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Study on radiochemical ageing of DGEBA/MDA filled with carbon black and glass powder under GAMMA irradiation

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ABSTRACT

In this work, we are interested in the study of radiochemical aging formulations of two epoxy composites with an epoxy resin model of diglycidylether of bisphenol A (DGEBA) crosslinked with methylene dianiline (MDA), which contains as filler carbon black (CB) and the glass powder (GP). Then we highlighted the thermal and radiochemical composites made by differential scanning calorimetric (DSC) and Fourier Transformer Infrared (FTIR). The study of this thermal and spectroscopic behavior shows an improvement in terms of performance thermal, mechanical and radiation hybrid materials made from the unfilled matrix. Monitoring changes in bands oxidation products has enabled us to establish a mechanism for radio-oxidation after irradiation.

KEYWORDS

Epoxy resin;
Gamma-ray;
Radiochemical ageing;
DSC;
Carbon black;
IR spectroscopy;
Radio-oxidation.

INTRODUCTION

In the case of a use in nuclear industry, the polymeric materials are more likely to be exposed with the ionizing rays. For an optimal use in the medium and long term and with an aim of risk prevention, it thus appears important to know the effect of these radiations on polymeric materials and/or their hybrids under these conditions. In particular, the composites with thermosetting matrices were introduced little by little into this industrial sector. The studies generally observe for these strongly aromatic polymers, a good behavior in severe conditions[1]. These materials are also easy to implement and their cost price remains interesting. They are largely used in the coating of the nuclear waste and the assembly or to replace certain parts of structure. In fact light materials have excellent mechanical properties sometimes even higher than alloys for largely lower densities.

One of the most current means to improve the performances of use of polymeric oxides is to add an inert filler, which would make it possible to increase the thermostability, to improve mechanical rigidity, to increase the viscosity of the uncrosslinked formulation, as well as the thermal behavior, to reduce the withdrawal to polymerization and also to strongly lower the price[2-4].

MATERIALS AND EXPERIMENTAL METHODS

Synthesis of the DGEBA

We used during this study, the epoxy resin diglycidyléther of bisphenol A (DGEBA), synthesized according to the method described by Castan[5,6]. Bisphenol A reacts with an epichlorhydrine excess, used like reagent and solvent[7,8], in the presence of soda according to the following diagram (Figure 1):

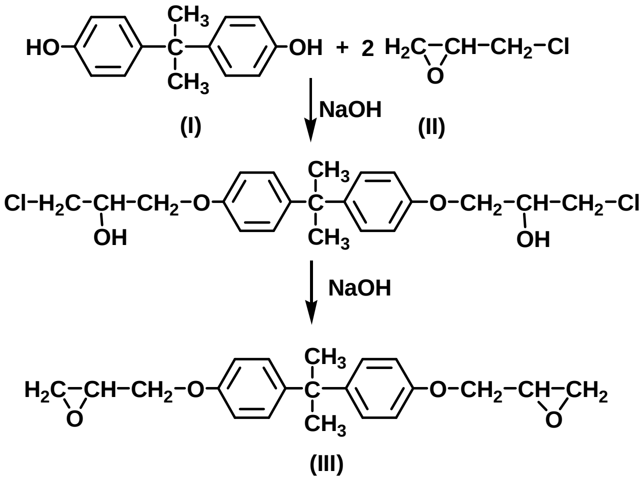

Figure 1 : Synthesis of the bisphenol diglycidyléther A (DGEBA)

Fillers

The selected loads have the following features:

Carbon black (CB)	Supplier: CABOT Carbon black of the type "Furnace" Code product: BP120 % in weight: >99 Density: 1.7 - 1.9 g/cm³ of 20°C Apparent bulk density: 20-380 kg/m3 (Fluffy)
Microballs of Glass	Supplier: AGP Density: 1,50 - 1,60 g/cm³ Chemical composition SiO_2 : 70 à 75 %, Na_2O : 12 à 15 % K2O : 1,5 %, CaO : 7 à 12 %, MgO : < 5 % Fe1O3 : < 0,5 %, Al2O3 : < 2,5 %

The filler glass beads (GB) is obtained by crushing of the microballs of glass and sifting with granulometry about 40-100µm, then washed with acetone in order to eliminate the fine particles.

