Elaboration and Viscosimetric, Viscoelastic and Rheological Studies of a New Hexafunctional Polyepoxide Polymer : Hexaglycidyl Ethylene of Methylene Dianiline

R. Hsissou[1*], M. El Bouchti[2], A. El Harfi[1]

[1]*Laboratory of Agricultural Resources, Polymers and Process Engineering (LARPPE), Team of Polymer and Organic Chemistry (TPOC), Department of Chemistry, Faculty of Sciences, Ibn Tofail University, BP 133, 14000, Kenitra, Morocco*
[2]*Laboratory REMTEX, ESITH (Hight School of Textile and Clothing Industries), Casablanca, Morocco*

Abstract

In this work, we studied the viscosimetric, viscoelastic and rheological behavior of a new hexafunctional epoxy polymer: hexaglycidyl ethylene of methylene dianiline (HGEMDA) which is synthesized in the laboratory and its natural phosphate-based composite as loading. In the first stage, after the synthesis of the macromolecular matrix (HGEMDA), we crosslinked and formulated it in order to produce a thermosetting technological composite material in the presence of natural phosphate loadings at different percentages (0% , 5%, 10% and 15%) by adding methylene dianiline (MDA) as hardener. Secondly, we studied the viscosimetric properties of this epoxy prepolymer by the use of an Ubbelohd VB-1423 capillary viscosimeter and the viscoelastic and rheological properties by the use of a RHM01 type rheometer -RD HAAKE. It was very important to specify the influence of natural phosphate in the rheological behavior of nanocomposites based on macromolecular matrix and natural phosphate.

1. Introduction

Epoxy polymers are technologically and nanotechnologically thermosetting macromolecular matrices which are universally used as hyperlinks in the formulation of composite materials [1-2]. They hold an important place in the industry thanks to the numerous properties: thermal property [3], mechanical property [4], electrical property [5], dielectric property [6], properties of morphological and electrical conductivity [7], thermophysical properties [8], Viscosimetric properties [9-10] and rheological properties [11-12]. They are used in several fields such as electronics [13], coatings [14], inhibition [15], burial of radioactive wastes [16-17], aeronautics [18] and spatial construction [19].

The rheological behavior in dynamic regime is applied to a material exhibiting a linear viscoelastic behavior, and the corresponding stress is also sinusoidal, but it has a phase shift [20].

These two parameters define the complex module G whose real part G ' and the imaginary part (G") respectively define the conservation module and the loss module. Being so, the complex modulus G* is defined at all times as the stress ratio on the deformation.

This shear module can be decomposed into a real part G' which is called storage module and an imaginary part G" which is called loss module:

The loss factor is defined as the loss ratio module on the storage module.

The complex viscosity η, which can be decomposed into a real part η' and an imaginary part η", can also be defined from the complex modules in [21].

The aim of our study is thus to exploit the epoxy polymer synthesized in the viscosimetric, viscoelastic and rheological behavior of thermosetting materials over a wide temperature range necessary for understanding and controlling storage conditions (Module G') and the loss conditions (the module G") [10-22]. The incorporation of a natural phosphate loading into the polymer materials is intended to give new properties of the

specific functions [23-24]. In other words, the presence of the aditifs which are dispersed in the macromolecular matrix is used to improve the rheological properties [22]. In order to optimize and control the dispersed system, it is very important to specify the influence of natural phosphate on the rheological behavior of nanocomposites based on the HGEMDA and the natural phosphate.

In this work, after the synthesis of the prepolymer (HGEMDA) [25], we were mainly interested in the viscosimetric properties which play an important role in the implementation phenomena, namely the flow of the macromolecular matrix [26-27]. Then, this prepolymer (HGEMDA) was crosslinked and formulated by the natural phosphate loading, in order to quantify its viscoelastic and rheological performances which are based on the influence of temperature on the (HGEMDA/MDA/PN) system [10-28].

2. Materials and methods
2.1. *Materials used*

In this work, several products have been used among which we have listed the hexafunctional epoxy prepolymer: Hexaglycidyl Ethylene of Methylene Dianiline (HGEMDA) synthesized in the laboratory [25]. Methylene dianiline, natural phosphate and methanol. These products have been marketed by Aldrich Chemical Co.

2.2. *Methods used*
2.2.1. *Viscosimetric analysis*

Viscosimetric analysis of the unbound standard epoxy prepolymer was monitored by using a Ubbelohd VB-1423 capillary viscosimeter on the liquid samples.

The measurement conditions retained by the Ubbelohd VB-1423 capillary viscosimeter are as follows:
➢ Size 1B viscometer for dilution series, 0.46 mm diameter capillary tube and Constant k = 0.051493;
➢ Measuring temperature in °C: 30 to 60;
➢ Number of measurements: 3 each time;
➢ Solvent: Methanol;
➢ The Hagenbach Correction was calculated according to the formula given in the norm DIN 51562 January1999 (Measurement of kinematic viscosity by means of the viscosimeter Ubbelohd);
➢ Solubilization of the epoxide prepolymers in methanol was carried out at 25 °C with magnetic stirring;
➢ The capillary viscosimeter consists essentially of three tubular parts (1, 2 and 3), the capillary tube (6) with the measuring sphere (5). Above and below the measuring sphere (5), the annular marks M_1 and M_2 are printed on the tube (3). These marks define the control volume for the experiments.

2.2.2. *Preparation of the samples analyzed by the Ubbelohd VB-1423 capillary viscometer*

In order to determine the viscosimetric behavior of the synthesized hexafunctional epoxide prepolymer HGEMDA according to weight percentage and temperature, we dissolve this prepolymer in methanol at different concentrations (5%, 10%, 15% and 20%). Afterwards, we studied their viscosities by using the Ubbelohd VB-1423 capillary viscosimeter at temperatures ranging from 30 °C to 60 °C.

2.2.3. *Viscoelastic and rheological analysis*

The viscoelastic and rheological analyzes of the new crosslinked and formulated epoxy prepolymer were followed by using the RHM01-RD HAAKE rheometer on the viscous samples.

