J. Mater. Environ. Sci. 7 (11) (2016) 3984-3992
ISSN : 2805-2508
CODEN: JMESCN

Study of mechanical properties of a composite based on a new tetra-functional epoxy polymer formula by TGEMDA and PTS

A. Bekhta *, O. Cherkaoui and A. El Harfi

[1] *Laboratory of Agroresource, Polymer and Process Engineering (LAPPE), Team of Organic and Polymer Chemistry (TOPC), Department of Chemistry, Faculty of Science, University Ibn Tofail, BP133, 14000, Kenitra, Morocco*

Received 30 Nov 2015, Revised 16 July 2016, Accepted 20 July 2016

**Corresponding Author. E-mail: abekhta@gmail.com ; Tel: (+212673545669)*

Abstract

In our work, we synthesized, characterized and made new composite materials based on epoxy matrix tetra glycidyl ether urea bisphenol S (TGEUBS) which we synthesized. The used hardener is the methylene dianiline (MDA) in the presence of two loads tri-sodium phosphate (TSP) and the resin tetraglycidyl methylene dianiline ether (TGEMDA) as an organic charge. The standard TGEUBS resin was characterized by the Fourier transform infrared spectroscopy (FTIR) and the nuclear magnetic resonance. So, we studied their visco-metric property using a capillary viscometer of hebbelod type while the cross-linked resins and the formulated tertiary and quaternary composites were studied by the rheometer.

Keywords: Composite materials, Epoxy matrix, tetraglycidyl ether urea bisphenol S, Viscometer, Rheometer.

Introduction

The different families of materials are crystals, polymers, and composites. A composite material is a material made up of several components [1, 2]: organic substances of nature or different other origins and various loads or organic and / or inorganic.
Thermosetting resins, including epoxy resins (ER) are important in the industry thanks to the many properties they offer and their easy implementation. They used in several areas especially electronics, sports, recreation, coatings, composites and radioactive wastes [3, 4], etc.
The polyepoxide resins are obtained by poly-condensation of two monomers having two opposing functions [5, 6]: epoxy pre-polymers derived from them are generally used in formulation in order to develop composites which comprise epoxy resins, fillers (mineral or organic) and a hardener as an additive. They often require viscosimetric and rheological studies [2] for applications in the packaging of radioactive waste (REI).

The knowledge of the rheological properties of these thermosetting materials on a wide range of temperature is necessary for understanding and mastering the storage conditions [7].The performance and quality of their implementation depends instinctively of their storage conditions. These rheological properties can also be related to the chemical structure or the degree of conversion of the prepolymer polyepoxide [8].

2. Materials and methods

2.1. The used equipment:

The basic chemicals are: Bisphenol S, urea, epichlorohydrin with a purity of 99%, methanol, triethyl amine, methylene dianiline, and tri-sodium phosphate. All these commodities were provided by the two companies Acros Chemical Co. and Aldrich Chemical Co. without any further purification.

2.2. The methods of analysis:

2.2.1. Nuclear magnetic resonance (NMR).

NMR (^{1} H) analyzes and NMR (^{13}C) were obtained by means of an apparatus of "AVANCE 300MHz Bruker" by dissolving the product in $CDCl_3$ at the ambient temperature. The chemical shifts are expressed in ppm and the couplings constant are expressed in Hz. The following abbreviations have been used: s, d, dd, t, q and m are respectively singlet, doublet, doubled doublet, triplet, quadruplet and multiplet.

2.2.2. Fourier transform Infrared analysis (FTIR).

The used IR spectrometer is BRUKER FTIR. The spectra were carried out in transmission on KBr pellets. The light beam passes through the sample to a thickness of about 2 * m. The analysis is performed between 600cm-1 and 4000cm-1.

2.2.3. The Viscosimetric analysis.

The viscosimetric analysis of the standard matrix was followed with a capillary viscometer of VB-1423 Ubbelohd tube.

