

Synthesis, Structural, Viscosimetric, and Rheological Study, of a new trifunctional phosphorus epoxyde prepolymer, tri-glycidyl ether tri-mercaptoethanol of phosphore (TGETMEP)

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Abstract: The aim of our work is to synthesize a new phosphorus tri-functional epoxy resin tri-glycidyl ether tri-mercaptoethanol of phosphorus (TGETMEP) in two stages. In the first stage, we got the precursor molecule of the epoxy matrix tri-mercaptoethanol phosphate (METR). The second step led us to the synthesis of tri-functional resin TMEP condensation with epichlorohydrin. The standard TGETMEP resin was characterized by the Fourier infrared transformation (FTIR) and nuclear magnetic resonance (NMR), on one hand. The viscosimetric analysis was investigated by the Hebbelod capillary viscometer and rheometer Rheomat 01, on the other hand. The cross-linked resins and tertiary formulated composites have been studied by the rheometer 01 which was observed by means of SEM.

Keywords: Epoxy resin, tri-functional, TGETMEP, structural characterization, hebbelod capillary viscometer, rheometer of rheomat 01.

Introduction

Thermosetting resins, including epoxy resins (ER) are important in the industry thanks to the many properties they offer and their easy implementation. They are used in several areas especially electronics, sports, recreation, coatings, composites and radioactive wastes¹⁻², etc.

The preparation of epoxy prepolymers requires two main methods: the first is the epoxidation by oxidation³⁻⁴ using a variety of oxidants agents formed mainly by peracids. The second way is the glycidylation via the condensation of epichlorohydrin with structures containing at least two labile hydrogens of the type: diacids⁵, diamines⁶, and polyphenols⁷. The preparation of an epoxy prepolymer by condensing epichlorohydrin was discovered almost simultaneously by the Swiss Castan and American Greenlee^{8,9}. These reactions are important to the extent that the actual functionality is lower than the theoretical functionality and the responsiveness with the hardener¹⁰ is therefore modified, which does not happen without any major influence on the characteristics of the final product.

In this work, we sought to synthesize new homologous products with structures similar to that

of DGEBA¹¹, which can have better properties, in order to be used in the field of protection and preservation of the environment and in the conditioning of radioactive waste thanks to their macromolecular matrices.

Materials and methods

Materials

All basic chemicals were supplied by Acros Chemical Co. and Sigma-Aldrich. Our composite materials are formulated from matrices consisting of mercaptoethanol, phosphate trichloride, tri-sodium phosphate, methylene dianiline and epichlorohydrin.

Synthesis of TGETMEP

The synthesis of the tri-glycidyl ether tri-mercapto ethanol phosphorus is made via the condensation of epichlorohydrin in two stages (**Scheme 1 and Scheme 2**).

Step 1: it presents the synthesis of intermediate product TMEP (tri-mercapto ethanol of phosphate) from mercapto ethanol and phosphate trichloride (Scheme 1) using a protocol adapted by the Italian chemist Pietro Biginelli in 1893^{12,13}.

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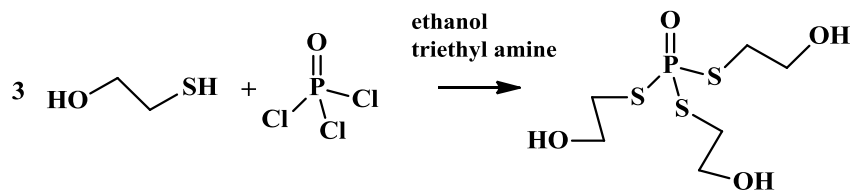
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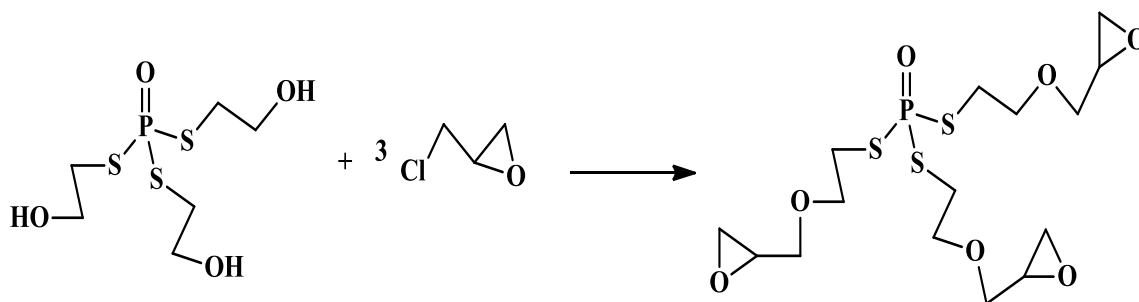
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Scheme 1: Synthesis of TMEP.