Preparation of the epoxy-NC and epoxy-PV composites

The protocol that we opted for the preparation of the composites epoxy-CB and epoxy-GP that the filler is mixed directly with resin DGEBA in a silicone mould before the addition of the curing agent methylene dianiline (MDA), and then one followed a cycle of cooking for the system at a temperature of 70°C during 24 hours[9-11]. After the chemical reaction, the crosslinked materials are hard, infusible and insoluble[12].

Following this protocol of implementation, we prepared a series of the samples of proportion from 0% to 5% in mass of CB and from 0% to 15% in mass GP in the epoxy matrix.

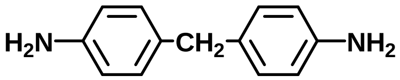

Figure 2 : Chemical structure of methylene dianiline (MDA)

Irradiation campaign

The samples based on DGEBA epoxy resin cured with MDA and filled with NC and PV were irradiated at room temperature and in air by the action of ionizing radiation Gamma guy at the National Institute of Agronomic Research (INRA). We used a radioactive source Cobalt (Co60), the total dose of irradiation campaign is of the order of 20 and 500 kGy.

Differential enthalpic analyses (DSC)

For this study, we used a modulated DSC Perkin Elmer TGA 4000 Termogravimetric analyzer. The mass of the samples is low close to 10 mg.

In our work, we measured the DSC spectra of the epoxy resin unirradiated and irradiated in a temperature range from ambient to 400 ° C, with ramps rise in temperature ranging from 1 to 15 ° C / min, under nitrogen.

Fourier transform infrared spectroscopy (FTIR)

Infrared analyzes were performed on a Fourier transform spectrometer type Nicolet Avatar 360 ESP. This equipment provides a resolution of 0.9 cm-1.

RESULTS AND DISCUSSION

Optimization of percentage of filler NC

We prepared six different formulations (from I to VI), each formulation contains a weight percentage different from the CB in an epoxy matrix (DGEBA/MDA) (Figure 3).

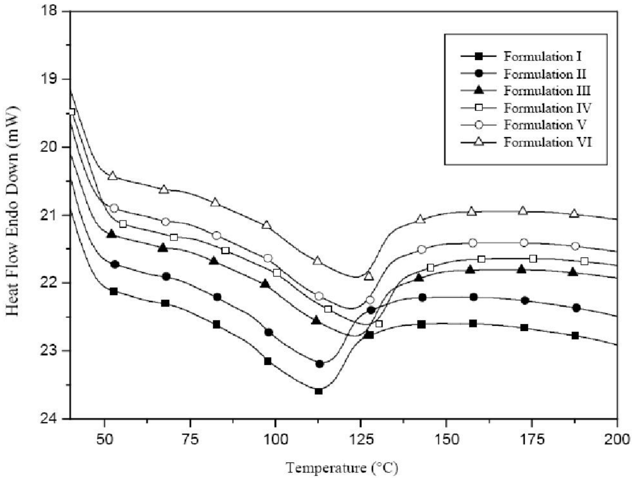

Figure 3 : Courbe DSC des formulations étudiées époxy-CB

The glass transition temperatures obtained for the different formulations are grouped in the following TABLE 1:

TABLE 1 : Evolution of Tg according to the percentage of CB

Formulation N°	Percentage of CB	Tg (°C)
I	0%	111,97
II	0,5%	113,23
III	1%	123,66
IV	2%	126,75
V	3%	122,07
VI	5%	123,32

The evolution of Tg, according to the percentage of CB, presents a maximum to 2% of 126.75 °C, which implies that the formulation presents a remarkable synergy in the vicinity of optimal percentage.