The measurement conditions adopted are as follows:

- Viscometer of 1B size for a series of dilution, capillary tube of 0.46 mm diameter
- Constant k = 0.051493.
- Measuring temperature in °C: 30 up to 45;
- Number of measurement: 4 in each case
- Solvent: Methanol
- Hagenbach correction was calculated using the formula given in the norm DIN 51562-1Janvier 1999 (Measurement of kinematic viscosity by means of the Ubbelohd of viscometer).
- Solubilizing epoxy resin prepolymers in methanol was carried out under magnetic stirring at 20 ° C.

2.2.4. Rheological analysis.

The rheological analysis of the standard and the crosslinked matrix composites were made and followed with a rheometer Haake RHM01-RD (HAAKE MARS) on sample liquids, pastes and solids.

The measurement conditions adopted are as follows:

- Measuring temperature in ° C: 150 ° C
- Speed Mode CR: 10-8 0 1500 rpm.
- Speed Mode CS: 10-7 to 1500 rpm.
- Frequency: 10-5 to 100 Hz.
- Strength: 0.01 to 50 N.
- Torsion: 5.10-8 to 0.2 N.m.
- Control software: RheoWin.

2.3. Experimental Protocol

2.3.1. Synthesis of TGEUBS resin

The mono or multifunctional epoxy resins are generally synthesized in two ways, the first of which is based on two stages and the second on a single stage. The TGEUBS tetraglycidyl ether urea bisphenol S resin was synthesized according to the literature procedures [9- 13] obtained in this case by two steps:

1st step: UBS Product synthesis (Urea Bisphenol S) from urea and bisphenol S, using a protocol adapted by the Italian chemist "Pietro Biginelli" in 1893 [14, 15] is shown in Figure 1.

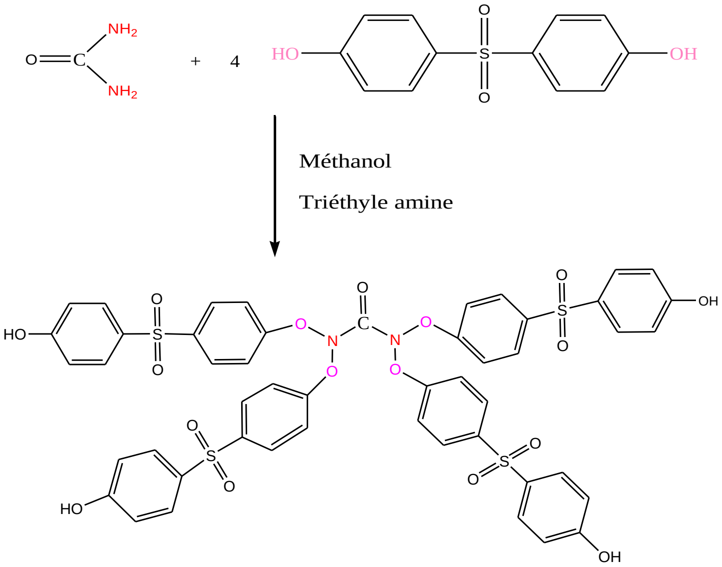

Figure 1: Synthesis of UBS.

2nd step: Polycondensation of epichlorohydrin on UBS are shown in Figure 2.

