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Theoretical and experimental studies of a new tri-functional polyepoxide: TriGlycidyl Ethylene Ether of Bisphenol A (TGEEBA). Optimisation of parameters by the experimental design and the formulation of a nano-composite

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Abstract

The objective of this work is to synthesize a new matrix polyepoxide triglycidyl Ethylene Ether of Bisphenol A (TGEEBA) for studying and modeling. Initially, we synthesized a new macromolecular binder in polyepoxide which we characterized by Infrared Spectroscopy Fourier Transform (TFIR) and by Mangetic Nuclear resonance of the proton (^{1}H NMR) and carbon (^{13}C). Secondly, we have applied this macromolecular matrix developing a thermoset composite material in the presence of loads of phosphate rocks at different percentages (0%, 5% and 10%) by the addition of methylene dianiline (MDA) as a hardener. The disperssion of nanoscale fillers in the matrix polyepoxide / hardener was followed using the Scanning Electron Microscope (SEM). Furthermore, we tried to optimize the synthesis of TGEEBA by the experimental design methodology.

Keywords: Macromolecular binder; TGEEBA; Natural phosphote nano-filler; formulation; nano-composite; SEM; design of experiments.

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1. Introduction

Epoxy polymers are important thermosets and have been widely used in many electronic industries (coating of electronic circuits), [1] fireproofing and flame retardants [2], aging with radioactive elements [3], adhesive coating [4] burial of radioactive waste [5-6]… For their outstanding

mechanical, thermal, chemical properties and electrical insulation [7-8-9], the most widely used method for the preparation of epoxy prepolymers is by glycidation via the condensation of epichlorohydrin to structures containing at least two labile hydrogens of the type: diacids [10], diamines [11], polyphenols [12 -13-14], or by epoxidation using peracids [15].

Epoxy resins certainly exhibit a wide range of reactivity and multiple choice of types of hardeners among which we find diols, diacids, anhydrides and diamines. Epoxidized polymers crosslinked with the diamine curing agent in particular such as methylene dianiline MDA have a very high glass transition temperature (> 100 ° C) [14-16-17]. They also have an excellent thermal stability and resistance to either standard or formulated chemicals [18-19-20].

To attain this objectif, we first synthesized the trifunctional epoxy resin: triglycidyl ether of bisphenol A ethylene (TGEEBA) which was characterized by the Fourier Infrared Spectroscopy Transform and confirmed by the Nuclear Magnetic resonance of the proton (^{1}H NMR) and carbon (^{13}C NMR).

The nanofiller's disperssion (trisodium phosphate) was followed by the scanning electron microscopy (SEM).

Furthermore, the design of experiments allowed us to optimize the performance of the polycondensation reaction and to achieve this without predicting the industrial nanocomposites which are applicable in many areas [21-22].

2. Materials and methods

2.1. Materials

2.1.1. Products used

The basic chemicals used in this study are namely: Methylene Benzenamine hardener (MDA) as crosslink [14-18-20] which is an aromatic primary diamine of the brute formula $C_{13}H_{14}N_2$. It has a functionality which is equal to four; the phosphate rock used as a load, which is a granulated product (2 µm); and the bisphenol A, trichloro ethylene, epichlorohydrin with a purity of 99%, methanol and latriéthylamine. All these commodities were supplied by Acros Chemical Company and Aldrich Chemical Co.

2.1.2. Synthesis

The synthesis of the TGEEBA epoxy resin was conducted in two steps:

The first step:

The condensation of the ethylenic trichloro on bisphenol A in the presence of methanol with magnetic stirring at room temperature for 4 hours (Fig. 1).

Step Two:

During the second step, we functionalized the Tris Bisphenol A epichlorohydrin Ethylene by magnetic stirrings at 70 ° C for 4 hours. The final product which is triglycidil ethylenically ether of bisphenol A TGEEBA is obtained by adding the basic triethyl amine with magnetic stirrings for 4 hours at 40 ° C (Fig. 2).

