

Synthesis and characterization of a new epoxy resin homologous to DGEBA (diglycidyl 3-Aminopropyl Triethyl Silane): a study of thermal properties

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ABSTRACT: In this work we have synthesized a new bifunctional epoxy resin namely diglycidyl 3-aminopropyl triethylsilane (DGAPTES).

This resin was synthesized in two steps: the first one is condensing the epichlorohydrin with 3-aminopropyl triethylsilane; the second is introducing the calcium carbonate as a base to form the oxirane cycle.

The resin obtained was characterized by infrared Fourier transformation spectroscopy (FTIR), its chemical structure was also confirmed by the nuclear magnetic resonance of ^1H and proton and carbon ^{13}C (^1H NMR and ^{13}C NMR) on the one hand, and we have improved the thermal properties of the standard resin (DGEBA) by adding an amount of (DGAPTES) as an organic load in the standard matrix, on the other hand. This formulation has been studied by thermogravimetry as a macroscopic approach. The uptake of humidity of the standard DGAPTES and the crosslinked DGEBA/DGAPTES/MDA according to 80%/20%/traces was studied in order to improve the Fickien behavior.

KEYWORDS: DGEBA; DGAPTES; formulation; thermogravimetry and humidity uptake.

1 INTRODUCTION

Among the thermosetting polymers there is the epoxy resin (ER) which contain in its molecule two or more oxirane functions [1]. Its use spreads in several areas, especially electronics, flame retardant, coatings (paints, varnishes, adhesives ...) and finally its composites. The most widely used method for the preparation of epoxy prepolymers is through the glycidylation, via the condensation of epichlorohydrin on structures containing at least two mobile hydrogens of the type: diacids [2], diamines [3] and polyphenols [4, 5] and the resin (DGEBA) as an industrial model [6]. While preparing an epoxy prepolymer by condensing epichlorohydrin, some secondary reactions may occur [7-8]. The formation of non déshydrohalogénables β -chlorohydrin is responsible for the opening of the regenerated oxiranes cycles and the homopolymerization of the prepolymer in the reactional medium [9].

Epoxy resins have a wide range of reactivity and multiple choices of types of hardeners among which we find diols, diacids, anhydrides and diamines. In particular, epoxy resins crosslinked with the diamine such as methylene dianiline MDA have a very high glass transition temperature ($> 100^\circ\text{C}$) [10-11]. They may also have an excellent thermal stability and good chemical resistance to chemical products [12].

In our work we tried to synthesize a new counterpart of DGEBA, which is the diglycidyl 3-aminopropyl triethylsilane (DGAPTES), to improve specific characteristics of the latter. We propose to incorporate the silane atom into the structure of DGAPTES, in view to its strong contribution to the level of thermal stability.

2 MATERIALS AND METHODS

2.1 MATERIALS USED

All basic chemicals were supplied by Acros chemical Co. and Aldrich Chemical Co. Our composite materials are formulated by matrices consisted of DGEBA and the new DGAPTES resin crosslinked by methylene diphenylamine MDAP.

2.2 SYNTHESIS OF THE EPOXY RESIN

2.2.1 SYNTHESIS OF THE NEW RESIN EPOXY BASED ON DIGLYCIDYL 3-AMINOPROPYLSILANE (DGAPTES)

The diglycidyl resin 3-aminopropyl triethylsilane (DGAPTES) is produced by the action of epichlorohydrin on the 3-aminopropyl triethylsilane. The synthesis is described by the following reactional scheme:

