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Synthesis and characterization of a new binding macromolecular Polycondensate hexafonctionnel Hexa Glycidyl Ethylene in Methylene Dianiline (HGEMDA). Formulation of nanocomposite based natural phosphate

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Abstract : In this work, we have synthesized the new binding macromolecular Polycondensate HexaGlycidyl Ethylene of Methylene Dianiline (HGEMDA) by polycondensation, by the arm of a spacer, which is methylene dianiline, and then we proceeded to the formulation of a nanocomposite (HGEMDA/MDA/PN) at the base of nanofilled phosphate and methylene dianiline as hardener.

As a first step, after its synthesis optimization, we characterized the new binding macromolecular Polycondensate infrared spectroscopy to transform of Fourier transform (TFIR). Its structure is confirmed by nuclear Magnetic Resonance (RMN ^{1}H) proton and carbon (RMN ^{13}C).

As a second step, we reticulate and formulated the new nanocomposite material thermoset ting in the presence of loads of phosphate at different percentages (0%, 5%, 10% and 15%) by the addition of methylene dianiline (MDA) as hardener. The dispersion of nanofillers in the polyepoxide hardener matrix was followed using the Electron Microscope at Scanning (SEM).

Key words: Macromolecular Binder, Polycondensate, HGEMDA, natural phosphate, cross-linking, formulation, thermosetting nanocomposite, SEM.

Introduction

Epoxy resins are thermosetting main macromolecular matrix binding in composites technology and/or very important nanotechnology and have been widely used in several industrial fields such as: electrical industry for applications such as cable or the coating of electronic circuits[1], fireproofing or flame retardant[2], aging[3], coating[4,5], thermal and electrical studies [6], electrical conductivity[7,8], inhibition[9], the packaging of radioactive waste[10,-11], rheology[12] and viscometric properties[13,14]. They are also used as adhesives, construction, aerospace (parts of cars and blades of a helicopter...) [15] and the space construction (heat shields rockets, parts of satellites and solar panels) [16,17] , for their exceptional mechanical properties, thermal and chemical Etc... [18,19,20,21,22]. This has led to develop so-called "thermostable" epoxy resins, i.e. including the feature or higher, but also a high density of connections containing for example, of aromatic nuclei [23]. Thus, among the resins multiepoxydes with high thermal resistance, we find epoxy novolac resins [24], tetraglycidyl methylene dianiline (TGMDA)[25,26], triglycidyl ether ethylene of bisphenol A (TGEEBA) etc...[27].

The method most widely used for the preparation of epoxy pre-polymers are madeby condensation of glycidol on compounds halogenated [28,29]. It is done in a single step: the formation of a nucleophile group by deprotonation using a database function glycidol hydroxyl, followed by a nucleophilic attack on the sites with the obtained compound halogen, or by the condensation of the epichlorhydrine structures containing at least two mobile hydrogens of the type: diacids, diamins, polyphenols [30] and or by oxidation of unsaturated in the presence of peroxides[31].

There are several hardeners for the cross-linking of polymers polycondensates, among which we find the deals, the diacids and anhydrides and dominoes. These are good hardeners for cross-linking of pre-polymers polycondensates, such as methylene dianiline MDA have a very high glass transition (> 100 ° C) temperature [30,32,33]. They have also excellent thermal stability and resistance to chemical product standard or formulated [34,35,36].

On the one hand, we have synthesized the prepolymer epoxy hexafonctionnel: HexaGlycidyl Ethylene of Methylene Dianiline (HGEMDA). It has been characterized by the infrared spectroscopy transformed of Fourier (IR) and confirmed its structure by the nuclear magnetic resonance (PMN ^{1}H) proton and carbon (RMN ^{13}C). On the other hand, we cross-linked and formulated by the phosphate nanofilled synthesized prepolymer (HGEMDA). Finally the dispersion nanofilled (phosphate) has been followed using an electron (SEM)[37,38].

Materials and methods

Materials

1-1- Products used

In this work, we used several products which we have listed methylene dianiline (MDA) used as a spacer arm and hardener [30,34,36], is a domain primary aromatic of formula$C_{13}H_{14}N_2$. It has functionality equal to four. As well as trichloro ethylene, epichlorhydrin with a purity of 99%. Methanol, the triethylamine and phosphate used as a load. All these commodities were provided by corporations Acros Chemical Co and Aldrich Chemical Co.

