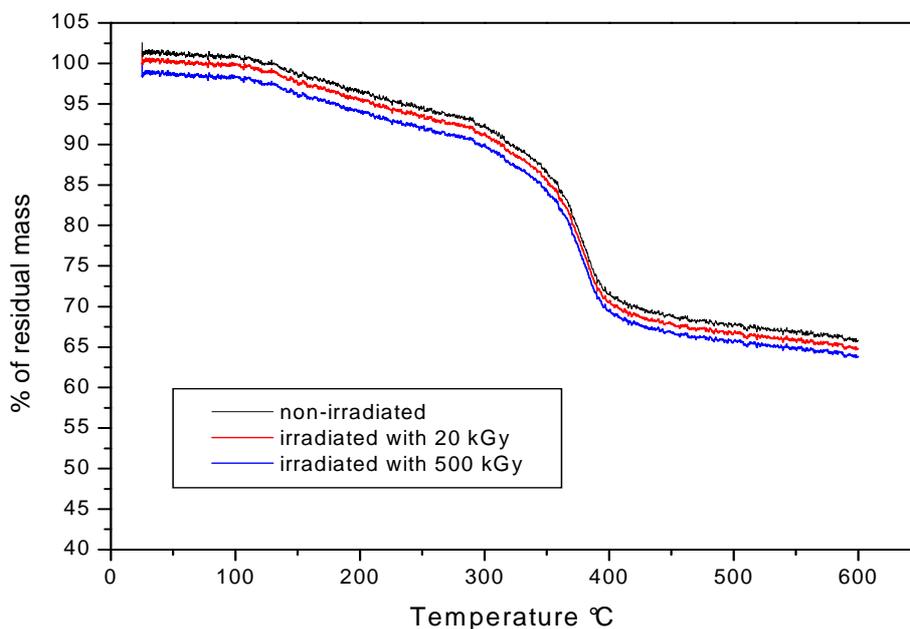


Fig.6: Evolution of the mass measured by TGA, resin DGEDDS / PDA unirradiated and irradiated respectively with 20 and 500 kGy

The main thermal characteristics of the resin extracted DGEDDS curves are presented in the table below (Table 5). From the results obtained in the above table, we also note a shift of onset temperature of degradation of the resin irradiated versus not irradiated.

We also realize that when the resin DGEDDS is cured with MDA, the starting temperature of degradation (250 °C) is higher than that cured with PDA (159 °C).

This resin has a residue at 500 °C above 60% due to the presence of the sulfone group in its structure, without really knowledge to mechanism of degradation due to the complexity of wave-matter interactions phenomena between the material and gamma radiation. [2,vii]

Table 5: Key features of heat extracted samples TGA diagrams DGEDDS/MDA DGEDDS/PDA unirradiated and irradiated with 20 and 500 kGy

Matrix DGEDDS / MDA	T _d (°C)	T ₁₀ (°C)	T ₅₀ (°C)	Sdr (°C)	R ₅₀₀ (%)
Unirradiated	250	312	-	294	65.87
Irradiated with 20 kGy	217	280	-	284	62.85
Irradiated with 500 kGy	180	264	-	260	60.73
Matrix DGEDDS / PDA	T _d (°C)	T ₁₀ (°C)	T ₅₀ (°C)	Sdr (°C)	R ₅₀₀ (%)
Unirradiated	159	320	-	287	67.81
Irradiated with 20 kGy	142	312	-	280	66.75
Irradiated with 500 kGy	128	295	-	279	65.73

4.2. Effects of aging on the surface

We followed by SEM and Microanalysis X evolution of the surface and the percentage of different elements on the surface of samples before and after irradiation.

4.2.1. Scanning Electronic Microscopy of DGEBA / MDA and DGEBA / PDA

SEM micrographs of DGEBA / MDA and DGEBA / PDA unirradiated and irradiated with 20 and 500 kGy in air are shown in Figure 10.