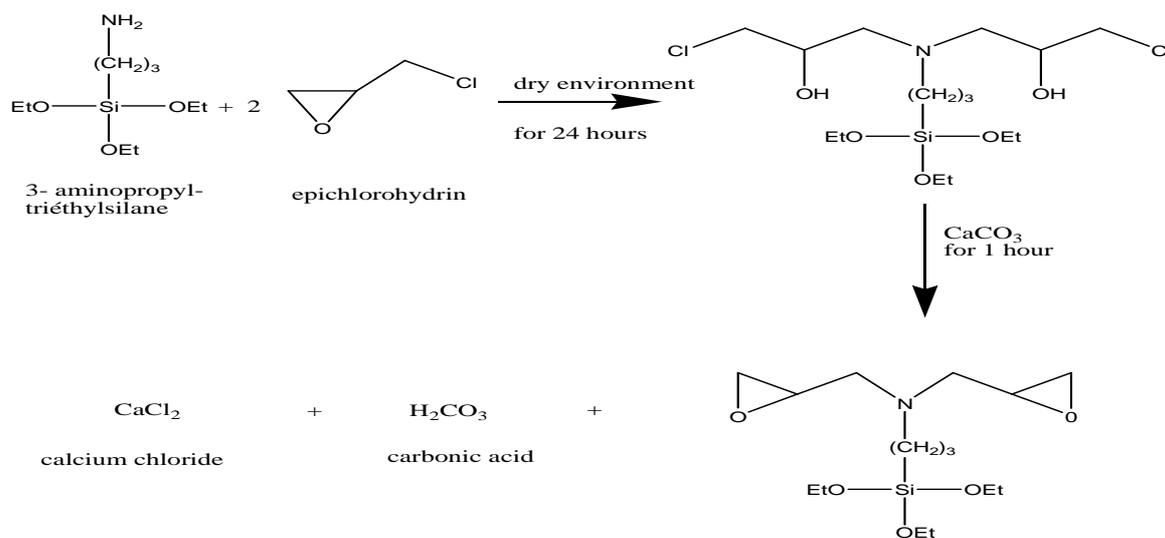


Fig.1. Synthesis of 3-aminopropyl diglycidyl triethylsilane (DGAPTES)

The hydrolysis of the silane function:

The reaction of hydrolysis of the silane function is shown in the following figure:

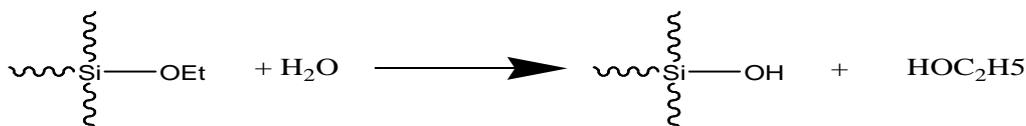


Fig. 2. Hydrolysis of the silane function

The use of the calcium carbonate instead of the sodium hydroxide is due to the fact that it can both rip out the acidic proton of the alcohol and cause a nucléophile attack on the silane.

Finally, the chlorure of calcium precipitates after a latency.

2.3 CHARACTERIZATION METHODS

2.3.1 INFRARED FOURIER TRANSFORMATION (FTIR)

The IR spectrometer used is a Fourier Transformation Spectrometer (FTIR) BRUKER. The light beam passes through the sample with a thickness of about 2 microns. The analysis is carried out between 4000 cm⁻¹ and 600 cm⁻¹.

2.3.2 NUCLEAR MAGNETIC RESONANCE (NMR)

^1H NMR analysis, ^{13}C were obtained by using a type of apparatus Bruker AVANCE 300, and the solvent CDCl_3 . The chemical displacements are expressed in ppm.

2.3.3 THERMOGRAVIMETRY ANALYSIS (TGA)

In our study which focuses on the degradation of the synthesized epoxy resin, we appealed to the technique of thermogravimetry analysis (TGA) [9]. The measures of kinetics of degradation by mass loss were made by using an apparatus SETARAM TAG 24S.

2.3.4 THE HUMIDITY UPTAKE

The humidity uptake of the crosslinked resin samples is expressed by the following formula:

$$P = (M_i - M_s) / M_s$$

P: The moisture uptake;

M_s : The mass of the dry sample;

M_i : The mass of the immersed sample;

3 RESULTS AND DISCUSSIONS

3.1 THE INFRARED FOURIER TRANSFORMATION (FTIR)

The FTIR absorption spectrum of the 3-aminopropyl diglycidyl triethylsilane is shown in Figure 3:

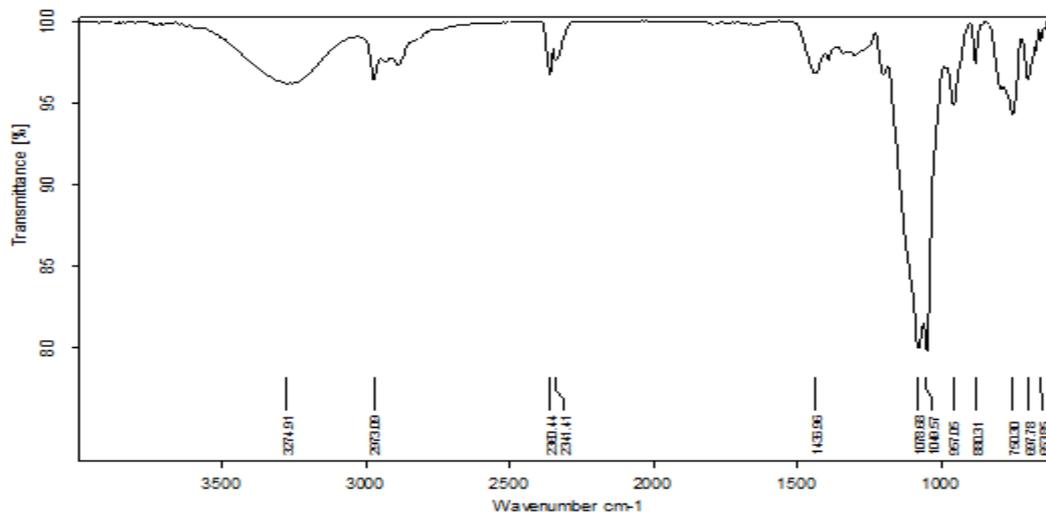


Fig.3. IR spectrum of the 3-aminopropyl triethylsilane diglycidyl resin

Table 1 summarizes the basic bands of the FTIR spectrum and their interpretations

Table 1. Bands of the diglycidyl 3-aminopropyl triethylsilane resin

Band position (cm ⁻¹)	Interpretation
3274 (3500-3050)	free or associated NH amine
2973 (3000-2500)	OH associated with carboxylic acid (carbonic acid)
1436 (1440-1393)	carboxylic acid coupled with OH (carbonic acid)
1078 (1100-1000)	siloxane Si-O-Si
880 (950-810)	Epoxide

3.2 NUCLEAR MAGNETIC RESONANCE (NMR)

3.2.1 NMR OF ¹H

The ¹H NMR of the product obtained shows the presence of different types of protons, so that the protons of methylene CH₂-N (C) provide a centered multiplet of 2.62-2.37 ppm, CH epoxide protons resonate as a centered multiplet of 2.77 ppm, the OCH₂ protons of the epoxide cycle appear as a centered distribution doublet at 2.38 and 2.63 ppm, NC methylene gives a multiplet centered at 2.36 ppm and then the methylene CH₂ proton Si-O-CH₂ CH₃ and proton CH₃ of methyl Si-O-CH₂-CH₃ respectively appear as a quadruplet and triplet centered at 3.83 ppm and 1.22 ppm.

3.2.2 NMR OF ¹³C

The NMR ¹³C of the obtained product shows the presence of different types of ¹³C, while the aliphatic carbon CN resonates as a centered singlet at 55.3 ppm. The carbon -CH of epoxide cycle gives a singlet centered at 49.5 ppm, the carbon -CH₂ of oxirane centered at 45.6, the aliphatic carbon -CH₂ 1Beta of -N gives a singlet centered at 23.6 ppm and finally the carbons -CH₂ and -CH₃ of Si-O- respectively give a centered singlet at 58.4 ppm and 18.4 ppm.

3.3 CROSSLINKING

3.3.1 AUTO-CROSSLINKING

Under the effect of temperature (60 °C for 48 h) the DGAPTES undergoes an auto-crosslink which may be explained either by a possible attack of hydroxyl of silane on the epoxide or by the attack of amines which did not react:

Both probable reactions are described below:

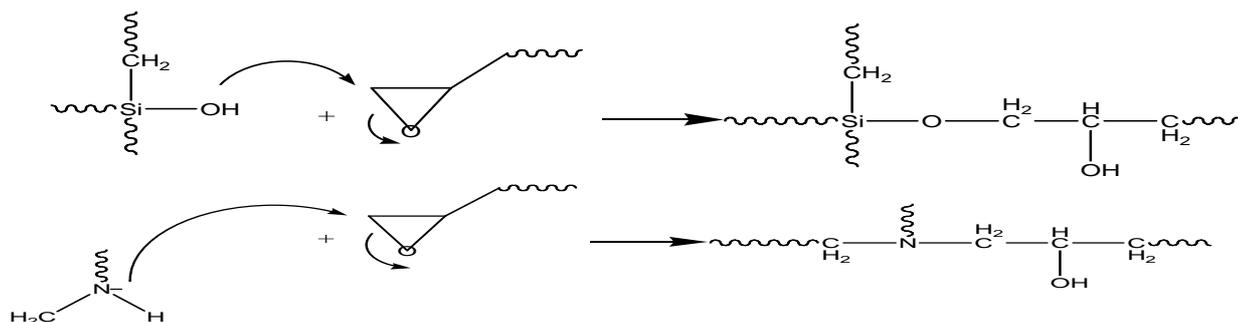


Fig.4. Reaction of the amine and the hydroxide with the epoxide

This leads us to propose a general scheme of our auto-crosslinked resin taking into consideration the different possibilities:

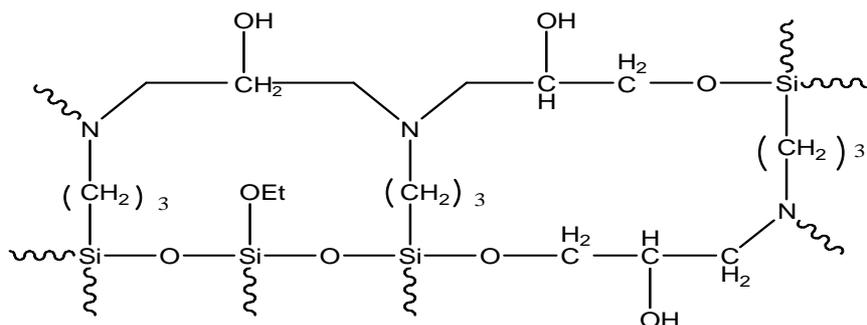


Fig.5. General scheme of the auto-crosslinked resin

Nevertheless, we notice a degradation of this material in the presence of water which can be due to the hydrolysis of the possible ether formed during the auto-crosslink that succeeds the reaction according to the reaction below.

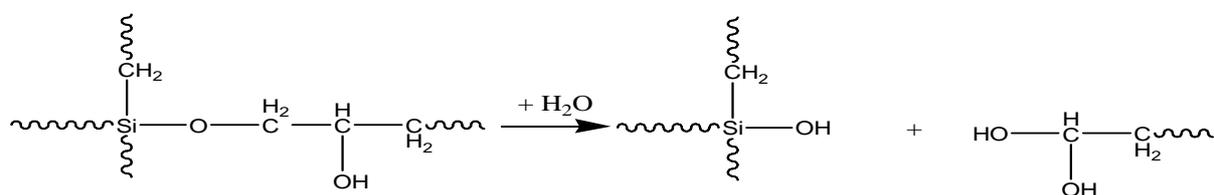


Fig.6. Diagram of hydrolysis of ether function during the auto-crosslink

3.3.2 THE CROSSLINK WITH THE MDA

The action of the methylene dianiline on the epoxide is described by the following reaction:

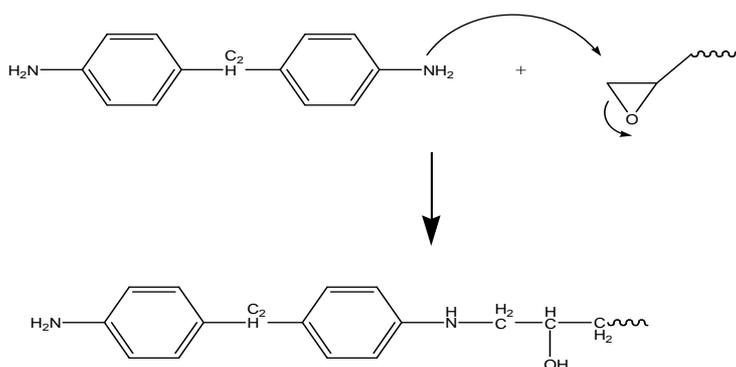


Fig.7. Diagram of the action of MDA on the epoxide grouping

The structure that describes this crosslink is shown in the figure 8 (we did not take into account the reactions of condensation induced by MDA amines)