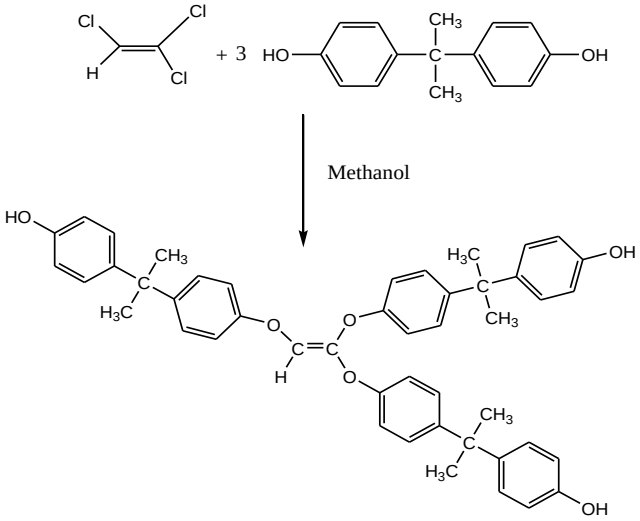


Fig. 1: form of synthesis of Ethylene's Bisphenol A

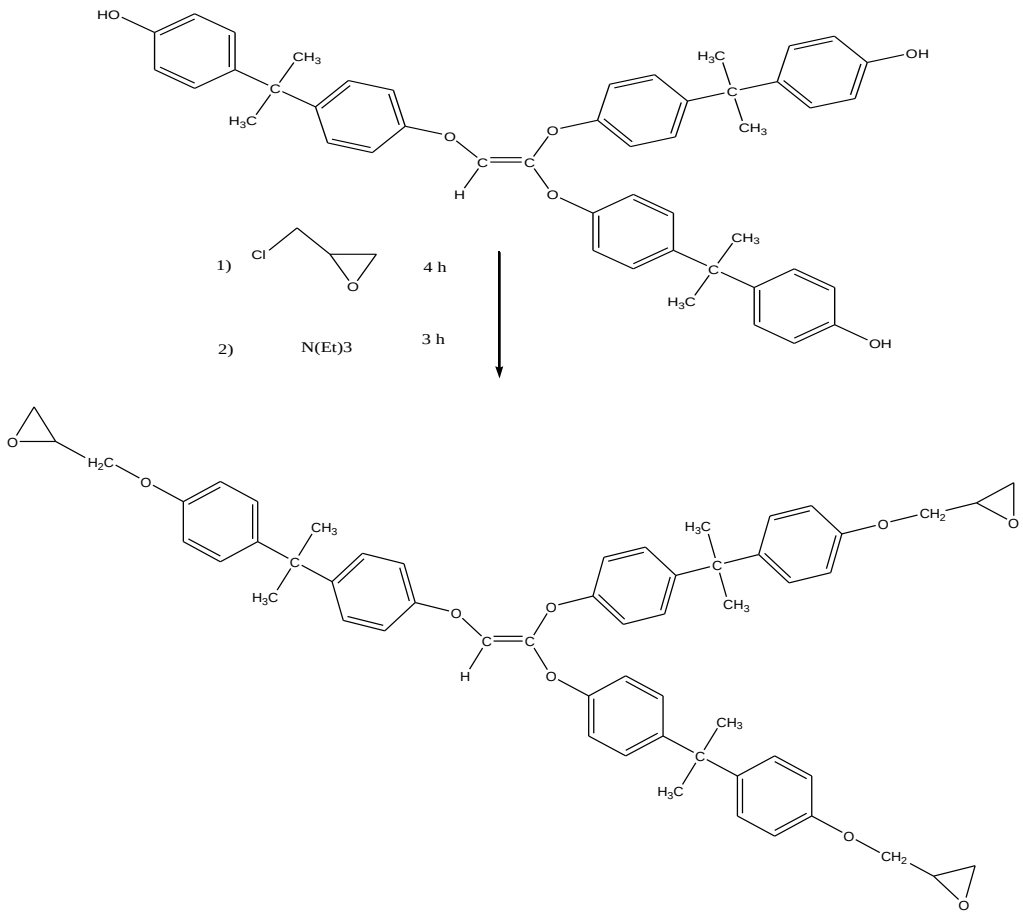


Fig.2: sythesis of triglycidyl ether of bisphenol A ethylene (TGEEBA)

2.1.3. The crosslinking of the TGEEBA matrix by the MDA

The crosslinking of TGEEBA in the presence of MDA as a hardner proceeds under the action of the temperature following the polycondensation reaction which leads to the three-dimensional as in figure 3.