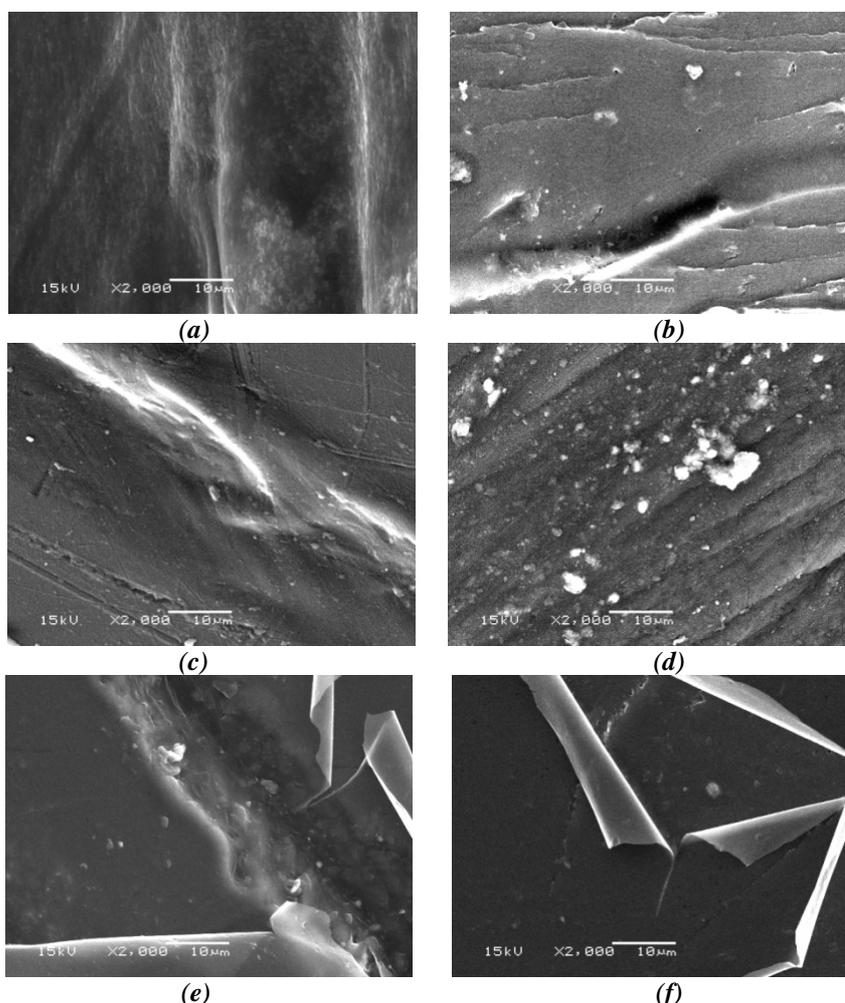


Fig.7: SEM photos of samples: (a) DGEBA / MDA unirradiated, (b) DGEBA / PDA unirradiated, (c) DGEBA / MDA-irradiated with 20 kGy, (d) DGEBA / PDA radiated with 20 kGy (E) DGEBA / MDA irradiated with 500 kGy, (f) DGEBA / PDA irradiated with 500 kGy,

From the SEM pictures obtained in Figure 10, we observed changes in surface form thin layers of bark for high doses.

4.2.2. Scanning Electronic Microscopy of DGEDDS / MDA DGEDDS / PDA

As before we show in Figure 11 below the SEM photos of the crosslinked resin DGEDDS with MDA and PDA.