1-2- Synthesis of hexaglycidyl ethylene of methylene dianiline

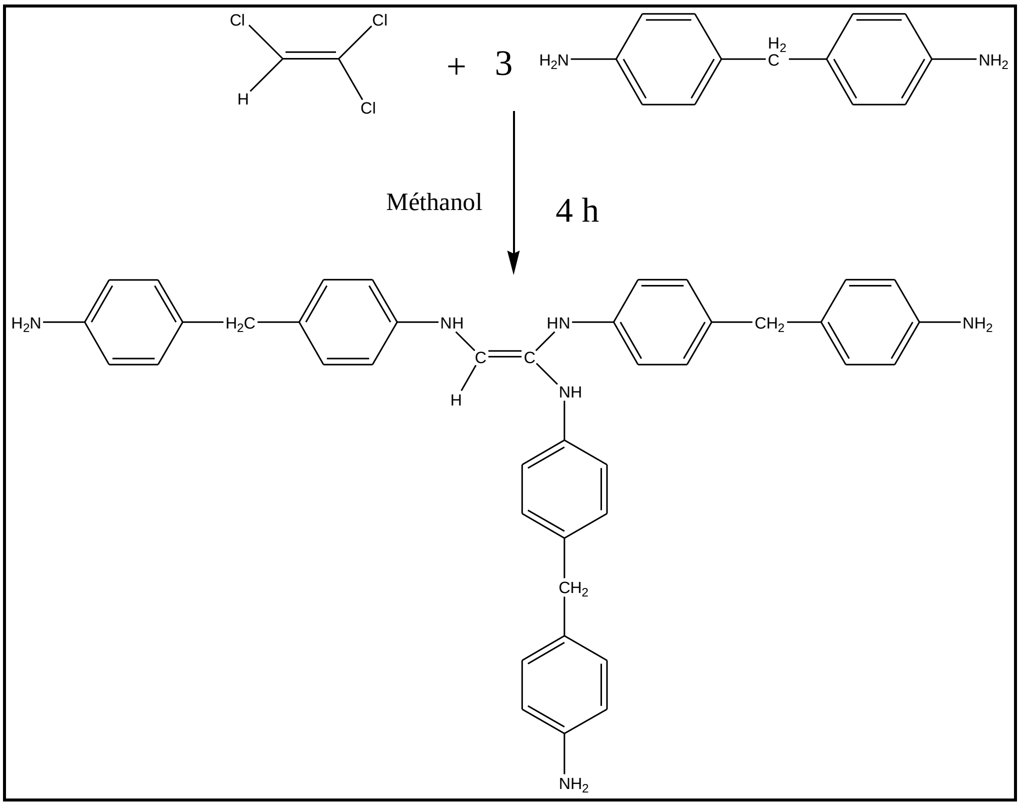
Synthesis of macromolecular binding polycondensate HGEMDA was performed in two phases:

1-2-1- The first phase

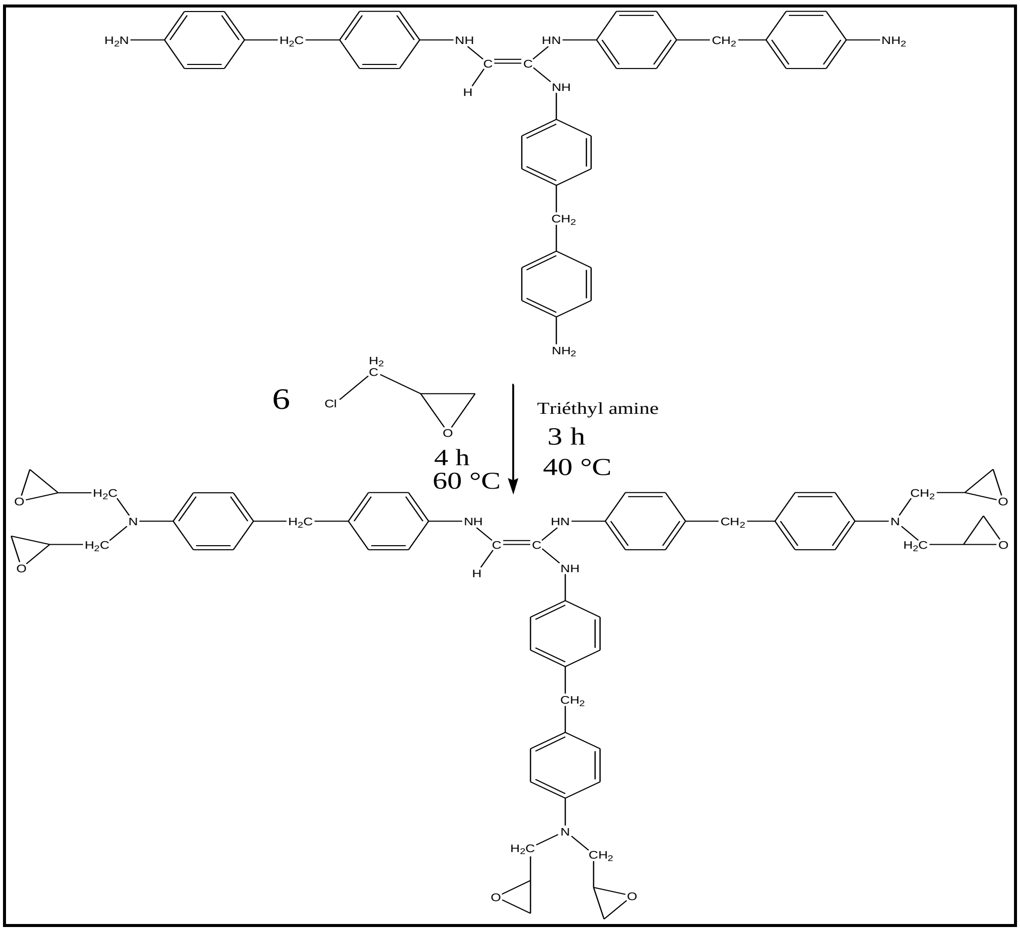
Condensation of 1 ml of trichloro ethylene and 6.6 g of ethylene dianiline in the presence of methanol with magnetic stirring at room temperature for 4 h, the reaction is shown in the Schema.

1-2-2- Second phase

The second phase we have added 6 ml of epichlorhydrine on the trees methylene dianiline of ethylene with magnetic stirring at 60°C for 4 h, the final product HexaGlycidyl Ethylene of Methylene Diamine (HGEMDA) is obtained by the addition of 9 ml of triethyl amine used a base with magnetic stirring for 3 hours at 40 °C, Schema 2 shows the second step of reaction.



Schema 1. Synthesis of the trees methylene dianiline of ethylene



Schema 2: Synthesis of HexaGlycidyl Ethylene of Methylene Dianiline (HGEMDA)

2- Methods of characterizations of the prepolymer hexaglycidyl ethylene in methylene dianiline

In this study, we employed the following methods:

2-1- Infrared spectroscopy with Fourier transforms (FTIR)

The IR spectrometer used is a spectrometer to transform of Fourier (FTIR) BRUKER. The light beam passes through the sample to a depth of about 2 µm. The analysis is performed between 4000 cm^{-1} and 600 cm^{-1}

2-2- Resonance Nuclear Magnetic (NMR)

Analysis of the proton and carbon 13 NMR, were obtained using a device of type advance 300 MHz of BRUKER. The solvent DMSO and chemical shifts are expressed in ppm.

2-3- Scanning Electron Microscopy (SEM)

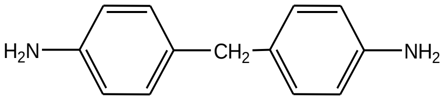
The scanning electron microscope was used to confirm the dispersion of nano filler in the macromolecular matrix. The observations were performed with a microscope JEOL-JSM-5500. This technique is based on the usage of a beam of accelerated electrons by a fixed potential which excites the sample surface. The interaction between the primary electrons with the material lead to the emission of secondary electrons, backscattered electrons, X-rays and Auger electrons.

Figure 1: Picture of the SEM device

2-3-1- Preparations of the samples analyzed by the scanning electron microscope

The presence of the epoxy prepolymer and methylene dianiline implementation produces a hardening of the prepolymer as a result of the crosslinking reaction. The Protocol consists of a preheating of stoichiometric amounts of the prepolymer and hardener. Methylene dianiline (MDA), is put in an oven at 120°C (a temperature above its melting temperature), whereas the prepolymer is increased to 60°C. When it is melted, the MDA is mixed with the prepolymer to give a single fluid phase, and then located at 70°C. Finally, leave the samples prepared in mussels the desired geometric formfor 24 hours at 70°C [27].