Optimization of percentage of load PV

We prepared six different formulations (from I ‘ to VI’), each formulation contains a mass percentage different from the GP in an epoxy matrix (DGEBA/MDA) (Figure 4).

The following TABLE 2 gathers the values of glass transition temperatures obtained by various formulations.

We note that the Tg increases to an optimum, which is 138.06 ° C corresponds to 10% of GP. After this value, any addition of GP becomes useless since it helps any increase in Tg, but on the contrary with its decline, it is because the fillers, when they exceed a threshold, tend to introduce much more spaces between the nodes of the three-dimensional network formed, which has the effect of lowering the crosslinking density causing a decrease in glass transition temperature. It should be noted that the glass transition temperature is intimately related to the crosslink density.

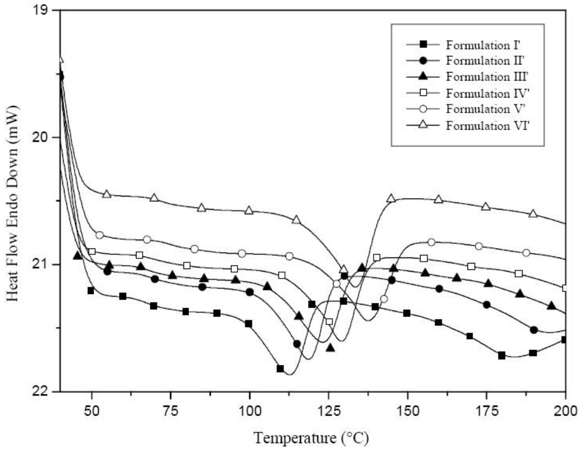

Figure 4 : Curve DSC of the epoxy-GP studied formulations

TABLE 2 : Evolution of Tg according to the percentage of GP

Formulation N°	Percentage of GP	Tg (°C)
I’	0%	111,97
II’	0,5%	117,48
III’	2%	126,24
IV’	5%	129,92
V’	10%	138,06
VI’	15%	133,61

It is visible that the incorporation of the load in an organic matrix improves its thermal stability.

Behavior of epoxy-CB composite under irradiation

The thermal diagram obtained for the system (IV) before and after irradiations with total doses 20 kGy and 500 kGy, is represented in the following figure 5:

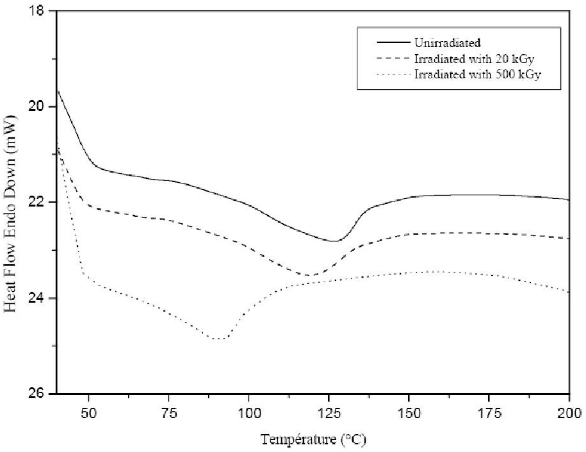

Figure 5 : Curve DSC of the formulation (IV)

The Tg extract the figure are grouped in the following TABLE 3:

TABLE 3 : Evolution of Tg of formulation DGEBA/MDA filled with CB

Formulation (IV)	Tg (°C)
unirradiated	126,75
Irradiated with 20 kGy	118,52
Irradiated with 500 kGy	90,82

Behavior of composite epoxy-GP under irradiation

The thermal diagram obtained for the system (V') before and after irradiations with total doses 20 kGy and 500 kGy, is represented in the following figure (figure 6):