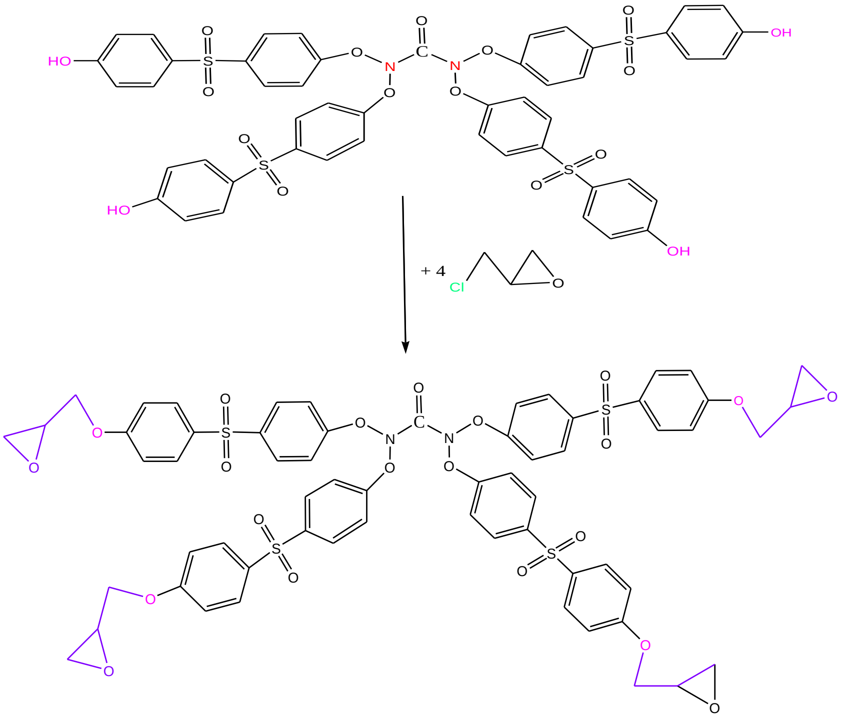

Figure 2: Synthesis of the new TGEUBS resin.

2.3.2. Sample preparation:

2.3.2.1. Preparation of viscosity:

To determine the viscometric behavior of the epoxy resin DGEUBS standard, we dissolved the resin in methanol at different concentrations (5%, 10%, 15% and 20%). Then, we studied their viscosities using a capillary viscometer of the type Ubbelohd at varying temperatures going from 30 °C to 50 °C.

2.3.2.1. Preparation of composites:

We thermally heated the following systems:

- TGEUBS / MDA
- TGEUBS / MDA / 5% TGEMDA
- TGEUBS / MDA / 5% PTS
- TGEUBS / MDA / TGEMDA 5% / 5% PTS

The systems are given below:

Image 1: Sample image obtained after the thermal heating.

3. Results and discussion

3.1. Structural study of the synthesized epoxy resin

We performed structural analysis of the epoxy resin obtained by the proton nuclear magnetic resonance (^{1}H NMR), carbon (^{13}C NMR), and confirmed the results by Fourier transform infrared spectroscopy. The results of structural analyzes which are given below have confirmed the structure of the synthesized epoxy resin TGEUBS.

3.1.1. Structural study by FTIR

The IR bands of the TGEUBS resin are shown in Figure 3.

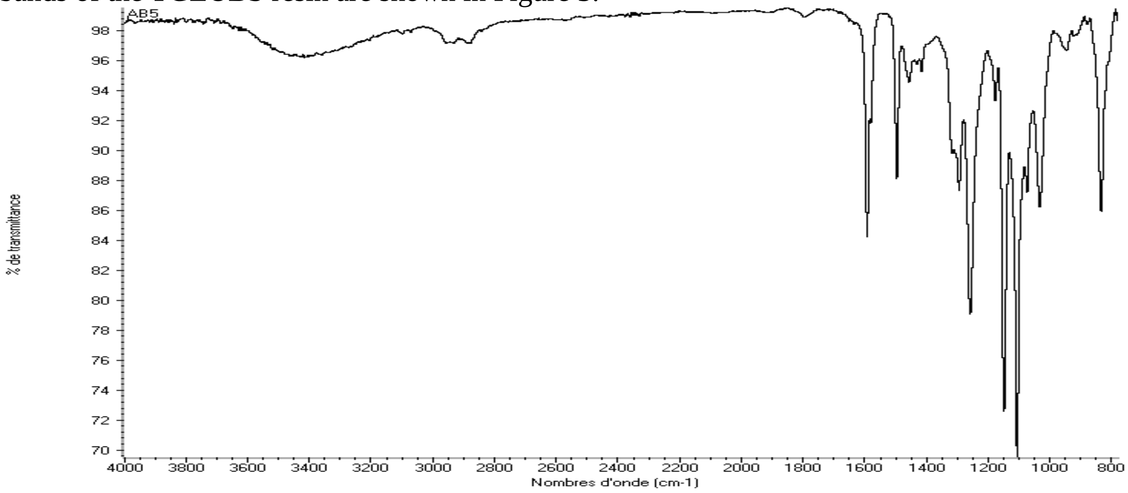

Figure 3: Analysis of the TGEUBS resin by FTIR.