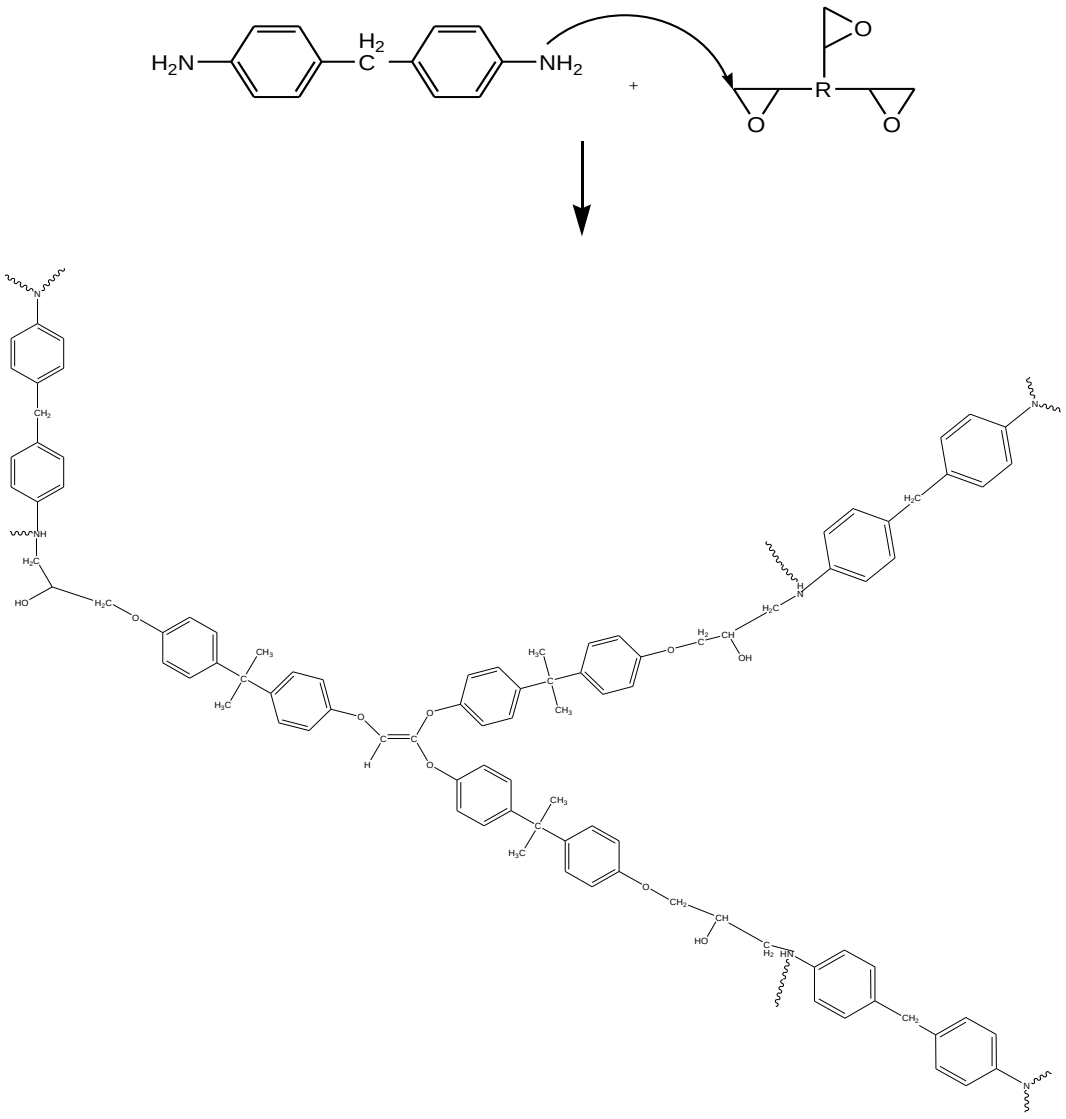


Fig. 3: cross-linking of the TGEEBA resin with MDA

2.2. Methods used in the development of TGEEBA

We used several methods among which we quote:

2.2.1. Method of experimental design (MEP)

The experimental design used to define the fewer experiences allows for a complete study of the influence of all parameters on given processes and their optimization. This is based on the search for a simple mathematical model which gives a good representation of the studied phenomenon [23].

The Mathematical Model:

$$y = b_0 + b_1 * X_1 + b_2 * X_2 + b_3 * X_3 + b_{12} * (X_1 * X_2) + b_{13} * (X_1 * X_3) + b_{23} * (X_2 * X_3)$$

The answers are described by a polynomial model of the following form:

By applying this model, we tested three factors at two levels [24-25-26].

The limit values of the parameters are defined in table 1:

Table 1: Areas of the Factors' variations

Settings	Temperature °C	Time (h)	Addition of the Trichloroethylene reagent
factors	X_1	X_2	X_3
Levels + 1	60	48	Fast
Levels -1	25	40	Slow

22.2.2. Fourier Transform Infrared Spectroscopy (FTIR):

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

2.2.3. Nuclear Magnetic Resonance (NMR):

The analyses NMR ^{1}H and ^{13}C were obtained using a type of apparatus of AVANCE 300 MHz BRUKER. The used solvent is $CDCl_3$ and the chemical deplacements are expressed in ppm.

2.2.4. Scanning Electron Microscopy (SEM)

The scanning electron microscope was used to make photographic images. The observations were performed on the JEOL-JSM- 5500 microscope. This technique is based on the use of an electron beam accelerated by a fixed voltage which excites the sample surface. The interaction between the primary electrons with the material lead to the emission of secondary electrons, retro-diffused electrons, X-rays and Auger electrons (Figure 4).

Fig. 4: SEM camera picture

3. Results and Discussions

3.1. Modeling

We based our work on the matrix of full factorial experiments to illustrate the best parameters influencing the performance by combining the studied interactions.

3.1.1. The graphic study of interactions between factors

3.1.1.1. The graphic study of interactions X_1X_2 (Temperature/Time)

According to this study, the following are the parameters, temperature (X_1) and time (X_2) as shown in figure 5.

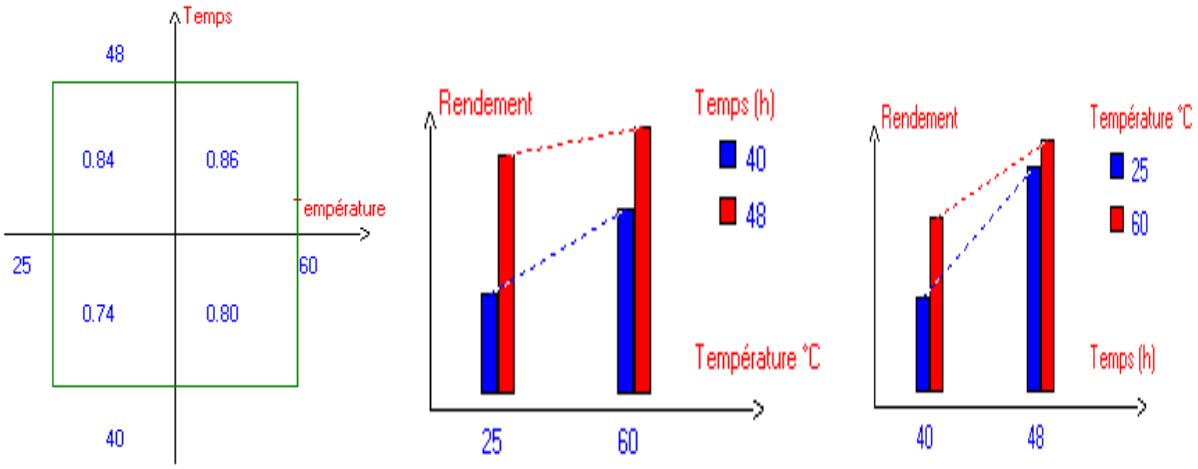


Fig. 5: Graphic system of X_1X_2 interaction

Under this system of interaction, it is apparent that the best yield is determined by the case of interaction where X_1 = 60 (temperature) and X_2 = 48 h (time).