Step 2: it shows the diagram of obtaining the TGETMEP resin by the effect of epichlorohydrin

on the TMEP in trimethylamine medium, according to the following reaction **Scheme 2:**



Scheme 2: Synthesis of TGETMEP.

Methods of analysis

Fourier Infrared Transformation (FTIR):

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

Nuclear Magnetic Resonance (NMR): The NMR analyzes ^1H , ^{13}C , ^{31}P were obtained by using a Bruker AVANCE 300 device, by dissolving the product in CDCl_3 . The chemical displacements are expressed in ppm.

Viscosimetric Analyses: The viscosimetric analysis of the standard matrix was performed through a capillary Ubbelohde viscometer VB-1423.

The selected measurement conditions are:

- Viscometer of 1B size for a series of dilution, capillary tube of 0.46 mm diameter.
- Constant $k = 0.051493$.
- Measurement of temperature in $^{\circ}\text{C}$: 30 up to 45;
- Number of measurement: 4 each time
- Solvent: Methanol
- The Hagenbach correction was calculated according to the formula specified in the norm DIN 51562-1 Janvier 1999 (Measurement of kinematic viscosity by means of the Ubbelohd viscometer).
- Solubilization of epoxy resin prepolymers in methanol was carried out under magnetic stirring at 20 $^{\circ}\text{C}$.

Rheological Analyses:

The rheological analysis of the standard matrix and crosslinked and formulated composites were followed with a rheometer of Haake RHM01-RD

(HAAKE MARS) on liquid, pasty, and solid samples.

The selected measurement conditions are:

- Measuring temperature: 150 $^{\circ}\text{C}$
- rotation speed Mode CR: 10-8 0 1500 rpm.
- rotation speed Mode CS: 10-7 to 1500 rpm.
- Frequency: 10-5 to 100 Hz.
- Strength: 0.01 to 50 N.
- Torsion: 5.10-8 0.2 N.m.
- Control software: RheoWin.

Electronic Scanning Microscope:

The scanning electron microscope was used to make photographic images. The observations were performed on a microscope JEOL-JSM-5500. This technique is based on the use of a beam of accelerated electrons by a fixed potential which excites the sample's surface. The interaction between the primary electrons with the material leads to the emission of secondary electrons, backscattered electrons, X-rays and Auger electrons.

Preparation of crosslinked and formulated Samples

In our study, we are interested in the mechanisms of reaction between the oxirane functions of epoxy prepolymers (TGETMEP) and amine functions of hardening agents (MDA). The protocol is the one adopted by S. Fetouaki¹⁴, which consists in preheating the stoichiometric amounts of the resin and the hardener¹¹⁻¹⁵ in silicon moles. Methylene dianiline (MDA) crystallized at room temperature is placed in an oven at 120 $^{\circ}\text{C}$ (a temperature above its melting point) while the resin is heated at 60 $^{\circ}\text{C}$. When melted, the MDA is mixed with the resin to provide a single fluid phase at 70 $^{\circ}\text{C}$.

The samples thus prepared were sealed into molds and subjected to the following firing cycle (**Figure 1**):

- 12 h to 70 ° C and 1 hour to 140 ° C.
- After demoulding, the sample is prepared according to the desired geometric shape.



Figure 1. Pictures of Sample preparation

The previous protocol was applied for cross-linking the loaded resin with tri-sodium phosphate at different percentages.

Results and Discussion

Microstructural Studies

We performed structural analysis of the epoxy resin obtained by means of infrared spectroscopy

and Fourier transform confirmed the results by the nuclear magnetic resonance of the proton (^1H NMR), carbon (^{13}C NMR) and phosphorus (^{31}P NMR). The results of structural analyzes are given below.

Infrared identification

The IR bands of the TGETMEP resin are shown in **Figure 2**.

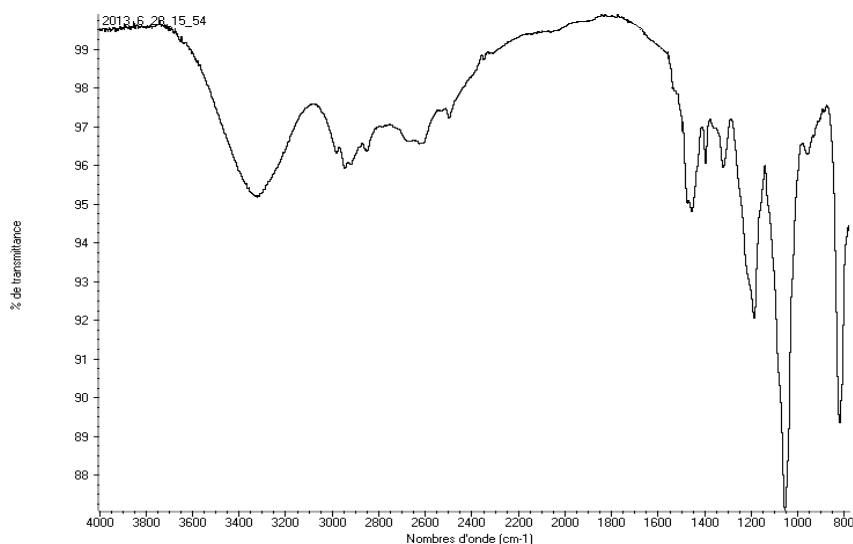


Figure 2. Analysis of the resin TGETMEP by FTIR.