The allocation of the different peaks obtained by means of infrared analysis in ATR mode is:
FTIR (cm^{-1}): 3400υ (residual OH), 1690 (C = O (carbonyl)), 1500 (aromatic C = C), 1300 (S = O = S (sulfone)), 1250 (O- aromatic), 1150 (CN), 1050 (CO) ethers, 815 (epoxide).

3.1.2. The NMR Structural study

We have strengthened the obtained results by the Infrared spectroscopic (IR) method by using 1H and 13C NMR. In ou case, we used CDCl3 as a solvent to solubilize the analyzed sample in the ambient temperature.

The results of the RMN the TGEUBS resin are respectively 3.1.2.1 and 3.1.2.2.

3.1.2.1. Nuclear Magnetic Resonance (NMR ^{1} H)

The Proton's NMR (NMR ^{1}H) in ppm: 2.3 and 2.4 (S. 2H of CH_2 of oxirane), 3.2 (S. 2H, oxirane CH), 4.2 (t 2H of CH_2 ether.), 5.4 and 5.6 (m, aromatic protons linked to O), 7.1 (s, aromatic protons bound to SO_2), 7.8 (s, aromatic protons linked to N).

3.1.2.2. Nuclear Magnetic Resonance (NMR ^{13} C)

The Carbon NMR (NMR ^{13} C) in ppm: 44.4 (S, CH_2 of the cycle oxiranes); 58, 1 (S, CH_2 linked to ether); 62,2-69,5 (S, CH of the cycle oxiranes); 115 3 (S, C = C of benzene linked to oxygen); 128.9 (S, C = C of benzene linked to O = S = O); 134.1 (S, C linked to oxygen); 143.3 (S, C the carbonyl (C=O)); 145, 1 (S, C the benzene linked to nitrogen); 162.4 (S, C linked to O = S = O).

3.2. The viscosimetric Study of the synthesized epoxy resin

As we mentioned previously, the viscosimetric properties can directly be related to the chemical structure or the degree of conversion of the reactive system [16- 19].

3.2.1. Viscosity according to Hebbelod type viscometer

The viscometric properties of the TGEUBS epoxy resin are studied by using a capillary viscometer of Ubbelohd type at varying temperatures going from 30 to 50 ° C. Determining the viscosimetric behavior of the epoxy resin is made after preparing the resin system / solvent. We dissolved the resin in methanol at different concentrations (5%, 10%, 15% and 20%), then studied their viscosity according to the massic concentration of the system resin/solvent by having the temperature fixed [12, 18] which is represented in Figure 4.

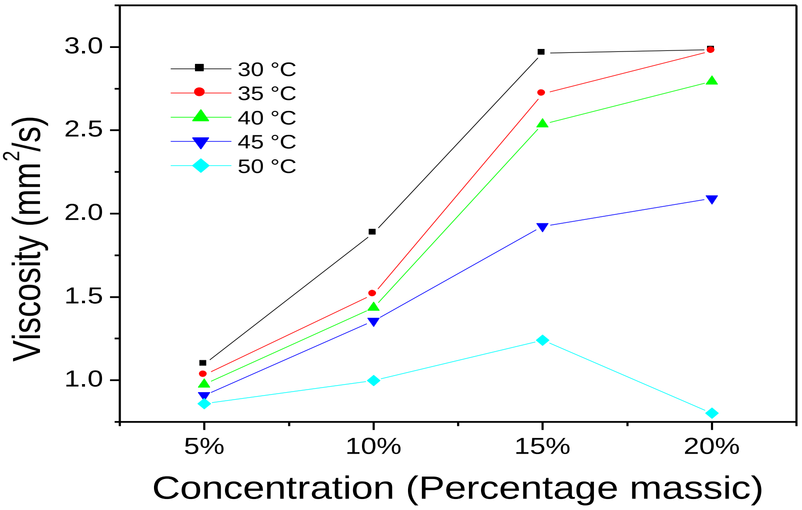

Figure 4: Mass concentration (%) effect on the viscosity (mm^2/s) of a pre-polymer TGEUBS/Methanol.