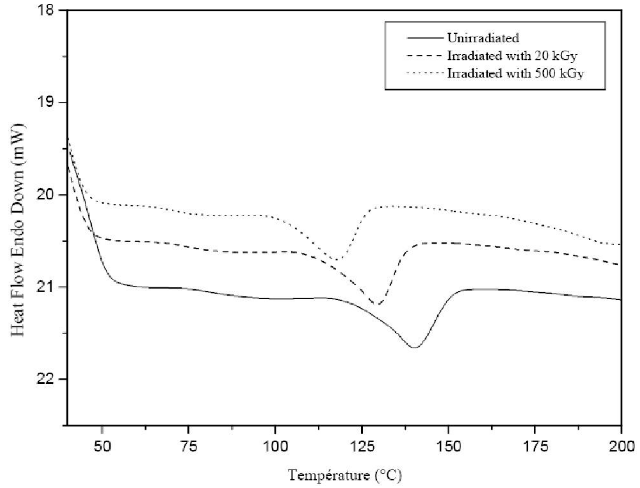

Figure 6 : Curve DSC of the formulation (V')

The Tg extract the figure are grouped in the following TABLE 4:

TABLE 4 : Evolution of Tg of formulation DGEBA/MDA filled with GP

Formulation (IV)	Tg (°C)
unirradiated	140,19
Irradiated with 20 kGy	129,34
Irradiated with 500 kGy	117,79

The analysis by DSC of the ageing of the epoxy resins under gamma ray shows a reduction in the glass transition temperature (Tg) and consequently a degradation from material in the different formulations of the resins.

It is noted that the most significant effect of the dose of irradiation is to shift the the glass transition temperatures to low temperatures and it is the case in the two types of formulations[13]. After irradiation, the Tg increased from 90.82 ° C to 126.75 ° C in the case of formulation (IV), and from 140 ° C to 117 ° C in the case of formulation (V ').

The reduction in Tg could be the result of cuts of chains which cause to decrease the number of junction points and thus to increase molecular mobility, as that was highlighted by the work of Yvette Ngono[14].

It was also observed that the value of the temperature of Tg in the case of formulation with GP is more important by contribution with the formulation with CB. Thus load GP adds to material an important thermostability and consequently a radioresistance with the gamma rays.

Evolution of oxidation products by infrared

In order to obtain information on the chemical modifications of the structure of our formulations under these conditions of irradiation, the samples were analyzed by FTIR spectroscopy in transmission mode before and after irradiation.

The IR spectra of the two epoxy formulations show the presence of the oxidation products, one band at around 1722 cm-1 attributed to ketone structures obtained by oxidation of hydroxyl crosslinking nodes near[15,16], band around 1760 cm-1 attributed to the formation of esters or carboxylic acid[17]. It is accompanied by a shoulder centered at 1670 cm assigned to the oxidizing species such as an aromatic ketone or amide[18].

