

Viscosimetric and rheological studies of a new trifunctional epoxy pre-polymer with noyan ethylene:Triglycidyl Ether of Ethylene of Bisphenol A (TGEEBA)

R. Hsissou^{*}, A. Bekhta, A. EL Harfi

Laboratory of Agricultural Resources, Polymers and Process Engineering (LARPPE), Organic Chemistry and Polymers Team (TOCP), Department of Chemistry, Faculty of Science, University Ibn Tofail, BP 133, 14000, Kenitra, Morocco.

Received 11 March 2016,
Revised 20 Sept 2016,
Accepted 28 Sept 2016

Keywords

- ✓ Viscoelastic,
- ✓ rheological behavior,
- ✓ TGEEBA,
- ✓ pre-polymer,
- ✓ natural phosphate,
- ✓ methylene dianiline
- ✓ nanocomposite

r.hsissou@gmail.com
Tel: +212 6 22 67 85 10

Abstract

In this work, we have studied the viscoelastic and rheological behavior of a new trifunctional epoxy pre-polymer: triglycidyl ether of ethylene of bisphenol A (TGEEBA) synthesized in our laboratory and its composite containing phosphate as load. In the first step, after the synthesis of (TGEEBA) we formulated this crosslinked epoxy pre-polymer to develop a thermoset nanocomposite material in the presence of loads of natural phosphate at different percentages (0%, 5%, 10 % and 15%) by the addition of methylene dianiline (MDA) as hardener in order to optimize and control the dispersed system in the macromolecular matrix. In the second step, we studied the viscometric properties of this epoxy prepolymer, using the capillary viscometer Ubbelohde VB-1423, and the rheological properties using the rheometer Haake RHM01-RD. It is very important to clarify the influence of the rock phosphate whose rheological behavior of nanocomposites based on TGEEBA and on natural phosphate.

1. Introduction

The epoxy polymers are thermosetting macromolecules widely used as hyperlinks in the formulation of composite materials because they represent the best compromise for an operating temperature which is about 150 Celsius continuously [1, 2]. The epoxy prepolymers have an important position in the industry thanks to numerous properties, and they are used in several areas such as: electronics [3], coatings [4], the burial of radioactive wastes [5, 6], leisure [7] and the rheology of nanocomposites etc ... [8, 9].

The aim of our study lies in the exploitation of the epoxy pre-polymer synthesized in the viscoelastic and rheological behavior of thermosetting materials over a wide temperature range which is needed for understanding and mastering the conditions of preservation or storage (module G') and the loss (module G'') [10, 11] and for linking the performance and the product quality with the conditions of implementation and the properties of the materials. The rheological properties can be directly related to the chemical structure or the degree of conversion of the polyepoxy prepolymers [12]. The incorporation of a rock phosphate load in the polymer materials aims at providing new properties or for specific functions [13, 14]. The behavior of composite materials is influenced by the presence of particles dispersed in the matrix. These insoluble additives such as phosphate are used to improve the rheological properties including the mechanical strength and the heat conductivity [11]. In order to optimize and control the dispersed system, it is very important to clarify the influence of phosphate on the rheological behavior of nanocomposites based on TGEEBA and the natural phosphate.

In this work, after the synthesis of the prepolymer (TGEEBA) [15], we cured and formulated this pre-polymer (TGEEBA) by the natural phosphate nano-filler to quantify its viscoelastic and rheological performance which is based on the influence of temperature on the (TGEEBA/methanol) and the (TGEEBA/MDA/NP) systems [10, 12]. Then we were principally interested in viscosimetric and rheological properties which play a crucial role in the flow of macromolecular matrix phenomena [16, 17].

2. Materials and Methods

2.1. Used materials

In this work, we used several products among which we list the trifunctional epoxy pre-polymer: Triglycidyl Ether of Ethylene of Bisphenol A (TGEEBA) synthesized in the laboratory [15].

The methylene dianiline (MDA), phosphate and methanol have been marketed by Aldrich Chemical Co.

2.2. Methods used in the preparation of the TGEEBA

In this work we used

2.2.1. Viscometric and Rheological analysis

The viscosimetric analysis of the standard epoxy pre-polymer was followed using the capillary viscometer Ubbelohd VB-1423 as well as using a rheometer Haake RHM01-RD (HAAKE MARS) on liquid and solid samples 1 and 2.