The allocation of the different strips obtained through infrared analysis in Fourier transform is

given in Table 1:

Table 1. Allocation of bands TGETMEP.

Band ν (cm^{-1})	Attribution
3390	O-H residual
2850, 2600	C-H de CH_2 du S
2350, 1450	C-H du O
1350	P=O
1038, 1150	C-O alcohols and ethers
1250, 815	Epoxy

Identification by NMR: The NMR of Proton

The NMR spectrum of the proton of the TGETMEP resin is shown in **Figure 3**:

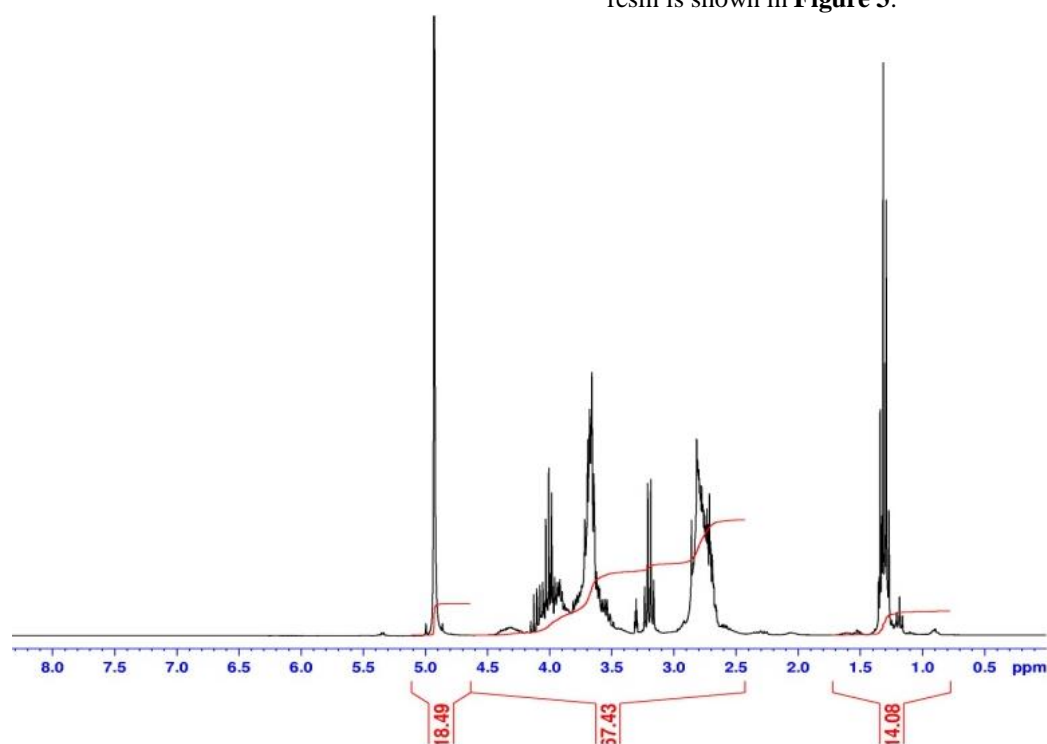


Figure 3. The NMR spectrum of the Proton of the TGETMEP resin.

The chemical shift in ppm of protons of the macromolecular matrix (tri glycidyl ether trimercaptoethanol phosphorus) is given according to the assignment of the peaks in the ¹H NMR spectrum: 1.26 and 1.34 (m 2H of CH₂ of oxirane.), 2.70-2,85 (m. 2H, CH oxiranes), 3.30 (t. 2H of

CH₂ bound to S), 3.5 and 4 (m, 2H of CH₂ linked with ether and CH of oxirane), 4.92 (s, 2H of CH₂ linked to CH₂ and ether).

The NMR of Carbon 13

Carbon 13 NMR spectrum of the TGETMEP resin is shown in **Figure 4**.