3.1.1.2. Graphic study of X_1X_3 interactions (temperature/addition of the tricholoéthylène reagent ClHC = CCl2)

In this study, the following are parameters: temperature (X_1) and the addition of the tricholoéthylène reagent (X_3) as shown in figure 6.

According to this interaction system, it is apparent that the best yield is determined by the case of interaction where the addition of the trichloroethylene reagent is rapid (X_3) and the temperature X_1 = 60 ° C.

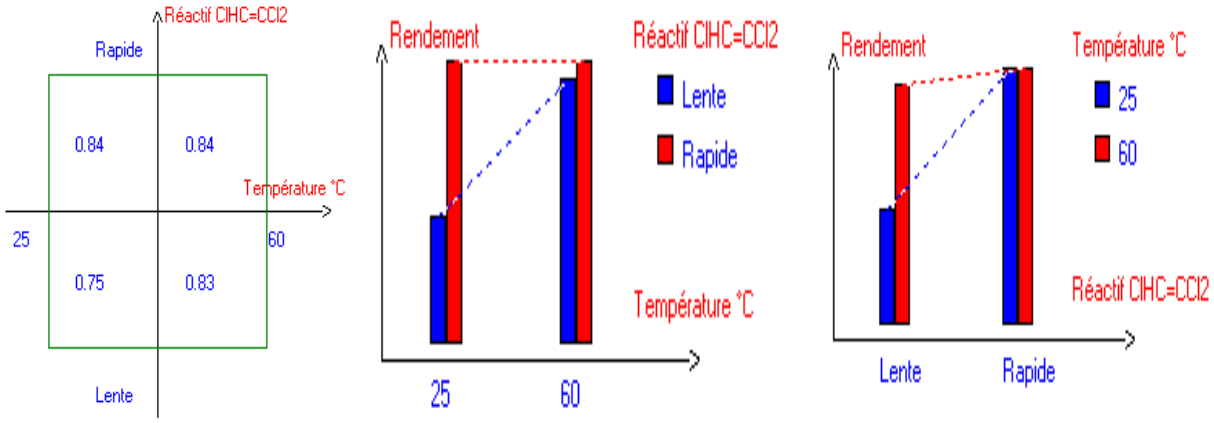


Fig. 6: Graphic system of the X_1X_3 interaction

3.1.1.3. Graphic Study of the X_2X_3 interactions (time/addition of the trichloroethylene reagent $ClHC = CCl_2$)

In this graphic study, the following are the parameters: the time (X_2) and the addition of the trichloroethylene reagent (X_3) as shown in Figure 7.

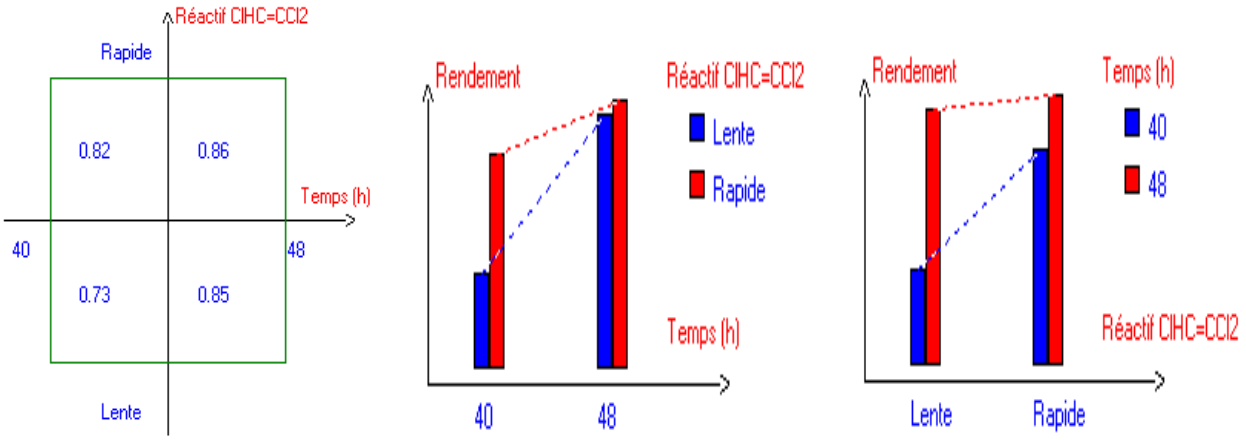


Fig. 7: Graphic system of the X_2X_3 interaction

According to this system of interaction, it appears that the best yield is determined by the case of the interaction where X_2 = 48h (time) and the addition of the trichlorethylene reagent is rapid (X_3).

3.1.2. The diagram of the average effects:

This diagram is highlighting the most influencing parameters on the reaction's yield. Indeed, we notice that the most active factors are given in a descending order of influence: time (b2), the addition of the trichlorethylene reagent (b3) and then temperature (b1).

3.1.3. Pareto diagram

The Pareto diagram is used to supplement the results as obtained using bar chart obtained above. This would determine the most influential factors (Figure 8). The Pareto chart shows well that the first three factors (time, addition of the trichloroethylene reagent and temperature) are acting in a descending order which are indeed, time (b2), addition of the trichloroethylene reagent (3) and temperature (b1) (Figure 9). This confirms the time of the optimized reaction that would be 48 hours.