Cross-linking reactions are carried out by a primary domain, methylene dianiline (MDA) [34], known for its excellent mechanical properties and good thermal stability it provides to the final product, compared to other hardeners. Its structure is given in Schema 3.



Schema 3: Formula of semi-developed of methylene dianiline

This hardener has a functionality equal to four, which means that when the reaction of cross-linking with a resin hexafonctionnelle (for example, HGEMDA), both amines react theoretically with twelve functions epoxide when in stoichiometric proportions [39,40]. The final product is a three-dimensional chemically bridged network. After the chemical reaction, cross-linked materials are tough, infusible and insoluble.

By using the previous Protocol to the reaction of crosslinking of the prepolymer in the presence of methylene dianiline as hardener and phosphate at different percentages (0%, 5%, 10% and 15%) as a charge, we got samples including the load well dispersed in the base, after an important mixing matrix [27].

2-3-2- Calculation of ration

2-3-2-1- Calculation of the stoichiometric coefficients

To obtain optimum when properties on hardened prepolymer multifunctional polycondensate in the presence of hardener (especially amines). It is desirable to make the prepolymer and the curing agent react to approximately stoichiometric amounts.

Epoxy equivalent calculation (Epoxy Equivalent Weight: EEW) synthesized prepolymer (HGEMDA).

$$EEW = \frac{M_w(HGEMDA)}{f}$$

With f is the feature of epoxy resin.
Where:

$$EEW = \frac{952}{6}$$

$$EEW = 158.7 g / éq$$

The calculation of the equivalent amine (Amine hydrogen Weight Equivalent: AHEW).

AHEW then constitutes the mass of hardener containing an equivalent amine.

$$AHEW = \frac{M_w(MDA)}{f}$$

Methylene dianiline:
M_w= 198 ; f=4

$$AHEW = \frac{198}{4}$$

$$EEW = 49.5 g / éq$$

2-3-2-2- Calculation of the weight ration

The ratio by weight of hardener to resin is calculated in the majority of cases, for 100 parts of resins or PHR (Parts per Hundered of Resin):

$$\text{PHR of amine} = \frac{\text{Amine H eqwt}}{epoxyequivalent} \times 100$$

In the case of the HGEMDA:

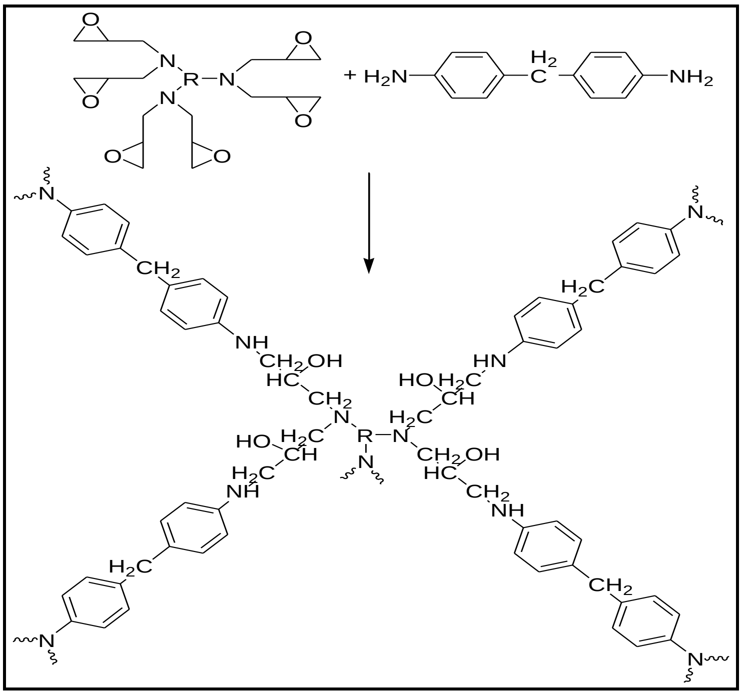
$$\text{PHR of amine} = \frac{49.5}{158.7} \text{x} 100$$

$$\text{PHR of amine} = 31 \text{g/eq}$$

So we need to react 31g of methylene dianiline for 100g of HGEMDA to achieve optimum properties when harden the prepolymer with methylene dianiline.

2-3-3- Cross-linking of matrix HGEMDA by the MDA

Cross-linking of HGEMDA in the presence of MDA as a hardener continues under the action of temperature following the polycondensation reaction which leads to the three-dimensional structure according to schema 4 and figure 2.