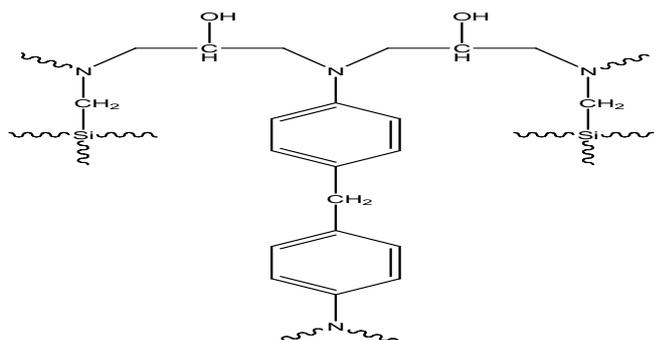


Fig.8. Diagram of the crosslinking with the MDA

3.3.3 CROSSLINKING A MIXTURE DGAPTES/DGEBA WITH MDA

The crosslink of a DGAPTES/DGEBA/MDA system follows the same principle described above. The structure describing this crosslink is shown in the figure 9:

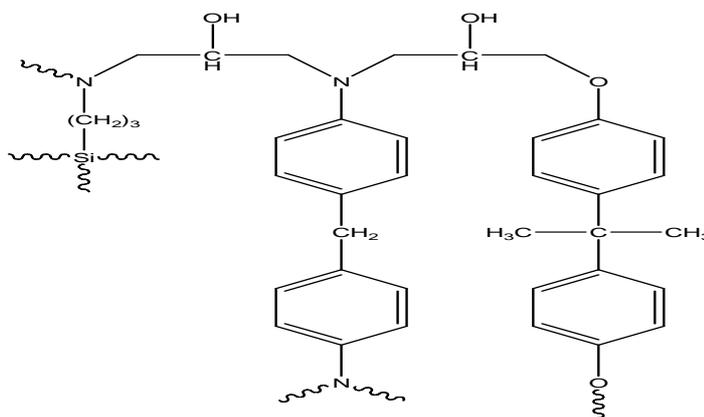


Fig.9. diagram of the crosslinking system DGAPTES/DGEBA/MDA

3.4 THERMAL DEGRADATION

By the thermogravimetric technique, we inspected the mass loss of three systems crosslinked with MDA: DGEBA, DGAPTES and a mixture of 10% of DGEBA and DGAPTES depending on the temperature when subjected to a thermal treatment.

Figures 10, 11, 12 respectively describe the thermal behavior of our crosslinked formulations.