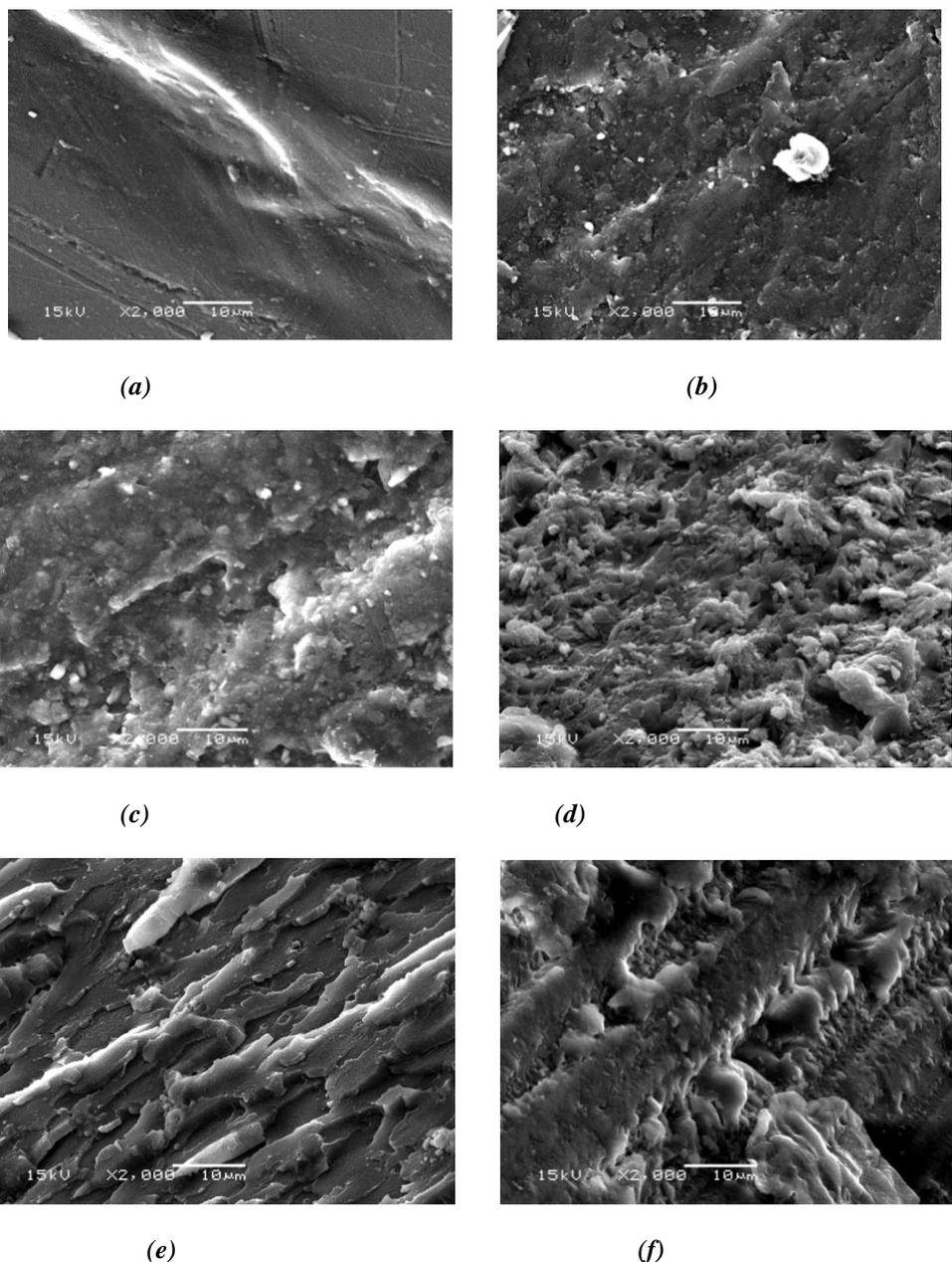


Fig.8: SEM photos of samples: (a) DGEDDS / MDA unirradiated, (b) DGEDDS / MDA irradiated, (c) DGEDDS / MDA irradiated with 20 kGy, (D) DGEDDS / PDA irradiated with 20 kGy (E) DGEDDS / MDA irradiated with 500 kGy, (f) DGEDDS / PDA irradiated with 500 kGy,

There is an analogy of the effect of radiation on the relative DGEDDS and DGEBA. The higher dose of irradiation that is aging more intense, mentioned by irregularities at the surface.

4.2.3. Microanalysis X

We performed X microanalysis for samples in question before and after irradiation in order to anticipate changes in the chemical composition of our materials (*Figure 12 and 13*).

Analysis of the spectra of microanalysis X of the two resins shows the existence of peaks of components. For the DGEBA resin are the peaks of the elements carbon, oxygen (essential components of the matrix), and traces of: silicon, chlorine, magnesium, aluminum (from a variety of impurities such as the pan and sandpaper surface treatment).

