

Synthesis and Microscopic Characterization Of The Urea Macromolecule Tetraglycidyl Ether Of Bisphenol A (TGEUBA): Optimizing The Parameters By The Experimental Design And The Formulation of A Nanocomposite By Trisodium Phosphate And TGEMDA.

A.BEKHTA * and A. El Harfi

^(a)Laboratory of Polymers, Radiation and Environment (LPRE), Team of Organic and Macromolecular Chemistry (ECOM), Department of Chemistry, Faculty of Science, University Ibn Tofail, BP133, 14000, Kenitra, Morocco

Abstract

The main objective of our work is to synthesize the standard matrix and formulate it by the tri-sodium phosphate: Urea tetraglycidyl ether of Bisphenol A (TGEUBA). We obtained the precursor molecule of the epoxy matrix Urea tetrabisphe  nol A (Utba) and then we tended towards the functionalization of the latter with epichlorohydrin. Microscopic characterization of the TGEUBA resin was obtained by using the Fourier Transform Infrared (FTIR) and was confirmed by the nuclear magnetic resonance (NMR). The dispersion power of the tri-sodium phosphate in the presence of an adjuvant in the TGEMDA TGEUBA prepolymer crosslinked and formulated at different percentages (0%, 10% PTS TGEMDA 10% and 10% TSP + 10% TGEMDA) was followed up by using the Scanning Electron Microscope (SEM). Moreover, we have optimized the synthesis with the erection of the TGEUBA by the method of experimental design (Nimrod W).

* *Corresponding author:*

abekhata@gmail.com

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1. Introduction:

Thermosetting materials are products resulting from the chemical transformation of macromolecular compounds according to the degree of their functionality. Among these materials, there are the epoxy molecular templates that contain in their structure two or more oxirane functions [1]. These resins obtained by polycondensation of epichlorohydrin on structures containing at least two labile hydrogens [2, 3]. The prepolymer is mono, bi, tri, tetra or multifunctional, modulating the crosslinking density nodes possessed by the final prepolymer. [4] Their polymerization is carried out by the opening of the oxirane ring under the effect of a crosslinking agent which can be amine or anhydride type [4]. The realization of the composite is made by two or more constituents (binder macromolecular, hardener and filler). In our case, the epoxy resin binders are widely used in industries for different applications like the coating of conductive and semi-conductives components and radioactive wastes [5,6].

The objective of this article is to synthesize a new epoxy prepolymer TGEUBA. The latter is crosslinked with the MDA hardener then formulated by a trisodium phosphate load and TGEMDA adjuvant. The composite consists of four major components, and the fillers are dispersed in a crosslinking-matrix mixture (TGEUBA / MDA resin). The evolution of the microstructure of the resin TGEUBA by infrared spectroscopy and nuclear magnetic resonance has been identified, followed by a study of the dispersion of the filler and followed by Scanning Electron Microscope.

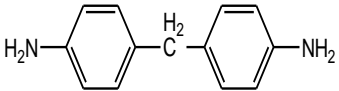
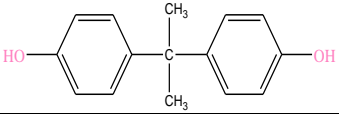
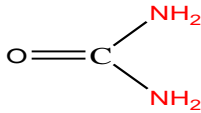
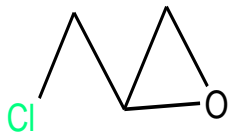
The optimization of the performance of polycondensation reaction was carried out by the design of experiments [7] according to the linear approach offered by the Nimrod W. software

2. Materials and methods

2.1. Materials:

The basic used chemicals in this article are presented in Table 1 below:

Table 1: Chemicals

Product Name	Function	Structure
Methylenedianiline (MDA) Curing [8-9-10]	Durcisseur [8-9-10]	
trisodium phosphate (TSP)	Charge	$\text{Na}_3\text{PO}_4^{2-}$
Bisphenol A (Bis A)	Precursor	
urea	precursor	
Epichlorohydrin with a purity of 99%	Epoxide	
Methanol CH3OH	Solvent	CH_3OH
Triethyl amine	Base	$\text{N}(\text{Et})_3$

All these commodities were provided by the companies Acros Chemical Co. and Aldrich Chemical Co.

2.2. Procedure:

The synthesized TGEUBA prepolymer in this work was obtained in two steps:

Step 1: In a round bottom flask, we mixed a mold of urea with 4 molds of bisphenol A diluted in methanol and triethyl amin as a base, then we heated it for 3 days at a temperature 65 ° C, the UBA product was extracted by the evaporation process.

Step 2: The obtained UBA product was dissolved in methanol and then mixed with a stoichiometric amount of epichlorohydrin. Then, we heated it for 3 hours at a temperature of 80 ° C to promote the condensation of epichlorohydrin and the hydroxyl functional UBA.