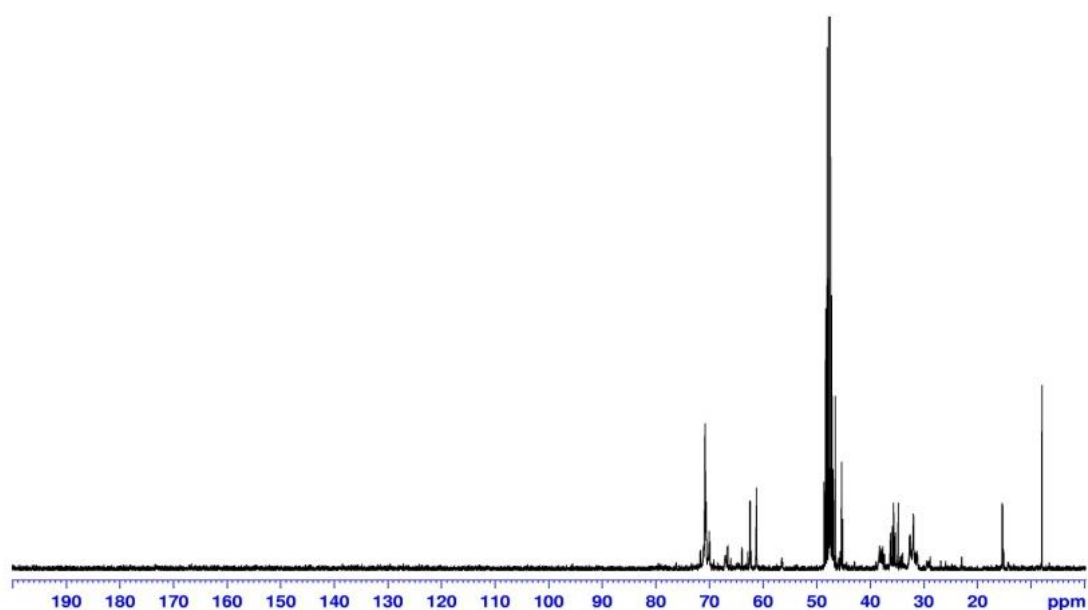


Figure 4. NMR Spectrum of carbon13 of the TGETMEP resin.

The chemical shift in ppm of prepolymer carbon (Tri glycidyl ether tri-mercaptoethanol of phosphorus) is given according to the assignment of peaks of carbon 13 (^{13}C NMR) as follows: 7.886-15- 22863-28748 (S, CH_2 linked with sulfur); 36.4 - 38.2 (S, CH_2 of oxirane); 45- 48.7 (S, CH

oxiranes); 61- 63.5 (S, CH_2 linked to oxygen and CH_2 of methylene); 66-71697 (S, CH_2 linked to CH of oxiranes and oxygen).

The NMR of phosphorus ^{31}P :

The spectrum of phosphorus 31 NMR of the TGETMEP resin is shown in **Figure 5**.

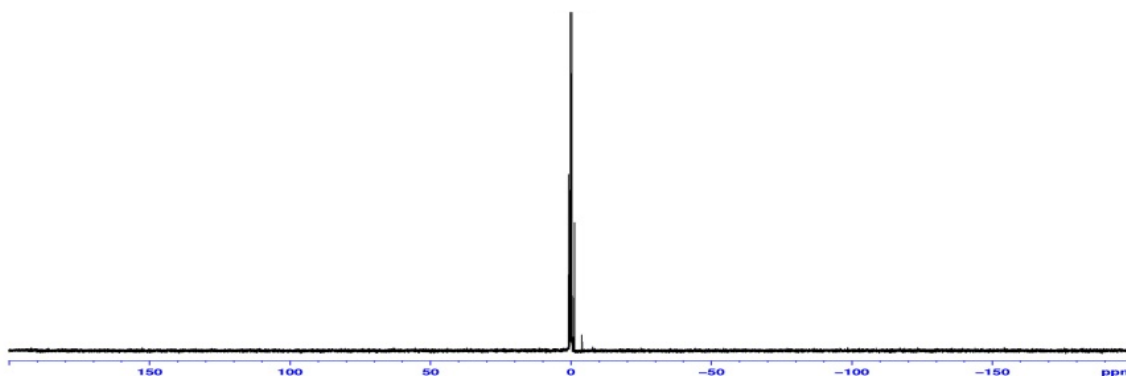


Figure 5. The spectrum of phosphorus 31 NMR of the TGETMEP resin.

The chemical shift in ppm of phosphorus (NMR ^{31}P) of this phosphorus resin is given as follows: 0703 S O = P (R)₃

Macrostructural analysis

Viscosimetric study of epoxy resin Tri-glycidyl Ether Tri-mercaptoethanol of phosphorus

As we mentioned before, the viscosimetric properties can be directly related to the chemical structure or the degree of conversion of the reacting system^{10,14-18}.

Evaluation of the viscosimetric behavior of the unbound prepolymer by using the UBBELHOD capillary viscometer

The viscosimetric properties of the TGETMEP epoxy resin are studied by using a capillary viscometer Ubbelohd at varying temperatures from 30 to 45°C. Determining the viscosimetric behavior of the epoxy resin is made after the preparation of TGETMEP solvent / resin system. We dissolved the resin in methanol at different concentrations ranging from 5% to 20%, and then we studied their viscosity according to the temperature by having a mass concentration of the fixed system resin/solvent¹⁰⁻¹⁵.