The measurement conditions used by the RHM01-RD HAAKE rheometer (Thermo Fisher (MARS)) are the following:
Temperature in °C: 80 °C;
Rotation speed CR mode: 10-8 0 1500 rpm;
Frequency: 10^{-5} to 100 Hz;
Force: 0.01 to 50 N;
Torsion: 5.10^{-8} to 0.2 Nm;
Control software: RheoWin.

2.2.4. *Preparations of the samples analyzed by the rheometer*

The presence of the epoxide prepolymer and methylene dianiline produces a curing of the prepolymer as a result of the self-crosslinking reaction. The protocol consists of preheating the stoichiometric amounts of the prepolymer and the hardener. The methylene dianiline (MDA), crystallized at ambient temperature, is placed in an oven at 120 °C (a temperature above its melting point), while the prepolymer is heated to 60 °C. Once melted, the MDA is then mixed with the prepolymer to give a single fluid phase at 70 °C for 1 hour. The crosslinking reactions are carried out by a primary diamine, methylene dianiline (MDA), known for its excellent mechanical properties and good thermal stability which it provides to the final product in comparison to the other hardeners [29]. Its structure is given in the diagram below.
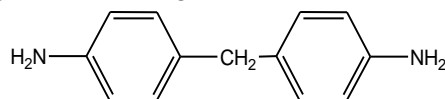
Scheme 1: Developed formula of methylene dianiline (MDA)

This hardener has a functionality which is equal to four, which means that during the crosslinking reaction with a hexafunctional resin (HGEMDA), the two amine functions theoretically react with twelve epoxide functions when they are in stoichiometric proportions [30-31]. By applying the above protocol to the reaction of the self-crosslinking of the prepolymer in the presence of methylene dianiline as a hardener and natural phosphate at different percentages (0%, 5%, 10% and 15%) as loading, we obtained the samples whose loading is well dispersed in the base matrix after extensive mixing.

2.2.5. *Ration calculation*
2.2.5.1. *Calculation of stoichiometric coefficients*

In order to obtain optimum properties when we have cured the multifunctional polyepoxide prepolymer in the presence of hardener (especially amines), it is desirable to make the prepolymer and the curing agent react in approximately stoichiometric amounts.
Calculation of the epoxy equivalent weight (EEW) of the synthesized prepolymer (HGEMDA)

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

With *f* as the functionality of the epoxy resin.

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

$$EEW = 158.7 g / eq$$

Calculation of the amine equivalent (Amine Hydrogen Equivalent Weight: AHEW)
The AHEW then constitutes the mass of the hardener containing an amine equivalent

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

Methylene dianiline:
$M_w = 198; f = 4$

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

$$EEW = 49.5 g / eq$$

2.2.5.2. *Calculation of the ration by weight*

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

$$A\min e \ \text{PHR} = \frac{AHEW}{epoxy \ \text{equivalent}} \times 100$$

In this case of the HGEMDA:

$$PHR \ \text{Amine} = \frac{49.5}{158.7} \times 100$$

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

Therefore, it will be necessary to react 31 g of methylene dianiline per 100 g of HGEMDA to reach the optimum of properties once we cure the prepolymer with methylene dianiline.

2.2.5.3. *Calculation of the ration to the quantity of the load*

We calculated the quantity of the desired charge according to the following equation:

$$y\% = \frac{x}{re\sin + MDA + x}$$

x shows the amount of the HGEMDA resin
y shows the amount of the natural phosphate charge

3. Results and discussion
3.1**.** *Viscosimetric behavior*
3.1.1. *Viscosimetric behavior of the standard prepolymer*

The different curves of the viscosity according to the weight percentage and the temperature of the synthesized epoxide prepolymer hexaglycidyl ethylene of methylene dianiline dissolved in methanol are shown successively in figures 1 and 2. From these figures, we have found that the viscosity values increase as the prepolymer mass concentration increases. This shows the progress of the homopolymerization reaction since the viscosity increases with the increase in the molecular mass of the solute. This is related to the chemical transformations undergone by the prepolymer [32-33].
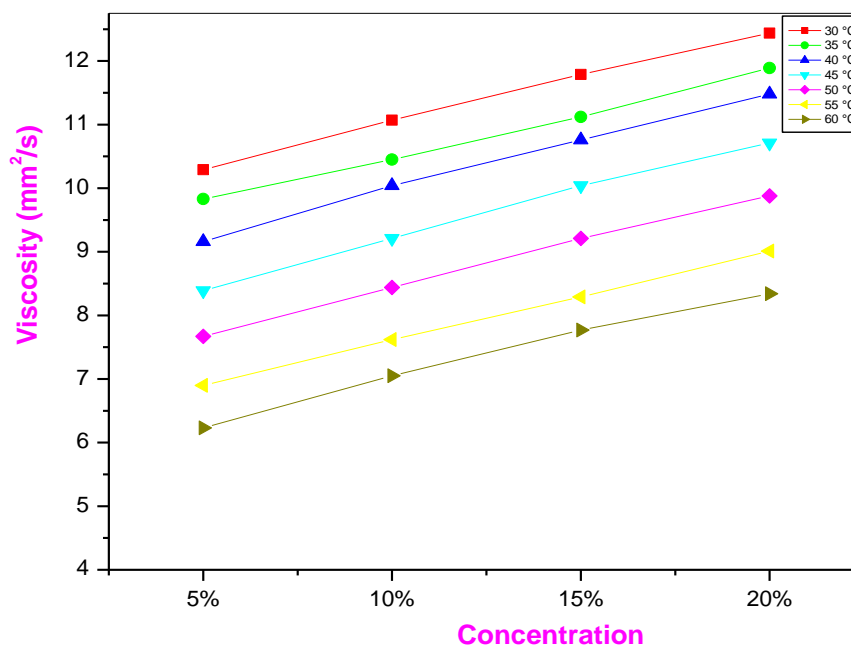