Regarding the resin DGEDDS, we find the same peaks as resin DGEBA with two peaks of more sulfur and chlorine, the first is due to the existence of the sulfone group in the structure and the second from rest epichlorohydrin and chloroform used during synthesis.

The following table (*Table 6*) includes all the mass percentages of the constituents of the surface of each sample.

Label A: 2c[15kv]

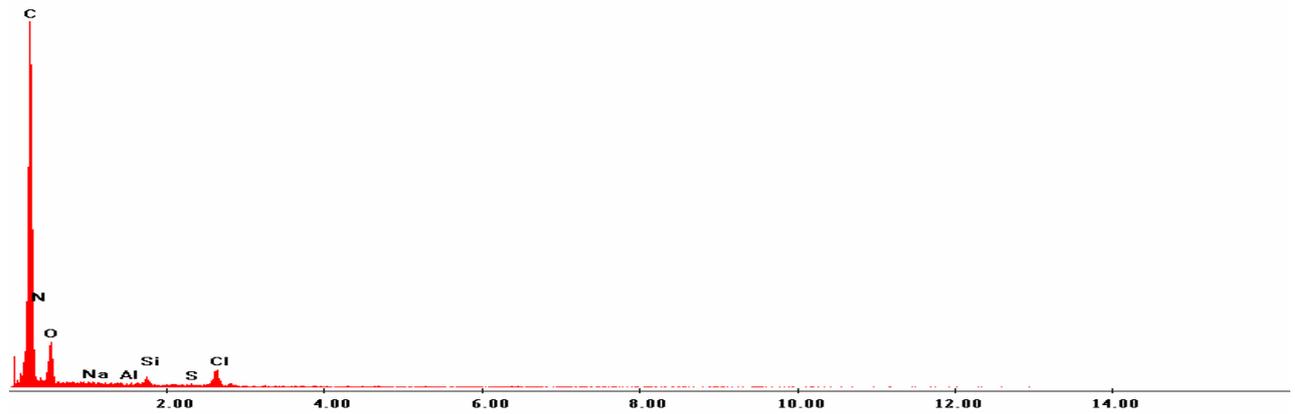


Fig. 9: Spectrum of the X microanalysis of resin DGEBA / MDA

Label A: 3n[15kEv]