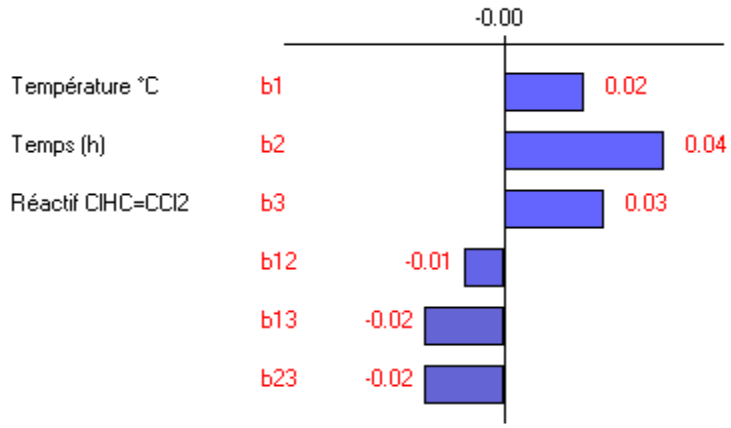


Fig. 8: bar chart diagram

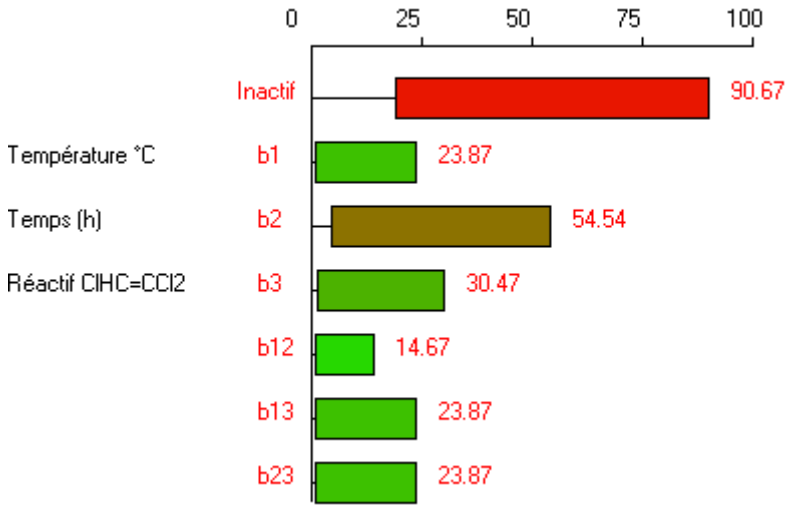


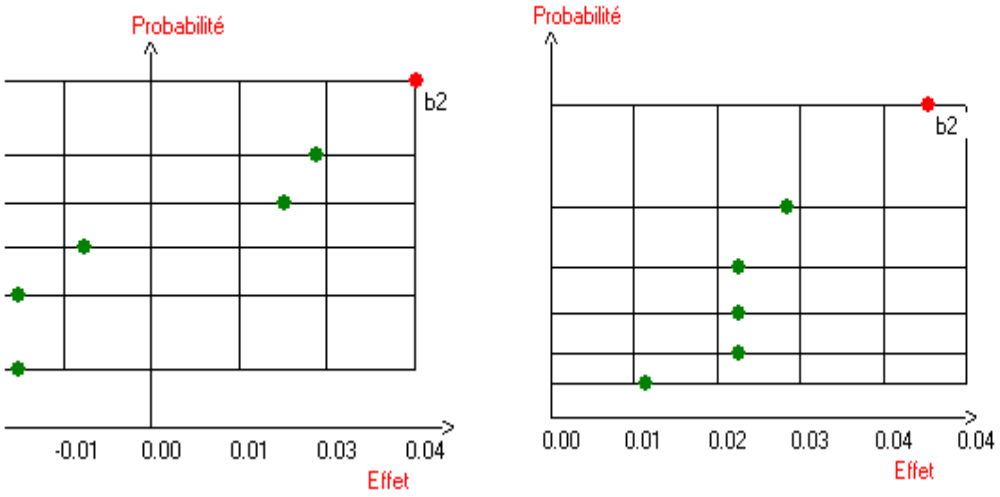
Fig. 9: Pareto chart for the yield's response

3.1.4. The method of HENRY's right

HENRY's method in Figure 10 is used to represent the function of the distribution of bj effects

on Gausso-arithmetic paper. It is giving two graphs: the first is Normal Plot with bj and the second is Half Normal Plot with $|bj|$. The effects that deviate from the right on the Normal Plot (below or above the top right is to say that the effects are positive or negative) are considered absolutely assets [26]. therfore we can distinguish the active coefficients though we are not given the exact meaning of the effect since we took just the absolute values of coefficient $|bj|$.

The following illustration shows the right of HENRY



a- The graph of the Normal Plot b- The graph of the half Normal Plot

Fig. 10: Right of HENRY (a, b).

From this figure, we find that the coefficient b_2 is absolutely active. This confirms the results obtained by the precedent methods.

3.1.5. the validation of the model:

The equation of the empirical model is only an approximation of reality and the implementation of the statistical tests should help to judge the results.

Table 2: Coefficients' Estimations and statistics

Standard deviation of the Response	0.057
R^2	0.898
R^2_a	0.287
Number of degrees of freedom	1

From table 2 we can conclude that all the responses obtained by this model of experimental

design has a satisfactory and descriptive quality because the R^2 correlation coefficient equal to 0.898 is closer to 1.

After the optimization of the factors (time, addition of the trichloroethylene reagent and temperature), we performed the synthesis of macromolecular matrix triglycidyl ether ethylene of bisphenol A (TGEEBA), according to the parameters optimized by modeling, which indeed led us to a very good performance of our matrix.