The reaction was continued by subsequently adding a mass concentration of solution of 10% of triethyl amine to the reaction mixture so as to obtain the closure of the oxirane cycle.

The reactive system at 60 ° C was brought to magnetic stirring for 60 minutes. Then the matrix of the TGEUBA resin was extracted by using a rotary evaporator.

2.3. Optimisation of theoretical synthesis of TGEUBA

The experimental plan allows defining the experiences reduced in number, hence allowing to a comprehensive study of the influence of all the parameters and their optimization on a given process. This is all based on finding a simple mathematical model which gives a good representation of the phenomenon. [20]

The mathematical model:

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

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

By applying this model, we tested three factors at two levels [21-22-23].

The limit values of the parameters are defined in Table 2:

Table 2: Factors variations Areas

Settings	Temperature ° C	Time (h)	Addition of the reagent Bisphenol A (BPA)
Factors	X ₁	X ₂	X ₃
Levels +1	75	72	Fast
Levels -1	25	3	Slow

2.4. Characterization methods of the synthesized prepolymer:

2.4.1. Infrared Fourier Tarnsform (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 .mu.m. The analysis is performed between 4000 cm⁻¹ and 600 cm⁻¹.

2.4.2. Nuclear Magnetic Resonance (NMR):

the analyzes of NMR 1H 13C were obtained by using an apparatus of Bruker AVANCE 300 by dissolving the product in CDCl₃. The chemical diplassements were expressed in ppm.

2.4.3. Scanning electron microscope (SEM) :

Scanning electron microscope was used to make photographic images. The observations were performed on the microscope JEOL-JEC-530. This technique was based on the use of a beam of accelerated electrons by a fixed potential which excites the sample surface. Picture 1 shows the SEM pictures of the device.



Picture 1: Photos of the device SEM.

2.5. Samples preparation for the Analyses by using SEM

We thermally heated the following systems:

- C1: TGEUBA / MDA
- C2: TGEUBA / MDA / 10% TGEMDA
- C3: TGEUBA / MDA / 10% PTS
- C4: TGEUBA / MDA / TGEMDA 10% / 10% PTS
- Results and Discussion

3.1. Modelization:

This work was based on the full factorial experiment matrix to illustrate the best parameters influencing the performance by combining the studied interactions.

3.1.1. The graphical study of interactions between factors:

- Graphic study of interactions X_1X_2 (Temperature / Time)

According to this study, the following parameters: the temperature (X_1) and time (X_2) are shown in Figure 1.

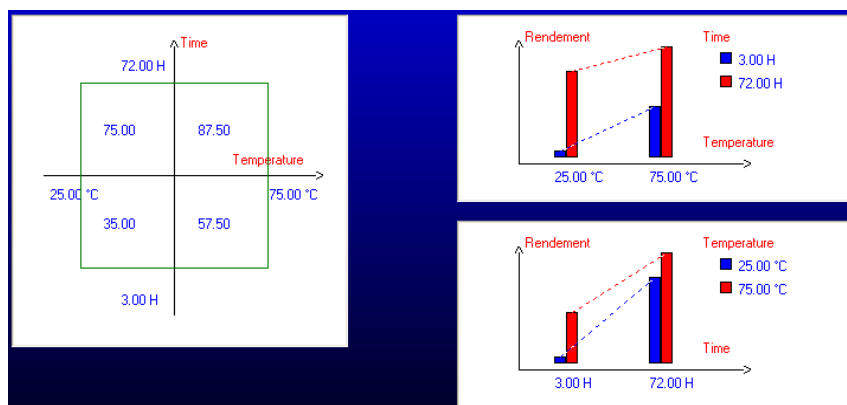


Figure 1: Graphical System X_1X_2 interaction

According to this system of interaction, it appears that the best performance is determined in the case of interaction where $X_1 = 75$ (temperature) and $X_2 = 72$ h (time).

Graphic study of interactions X_1X_3 (temperature / reagent addition PBA)

According to the study, the following parameters: temperature (X_1) and the addition of BA reagent (X_3) are shown in Figure 2.