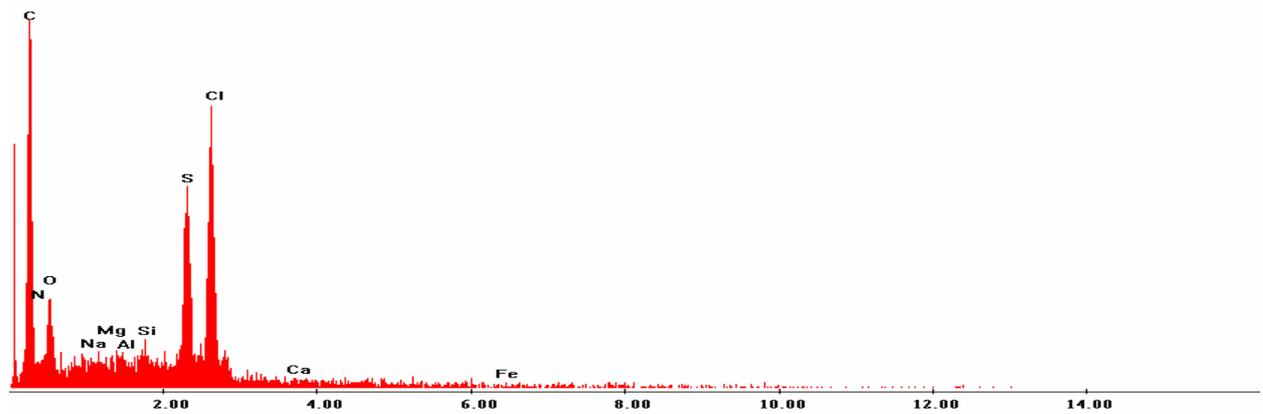


Fig. 10: Spectrum of the resin Microanalysis X DGEDDS / MDA

Table 6: Elements of the surface before and after irradiation

Element (Wt%)	DGEBA / MDA unirradiated	DGEBA / MDA irradiated with 20 kGy	DGEBA / MDA irradiated with 500 kGy	DGEDDS / MDA unirradiated	DGEDDS / MDA irradiated with 20 kGy	DGEDDS / MDA irradiated with 500 kGy
CK	78.82	78.80	76.39	68.36	68.30	67.59
NK	7.19	7.17	6.06	7.41	7.38	8.67
OK	11.48	11.52	14.70	12.64	12.70	15.41
NaK	0.62	0.66	0.11	0.14	0.17	0.22
AlK	0.30	0.26	0.04	0.20	0.22	---
SiK	0.63	0.60	0.57	0.18	0.16	---
SK	---	---	0.11	6.36	6.30	5.50
ClK	0.66	0.67	2.02	4.72	4.78	2.61
CaK	0.29	0.31	---	---	---	---
Total	100.00	100.00	100.00	100.00	100.00	100.00

The percentage changes of these elements show that there is an increase of the mass concentration of oxygen at the surface after irradiation for both resins depending on the dose.

Various authors have reported the oxidation surface during aging of polymers under air [10]. As we saw earlier, the degraded surface layer would be due on the one hand the diffusion of atmospheric oxygen to the heart of the polymer and, secondly, determination of the oxygen the network by oxidation reactions. This surface oxidation can explain the color change of samples during aging radiochemical passing the initial gray to green to brown.

On the one hand, the evolution of the mass concentration of oxygen as a function of radiation dose on the surface of a sample aged in air and an unaged sample helps explain the appearance of strips of bark surface level power at higher doses.

On the other hand, at low doses there is a slight change in the surface compared with higher doses which is explained by the radiation resistance of our materials.

5. Conclusion

In this study, we developed the assessment thermostability and therefore the radiosensitivity of these epoxy resins by thermogravimetric analysis that gave us an insight into the thermal degradation of various products. The irradiation causes mainly a shift of the onset temperature of degradation and a decrease in the number of junctions. These effects can be attributed to destruction of the nodes of crosslinking within the matrix and / or divisions of chains in the molecular structure.

The experimental data show that curing with MDA offers all resins, radiochemical and thermal stability remarkably higher than those cured by the PDA. Indeed, the two aromatic rings present in the MDA provide a rigid macromolecular structure difficult to access with PDA.

The results of X microanalysis allowed us to highlight the phenomenon of surface oxidation, observed by SEM, which is responsible for triggering the process of aging due to changes resulting, first, direct effects radiation, and secondly, the consequences induced by the conditions of use of the material after irradiation.

6. References

1. Ochi, M., Takashima H., *Polymer*, 42 (2001) 2379.
2. Devanne, T., "vieillessement radiochimique d'un réseau époxy", Thèse de Doctorat : École Nationale Supérieure d'Arts et Métiers, Centre de Paris, (2003).
3. Fetouaki, S., El Harfi, A., Belkbir, L. *Eur. Polym. Journal* 38 (2002) 787.
4. Castan, P.; US Patent, 2444333 (1948).
5. Meghraoui, H., Rami, N., Toufik, M., Elharfi, A., Achour, M. E., Carmona, F., Outzourhit, A. *Phys. Chem. News* 38 (2007) 84.
6. Levan, Q., Thèse de Docteur-Ingénieur, INP Toulouse, France. (1981).
7. Rami, N., Meghraoui, H., Grich, M., Fetouaki, S., Elharfi, A. *Ann. Chim. Sci. Mat.* 33 (2009) 479.
8. Fetouaki, S., Toufik, M., Meghraoui, H., Elharfi, A. *Phys. Chem. News* 27 (2006) 131.
9. Cporricio, G., Bargigia, G.; Brevet Français n° 2258411, (1975)
10. Pistor, J., Pauli, A.M., Arfi, C., *Analysis (F)* 6(3), (1978) 121
11. Vignoud, L., David, L., Sixou, B., Vigier, G. *Polymer* 42, (2001) 4657