Figure 1: Variation of the viscosity of the standard prepolymer according to weight percentage at different temperatures
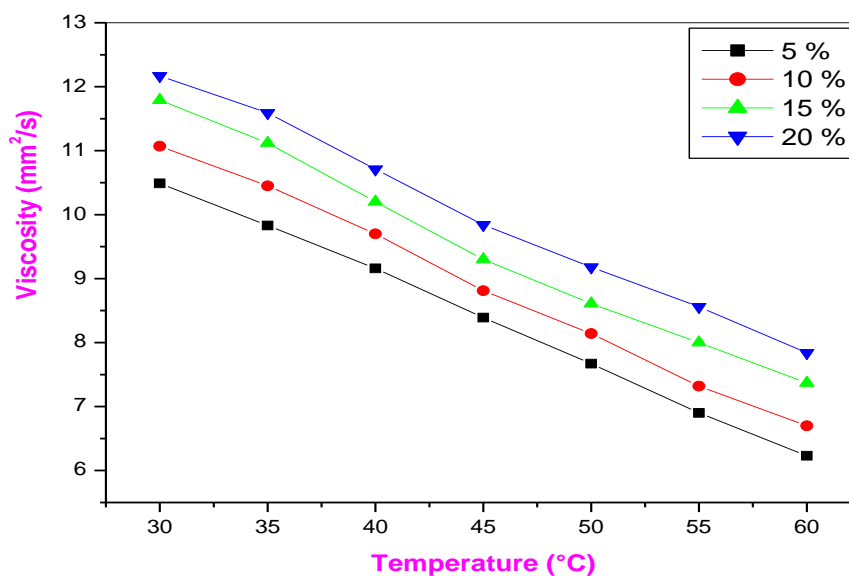
Figure 2: Variation of the viscosity of the standard prepolymer according to temperature at different concentrations

Indeed, the increase in temperature implies that the HGEMDA prepolymer changes from a viscous state to a liquid state, which explains the fall in the observed viscosity (figure 2) [34].

We can therefore cite the following causes:

The addition of the epichlorohydrin was not complete because of the steric hindrance of the NH_2 groups;

The intervention of the opening reactions of regenerated epoxy cycles;

An anomaly of addition of the epichlorohydrin to the amine which can be schematized by the following reaction:

Scheme 2: Addition of epichlorohydrin to the amine

All these factors can have an influence on the functionality of the obtained product, therefore, allowing us to have the residual amines and the hydroxyls which exhibit the labile protons. The latter are both responsible for self-crosslinking of the prepolymer by acting as a hardener.

It emerges from these analyzes that the hexafunctional prepolymer, hexaglycidyl ethylene of methylene dianiline (HGEMDA), has a thermostability which makes it possible to avoid self-crosslinking during storage.

3.1.2. *Viscoelastic behavior of the cross-linked prepolymer*

Rheology relates to the study of the flow, deformation, elasticity and viscosity of the material in question, but we have been interested in the viscoelastic behavior of the crosslinked prepolymer (HGEMDA/MDA) since it plays a primordial role in the phenomena of flow of the macromolecular matrix. Our rheological study of the standard matrix based on epoxy prepolymer HGEMDA and MDA yields the viscosity under the effect of rotation constraint and under a controlled atmosphere in view of temperature is presented in figures 3. Figure 3 shows the characteristics of the rheological behavior of the crosslinked hexafunctional resin in view of temperature. The gelling time for different temperatures decreases with the increase of temperature because the supplied heat accelerates the depolymerization process of the resin. In this figure, we notice the plot of four phases, namely:

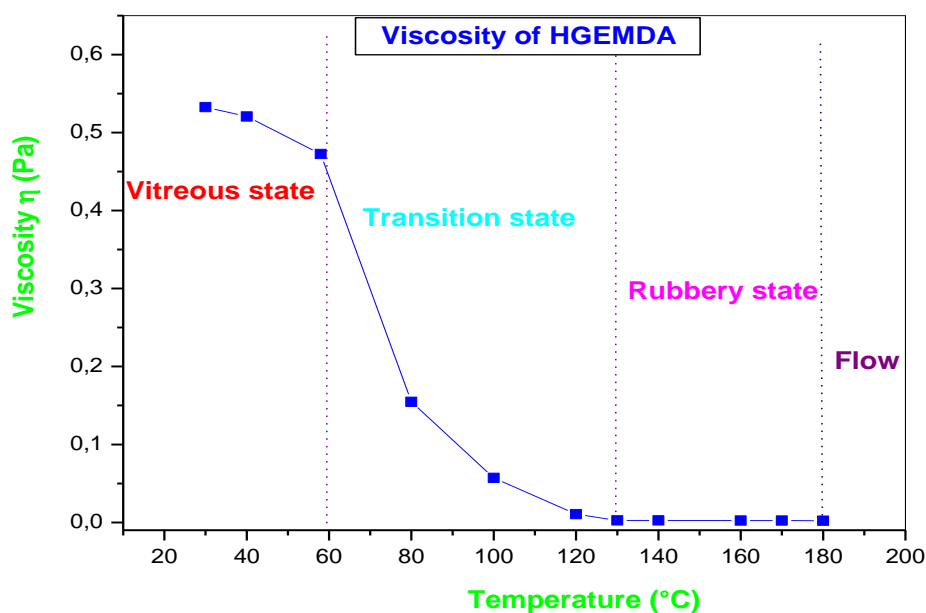Vitreous state: At low temperature and reduced viscosity, the molecular mobility is high.

Figure 3: Different states of the viscoelastic ɳ of the crosslinked prepolymer in view of temperature T

Transition state: A slight increase in temperature can induce a significant increase in the molecular mobility and a decrease in viscosity.

Rubbery state: At higher temperature and high molecular mobility, the viscosity is not limited. It is flexible, but has no flow.

Flow: At high temperature and totally free molecular mobility, the viscosity is reduced.

The viscosity depends strongly on temperature to maintain a sense of measurement in which we specify the temperature at which it was made. In a liquid, the viscosity decreases rapidly in view of temperature. This result allowed us to confirm the study of the viscosimetric behavior of Ubbelohd type.

3.2. *Experimental determination of the temperature of the vitreous transition Tg*

The thermal behavior of the viscoelasticity clearly shows the existence of the phase transition, that is to say the transformation of the viscous state into the rubbery state. From figure 3, we have deduced the glass transition temperature which is equal to 130 °C.