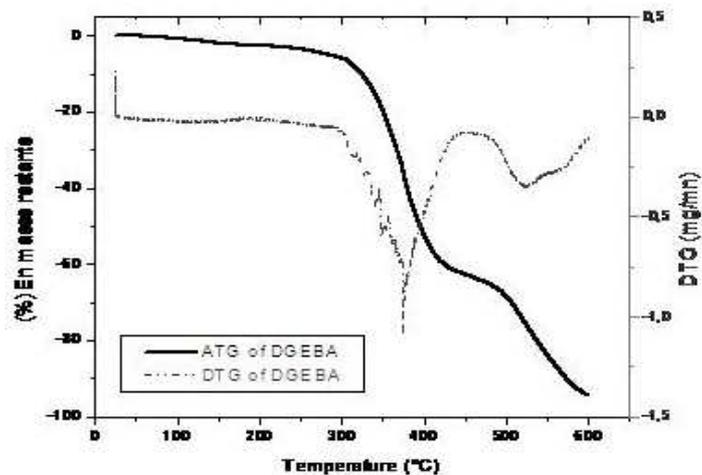


Fig.10. Thermal behavior DGEBA/MDA

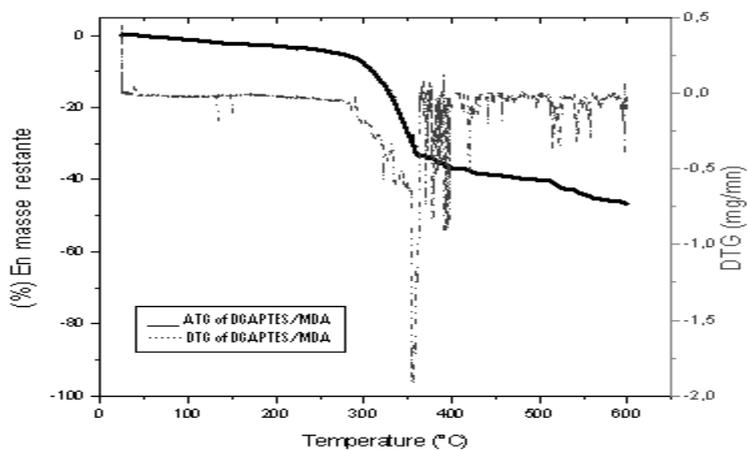


Fig.11. Thermal behavior DGAPTES/MDA

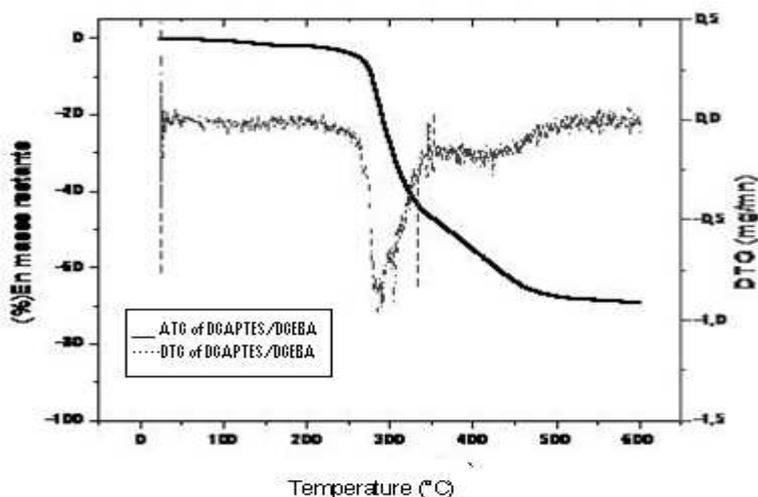


Fig.12. Thermal behavior DGEBA/10% DGAPTES/MDA

In addition, we have classified the main thermal characteristics of the resins studied and extracted from the curves of the thermo-gram in Table 2, according to conventional standards by:

T_d : Temperature of the onset of decomposition (loss of weight of 2%).

T_{10} : Temperature at 10% of mass loss.

T_{50} : Temperature at 50% of mass loss.

S_{dr} : Threshold of rapid decomposition.

R_{500} : Fraction of residue at 500 ° C.

Table 2. The Main characteristic of pyrolysis of the studied samples

Samples	T_d (°C)	T_{10} (°C)	T_{50} (°C)	S_{dr} (°C)	R_{500} (%)
DGEBA/MDA	157,27	324,24	395,74	294,50	32
DGAPTES/MDA	134,79	310,69	-	300,28	60
DGEBA/10% DGAPTES/MDA	181,50	279,01	369,34	274,32	35

The comparative study shows that despite the moderate temperature of the starting decomposition of DGAPTES/MDA, which is of the order of 134.79 °C as compared to that of DGEBA/MDA which is of the order of 157.27 °C. We note, by contrast, at the level of % R_{500} that the DGAPTES/MDA resists better than DGEBA/MDA whose values are 60% and 32% respectively.

The addition of 10% of the DGAPTES to DGEBA increases its temperature of the starting decomposition of 24 °C. but above this temperature this addition adapts a less interesting behavior. Finally, we see an increase of 35% of mass loss compared to DGEBA/MDA.

3.5 HUMIDITY UPTAKE

We measured the humidity uptake of the two samples namely the DGAPTES and a mixture of DGEBA/20%DGAPTES/MDA.