- **Depending on mass concentration:** The results are shown in **Figure 6**.

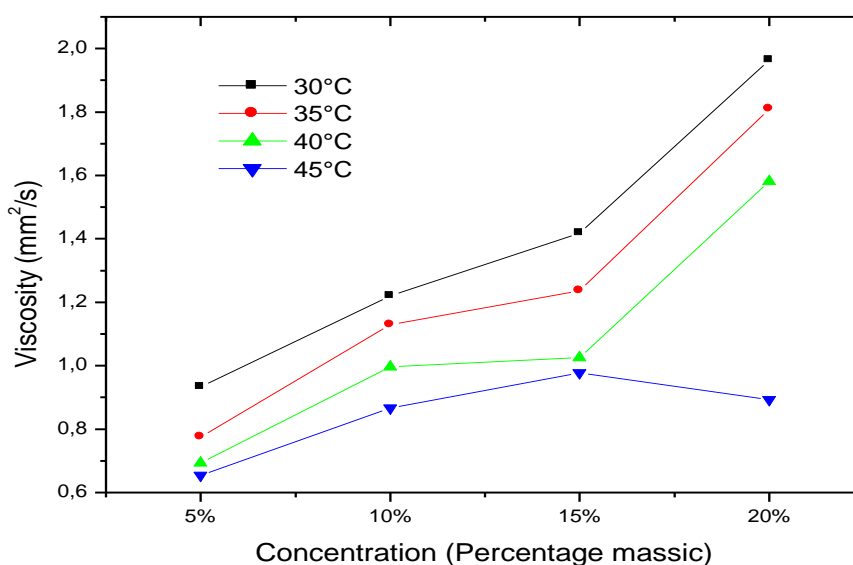


Figure 6: Mass concentration (%) effect on the viscosity (mm²/s) of a pre-polymer TGETMEP/Methanol.

The results shown in **Figure 6** are quite logical and expected, and the viscosity of the solution increases gradually as the massive percentage of the TGETMEP/methanol increases.

The drop observed at the temperature 45 ° C to 15% corresponds to the passage of the TGETMEP resin from the viscous state to the liquid state.

- **Depending on the temperature:**

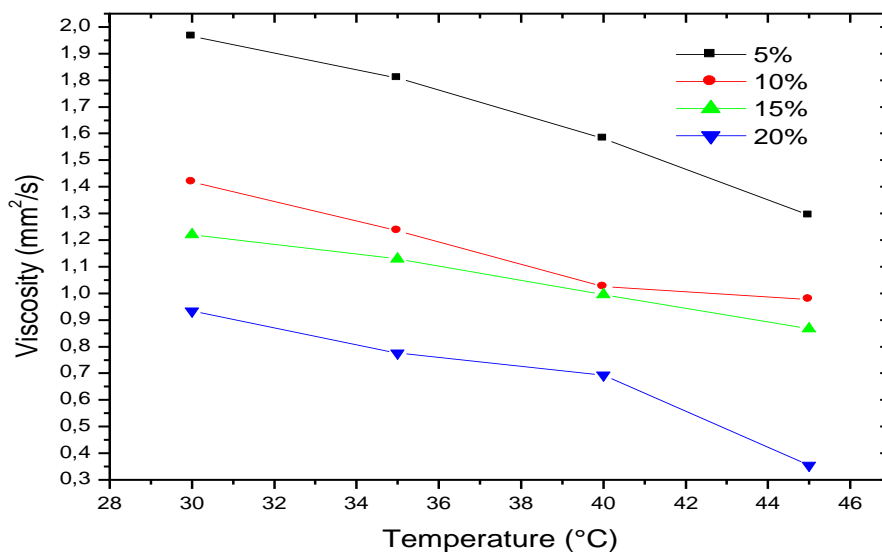


Figure 7. Temperature effect on the viscosity (mm²/s) of a pre-polymer TGETMEP.

The results shown in this graph are quite logical and expected by another authors¹⁷⁻²². The viscosity of the solution increases gradually as the temperature TGETMEP / methanol increases.

Likewise, the drop observed at the temperature 40 ° C to 20% is making the TGETMEP resin go from the viscous state to the liquid state.