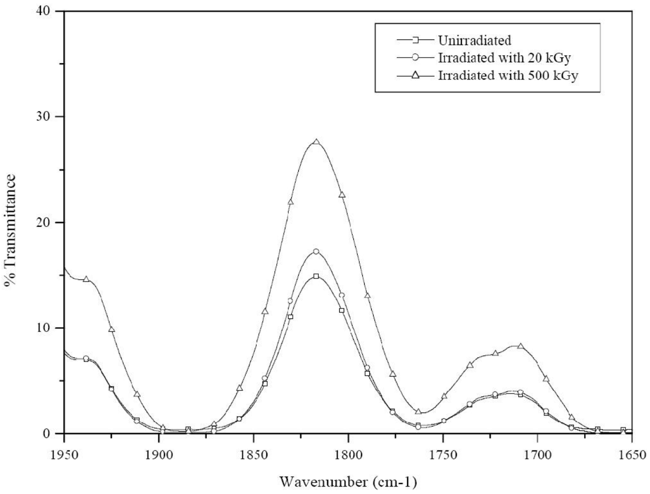

Figure 7 : IR spectra of DGEBA/MDA unfilled

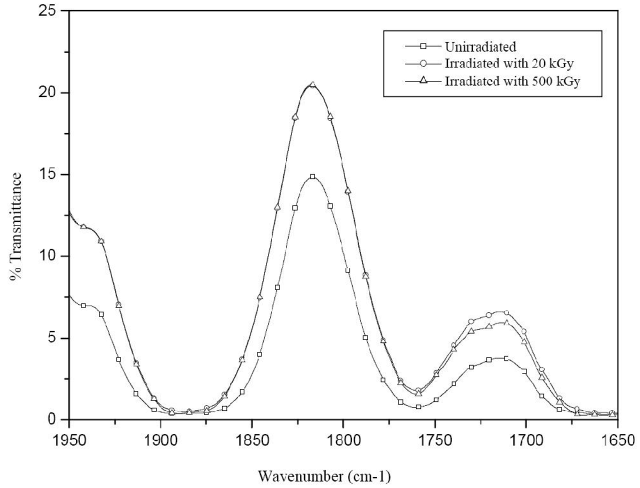

Figure 8 : IR spectra of the formulation DGEBA/MDA filled with CB

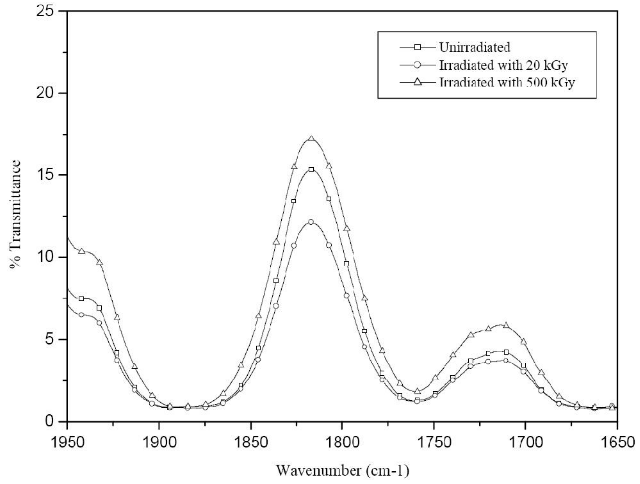

Figure 9 : IR spectra of formulation DGEBA/MDA filled with GP

According to the results obtained by FTIR of the Epoxy-CB formulation (Figure 8), the exposure radiolysis produces the same oxidation products with the same intensity whatever the dose applied. Against by the effect of radiation on the Epoxy-GP formulation (Figure 9) caused a slight decrease in the intensity of oxidation products at 20 kGy, presenting the radioresistance of this formulation to low dose, in contrast for the dose of 500 kGy one notes an increase in the intensity of the bands of oxidation.

Mechanism of radio-oxidation

The epoxy/polymer interaction led to a nonselective rupture of the bonds, thus forming a macroradical. The evolution of this macroradical is conditioned by the atmosphere. In the presence of oxygen, the macroradical starts a mechanism of oxidation and form of new species.

The mechanism of radio-oxidation suggested is schematized in the following figure 10.

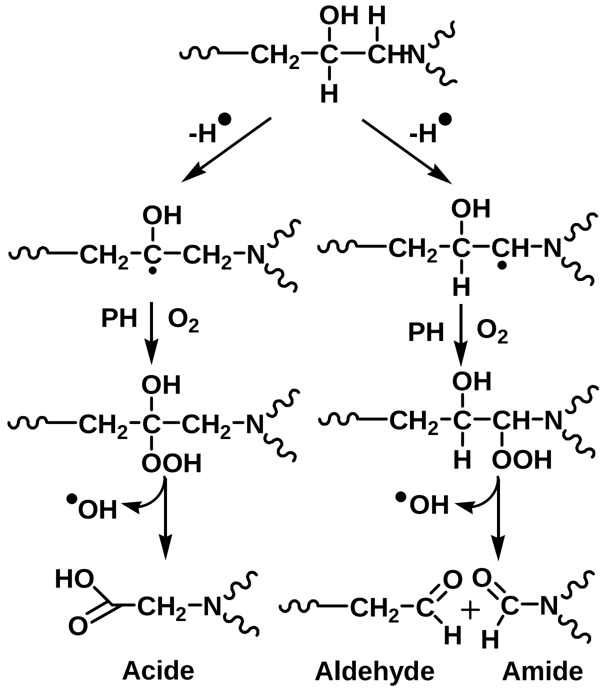

Figure 10 : Degradation mechanism of DGEBA/MDA irradiation

Radio-oxidation shows a profile of distribution very marked and products of oxidation: formate, ester and carboxylic acid.