Schema 4: Resin crosslinking reaction HGEMDA with the MDA

Figure 2: Photos of the composite formula to different percentage of phosphate

2- Results and discussion

2-1- spectral characterization of the synthesized epoxy prepolymer

We conducted a structural analysis of prepolymer epoxy synthesized by the infrared spectroscopy transformed of Fourier (FTIR) and confirmed the results obtained by the Nuclear Magnetic Resonance (^{1}H NMR) proton and carbon (^{13}C NMR). The letters s, d, t, q, and m mean respectively Singlet, doublet, triplet, quadruplet and multiplied. The results of structural analyses, given below, confirm the structure of the synthesized polycondensate prepolymer.

2-1-1- Infrared spectroscopy with Fourier transforms (FTIR)

Prepolymer polycondensate synthesized, was characterized by an infrared analysis in Fourier-transform. The latter has been exposed in its viscous State to infrared radiation under mode ATR. The results are shown in figure 3.

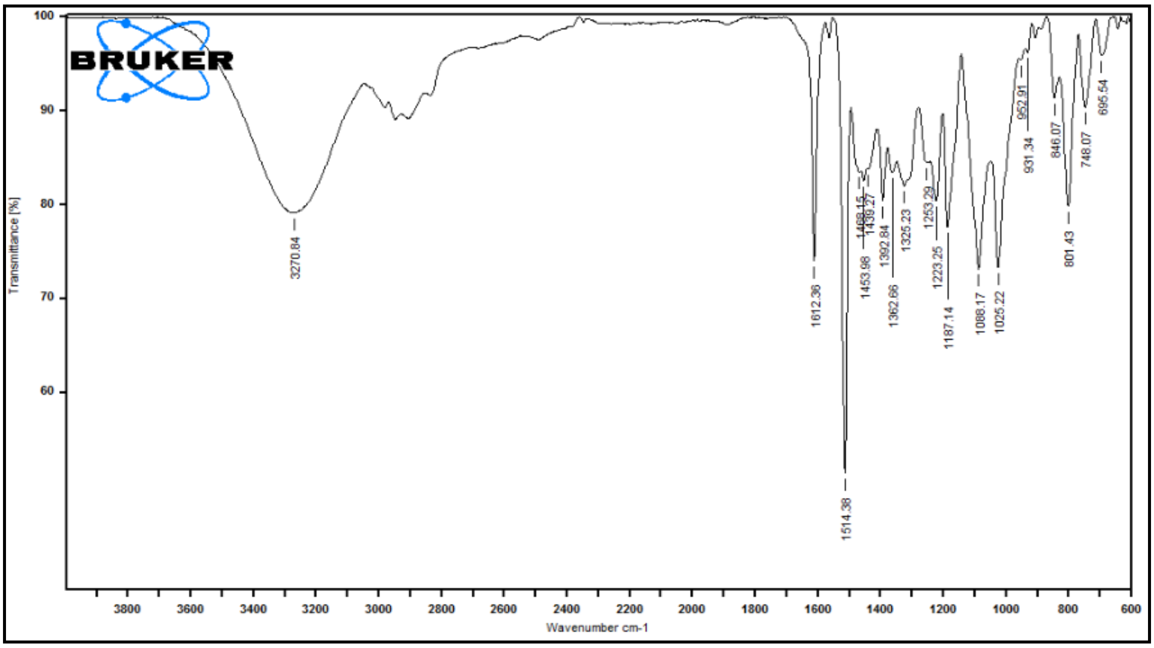


Figure 3: IR spectrum of the epoxy resin synthesized hexa glycidyl ethylene of methylene dianiline

The allocation of different bands obtained through infrared analysis under mode ATR is given in table 1 below:

Table (1): Analysis of the Infrared of the epoxy resin synthesized

Band υ (cm-1)	Assignments
3270.84	Vibration of the N - H bond of secondary amines
1612.36	Vibration of the C = C of SP2 carbon bond
1514.38	Deformation of the N - H bond in the plan
1453.98	Deformation of the CH2 bond in the plan
1392.84	Deformation of the C - H bond in the plan
1187.14; 1223.25; 1253.29	Elongation of the binding of aliphatic amines
1025.22; 1088.17	The C - O bond vibration
931.34	The H - C = bond stretching
801.43	Epoxy group

2-1-2- Resonance Nuclear Magnetic

2-1-2-1- NMR ^{1}H

Proton NMR Spectra (^{1}H) of the prepolymer Polycondensate hexafonctionnel synthesized is presented in figure 4, confirms the structure of the HGEMDA. The assignment of chemical shifts of the HGEMDA is regrouped in table 2.