The measurement conditions used by the capillary viscometer Ubbelohd VB-1423 are:

- viscometer of 1B size for a series of dilution, capillary tube of 0.46 mm diameter and constant $k=0.051493$;
- Measuring temperature in °C: 30 up to 60;
- Number of measurement: 3 in each case;
- Solvent: Methanol;
- The Hagenbach correction was calculated using the formula specified in the DIN standard 51562-1 January 1999 (Measurement of kinematic viscosity by means clustering of the Ubbelohd of viscometer);
- The solubilization of the epoxy pre-polymer in methanol was performed at 25 °C under magnetic stirring;
- The capillary viscometer consists principally of three tubular portions (1, 2 and 3), the capillary tube (6) with the measuring sphere (5). Above and below the measuring sphere (5), the ring marks M_1 and M_2 are printed on the tube (3). These marks define the volume of control for the experiments.



Figure 1: viscosimetric measurement device Ubbelohd VB-1423

The measurement conditions used by a rheometer Haake RHM01-RD (Thermo Fisher (MARS)) are:

- Temperature in °C : 150 °C;
- Rotation Speed Mode CR: 10-8 0 1500 rpm;
- Frequency: 10^{-5} to 100 Hz;
- Strength: 0.01 to 50 N;
- Twist: $5 \cdot 10^{-8}$ to 0.2 N.m;
- Control software: RheoWin.

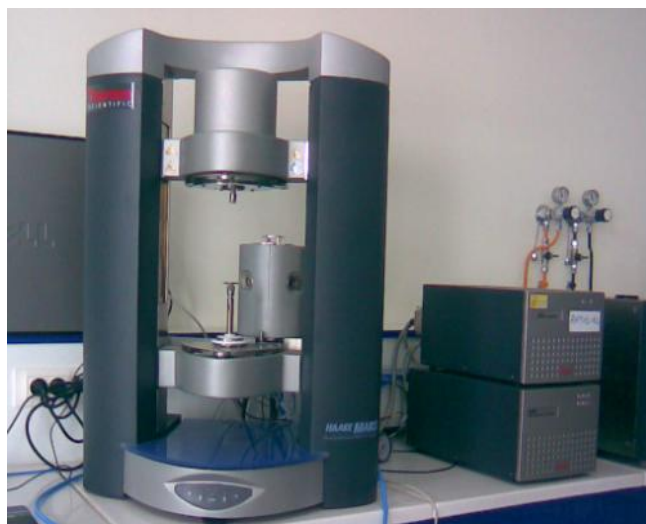


Figure 2: rheometer Haake RHM01-RD Device

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

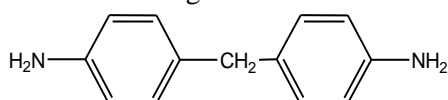
To determine the viscosimetric behavior of the trifunctional synthesized epoxy pre-polymer TGEEBA, we dissolved the prepolymer in methanol at different concentrations (5%, 10%, 15% and 20%) then, we studied their viscosities through a capillary viscometer Ubbelohd VB-1423 at varying temperatures from 30 to 60 °C.

2.2.3 Preparations of the samples analyzed by the rheometer.

The presence of the epoxy pre-polymer and methylene dianiline produce a hardening of the pre-polymer due to the crosslinking reaction. The protocol consists of a pre-heating stoichiometric amounts of the prepolymer and the hardener. The methylene dianiline (MDA), crystallized at room temperature, is placed in an oven at 120 °C (a temperature above its melting point), while the prepolymer is brought to 60 °C. When melted, the MDA is mixed with the prepolymer to give a single fluid phase being then at 70 °C.

The samples thus prepared were sealed in molds and have undergone the following curing cycle: 12 hours at 70 °C and then 1h at 140 °C. After demoulding, the sample is brought into the desired geometric shape.

The crosslinks' reactions are carried out by a primary diamine, and methylene dianiline (MDA), known for its excellent mechanical properties and the good thermal stability it provides to the final product, compared with other hardeners [18]. Its structure is shown in the diagram below.



Schema 1: Formula of methylene dianiline (MDA)

This hardener has a functionality equal to four, which means that during the crosslinking reaction with a trifunctional resin (eg, TGEEBA), the two amine functions theoretically react with six epoxide functions when they are in stoichiometric proportions [19, 20]. The final product is a chemically bridged in a three-dimensional network. After the chemical reaction, the crosslinked materials are hard, infusible and insoluble.