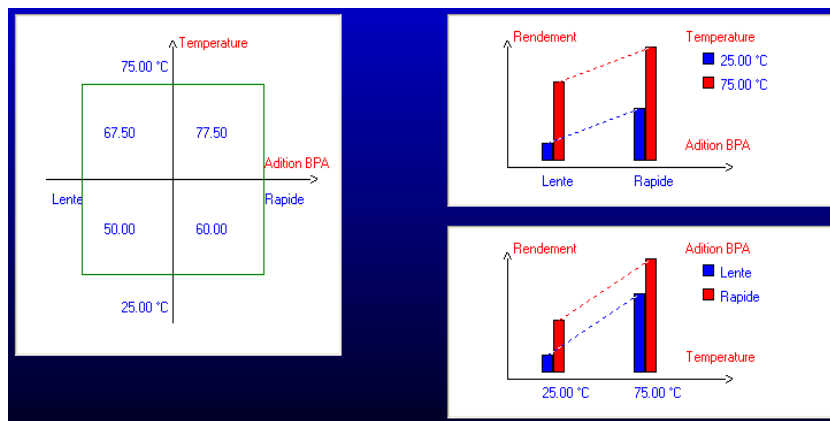


Figure 2: Graphic system of interaction X_1X_3

From this interaction system, it appears that the best performance is determined in the case of interaction where the addition of the reagent Bisphenol A is fast (X_3) X_1 and temperature = 75°C .

Graphic Study of X_2X_3 interactions (time / Addition BPA reagent)

In this graphic study, the following parameters: the X_2 time and adding the reagent of Bisphenol A (X_3) are shown in Figure 3.

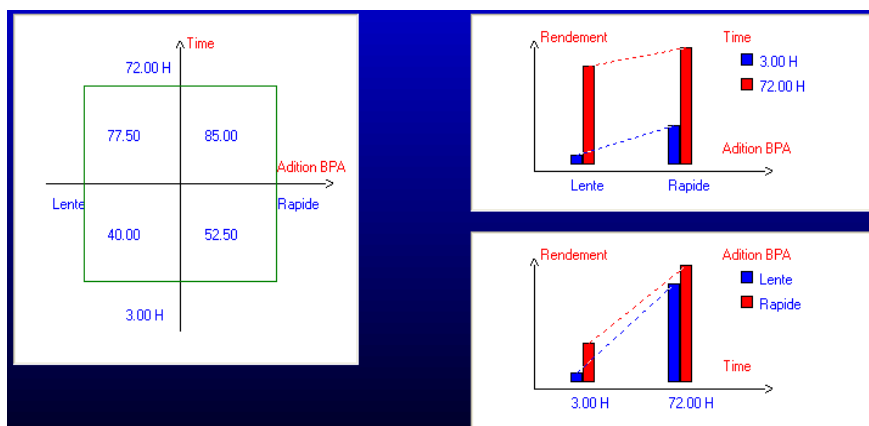


Figure 3: Graphical System X_2X_3 interaction

According to this system of interaction, it appears that the best performance is determined in the case of interaction where $X_2 = 72$ h (time) and the reagent addition bisphenol A (PBA) is fast (X_3).

3.1.2. Struck through the diagram layout of the average effects:

The bar diagram highlights the most influencing parameters on the reaction yield.

Indeed, we notice that the most driving factors are given in descending order of influence. The addition of BPA reagent (b_3), the time (b_2) and the temperature (b_1).

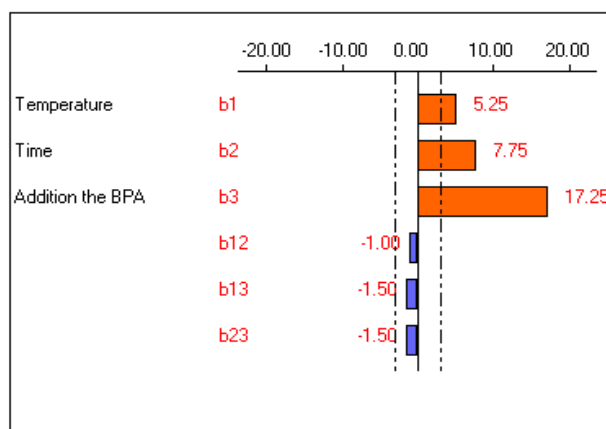


Figure 4: bar diagram

3.1.3. Pareto diagram:

The Pareto diagram is to supplement the results as obtained by the using bar diagram obtained previously. This would determine the most influencing factors.