Throughout the obtained curves of viscosity, we notice that the viscosity values increase with the concentration. This shows the progress of the reaction of the homopolymerization since viscosity

increases with increasing molecular weight of the solute. This may be related to the chemical transformations of the resin^{19,20}. We can expect the following actions:

- The addition of epichlorohydrin was not complete for the steric hindrance of the OH groups of the TMEP;
- The intervention of opening reactions of the regenerated epoxide cycles;
- An abnormality of adding the epichlorohydrin to the alcohol which can be represented Schematically by the following reaction:

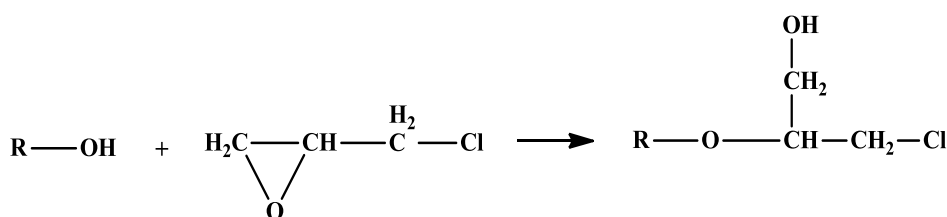


Figure 8. The addition of epichlorohydrin to the alcohol.

All these factors may influence the functionality of the obtained product. Therefore we would have the residual amines and hydroxyl which are presenting labile protons, which may be responsible for a self-crosslinking of the pre-polymer by adding the hardener¹⁹⁻²¹.

At 45 ° C and 20% of mass concentration²², the studied epoxy resin change from a viscous state

to a liquid state which explains the falling viscosity observed in **figure 6** and **7**.

Viscoelastic behavior of the prepolymer with the Rheometer Haake type Rheomat 01:

In this study, we have varied the viscosity according to temperature with the fixation of speed, which is represented in **Figure 9**.

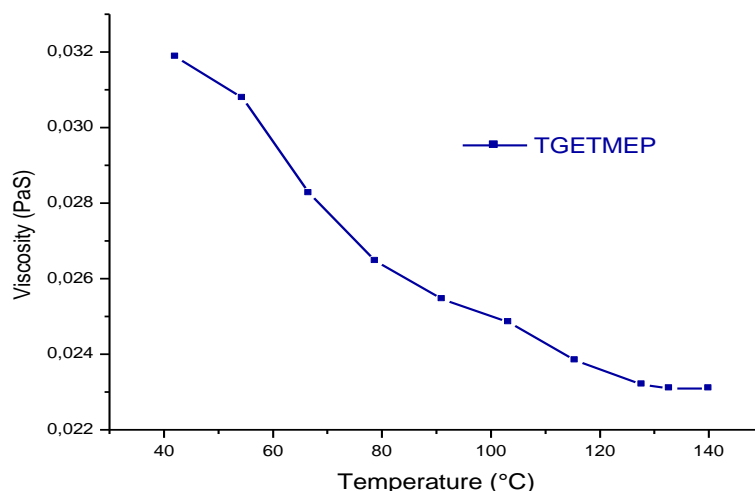


Figure 9. Viscosity according to temperature.

The viscosity of the TGETMEP resin decreases progressively with the increase of the temperature from 0 to 140 °C. From a temperature of 130 °C, the studied TGETMEP epoxy resin changes from a viscous state to a liquid state, this explains the constant in the observed viscosity.

The Rheological properties of the TGETMEP resin hardened and formulated by the tri-sodium phosphate Na_3PO_4 :

We studied the rheological behavior at fixed temperature of the standard TGETMEP resin and its composites TGETMEP / MDA, TGETMEP / MDA / 10% PTS TGETMEP / MDA / PTS 15%, according to the approach of the literature¹⁴ in order to get a better understanding of the structure / the rheological behavior namely the storage modulus G' and the loss modulus G'' . This technique is most often the key to understanding and improves the whole implementation. In this part, we focused on the study of the rheological behavior of the crosslinked matrix and its composites which consist of a dispersion of particles of the PTS load in the

epoxy matrix (TGETMEP). The rheological analyzes are obtained at the fixed temperature of 150 °C at a frequency range of 0.1 to 600 rad / s. Figures 10 and 11 show the storage modulus G' and the loss modulus G'' , for the cross-linked matrix and the formulations obtained by the dispersion of the filler at 10 and 15%. From the obtained results, we notice that adding the PTS load in the TGETMEP prepolymer significantly increases G' , and a slightly increases G'' . These changes of G' and G'' are consistent with the results obtained by Grich et al.²³ at the level of the dispersions of the load. They are equally consistent with the results found by Advani and Fan²⁴ who showed that the rheological properties depend on the optimization of the dispersion of the filler in the formulated matrix. The dispersed systems described in this study showed similar rheological properties to the previous work^{23,24} and these rheological results are synonyms to improve the physical properties of our formulated materials. In addition, and through these results we found that the addition of the PTS load gives a much observed increase with the percentage increase of the load.