Applying the previous protocol to the crosslinking reaction of the prepolymer in the presence of methylene dianiline as a hardener and natural phosphate at different percentages (0%, 5%, 10% and 15%) as a filler, we obtained some samples with the well dispersed filler in the base matrix after a major stir.

2.2.4 Ration Calculation

2.2.4.1 Calculation of stoichiometric coefficients

In order to get the optimum properties when we harden a multifunctional epoxy resin with a hardener (especially amines), it is desirable to make the resin react and the hardening agent into approximately stoichiometric amounts.

Calculation of the equivalent epoxy (Epoxy Equivalent Weight: EEW) of the TGEEBA resin.

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

Where f is the functionality of the epoxy resin. In which:

$$EEW = \frac{874}{3}$$

$$EEW = 292 \text{ g/eq}$$

Calculating the equivalent amine (Amine Hydrogen Equivalent Weight: AHEW).

AHEW is then on the weight of hardener containing an amine equivalent.

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

Methylene dianiline:

$$M_w = 198 ; f = 4$$

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

$$AHEW = 49.5 \text{ g/eq}$$

2.2.4.2. Calculating the weight ration

The weight ratio of hardener in view of the resin is calculated in the majority of cases for 100 parts of resins or PHR (Parts per hundred of Resin)

$$PHR(\text{amine}) = \frac{\text{Amine H eq wt}}{\text{equivalent epoxy}} \times 100$$

In this case of the TGEEBA:

$$PHR \text{ amine} = 49.5/292 \times 100$$

$$PHR \text{ amine} = 17 \text{ g/eq}$$

So, we have to react 17g per 100g of methylene dianiline TGEEBA to achieve the optimum properties when we harden the resin with methylene dianiline.

3. Results and discussion

3.1. Viscosimetric behavior

3.1.1. Viscosimetric behavior of the Standard pre-polymer (unbound) analyzed by Ubbelohd VB-1423 viscometer

The different curves of the obtained viscosity of the epoxy pre-polymer synthesized triglycidyl ether of ethylene of bisphenol A (TGEEBA) in methanol are shown in figures 3 and 4.

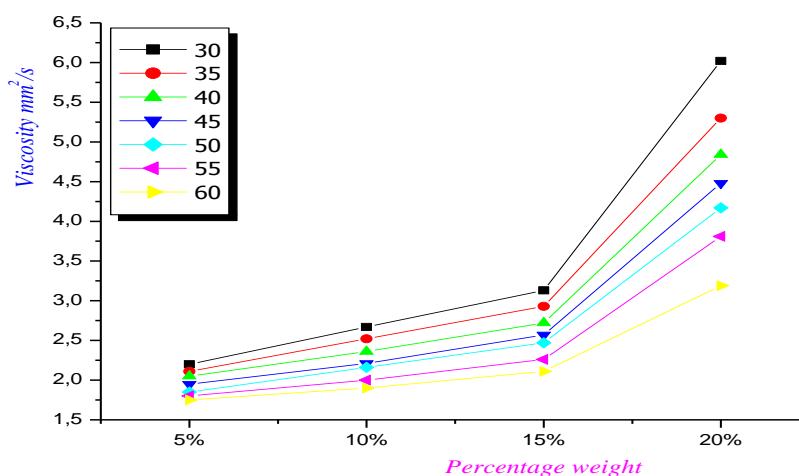


Figure 3: Variation of the standard pre-polymer's viscosity in view of the massive percentage with different temperatures

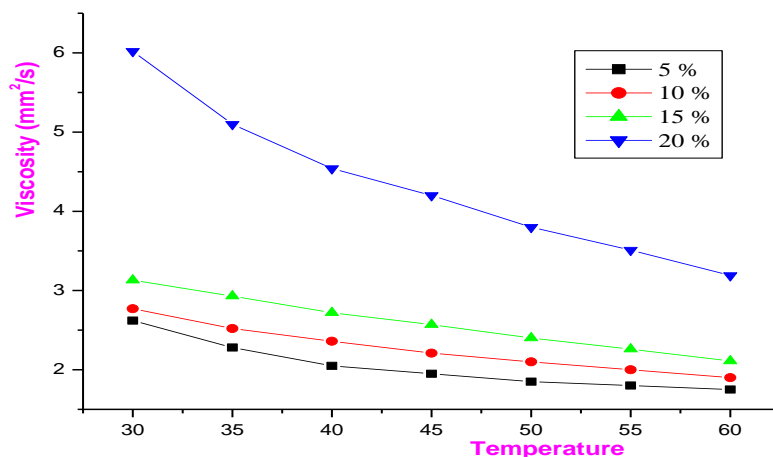


Figure 4: Variation of the standard pre-polymer's viscosity in view of temperature at different concentrations

According to figures 3 and 4, we found that the viscosity values increase progressively as the mass concentration of the prepolymer increases. This demonstrates the progress of the reaction of the homopolymerization since the viscosity increases with the increase of the molecular weight of the solute. This is related to the chemical transformations of the pre-polymer [21, 22].