The results shown in this graph are quite logical and expected by another authors [16, 24]. The viscosity of the solution increases gradually as the concentration TGEUBS/Methanol increases. The observed decrease at the temperature of 50 ° C and 20% of TGEUBS/Methanol corresponds to the passage of the TGEUBS resin from the viscous state to the liquid one.

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 [20-22]. We can expect the following actions:

- The addition of epichlorohydrin was not complete for the steric hindrance of the OH groups of the UBS;
- 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:

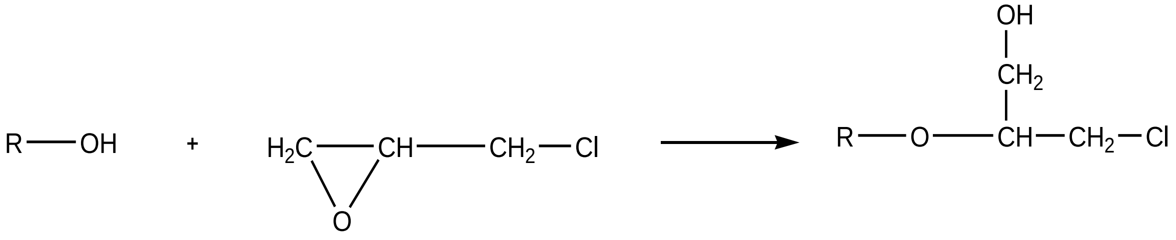

Figure 5: The addition of epichlorohydrin to the alcohol.

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 hardener [20, 22 and 23].

At 50 ° C and 20% of mass concentration [24], the studied epoxy resin change from a viscous state to a liquid state which explains the falling viscosity observed in figure 4. The chemical explanation of the temperature 50°C and the concentration massic 20% effect is the heat supplied accelerates the depolymerization process of the resin that it explains the observed fall.

3.2.2. Viscosity according to the rheometer of Rheomat 01 type

The viscometric property of the TGEUBS epoxy resin is studied by using a rheometer of Rheomat 01 type at varying temperatures from 0 to 180. In this study, we have varied the viscosity according to temperature with speed fixation. This is represented in Figure 6.

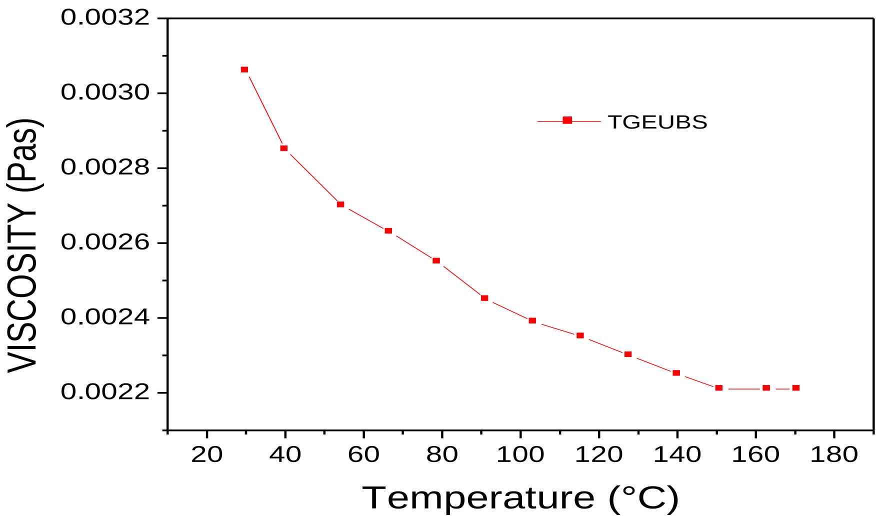

Figure 6: viscosity according to temperature.