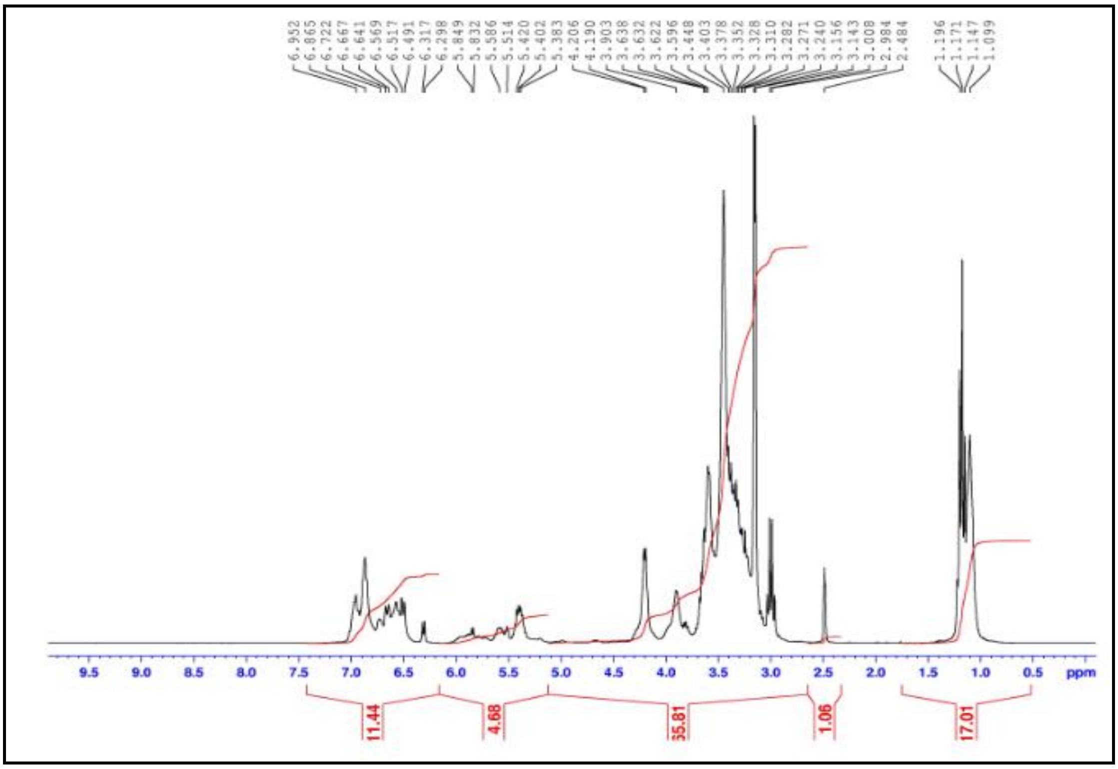


Figure 4: Spectrum of the proton RMN of the epoxy resin synthesized from ethylene hexa glycidyl methylene dianiline (HGEMDA)

The powers of the peaks of epoxy synthesized HGEMDA observed are given in table 2.

Table (2): Analysis of the proton RMN of the epoxy resin synthesized

δ ppm	The protons and the interpretation
1.3	(d; 12H) CH2 oxirane
2.5	(d;12H) CH2 associated with oxirane
3 - 3.6	(m;6H) CH oxirane
3.9	(s;3H) methylene
4.2	(s.3H) N — H
5.4	(s;1H) CH ethylene
6.34 - 6.5 - 6. 65 - 6.9	(d;24H) Aromatic HP

2-1-2-2- NMR carbon (^{13}C)

Macromolecular structure ^{13}C NMR spectrum HGEMDA, figure 5 confirms that of the proton NMR spectrum. The allocation of different carbon chemical shifts of the HGEMDA is grouped in the table 3.