Indeed, the rise in temperature implies that the pre-polymer TGEEBA passes from a viscous state to a liquid state, which explains the observed collapse in viscosity (Figure 4) [23].

3.1.2. The viscoelastic behavior of the crosslinked pre-polymer analyzed by the type of rheometer RHM01-RD Haake

Rheology refers to the study of the flow, deformation, elasticity and viscosity of the considered material. We were interested in the viscoelastic behavior of the crosslinked prepolymer (TGEEBA/MDA) since it plays a crucial role in the flow phenomena of macromolecular matrix, and more generally the viscosity of the material under the effect of the applied stress. Our rheological study of the standard matrix of the epoxy pre-polymer TGEEBA and MDA gives the viscosity under the rotational effect of stress and under a controlled atmosphere in view of temperature. Figure 5 shows the characteristics of the rheological behavior of the tri-functional reticulated resin depending on the temperature. The jellification time at different temperatures decreases with increasing temperature because the supplied heat accelerates the depolymerization process of the resin.

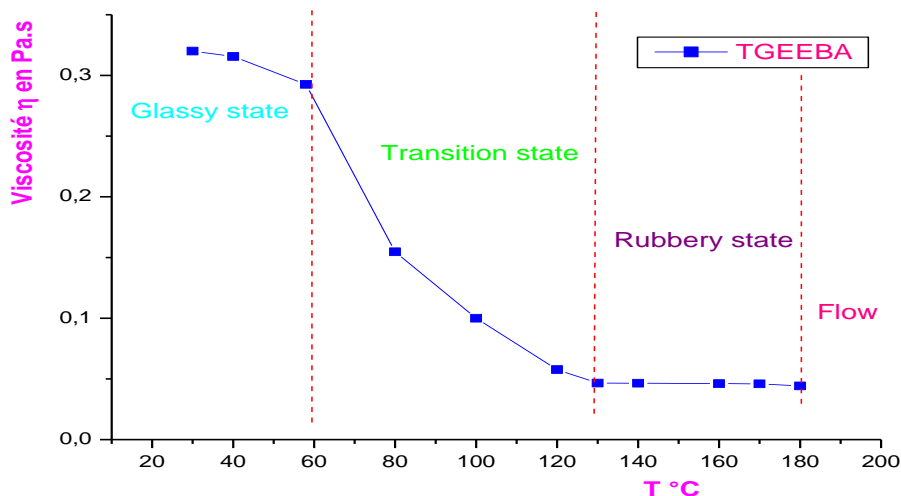


Figure 5: Different states of the viscoelastic of the crosslinked pre-polymer according to temperature

In this figure, we see the course of four phases, namely:

Glassy state: At low temperatures and reduced viscosity, the molecular mobility is high.

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

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

Flow: at high temperature and molecular mobility completely free, the viscosity is reduced.

The viscosity depends greatly on the temperature to maintain a sense of the extent to which we specify the temperature at which it was made. In liquids, the viscosity rapidly decreases with temperature.

3.1.3. Elastic behavior G' of the crosslinked and formulated pre-polymer in view of temperature.

The studied nanocomposite polymers (TGEEBA/MDA/NP) were introduced in the cell of the rheometer RHM01-RD Haake at high temperatures, for which the behavioral measures G' show that the response of polymeric materials are liquid-like. The experiments carried out with increasing temperatures show that there is a temperature T_0 below which the response G' is spontaneously replaced by a resilient plate ($G' = \text{constant}$). Figure 6 shows the behavior G' in view of temperature.