3.2. Spectral characterization of the synthesized epoxy resin

We performed a structural analysis of the resin synthesized by Infrared Spectroscopy Fourier Transform (FTIR) and confirmed the results obtained by the nuclear magnetic resonance proton (^{1}H NMR) and carbon (^{13}C NMR). The letters s, d, t, q, and m are respectively singlet, doublet, triplet, quadruplet and multiplet. The results of structural analyzes, given below, confirm the structure of the synthesized epoxy resin.

3.2.1. Fourier Transform Infrared Spectroscopy (FTIR)

The synthesized epoxy resin was characterized by means of infrared analysis of Fourier transform. The latter was in its viscous state exposed to infrared radiation in ATR mode. The results obtained are illustrated in figure 11.

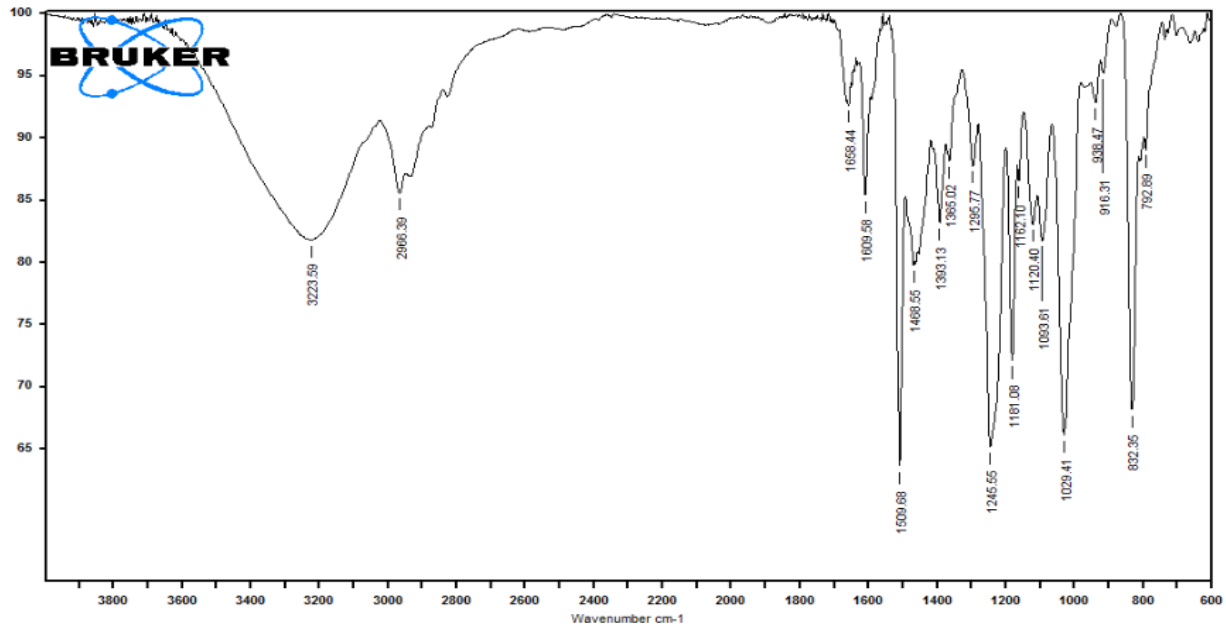


Fig. 11: IR spectrum of the synthesized resin TriGlycidyl Ethylene Ether of Bisphenol A

The allocation of the different strips obtained through infrared analysis with ATR mode is given in table 3 below:

Table 3: Infrared analysis with ATR mode of the synthesized resin

Band υ (cm-1)	attributions
3223.59	=C-H stretching
2966.39	C-H stretching vibration CH_3
1658.44	C=C stretching vibration
1509.68 ; 1609.58	Double link C = C aromatic Stretching vibration
1468.55	C-H CH3 elongation
1181.08 ; 1245.55 ; 1295.77	Link CO of aromatic ethers (Ph-O-) vibration of valence
1029.41	Elongation C-O de $–CH_2$-O-C
916.31 ; 938.47	of CH Link of stretching vibration of HC =
832.35	epoxy Group

3.2.2. Nuclear Magnetic Resonance NMR

3.2.2.1. NMR ^1H

The NMR ^{1}H spectrum of the synthesized tri-functional resin in figure 12 confirms the TGEEBA structure. The attributions of the chemical shifts of TGEEBA are regrouped in table 4.