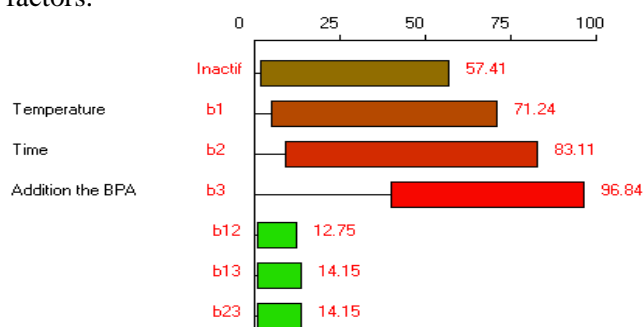
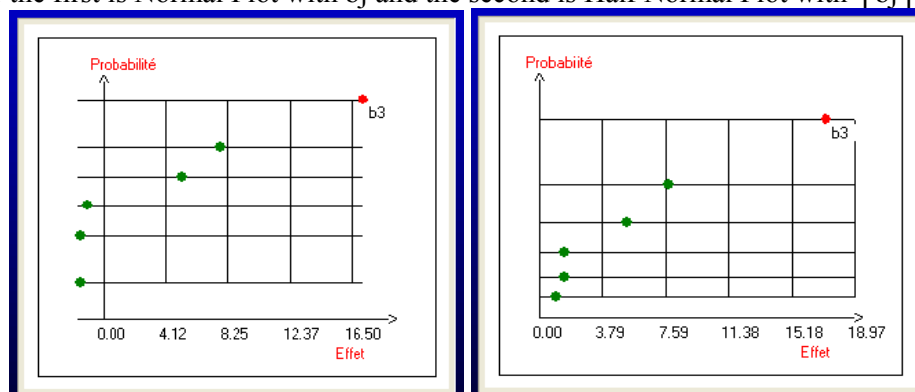


Figure 5: Pareto diagram for the yield response

The Pareto chart makes it clear that the first three factors (EPS reactive, time and temperature) are acting in descending order and are in fact the addition of the BPA reagent (b3), time (b2), and temperature (b1). This confirms the added reagent time of the optimized reaction would be 72h.

3.1.4. Method of the right of HENRY:

The HENRY method in Figure 6 is used to represent the distribution function b_j effects on gaussian arithmetic papers. It gives two graphs: the first is Normal Plot with b_j and the second is Half Normal Plot with $|b_j|$.



a- The graph of Normal Plot

b- The graph of Half Normal Plot

Figure 6: Right of HENRY (a, b).

The effects which deviate from the right on the Normal Plot (below or above the right that is to say that the effects are positive or negative) are considered absolutely assets. [26]. It distinguishes the active coefficients, but it does not give the exact meaning of the effect since we took just the absolute values of the coefficient $|b_j|$. The following illustration shows the HENRY right. From this figure, we find that the coefficient b_3 is absolutely active. This confirms the results obtained by the former methods.

3.1.5. Validation of the model:

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

Table 3: Estimated coefficients and statistics.

Standard deviation of the response	0.707
R2	1.000
R2A	0.999
Number of degrees of freedom	1

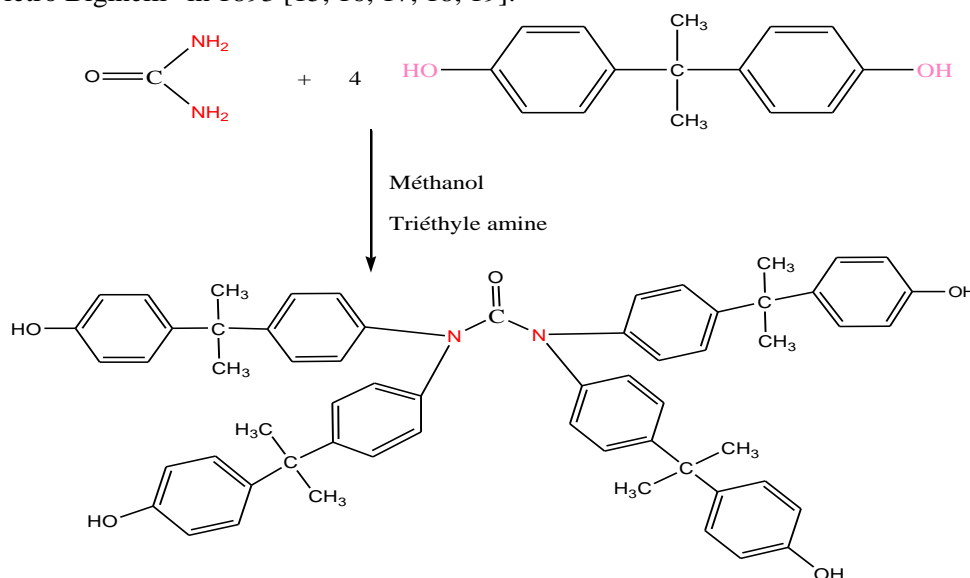
From Table 2, we can conclude that all the responses obtained by this model of experimental plan have a satisfactory descriptive quality since the correlation coefficient R_2 is equal to 1.000.

After the optimization of the factors influencing the performance of the polycondensation reaction shows that the factors (BPA reagent, time and temperature) are predominant, this allowed us to process for the synthesis of macromolecular triglycidylisocyanurate matrix ether urea bisphenol A (TGEUBA), according to the parameters optimized by modeling, which led us in fact to a very good performance of our matrix.