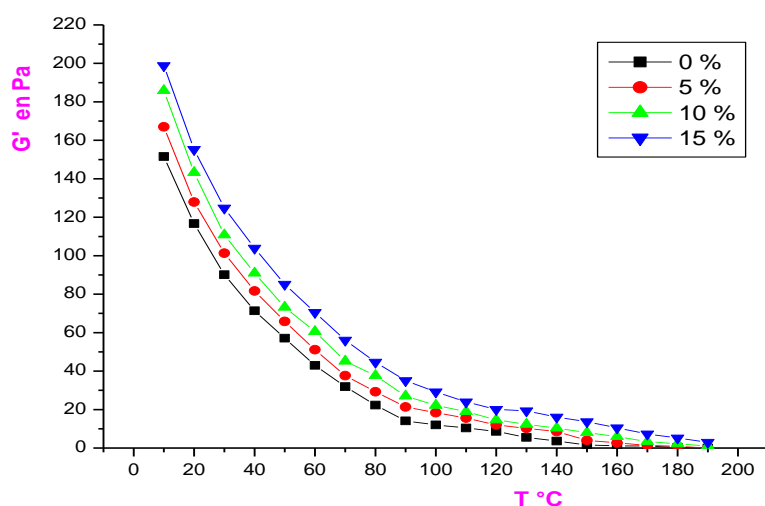


Figure 6: Variation of the elastic behavior G' of the crosslinked and formulated pre-polymer in view of temperature

From this figure, we found that the change in behavior G' with the increase of the temperature decreases to the gelling temperature T_0 , above which the low frequency response of the prepolymer is liquid-like and below which it is gel-like. The rheological measurements clearly show that the increase in temperature induces a transition from a solid behavior to a viscoelastic liquid one.

3.2. Rheological elastic (module of conservation or storage G') and vitreous (module of loss G'') behavior

The literature on the rheological behavior of nanocomposites often leads to a better understanding of the structures and the relationships which are responsible for strengthening the polymers by rock phosphate as a filler. Rheology is placed here on the border between the determination of the structure and the physical properties of nanocomposites. This of technique often plays the key to understanding and improving the implementation. In this work, we focused on the study of the rheological behavior of nanocomposites consisting of dispersing the phosphate load in an epoxy matrix (TGEEBA). Figures 7 and 8 respectively show the elastic behavior (module of conservation or storage G') and the glassy behavior (module of loss G''). The rheological analyses of nanocomposites (TGEEBA/MDA/NP) were performed in 150 °C under the action of a range of variable frequencies from 0.1 to 100 rad/s.

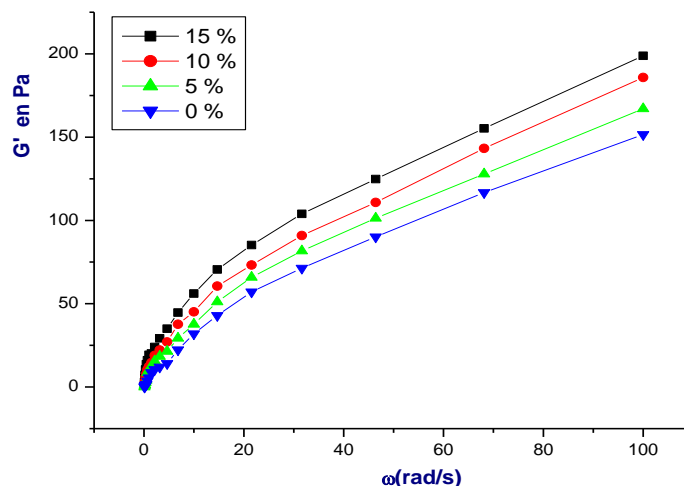


Figure 7: Elastic behavior of formulations TGEEBA/MDA/NP

Figure 7 shows the module of conservation or storage G' on the one hand, and the increase of the latter according to the frequency and the variation of G' which increases with the percentage of the load (natural phosphate) on the other. This could explain that the formulation of the composite (TGEEBA/MDA/NP) was hardened. Figure 8 shows the module of loss G'' on the one hand, and the increase of the latter depending on the frequency and the variation of G' which increases with the percentage of the load (natural phosphate). This has enabled us to confirm the study of elastic behavior of G' .