3.3. *Experimental determination of the activation energy Ea*

Activation energy is a concept introduced in 1889 by the Swedish scientist Svante August Arrhenius after having noticed the empirical law that describes the evolutions of viscosity with temperature. In this law, there appears a term called activation energy. The Arrhenius equation $ɳ = ɳ_0 \exp(-Ea/RT)$ allowed us to calculate the activation energy value from the Arrhenius slope as in figure 4.

$ɳ$: Viscosity (Pa);

$ɳ_0$: obtained viscosity whose ordinate at the origin (Pa);

E_a: Activation energy (J / mole);

R: Perfect gas constant (8.314 J.mol^{-1} K^{-1});

T: Temperature in Kelvin ($\Theta + 273$).

Figure 4 shows the variation of the logarithm of the viscosity in view of the inverse of temperature. This variation is a straight line which is based on the Arrhenius relation and from which we calculated the activation energy. From this figure, we have obtained a straight line whose slope (Ea/R) is equal to **0,57**. Finally, we obtained the activation energy which is equal to **4, 7314 J / mole**.
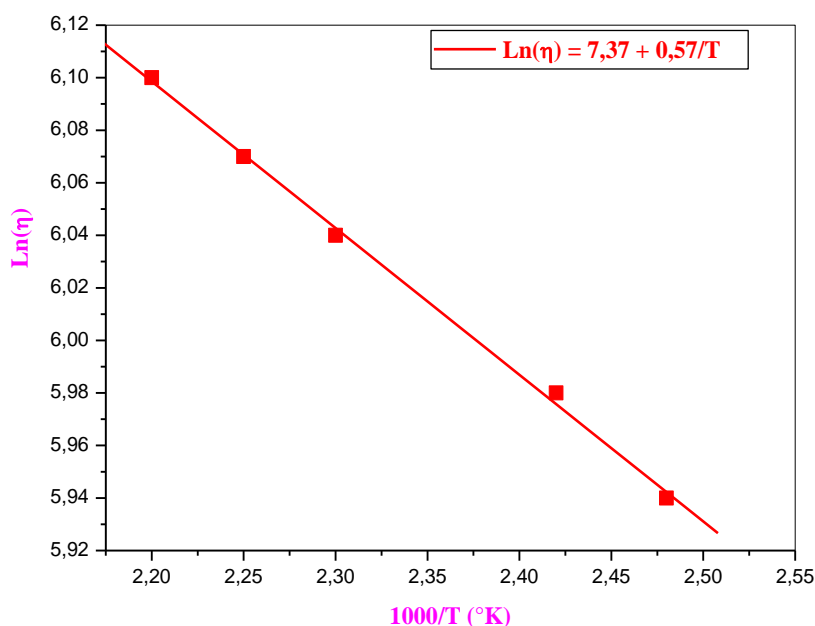
Figure 4: Variation of Ln (Ɲ) in view of the inverse of the temperature

3.4. *Determinations of thermodynamic parameters*

3.4.1. *Determinations of the Enthalpy variation of activation ΔHa, the variation of Entropy of activation ΔSa and the variation of the activation free Energy ΔGa*

An alternative formula of the Arrhenius equation allows the determination of the enthalpy variation and the entropy variation according to the following equation.

$$\eta = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a}{R}\right)\exp\left(\frac{\Delta H_a}{RT}\right)$$

$$Ln(\frac{\eta}{T}) = Ln(\frac{R}{Nh}) + \left(\frac{\Delta S_a}{R}\right) + \left(\frac{\Delta H_a}{RT}\right)$$

N: Number of Avogadro (6.023×10^{23} mole^{-1});

h: Planck constant (6.62×10^{-34} J.S);

ΔHa: Enthalpy variation of activation;

ΔSa: Variation of activation Entropy.

Figure 5 shows the variation of the Ln (Ɲ/T) in view of the inverse of the temperature. We have obtained a straight line whose intercept is equal to (ln (R/Nh) + ΔSa / R) and a slope equal to (ΔHa/R). From this figure, we have deduced the values of the activation enthalpy variation ΔHa and the activation entropy variation ΔSa, which are respectively equal to **- 8.1726 J / mole** and **- 77.990 J / mole**. The negative value of the activation enthalpy variation ΔHa means that the reaction is exothermic. This explains the released heat which accelerates the process of depolymerization of the hexafunctional resin. The negative value of the entropy variation means that there is a decrease in the disorder during the depolymerization of the hexafunctional resin.

The variation of activation free energy ΔGa is the difference between the variation of the free enthalpy of the activated and non-activated states which is expressed in view of ΔHa as the change in enthalpy of activation and ΔSa as the variation of Entropy of activation by the following equation: ΔGa = ΔHa - T ΔSa.

From this relation, we have deduced the variation of activation free energy ΔGa equal to **- 23.249 KJ / mole.**
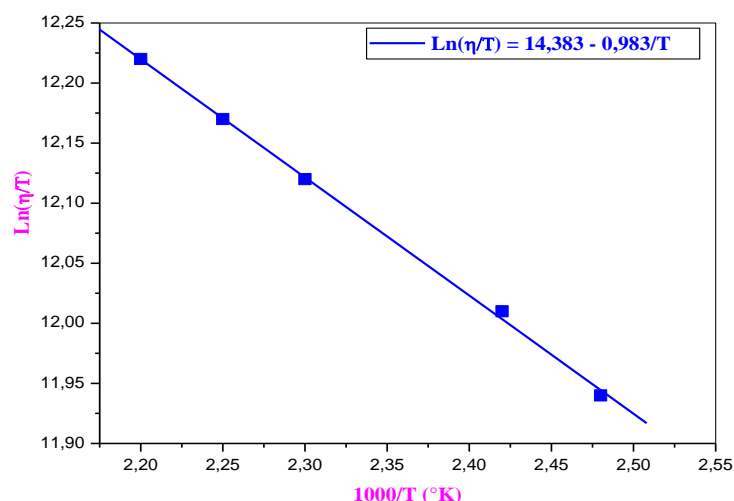
Figure 5: Variation of Ln (Ɲ / T) in view of the inverse of the temperature