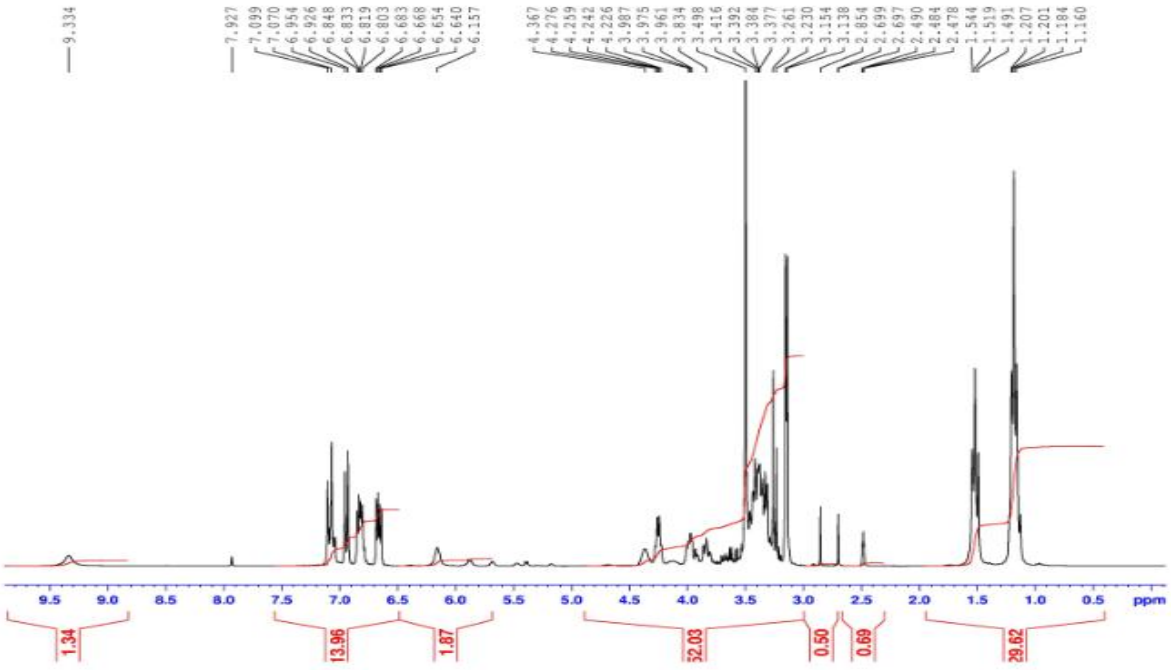


Fig. 12: the Proton's NMR spectrum of the synthesized epoxy resin TriGlycidyl Ethylene Ether of Bisphenol A

The attributions of the peaks of the observed TGEEBA resin are as follows:

Table 4: The proton's NMR analysis of the synthesized resin

δ ppm	Protons and interpretation
1-1,5	CH_3 Protons' grouping (s, 18H)
2,6	The CH_2 protons' grouping (d, 6H) of oxirane
3,5	The CH protons' grouping (t, 3H) of oxirane
4,3	CH_2 protons' grouping (d, 6H) of ester
6,2	Hydrogene's grouping HC = C (s, 1H)
6,5-7,2	The aromatic protons 6.5 to 7.2 (m, 24)

3.2.2.2. the NMR ^{13}C

The spectrum of Carbon 13 of the TGEEBA macromolecular structure in Figure 13 confirms this proton's NMR spectrum. The attribution of the chemical shifts of the different carbons of TGEEBA is grouped in table 5.

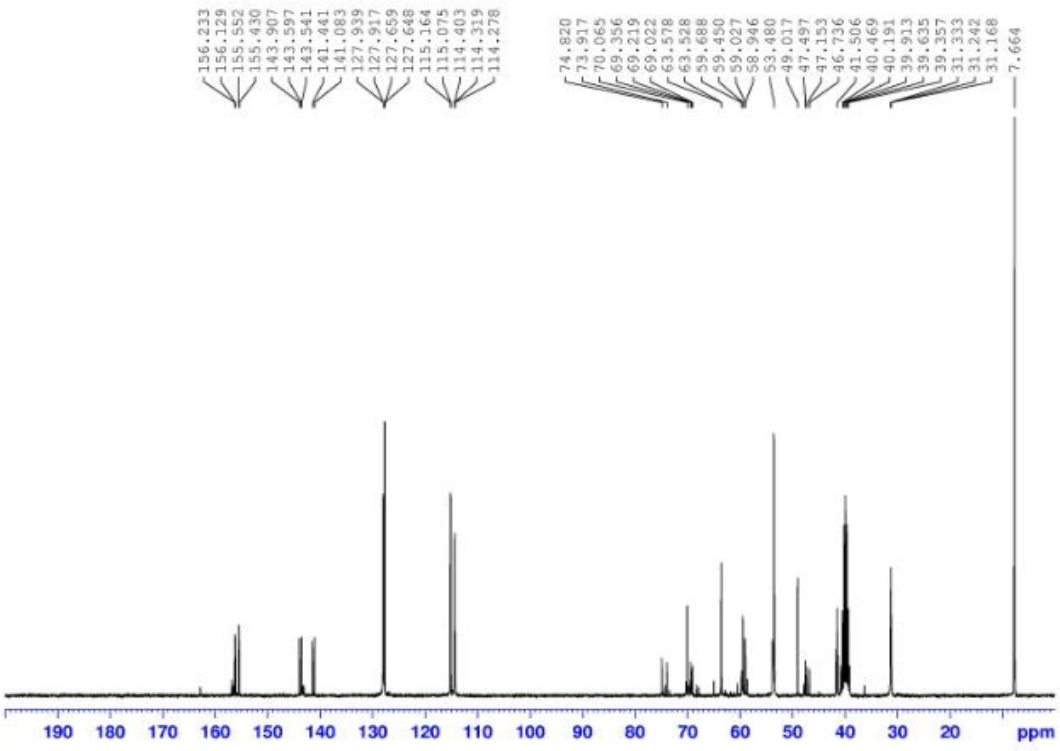


Fig. 13: Carbon's NMR spectrum of the epoxy resin synthesized TriGlycidyl Ethylene Ether of Bisphenol A

The attributions of the peaks of the observed TGEEBA resin are as follows:

Table 5: Carbon's NMR analysis of the synthesized resin

δ ppm	Carbones and interpretation
7,66	(S, CH_3)
31	(S, CH_3)
41	(S, CH_2 oxirane)
46	(S, CH_2 oxirane ether)
54	(S, CH oxirane)
127	(S, CH aromatic)
141	(S, C-C aromatic)

3.3. Scanning electron microscopy (SEM)

In order to identify the morphology of the good dispersion of the filler immerged in the resin epoxy matrix and to confirm the result, we used a surface analysis by the scanning electron microscope (SEM). The morphological results are represented by the SEM pictures as shown in figure 14.