3.2. Preparation of the epoxy resin

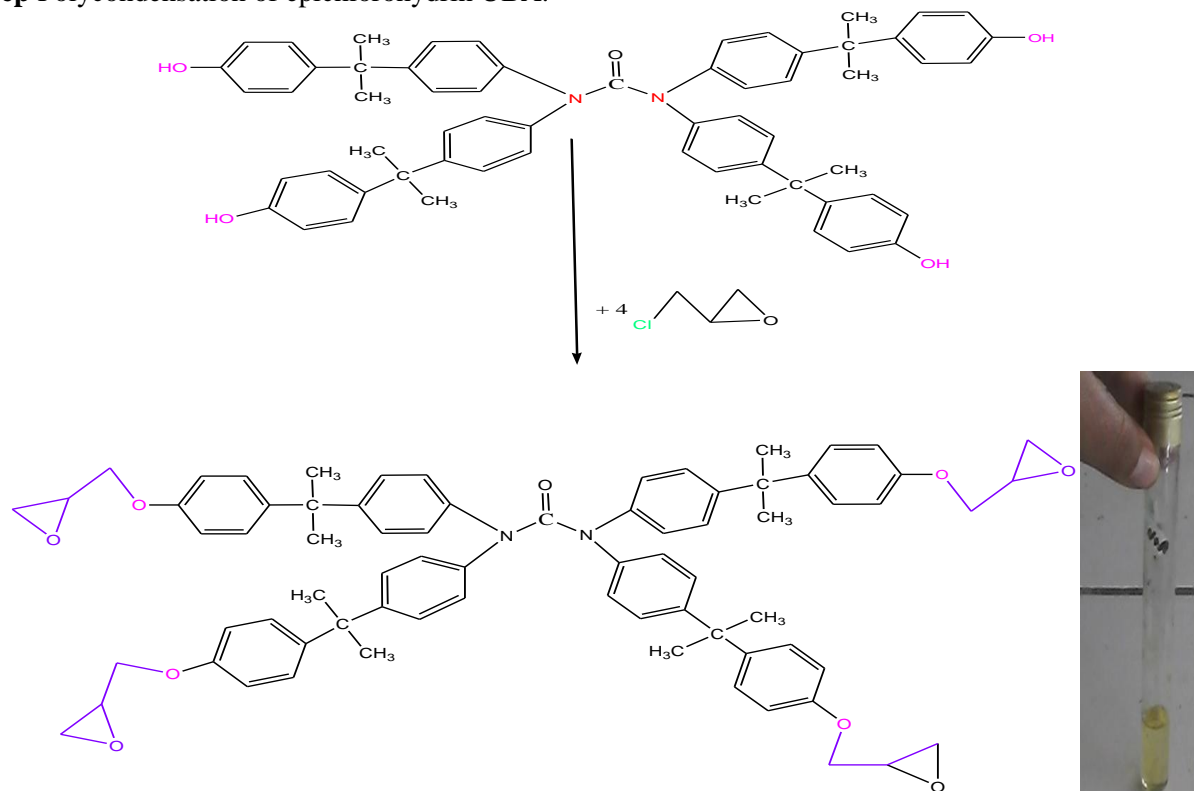
The tetraglycidyl ether resin TGEUBA urea bisphenol A is synthesized according to procedures of the literature [11, 12, 13, 14] obtained in this case by two steps:

- **1st step:** Product Summary UBA (Urea Bisphenol A) from urea and bisphenol A, using a protocol adapted by the Italian chemist "Pietro Biginelli" in 1893 [15, 16, 17, 18, 19].



Scheme 1: Summary of UBA.

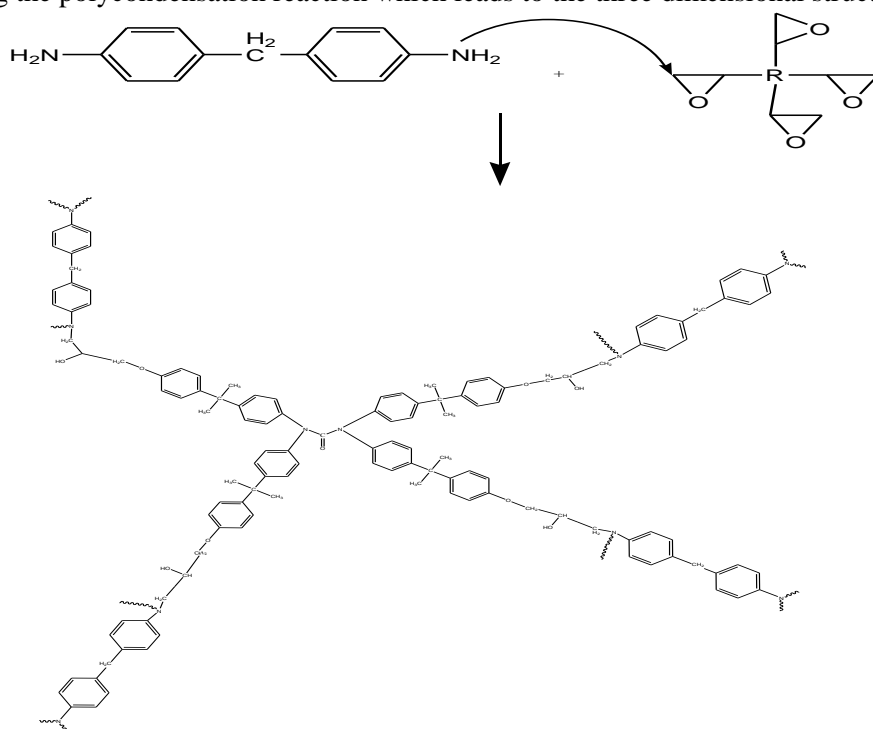
- **2nd step** Polycondensation of epichlorohydrin UBA.