3.5. *Behavior of the complex viscosity of the crosslinked prepolymer*

Figures 6 and 7 reciprocally show the evolution of the complex viscosity of the crosslinked prepolymer according to frequency and angular velocity, corresponding to an increasingly marked exfoliation. We therefore understand that it should be possible to relate these rheological data to a parameter characterizing the level of exfoliation. Finally, the obtained structures are in fact relatively complex and can evolve in view of frequency and the angular velocity of the flow conditions.
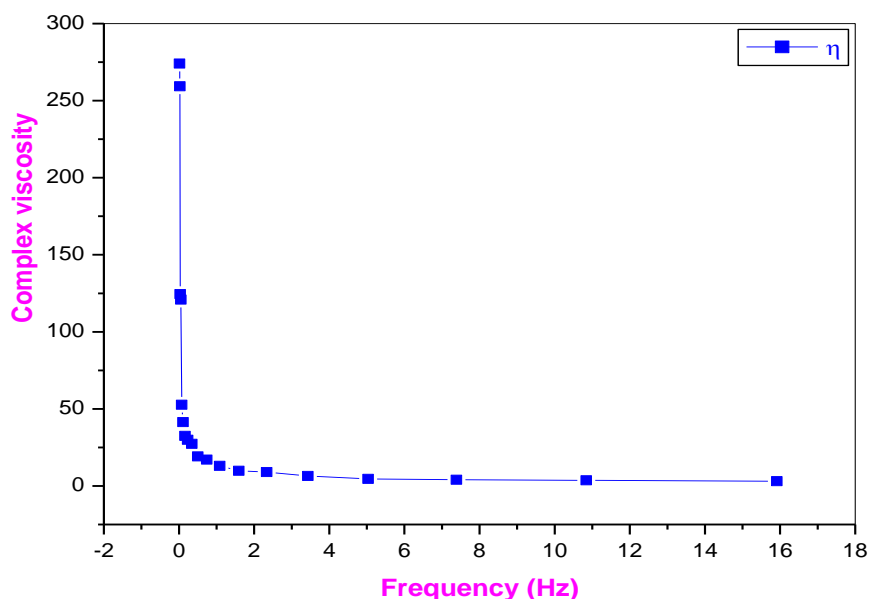

Figure 6: Variation of the complex viscosity in view of frequency

Figure 6 clearly show the behavior of the complex viscosity and that the complex viscosity decreases with increasing frequency. Indeed, the increase in frequency implies that the HGEMDA prepolymer passes from a viscous state to a liquid state, which explains the drop in the observed viscosity, on the other hand. Therefore, it is necessary to store the synthesized prepolymer at low frequency (0.5 Hz).
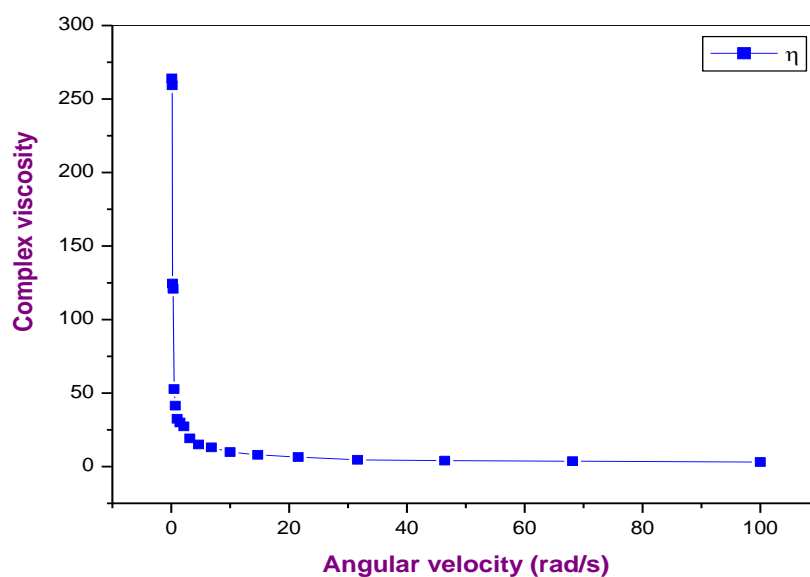
Figure 7: Variation of the complex viscosity in view of angular velocity

Figure 7 clearly shows once again the behavior of the complex viscosity and that the complex viscosity decreases with the increase of the angular velocity on the one hand. The increase in angular velocity implies that the prepolymer HGEMDA passes from a viscous state to a liquid state, which explains the fall in the observed viscosity on the other hand. This result confirms the result of the complex viscosity in view of frequency and that of the viscosity in view of temperature. Therefore, it is necessary to store the synthesized prepolymer at low frequency and at low temperature.

3.6. *Elastic rheological behavior (conservation or storage modulus G') and vitreous (loss modulus G'') of the crosslinked and formulated prepolymer*
In this part of the work, we focused on respectively the study of the elastic behavior, rheological properties (storage modulus or storage G') and the glassy behavior (loss modulus G''). The polymer nanocomposites (HGEMDA/MDA/PN) studied in different formulations were introduced into the cell of the rheometer Haake RHM01-RD. The rheological analyses of nanocomposites (HGEMDA/MDA/PN) were carried out at 150 °C under the action of a range of variable frequencies of 0.1 to 100 rad/s.

3.6.1. *Variation of the elastic behavior G' and glassy G'' in view of rotation speed*
Figures 8 and 9 respectively show the elastic behavior G' (storage modulus) and of the glassy behavior G'' (loss modulus) of the prepolymer crosslinked and formulated according to the rotational speed. These measurements of elastic behavior G 'and glassy G'' show that the response of the polymeric materials is of a liquid type.

According to these figures, we found that the variation in elastic behavior G' and glassy behavior G'' of the prepolymer crosslinked and formulated with the increase of the rotational speed decreases to the initial deformation γ_0, above which the response of the prepolymer is of a gel type and below which it is of a liquid type. The measurements of elastic behavior G' and glassy behavior G'' clearly show that the increase of the rotation speed induces a transition from a gel behavior to a liquid behavior.