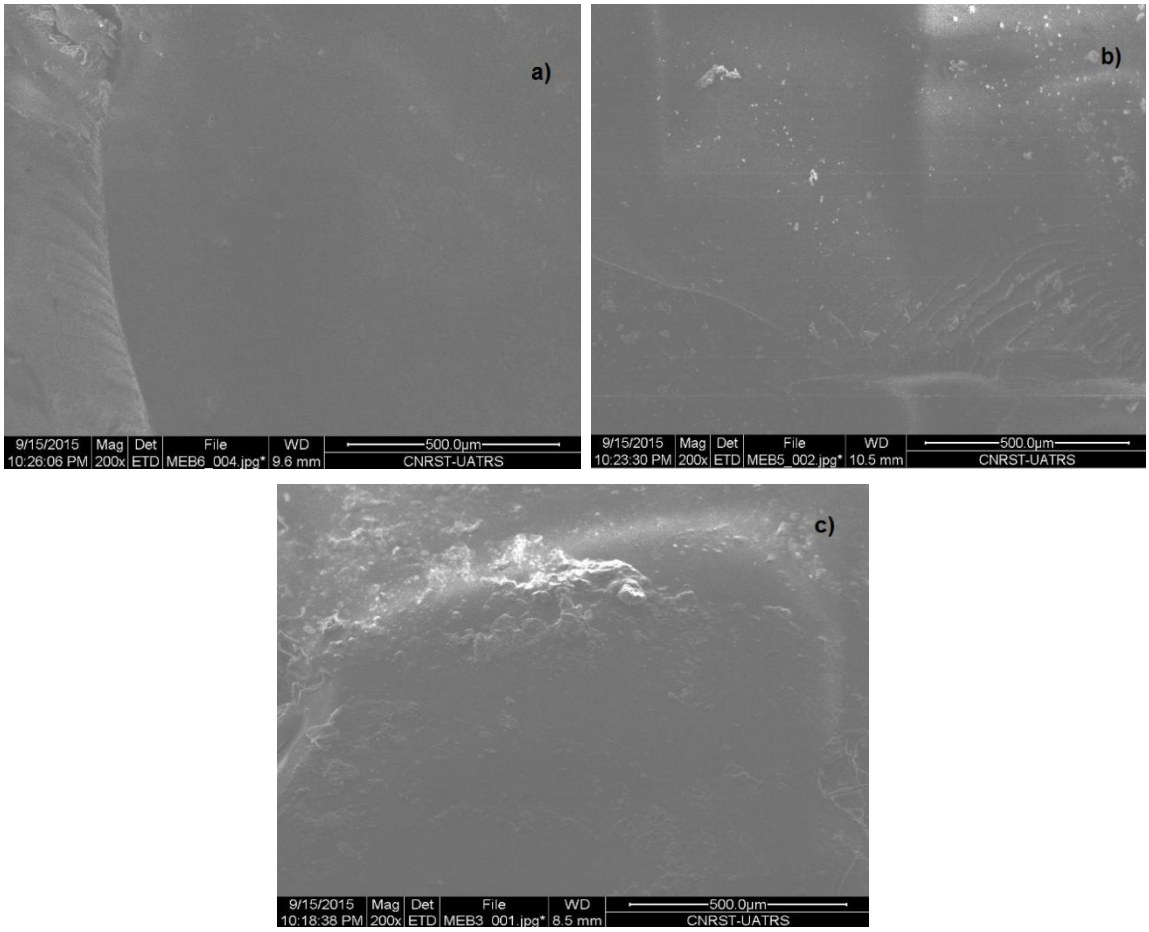


Fig. 14: the SEM of the epoxy resin synthesized and cross-linked by MDA of 0% (a), 5% (b) and 10% (c) of the natural phosphate load.

According to the observations of the morphology of the nano-composites prepared by TGEEBA/MDA/rock phosphate by SEM, we have therefore clearly demonstrated the appearance of natural phosphate loads which are well dispersed on the surfaces of the tested samples as indicated in these pictures.

Conclusion

The objective of this work is the synthesis of a tri-functional epoxy matrix of spacer arm bisphenol A to design a nanocomposite based on nano-scale filler (rock phosphate) which is an excellent binder and dispersing agent of the latter. To meet this goal, we initially optimized the factors (time, temperature and addition of the trichloroethylene reagent) to achieve a good yield from the reaction on one hand, and to achieve a consequent epoxide functionality in order to present the optimal conditions namely: the reaction temperature of 60 ° C, the time course of the reaction which is of the order of 48 hours, and the addition of the trichloroethylene reagent, by using of course the design of experiments method.

We then synthesized the macromolecular binder (TGEEBA) with a good yield and a functionality which is equal to 3.

The structure of this resin was characterized and confirmed by FTIR and nuclear magnetic resonance (NMR ^{1}H and NMR^{13}C). The new composite material provided for tri-functional epoxide matrix is obtained according to the optimized formulation in the presence of the curing agent (MDA) and the rock phosphate loaded with different percentages (0%, 5% and 10%). The morphological study of the nano-composite is identified by the SEM.

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