Scheme 2: Summary of new TGEUBA resin.

3.3. Crosslinking the TGEUBA matrix by the MDA

The crosslinking of TGEUBA in the presence of MDA as the curing agent proceeds under the action of the temperature following the polycondensation reaction which leads to the three dimensional structure in Scheme 3.



Scheme 3: Scheme of the crosslinking of the TGEUBA resin by MDA.

3.4. Microstructure study:

In this study, we characterized our resin by the infrared and confirmed its structure by the spectroscopic method of Nuclear Magnetic Resonance (NMR) of the proton and carbon 13. The allocation of the different peaks obtained by means of infrared analysis in Fourier transform (FTIR) is given in Table 3:

3.4.1. Infrared identification:

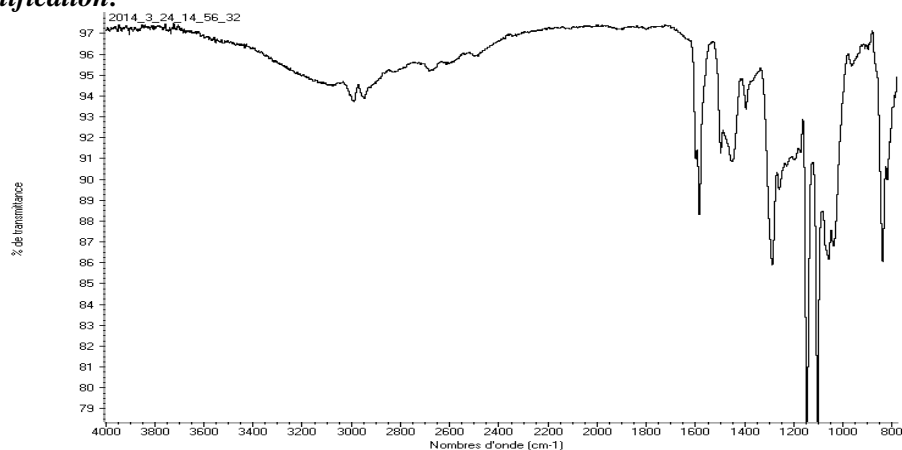


Figure 7: Analysis TGEUBA resin by IR.

Table 3: Allocation peaks of TGEUBA

Band ν (cm ⁻¹)	Functions
3000	O-H residual
2600	C-H de CH ₂
1590	C=C
1420	CH ₃
1300,1540	C=O
1150	C-O the alcohols and ethers
1100	C-C
1020	C-N
1250,815	Epoxy

3.4.2. Identification by NMR:

The NMR of Proton-1:

The NMR spectra of the proton of the TGEUBA resin is shown in Figure 8: The Proton NMR (NMR ¹H) in ppm: proton NMR (NMR 1H) in ppm: 1.67 (s, 3H CH₃), 3.64-3.71 (m, 2H, CH₂ oxiranes), 4.103 (t CH 2H. oxiranes), 4.84 (t, 2H of CH₂ linked with ether), 4.84 (dd, benzene H).

The NMR of Carbon-13:

The carbon 13 NMR spectra of the TGEUBA resin is shown in Figure 9. The Proton NMR (NMR 13 C) in ppm: 31 (s, CH₃); 42.4 (s, tertiary carbon); 44.2 (s, CH₂ oxirane); 50 (s, oxirane CH); 69.5 (s, CH₂ bound with oxirane); 114.9 - 116.4 - 128.9 - 129.7 (s, aromatic CH); 137.7 - 138.7 (s, aromatic tertiary carbon bonded to the tertiary carbon) and 146 - 155 (s, aromatic tertiary carbon bonded to the oxygen).