3.6.2. *Evaluation of the elastic behavior G' and glassy behavior G'' in view of the frequency and the angular velocity of the crosslinked and formulated prepolymer*
According to the literature in the elastic and glassy rheological behavior in view of frequency and angular velocity of nanocomposites show a better understanding of structure , their flow and their implementation depending on the nature of the loading namely the Phosphate.
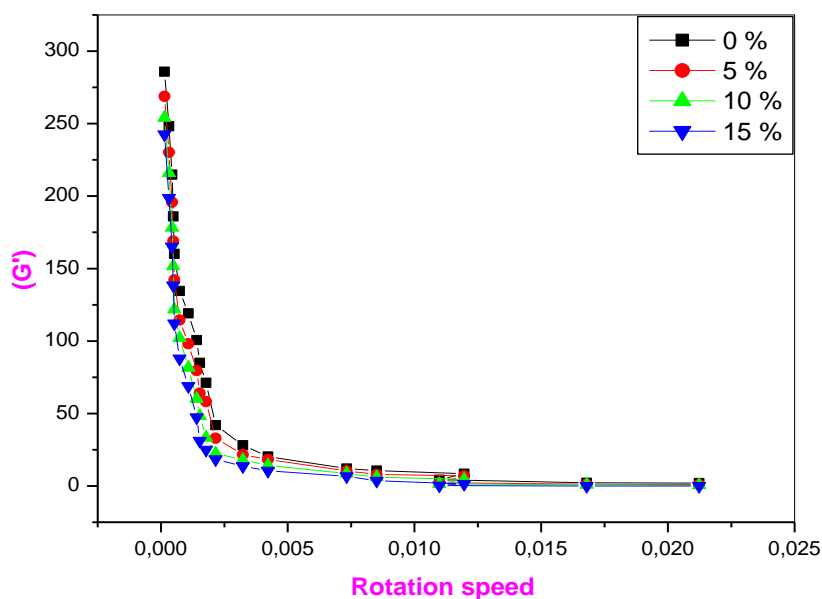
Figure 8: Elastic behavior G' in view of the rotation speed of the formulations (HGEMDA/MDA/PN)
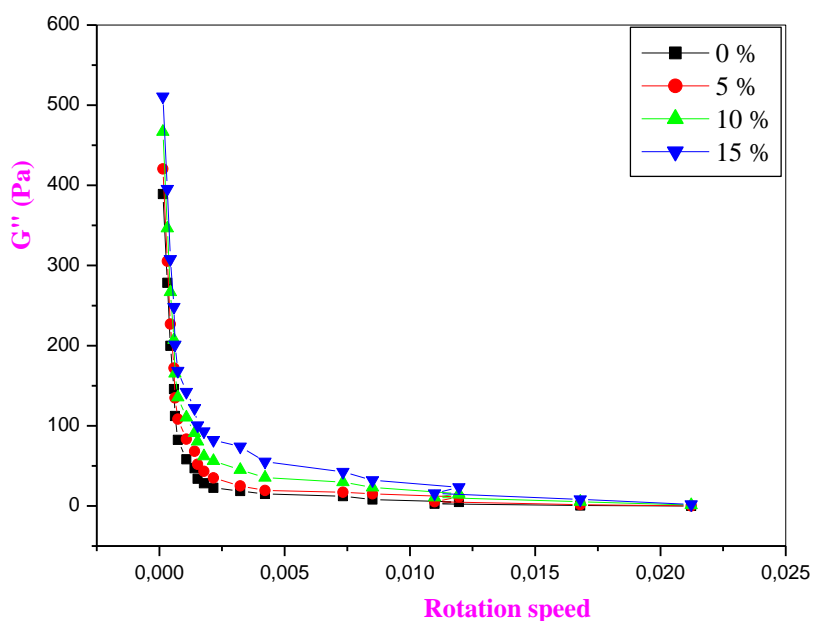

Figure 9: Glass behavior G " in view of the rotation speed of the formulations (HGEMDA/MDA/PN)

These rheological behaviors of the nanocomposite in view of frequency and angular speed have been studied at low constraint (typically 0.1 Pa) to be placed in the well linear viscoelastic region. The rheological behavior of the (HGEMDA/MDA/PN) is presented in the following figures 10, 11, 12 and 13.

Figures 10 and 11, which are showing the storage module G' and the loss module G" in view of frequency, also show the increase of these latter in view of frequency. They also show that the variation of elastic behavior G' and of vitreous behavior G" increases with the percentage of the charge of the natural phosphate incorporated in the epoxy matrix. This explain the fact that the formulation of the composite (HGEMDA/MDA/PN) is well cured.
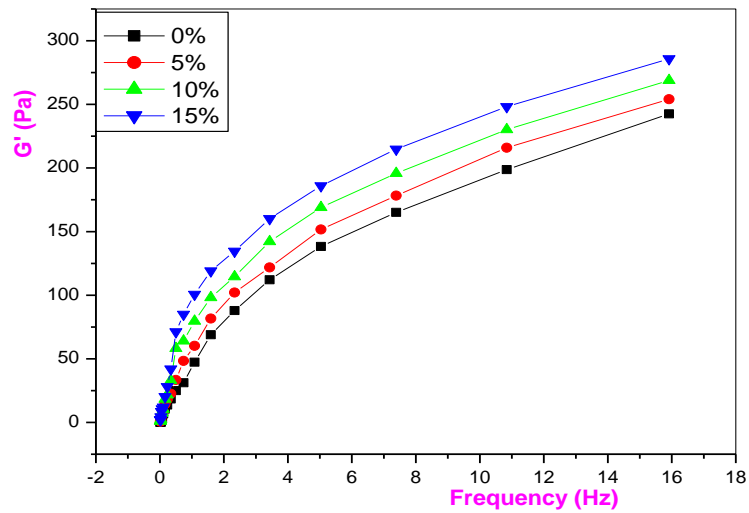
Figure 10: Variation of the elastic behavior G' in view of formulations' frequency (HGEMDA/MDA/PN)
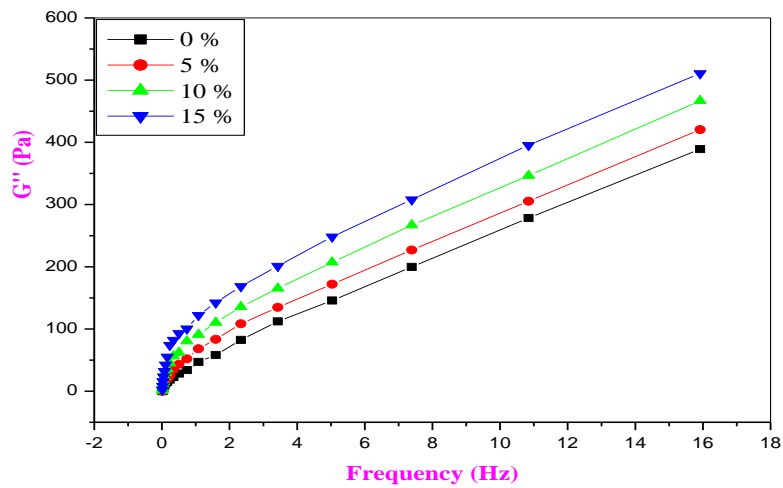