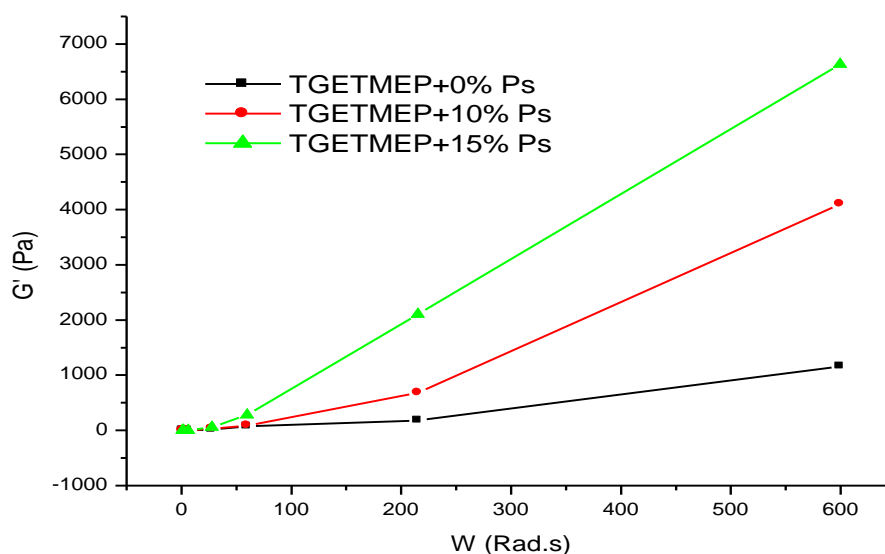


Figure 10. The modulus G' of composites according to a frequency range.

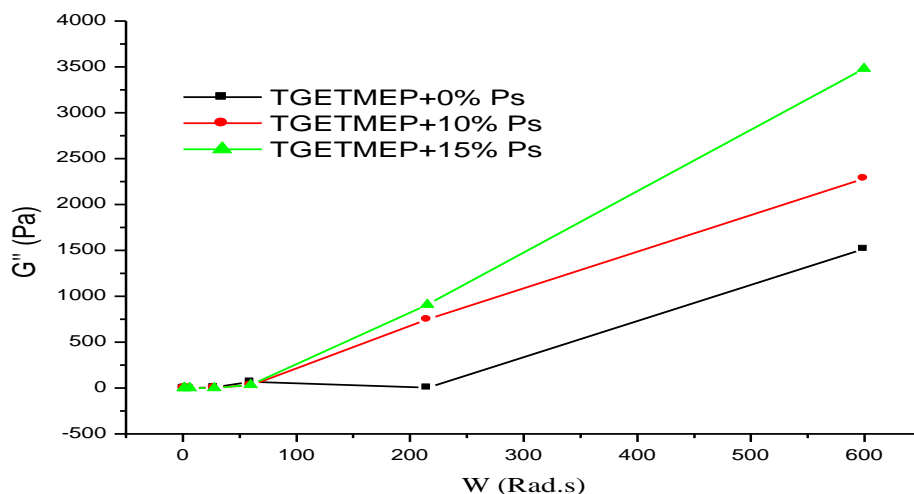


Figure 11. The modulus G'' of composites according to a frequency range.

Scanning electron microscope (SEM)

The study of the dispersion of the PTS load on the matrix TGETMEP by SEM, gave us an observation

of the morphology of the surface of our resin, with and without the load. Figure 12 shows the SEM morphologies of the state surface of our samples.

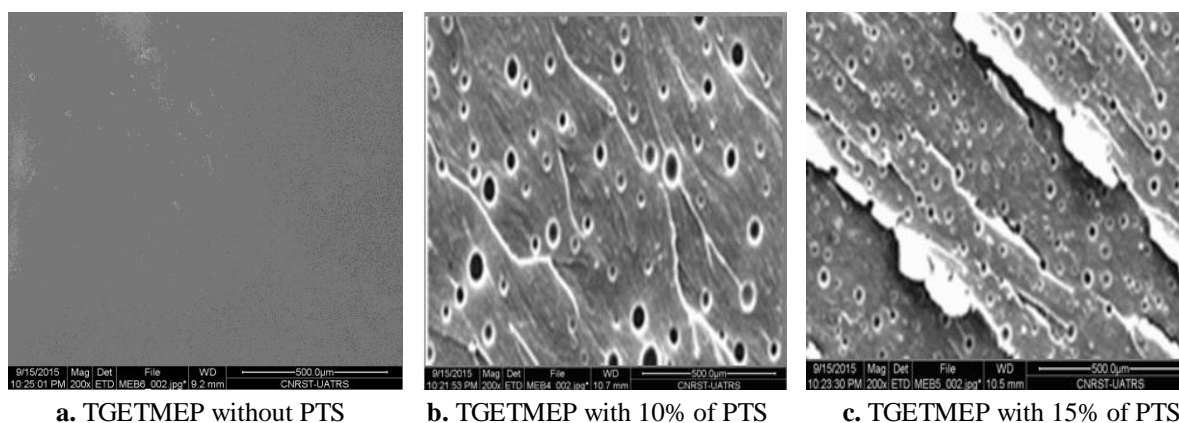


Figure 12. SEM morphologies of the surface of the crosslinked TGETMEP resin (a) without and with the PTS load (b and c).