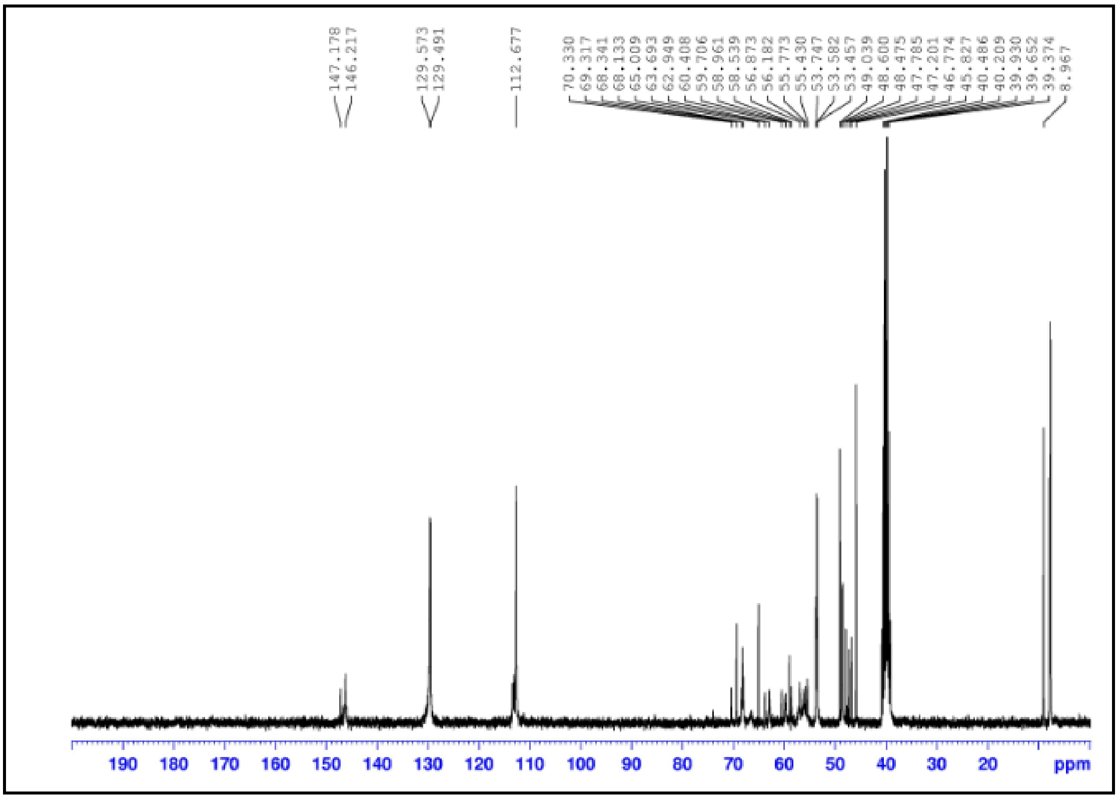


Figure 5: Spectrum of carbon RMN of the epoxy resin synthesized hexaglycidyl methylene diamine ethylene (HGEMDA)

The powers of the peaks of the synthesized epoxy resin (AGENDA) observed are grouped in Table 3.

Table (3): Analysis of the carbon NMR of the epoxy resin synthesized

δppm	Carbons and interpretation
46	(S; CH2 of the oxirane)
47	(S; Aliphatic CH2)
49	(S; CH of the oxirane)
58	(S; CH2 oxirane-related)
68	(S; CH ethylene)
112	(S; C ethylene)
129	(S; Aromatic HP)
147	(S; C - aromatic C)

2-2- The Scanning Electron Microscopy (SEM)

To identify the correct morphology dispersion of load in the matrix nanocomposite thermosetting (HGEMDA/MDA/PN) and to confirm the result, we used the surface analysis using electron microscopy (SEM).The morphological results are represented by photos of SEM in figure 6.