The samples are first weighed and then immersed in water a weight measurement according to time makes us establish the percentage of the mass uptake and then the mass to saturation.

The results are respectively represented by the following two figures 13 and 14:

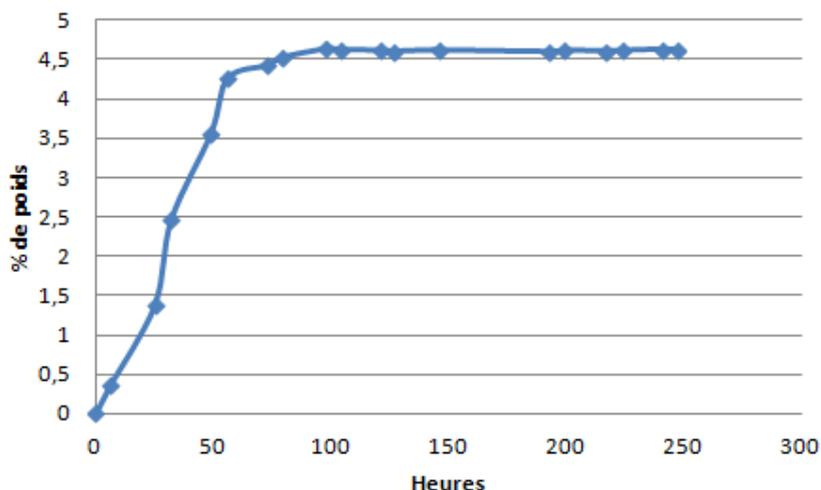


Fig.13. Test of humidity uptake of DGAPTES/MDA

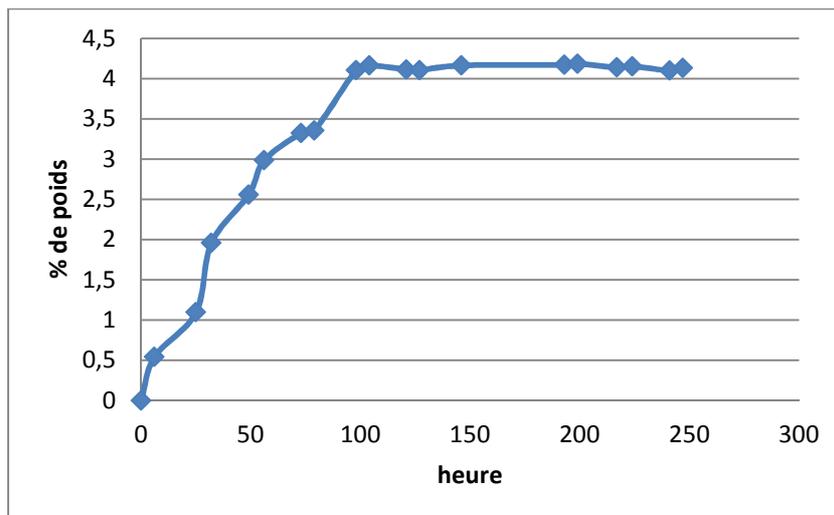


Fig.14. Tests of the DGEBA/DGAPTES/MDA humidity uptake

According to Figures 13 and 14 we found that the humidity diffusion adapts a Fickien behavior and we observed a maximum of diffusion according to time. Thus, the maximum of water absorption of the samples are respectively 4.63% for (DGAPTES/MDA) and 4.18% for (DGEBA/DGAPTES/MDA).

4 CONCLUSION

In this study, we developed a new epoxide resin which is silicon-bifunctional and to which we conducted a microscopic (IR, ^1H NMR, ^{13}C NMR) and macroscopic (ATG) study of both the standard resin and the DGEBA supported by the DGAPTES. We have shown, on the other hand, a synergy of thermal properties of a mixture of two bifunctional epoxy resins (DGEBA and DGAPTES) crosslinked with the MDA. Finally, a study of humidity uptake of two samples DGAPTES and a mixture of DGEBA/20% DGAPTES/MDA was accomplished.

The thermogravimetric analyses show that these formulations have the characteristics of an enhanced thermal stability, which would allow them for an eventual use in a temperature range up to 300 °C without any risk of degradation.

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