The viscosity of the TGEUBS resin decreases progressively with the increase of temperature from 0 to 150 ° C. According to the temperature of 150 ° C, the TGEUBS epoxy resin goes from a viscous to a liquid state, which explains the constant in the observed viscosity.

3.3. Rheological studies of our synthesized products

We studied the rheological behavior of the standard TGEUBS resin and its composites TGEUBS / MDA, TGEUBS / MDA / PTS, TGEUBS/ MDA / TGEMDA, TGEUBS/ MDA / TGEMDA / PTS according to the approach of the literature [2] with the aim of a better understanding of the structure / rheological behavior. This technique is most often the key for understanding and improving the implementation. In this part, we focused on the study of the rheological behavior of the standard matrix, and the cross-linked composites which consist of a dispersion of particles of two charges in an epoxy matrix (TGEUBS). The rheological analysis of the matrix and composites were performed at 150 ° C at a frequency ranging from 0.1 to 600 rad / s. Figures 7, 8 and 9 show the storage module G' and the loss module G" for the matrix and the formulations obtained by the dispersion of the fillers of 5%. While the addition of fillers in the TGEUBS prepolymer considerably increases G ', there is only a slight increase in G ". These changes of G 'and G "are consistent with the results obtained by Grich et al. [2] for the dispersions of the filler, and by Fan and Advani [25] who showed that the rheological properties depend on the method of dispersion, the charge of ratios aspect, concentration, and the interaction between charges. As mentioned above, the dispersed systems described in this work showed rheological properties similar to previous works. These rheological results are synonymous, which improve the physical properties of our formulated materials. Moreover, in these results we found that the addition of the TGEMDA organic filler gives an increase better than the addition of the inorganic filler PTS. The addition of the two fillers (TGEMDA and PTS) provides a well observed increase.

3.3.1. Rheological properties of the standard resin

Figure 7 show the storage module G' and the loss module G" for the standard TGEUBS resin.

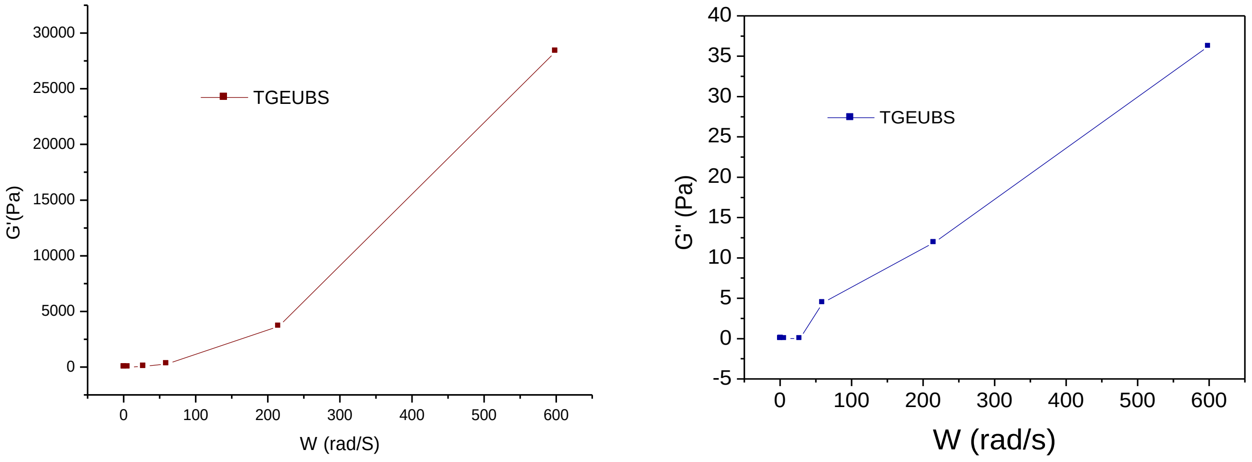

Figure 7: the modules G 'and G" of TGEUBS according to a frequency range.