Figure 11: Variation of the glassy behavior G" in view of formulations' frequency (HGEMDA/MDA/PN)
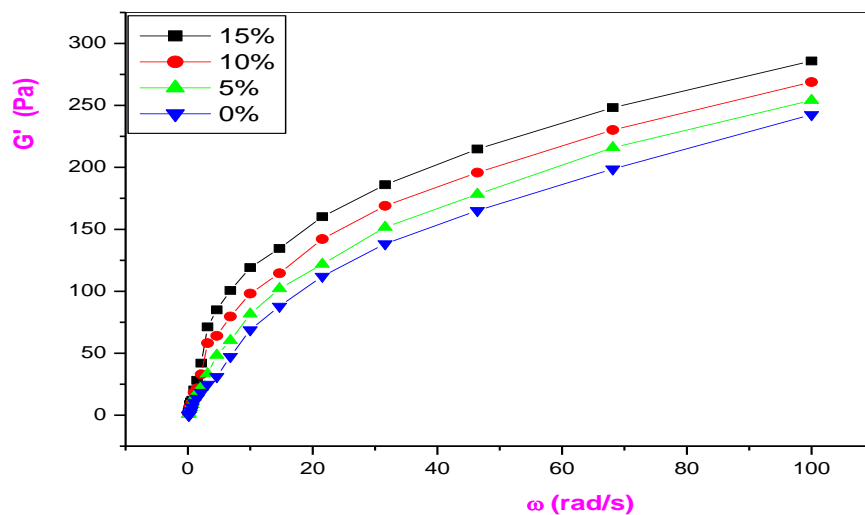

Figure 12: Variation of the elastic behavior G' in view of the angular velocity of the formulations (HGEMDA/MDA/PN)
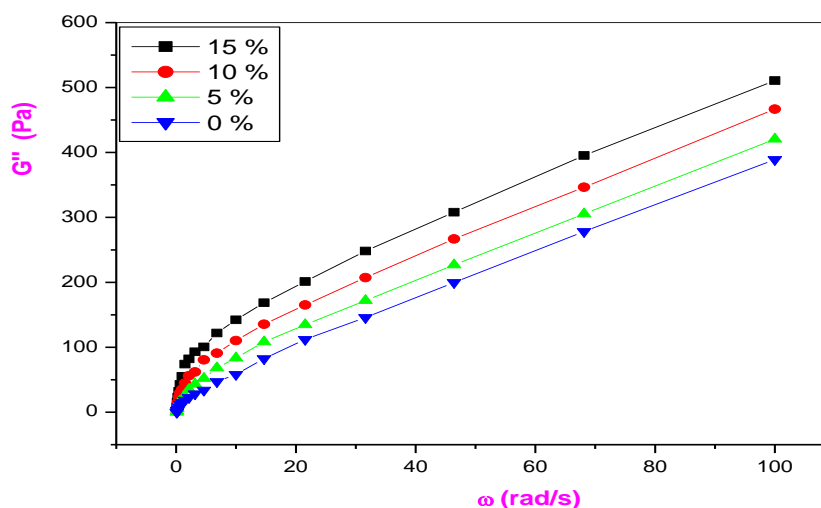
Figure 13: Variation of the glassy behavior G " in view of the angular velocity of the formulations (HGEMDA/MDA/PN)

Figures 12 and 13 - presenting the conservation or storage module G' and the loss module G'' in view of the angular velocity - clearly show the increase of the latter in view of the angular velocity. On the one hand, we observed a regular increase in the elastic behavior G' and the vitreous behavior G" with low-frequency, indicating the progressive reorganization of the structure. On the other hand, we observed that the variation in the elastic behavior G' and the vitreous behavior G" increases with the percentage of the charge of the natural phosphate incorporated in the epoxy macromolecular matrix. These results of the studies of the elastic behavior G 'and the glassy behavior G" as a function of the angular velocity confirm the results of the elastic behavior and of glassy behavior as a function of the frequency.

Conclusions

In this work, we synthesized the standard epoxy hexaglycidyl ethylene prepolymer of methylene dianiline (HGEMDA) from which we developed a hexafunctional polymer cured through MDA and formulated by natural phosphate. We carried out, through these structures, the viscosimetric studies in view of the mass concentration and the temperature by using an Ubbelohd VB-1423 capillary viscosimeter on the one hand, and the rheological study of the crosslinked prepolymer formulated at by natural phosphate by using a rheometer of type RHM01-RD HAAKE, on the other hand. The results obtained from the viscosimetric study of the standard hexafunctional epoxy prepolymer allowed us to have a clear and precise idea of its viscoelastic properties since the variation of the viscosity in view of the concentration increases and that of temperature decreases. This confirms the results of the viscoelasticity. In other words, for this crosslinked product, we have deduced the different viscoelastic states of the thermal behavior of the thermosetting polymers in view of temperature. This result allowed us to notice a plot of four phases, namely the vitreous state, the transitory state, the rubbery state and the flow state), which conform to the appearance of the multifunctional epoxy prepolymers synthesized in the laboratory (triglycidyl ether ethylene of bisphenol A (TGEEBA)). We have noticed the variation of the complex viscosity which decreases in view of rotation speed. In the context of the study of the behavior of the crosslinked prepolymer, this result is comparable with the previous study of multifunctional resin (TGEEBA). As for the accomplished study carried out on the three matrices, the elastic behavior G' (conservation module) and the vitreous behavior G" (loss module) were crosslinked and formulated in view of Rotation speed, frequency and angular velocity since viscosity in the liquid state and viscoelasticities decrease in view of temperature. Finally, the study of the elastic and vitreous behavior respectively characterized by G' and G" of the composite increases in view of frequency and angular velocity. This would confirm the hardening of the selected formulations. It should be noticed that the rheological behavior of the composite materials is made