The images obtained by the SEM clearly show the homogeneity of our composite surfaces made by different percentages of tri-sodium phosphate (TSP). This dispersion confirms the increase in rheological properties with increasing mass percentage. Indeed, a good dispersion of the filler in different percentages PTS is displayed in Figure 11 (b) and (c) respectively to 10 and 15% according to figure 12 (a) without the pre-load.

Conclusion

In this work, we synthesized, characterized and formulated new composite materials based on epoxy matrix triglycidyl ether Tri-Mercapto EthanPhosphore (TGETMEP). The used hardener is the methylene dianiline in the presence of the inorganic filler which is trisodium phosphate (TSP).

The prepared composite standards were studied by means of viscosimetric and rheological analysis. It is well noticed that the adding of the charge gives a clear idea on the flow properties and mechanical properties of the standard resin and crosslinked and formulated materials.

The results obtained from the addition of the load on the standard matrix gave an improvement of the rheological properties (storage modulus G' and loss modulus G'') which are improved by a dispersion of the TSP loading. The latter was well confirmed by the study in which we performed a measurement by the SEM.

References

- 1- A. Bekhta, T. EL Lambarki Alloui, A. Bouih, B. El Hilal, and A. EL Harfi, IJIAS, Aug. 2014, 7, pp. 1057-1070.

- 2- Z. Faiz; S. Fakhi; A. Bouih; A. Idrissi; Mr. Mouldouira, *J. Mater. About. Sci.* July **2012**, 3, pp 1129-1136.
- 3- B. Phillips, PS. Starcher, DL. Heywood, *Brevet francais no*, **1959**. 1,184, 527.
- 4- B. Phillips, FC. Frostick, *Brevet francais no*. 1,218,079, **1959**.
- 5- P. Schrade, *Brevet allement no*. 1,176,122, **1965**.
- 6- J. Leseq Bruneau, *Brevet francais no*. 1,562, 200, **1969**.
- 7- P. Castan, *Brevet anglais no*. 518,057, **1933**.
- 8- P. Castan, *Brevet US no*. 2,444,333, **1948**.
- 9- P. Castan, *Brevet anglais*, 518, 57, **1933**.
- 10- M. El Gouri, A. El Harfi, M. Rafik, S.E.Hegazi, M. Grich and H. Meghraoui, *Ref. O241008/83. Ph&Ch News* (**2009**).
- 11- R. Ziraoui, M.Grich, H. Meghraoui, A. Elharfi, *Ann. Chil. Sci. Mat.*, **2010**, 35, pp. 99-112.
- 12- P. Biginelli, *Aldehyde Urea Derivatives of Aceto- and Oxaloacetic Acids. Gazz. Chim. Ital.* 23, **1893**, pp.360-413.
- 13- Suresh Maddila and B. Sreekanth, *Jonnalagadda, Bull. Chem. Soc. Ethiop.*, **2012**, 26(1), pp. 121-126.
- 14- S. Fetouaki, A.Elharfi, L. Belkebir, *J. European. Polymer.* **2002**, 38, pp. 787-793.
- 15- A. Bekhta, and Ahmed EL Harfi, *IJIAS*, Aug. **2014**, 7 pp. 662-673.
- 16- A. Bekhta, *MJC, Mor. J. Chem.* **2015**, 3, pp. 458-464.
- 17- R. Hsissou and A. ELHarfi, *IJIAS*, Dec. **2014**, 9(4), pp.1651-1658.
- 18- P.G. De Genne, *Polymer Phys*, **1979**.
- 19- M. El Gouri, A. El Harfi, M. Rafik, S. E. Hegazi, M. Grich, H. Meghraoui, *J. Phys. Chem. News*, **2010**, 52, pp. 112-128.
- 20- De-Genne P. G., *J. Chem. Phys.*, **1968** 49, pp. 1032-1035.
- 21- I. Z. Chernin, F. F. M. Smekhov, Y. M. Zherdyaev., *J. Applied.Chemistry*, **2006**, 79 pp. 1673-1680.
- 22- J. El Azzaoui, N. El-Aouni, A. Bekhta, A. El Harfi, *Mor. J. Chem*, **2015**, 3, pp. 338-345.
- 23- M. Grich, M. El gouri, R.Ziraoui, N.Rami, H. Meghraoui, O.Cherkaoui, A.El harfi, *J. Mater. Environ. Sci.* **2014**, 5, pp. 374-379.
- 24- Z.Fan, S.G. Advani, *J. Rheol.* **2007**, 51, pp 585.