3.3.2. Rheological properties of composites:

Figures 8 and 9 show the storage module G' and the loss module G" for the matrix and the formulations obtained by the dispersion of the fillers of 5%. While the addition of fillers in the TGEUBS prepolymer of composites according to frequency range.

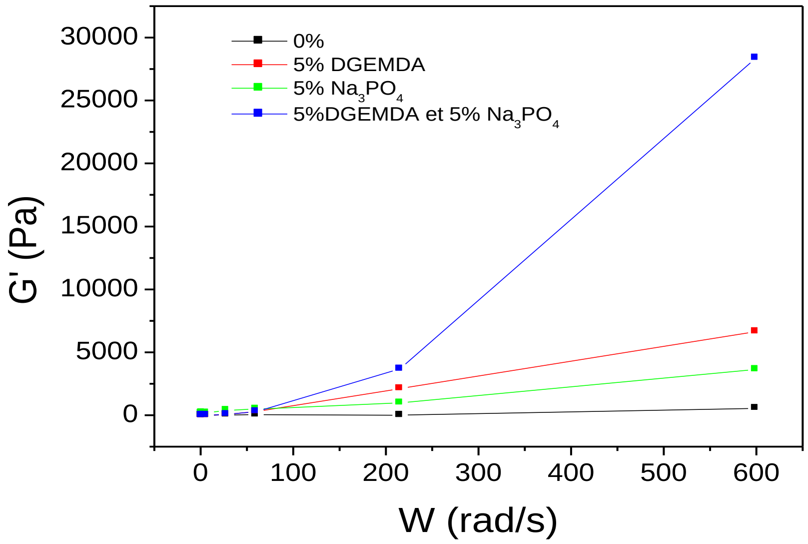

Figure 8: the module G' of composites according to frequency range.

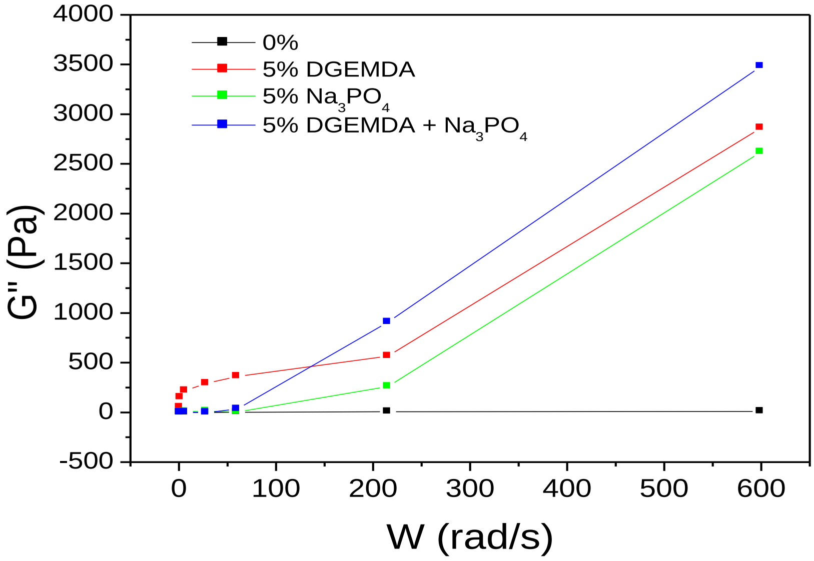

Figure 9: the module G'' of composites according to frequency range.

Conclusion

In this work, we synthesized, characterized and formulated new composite materials with epoxy matrix tetraglycidyl ether urea bisphenol S (TGEUBS). The used hardener is the methylenedianiline in the presence of two fillers namely tri-sodium phosphate as the inorganic filler and the tetraglycidyl methylenedianiline Ether resin (TGEMDA) as the organic filler.

The prepared composite standards were studied by means of viscosimetric and rheological analysis. It is well noticed that the adding of two charges gives a clear idea on the flow properties and mechanical properties of the standard resin and crosslinked and formulated materials. The results which are obtained from the addition of the two loads on the standard matrix give an improvement in the rheological properties over a single charge.