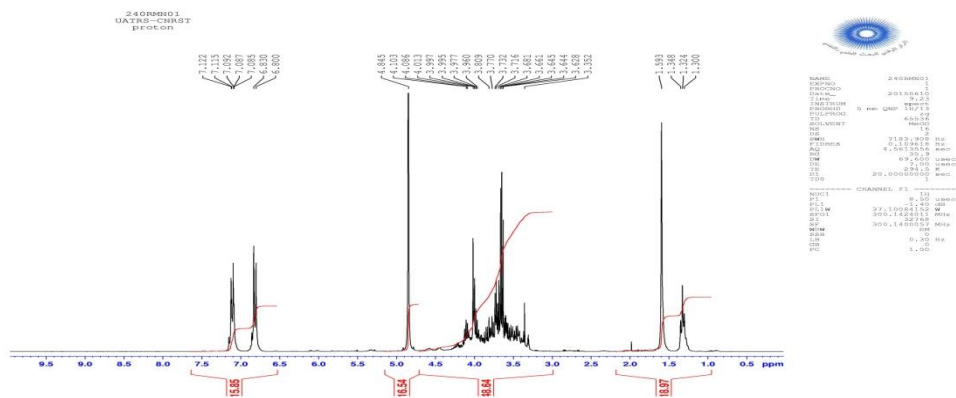


Figure 8: Analysis of TGEUBA resin by NMR ^1H .

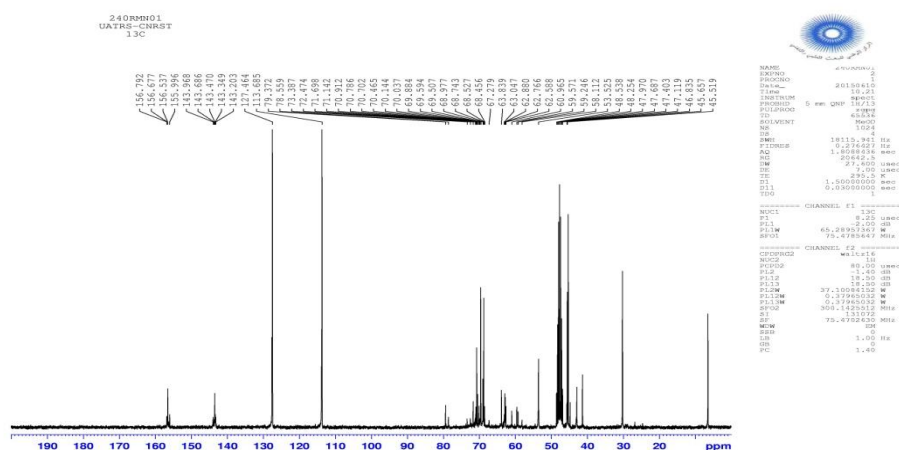


Figure 9: Analysis of the TGEUBA resin by NMR ^{13}C .

3.5. Study of the dispersion of trisodium phosphate load in the TGEUBA prepolymer matrix.

Our composite materials (C1, C2, C3, C4) were analyzed by scanning electron microscopy. The obtained results are respectively shown in Figure 10: According to observations by the SEM, the developed composite based on TGEUBA, we are clearly shown that the appearance of spherical fillers of trisodium phosphate are well dispersed on the analyzed surface according to Figure 10.

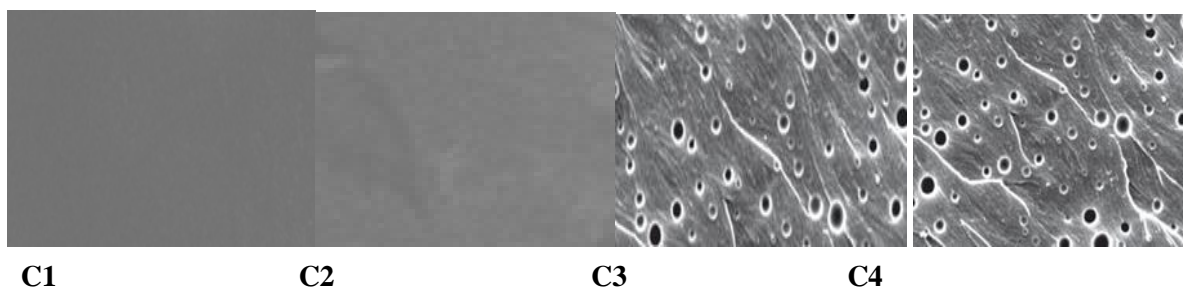


Figure 10: The microscope of TGEUBA resin crosslinked by MDA to 0% (C1), 10% TGEMDA (C2), 10% PTS (C3) and 10% + 10% TGEMDA PTS (Na_3PO_4) (C4).