difficult by the relative chemical structure of this multifunctional prepolymer. This obliged us to store the prepolymer at a low temperature.

References

1. Hsissou R., Bekhta A., El Hilal B., El Aazaoui J., Dagdag O., Abouelouafa K., El Harfi A., *Inter. J. Sci. Eng. Res.,* 8 (1) (2017) 1181-1188
2. Hsissou R., El Rhayam Y., El Harfi A., *Inter. J. Innov. App. Stud.,* 7(2) (2014) 674-682
3. El Gouri M., El Bachiri A., Hegazi S.E., Rafik M., El Harfi A., *Polym. Degrad. Stab.,* 94 (2009) 2101-2106
4. Sumeera I., Arshad M., *Op. J. Syn. Theo. and Appl.,* 1 (2012) 36-43
5. Vijayalakshmi A., Vidyavathy B., Chithra B., Hemamalini M., *Inter. J. ChemTech Res.,* 8(12) (2015) 638-42
6. Murugavel S., Malathi M., *Inter. J. ChemTech Res*., 9 (3) (2016) 616-622
7. Manikandan S., Ramanathan S., Ramakrishnan V., *Inter. J. ChemTech Res.,* 9 (2) (2016) 10-19
8. Selvarani K., Mahalakshmi R., *Inter. J. ChemTech Res.,* 9 (1) (2016) 113-120
9. Hsissou R., Dagdag O., EL Harfi A., *Mor. J. Chem.,* 3 (4) (2015) 791-797
10. Hsissou R., Elharfi A., *Mor. J. Chem.,* 4 (2) (2016) 315-323
11. Bekhta A., El Harfi A., *Mor. J. Chem.,* 4 (1) (2016) 61-67
12. Hsissou R., Bekhta A., El Harfi A., *J. Mater. Environ. Sci.,* 8 (2) (2017) 603-610
13. Fetouaki S., Toufik M., Meghraoui H., El Harfi A., *Phy.Chem. N. J.,* 27 (2006) 131-140
14. Hsissou R., Benassaoui H., Benhiba F., Hajjaji N., ElHarfi A., *J. Chem. Tech. Metall.,* 52(3) (2017) 431-438
15. Dagdag O., El Gouria M., Galai M., Ebn Touhami M., Essamri A., Elharfi A., *Der Pharma Chemica,* 7(4) (2015) 114-122
16. Bekhta A., Lambarki El Allioui T., Bouih A., El Hilal B., El Harfi A., *Inter. J. Innov. Appl. Stud.,* 7 (3) (2014) 1057-1070
17. El Hilal B., Lambarki EL Allioui T., Bouih A., Rafik M., Elharfi A., *Mor. J. Chem.,* 4 (1) (2016) 215-222
18. Chenard J. Y., *High performance composites. Stake* 25 (1982) 63
19. Gohardani O., Williamson D. M., Hammond D. W., *J. Wear.,* 294–295 (2012) 336-346
20. Heinrich G., Kluppel M., *Adv. Polym. Sci.,* 160 (2002) 1-44
21. Macosko C. W., *Rheology- Principales, measurements and applications, New-York: VCH,* (1994) 109-126
22. Grich M., El gouri M., Ziraoui R., Rami N., Meghraoui H., Cherkaoui O., El harfi A., *J. Mater. Environ. Sci.,* 5 (2) (2014) 374-379
23. Brito Z., Anchez G. S., *Composite Structures,* 48 (2000) 79
24. Rami N., Meghraoui H., Ziraoui R., El khoukhi T., Mouhib M., El Harfi A., *J. Mater. Environ. Sci.,* 1 (2010) 277-288
25. Hsissou R., El Harfi A., *Inter. J. PharmTech Res.,* 10 (2) (2017) 891-902
26. El Azzaoui J., El-Aouni N., Bekhta A., El Harfi A., *Mor. J. Chem.,* 3 (2) (2015) 338-345
27. El Aouni N., El Azzaoui J., El Harfi A., *Mor. J. Chem.,* 4 (1) (2016) 53-60
28. EL Gouri M., EL Harfi A., Rafik M., Hegazi S.E., Grich M., Meghraoui H., *Phys. Chem. News,* 52 (2010) 112-128
29. Ziraoui R., Meghraoui H., Rami N., Cherkaoui O., Choukri A., Hakam O., Elharfi A., *Ann. Chim. Sci. Mat.,* 37 (2012) 85-96
30. Raskin A., Salomon J. P., Sabbagh J., *Clinical Concepts: Editions SNPMD, Paris,* (2007) 7-21
31. Meghraoui H., Rami N., Grich M., Echchelh A. , Elharfi A., *Ann. Chim. Sci. Mat.,* 34(3) (2009) 141-153
32. Rami N., Meghraoui H., Grich M., Fetouaki S., Elharfi A., *Ann. Chim. Sci. Mat.,* 33(6) (2008) 479-492
33. Chernin I. Z., Smekhov F. M., Zherdyaev Yu. M., *Moscow: Khimiya,* 1982
34. Hsissou R., Rafik M., Hegazi S. E., El Harfi A., *Arab. J. Chem. Envir. Res.,* 3 (1) (2016) 35-50

(2017) ; http://www.jmaterenvironsci.com