Effect of the filler under irradiation

For follow the effect of the load on our material under irradiation, we followed the evolution of the intensity of oxidation products according to the load used and the dose of irradiation (Figures 11 and 12).

According to these results one can conclude that:

- The addition of load GP decreases the intensity of the bands of the oxidation products in the case the two doses of irradiation what gives to material a protection with oxidation and consequently better a radioresistance with the irradiations.
- The addition of load CB with the dose of 20 kGy gives an increase in the intensity of the bands of oxidation, can be explained by the oxidation of filler CB and the matrix, on the other hand the irradiation with the dose of 500 kGy gives a reduction in the intensity of the bands of oxidation explained by a re-

crosslinking of material. Molecular mobility makes it possible the radicals to be coupled to give new junctions[20].

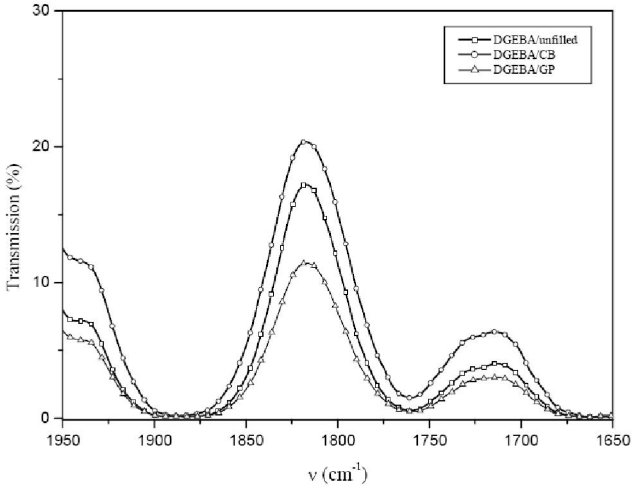

Figure 11 : IR spectra of DGEBA/MDA unfilled resin, DGEBA/MDA filled with CB and DGEBA/MDA filled with GP (irradiated with 20 kGy)

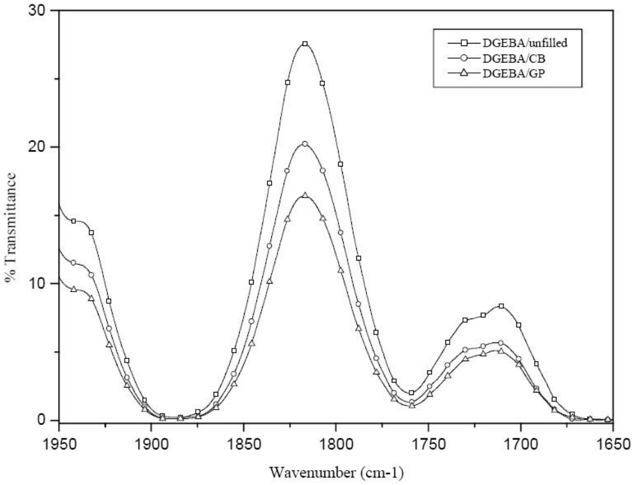

Figure 12 : IR spectra of DGEBA/MDA unfilled resin, DGEBA/MDA filled with CB and DGEBA/MDA filled with GP (irradiated with 500 kGy)

CONCLUSION

During this study, we optimized an implementation of two epoxy materials formulated with two types of loads: black carbon and glass powder, in order to increase to them radioresistance with the gamma rays.

Before studying the effect of the irradiation on our formulations, optimization made it possible to choose the best percentage of filler added. One observed a better improvement of Tg compared to the unfilled resin to give improved thermal stability, allows the use in a temperature range up to 300 ° C without any risk of degradation.