Conclusion:

In this work, we have optimized, synthesized, characterized and made new composite materials with epoxy matrix tetraglycidyl ether urea bisphenol A (TGEUBA). The used hardener is the methylenedianiline in the presence of a filler namely tri-sodium phosphate as a mineral filler and an adjuvant which is the tetraglycidyl ether methylenedianiline (TGEMDA) as organic filler. To meet this objective, at first, we optimized the factors influencing the efficiency of the polymerization reaction (reagent addition bisphenol A, time and temperature).

Indeed the optimal settings for this polycondensation are: Reactive Bisphenol A (fast) / time (72h) / temperature (75 °a C). Then the structure of this resin was characterized and confirmed by Fourier transform infrared spectroscopy and nuclear magnetic resonance (NMR 1H and NMR 13C). The prepared composites were examined by the SEM. It is clear that the addition of trisodium phosphate load in the presence of the TGEMDA adjuvant allowed us to have an optimal composite of charge dispersion.

References:

- [1]: P. Castan, Brevet US 2444333 (1948).
- [2]: El Gouri M., El Harfi A., Rafik M., Hegazi S.E., Grich M. and Meghraoui H., Ref. O241008/83. Ph&Ch News (2009).
- [3]: M. Grich, M. El gouri, R. Ziraoui, N. Rami, H. Meghraoui, O. Cherkaoui, A. El harfi. J. Mater. Environ. Sci. 5 (2014) 374-379.
- [4]: Toufik DJILALI «Élaboration d'une solution de collage pour les assemblages travaillant à haute et basse température : le Joint Multi-Adhésifs. Mise en œuvre de la solution technologique et prédiction de son comportement en service » thèse N° d'ordre : 2584 (2007) TOULOUSE.
- [5]: Atiqa BEKHTA, Touria EL Lambarki Alliou Abderrahim Bouih, Bouchra El Hilal, and Ahmed EL Harfi, IJIAS, 7 (1057-1070) Aug. 2014
- [6]: EL hilal B., Lambarki el Alliou T., Bouih A, Bekhta A., EL Harfi A.,IJIAS, 7(2014)
- [7]: GOUPY Jacques ' Introduction aux plans d'expériences' Dunod. Paris. 303 pages. 2001
- [8]: Atiqa BEKHTA and Ahmed EL HARFI, IJIAS , 7 No 2 (Aug. 2014), pp. 662-673.
- [9]: R. HSISSOU, Y. EL RHAYAM & A. EL HARFI. International Journal of Innovation and Applied Studies. Vol. 7 No. 2 Aug. 2014, PP. 674-682.
- [10]: ZIRAOUI R., MEGHRAOUI H., RAMI N., CHERKAOUI O., CHOUKRI A., HAKAM O. et ELHARFI A. Ann. Chim. Sci. Mat., 2012, 37 (2-4), pp. 85-96.
- [11]:A. Bekhta, J. El Azzaoui, N. El-Aouni, B. El Elhilal and A. Elharfi, Mor. J. Chem.3 (2015) 458-464
- [12]: J. El Azzaoui, N. El-Aouni, A. Bekhta, A. El Harfi, Mor. J. Chem.3 (2015) 338-345
- [13]: S. Fetouaki, A. El Harfi, L. Belkebir, J. European Polymer., 38 (2002) 787-793.
- Biginelli, P. Aldehyde Urea Derivatives of Aceto- and Oxaloacetic Acids. Gazz. Chim. Ital. 23(1893) 360-413.
- [14]: P. Castan, Brevet US 2444333 (1948).
- [15]: P. Castan, English Patent no. 518057 (1933).
- [16]: J. Canadell, A. Mantecón, V. Cádiz, Polym. Degrad. Stab., 92 (2007)1934.
- [17]: L. Weichang, J.V. Russell , P.S. George, Polym., 48 (2007) 2351.
- [18]: El Gouri M., El Harfi A., Rafik M., Hegazi S.E., Grich M. and Meghraoui H., Ref. O241008/83. Ph&Ch News (2009).
- [19]: James E. Mark, Physical Properties of Polymer Handbook, Springer, 2007, 2e éd, 1076 p. (ISBN 0387690026) 1 mars 2013)], p. 294.
- [20]: R. L. Plackett, J. P. Burman. Biometri. (33) (1946) 305 – 325.
- [21]: M. Berradi, A. El Harfi. Moroc. Jour. Chem. 3(1) (2015) 142-146.
- [22]: A. L. Ahmad, S. S. Wong, T. T. Teng, A. Zuhairi. Jour. Hazar. Materi. (145) (2007) 162 – 168.
- [23]: Y. Elrhayam, A. El Harfi. Jour. Environ. Scien. Engine. B (3) (2014) 18 - 23.