References

1. Ziraoui, R., Meghraoui, H., Rami, N., Cherkaoui, O., Choukri, A., Hakam O. K., Elharfi, A., J. *Ann. Chim. Sci. Mat.* 37 (2012) 85-96.
2. Grich, M., El gouri, M., Ziraoui, R., Rami, N., Meghraoui, H., Cherkaoui, O., El harfi, A., *J. Mater. Environ. Sci*. 5 (2014) 374-379.
3. BEKHTA, A., EL Lambarki Allioui, T., Bouih, A., El Hilal, B., EL Harfi A., *IJIAS*, 7 (2014) 1057-1070.
4. Faiz, Z., Fakhi, S., Bouih, A., Idrissi, A., Mouldouira, Mr., *J. Mater. About. Sci.* 3 (2012) 1129-1136.
5. Fetouaki, S., Elharfi, A., Belkebir, *L., J. European Polymer*. 38 (2002) 787-793.
6. Ziraoui, R., Grich, M., Meghraoui, H., Elharfi, A., *Ann. Chil. Sci. Mat*., 35 (2010) 99-112.
7. Ghosh, N. N., Kiskan, B., Yagci, Y., *J. Progress in Polymer Science*. 32 (2007) 1344-1391.
8. Lipatov Yu, S., physicochemical Foundations of Polymer Filling, *Moscow Khimiya Livre* (1991).
9. Castan, P., *English Patent*, No. 518.057 (1933).
10. Canadell, J., A. Mantecon, Cadiz, V., "*Polymer Degradation and stability"*, 92 (2007) 1934-1941.
11. Weichang, Liu., Varly Russell, J., Simon George, P., "*Polymer"*, 48 (2007) 2351.
12. BEKHTA, A., EL Harfi, A., *IJIAS,* 7 (2014) 662-673.
13. BEKHTA, A., El Azzaoui, J., El-Aouni, N., El Elhilal, B., Elharfi, A., *Mor. J. Chem.* 3 (2015) 458-464
14. Biginelli, P., Urea Derivatives Aldehyde of acetone and Oxaloacetic Acids. *Gazz. Chim. Ital.* 23 (1893) 360-413.
15. Suresh, M., and Sreekanth Jonnalagadda, B., *Bull. Chem. Soc. Ethiop.*, 26 (2012) 121-126.
16. Hsissou, R., Dagdag, O., EL Harfi, A., *J. Mor. Chem.* 3 (2015) 791-797
17. Genne P. G., *J. Polymer*, *Phys*, 1979.
18. El Gouri, M., El Harfi, A., Rafik M., Hegazi SE, Grich, M., Meghraoui H., *Ch Ph & News Ref.* O241008 / 83. (2009).
19. Ziraoui, R., Grich, M., Meghraoui, H., Elharfi, A., *Ann. Chil. Sci. Mat.*, 35 (2010) 99-112.
20. El Gouri M., El Harfi A., Rafik M., Hegazi S. E., Grich M., Meghraoui H., *J. Phys. Chem. News*., 52 (2010) 112-128.
21. Krasovskii A. N., Novikov D. V., Filippov V. N., Khim Russi P., *J. Chemis of Appli.* 77 (2004) 1382-1388.
22. De-Genne P. G., *J. Chem. Phys*., 49 (1968) 1032-1035.
23. Chernin I. Z., Smekhov F. F. M., Zherdyaev Y. M., *J. Applied. Chemistry*., 79 (2006) 1673-1680.
24. El Azzaoui J., El-Aouni N., Bekhta A., El Harfi A., *Mor. J. Chem*. 3 (2015) 338-345.
25. Bekhta A., El Azzaoui J., El-Aouni N., El Elhilal B., Elharfi A., *Mor. J. Chem*. 3 (2015) 458-464
26. Fan Z., Advani S. G., *J. Rheol.* 51 (2007) 585.

(2016) ; http://www.jmaterenvironsci.com/