The study of the radiolysis of phenoxy polymer by DSC shows a major mechanism of chain scission. This result is confirmed by an increase in the molecular mobility which is confirmed by the decrease of Tg

Structural analysis by FTIR can identify most of the products formed during radiolysis. The quantitative correlation of the experimental results allows establishing the principal mechanism of radio-oxidation.

The reductions in the intensities cause a reinforcement of the network via the particles of the PV filler, which attenuates the effect of the cuts of chain under irradiation. What enabled us to note that load PV gives to materials better a radioresistance by report filler CB.

REFERENCES

[1] T.Devanne; Radiochemical ageing of an epoxy network, PhD Thesis: Ecole Nationale Supérieure d'Arts et Métiers, Paris Center, **(2003)**.

[2] Z.Brito, G.Sanchez; Composite Structures, **48**, 79-81 **(2000)**.

[3] H.Lee, K.Neville; Characterization of uncured epoxy resins and epoxy-resin curing mechanisms. Chap 4 et 5 In: Handbook of Epoxy Resins, Ed. New York, McGraw-Hill, **(1982)**.

[4] M.Grich, H.Meghraoui, R.Ziraoui, M.Elgouri, A.Elharfi; Ann.Chim.Sci.Mat., **36(1)**, 1-10 **(2011)**.

[5] P.Castan; Brevet US 2444333, **(1948)**.

[6] P.Castan; Brevet US 2324483, **(1943)**.

[7] L.R.Snyder; Anal.Chem., **41(8)**, 1084-1094 **(1969)**.

[8] B.J.Mair, P.T.R.Hwang, R.G.Ruberto; Anal.Chem., **39(7)**, 838-840 **(1967)**.

[9] S.Fetouaki, A.Elharfi, L.Belkebir; Eur.Polym.J., **38(4)**, 787-793 **(2002)**.

[10] N.Rami, H.Meghraoui, M.Grich, S.Fetouaki, A.Elharfi; Ann.Chim.Sci.Mat., **33(6)**, 479-492 **(2008)**.

[11] M.El Gouri, A.El Bachiri, S.E.Hegazi, M.Rafik, A.El Harfi; Polym.Degrad.Stab., **94(11)**, 2101-2106 **(2009)**.

[12] N.A.St.John, G.A.George; Diglycidyl amine - epoxy resin networks: Kinetics and mechanisms of cure. Progress in Polymer Science, **19**, 755-795 **(1994)**.

[13] N.Rami, H.Meghraoui, R.Ziraoui, T.El Khoukhi, M.Mouhib, A.El Harfi; J.Mater.Environ.Sci., **1(4)**, 277-288 **(2010)**.

[14] Y.Ngono; «Long-term behavior of thermosetting resins by irradiating medium: The role and action of water», PhD Thesis: University Joseph Fourier – Grenoble 1, 196 **(1999)**.

[15] N.Longie´ras, M.Sebban, P.Palmas, A.Rivaton, J.L.Gardette; Journal of Polymer Science Part A: Polymer Chemistry, **44**, 865e87 **(2006)**.

[16] A.Rivaton, L.Moreau, J.L.Gardette; Polymer Degradation and Stability, **58**, 321e32 **(1997)**.

[17] Y.Ngono, Y.Mare´chal; Journal of Polymer Science, Part B: Polymer Physics, **38**, 329e40 **(2000)**.

[18] H.P.Gilfrich, H.Wilski; Radiation Physics and Chemistry, 39-401 **(1992)**.

[19] V.Bellenger, J.Verdu; Oxidative skeleton breaking in epoxy–amine networks, J.Appl.Polym.Sci., **30(1)**, 363-374, 364 **(1985)**.

[20] O.Debre; «Effects of ionizing radiation on polymers associated with nuclear waste. Technical contribution of HSF-SIMS», PhD Thesis: University Claude Bernard in Lyon, 131 **(1997)**.