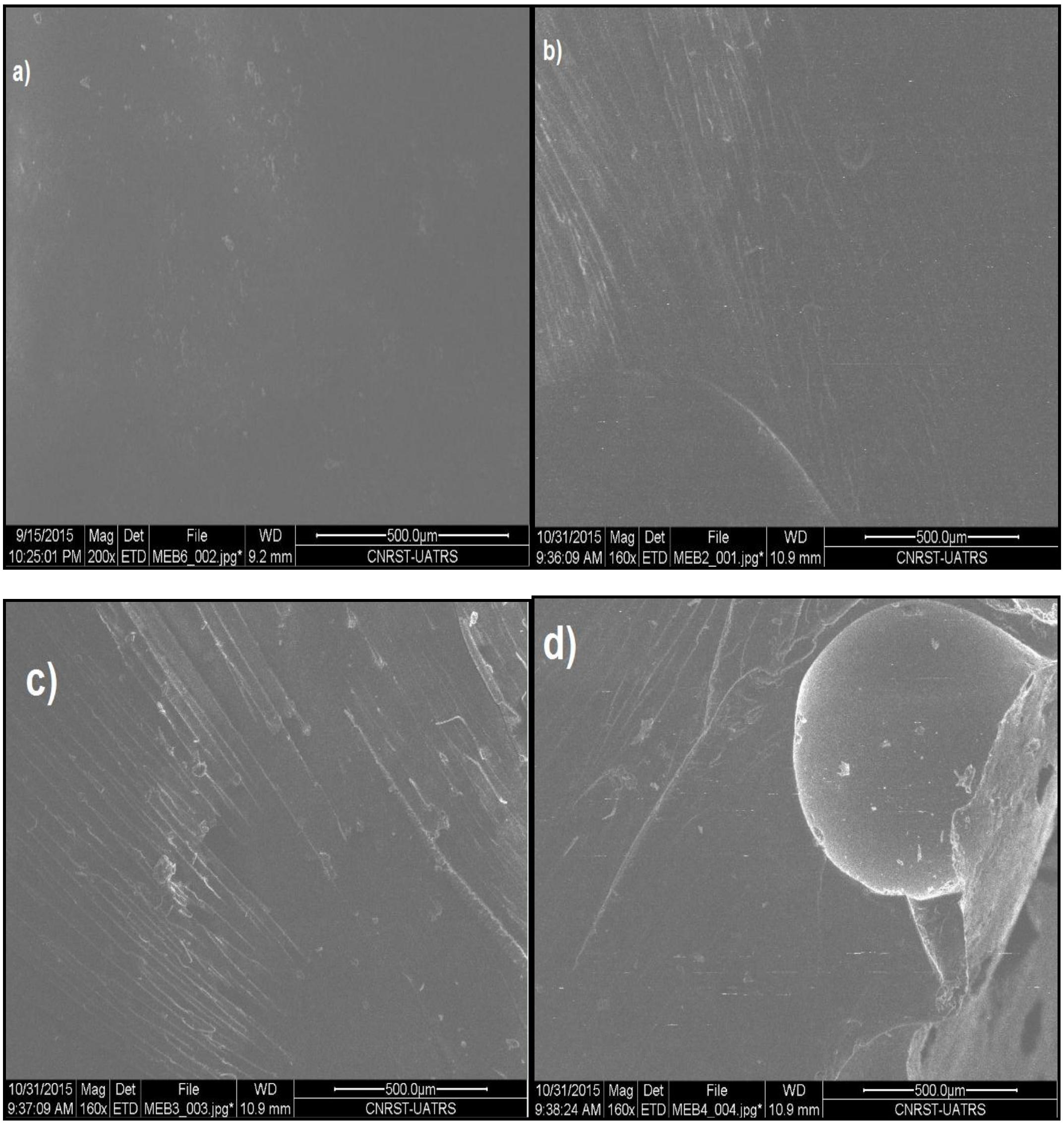


Figure 6.Photos of microscopic electronic scanning of the epoxy prepolymer synthesized cross-linked by MDA and formulated with 0% (a), 5% (b), 10 (c) and 15 per cent (d) of the burden of natural phosphate.

These observations using the morphology of the thermosetting nanocomposite SEM (HGEMDA/MDA/PN) developed, we thus showed clearly the good dispersion of load of phosphate in the macromolecular matrix epoxy, newly synthesized and this through the pictures a, b, c, d in figure 6.

Conclusion

The objectives of this work are the synthesis of a new spacer arm-bending macromolecular polycondensate hexafonctionnel methylene dianiline to reticle and then formulate a nanocomposite based phosphate at different percentages as a charge in the presence of methylene dianiline as hardener.

This synthesized polycondensate prepolymer structure has been characterized and confirmed by infrared spectroscopy (FTIR) Fourier transform and the proton and carbon-13 nuclear magnetic resonance (NMR ^{1}H and^{13}C NMR). Firstly, after the synthesis ofprepolymer polycondensate hexafonctionnel, we cross-linked and formulated the material thermoset nanocomposite, in the presence of the hardener (MDA) and phosphate at different percentages (0%, 5%, 10% and 15%) as. On the other hand, we followed the dispersion of load of phosphate rock in the material nanocomposite (HGEMDA/MDA/PN), using a scanning electron microscope, which revealed as a good dispersion.

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