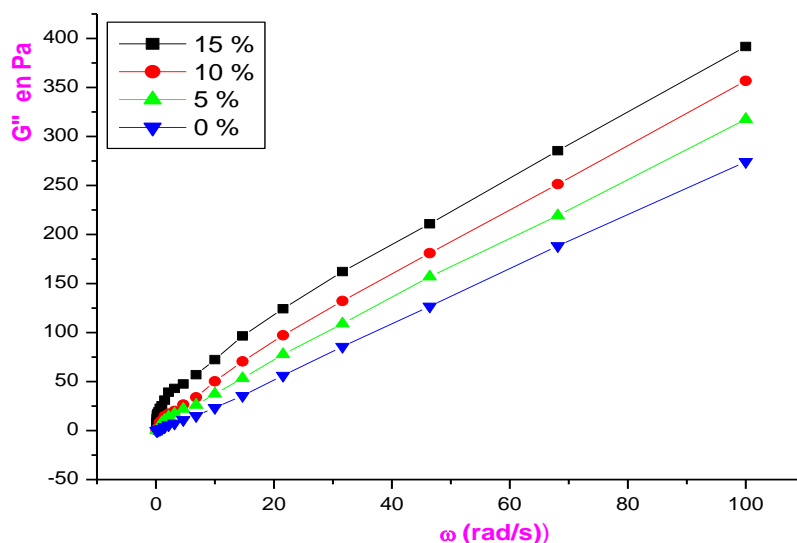


Figure 8: Glassy behavior formulations TGEEBA/MDA/NP

Conclusions

In this work, we synthesized the standard epoxy pre-polymer triglycidyl ether ethylenically of bisphenol A (TGEEBA) from which we have developed a tri-functional polymer hardened via the MDA and formulated by the NP. Through these structures we proceeded to the viscometric studies based on the mass concentration and temperature using a capillary viscometer Ubbelohd VB-1423 on the one hand and the rheological study of the crosslinked and formulated pre-polymer of rock phosphate with a RHM01-RD rheometer Haake on the other hand. The results of the viscosimetric study of the standard tri-functional epoxy pre-polymer has allowed us to have a clear and accurate picture of its viscoelastic properties since the change in viscosity in view of

concentration increases and that the temperature decreases. This confirms the results of the viscoelasticity. As for the crosslinked product, we studied the different viscoelastic states depending on the temperature, and the results allowed us to observe a four-phase plot (the glassy state, the transition state, the rubbery state and the flow state) in the context of studying the behavior of the cross-linked pre-polymer and the cross-linked and formulated one. The study that we conducted on the three matrices was confirmatory since the viscosity, the viscoelastic state and the elastic behavior G' decreases with the temperature. Finally, the study of elastic and glassy behavior respectively characterized by G' and G'' of the composite increases with the frequency. This confirms the hardening of the selected formulations.

It must be noticed that the rheological behavior of composite materials are complicated by the chemical structure which is relative to this multifunctional pre-polymer. This obliged us to store the pre-polymer in low temperatures.

Acknowledgments- My sincere thanks for their encouragement to Ahmed Elharfi professor, of Department of Chemistry, Faculty of Science, University Ibn Tofail, BP133, 14000, Kenitra, Morocco, as well as to all those who allowed us the rheological characterization.

References

1. Chrétien G., *Matér. Comp., Tech. et Doc. (Lavoisier), Paris.* (1986) 107.
2. Hsissou R., El Rhayam Y., El Harfi A., *Inter. J. Inno. App. Stu.*, 7 (2) (2014) 674-682.
3. Fetouaki S., Toufik M., Meghraoui H., A. El Harfi. *Phys. and Ch. Ne. Jo.*, 27 (2006) 131- 140.
4. Dagdag O., M. Galai, M. Ebn Touhami, A. El Harfi. *Inter. J. Inno. App. Stu.*, 10 (1) (2015) 295-304.
5. Bekhta A., T. Lambarki EL Allioui, A. Bouih, B. EL Hilal, A. EL Harfi. *Inter. J. Inno. App. Stu.*, 7 (3) (2014) 1057-1070.
6. EL Hilal B., A.ELHarfi, *Inter. J. Inno. App. Stu.*,7 (2014) 729-735.
7. Fetouaki S., El harfi A., Belkebir L., *Eur. Polym. J.* 38(2002) 787-793.
8. Bekhta A., El harfi A., *Mor. J. Chem.* 4 (1) (2016) 61-67.
9. EL Azzaoui J., EL-Aouni N., EL Harfi A., *Mor. J. Chem.* 4 (1) (2016) 14-23.
10. Hsissou R., Dagdag O., EL Harfi A., *Mor. J. Chem.* 3 (4) (2015) 791-797.
11. 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.
12. EL Gouri M., EL Harfi A., Rafik M., Hegazi S.E., Grich M., Meghraoui H., *Phys. & Ch. Ne.*, 52 (2010) 112-128.
13. Brito Z., Anchez G. S., *Comp. Stru.*, 48 (2000) 79.
14. Rami N., Meghraoui H., Grich M., Fetouaki S., El Harfi A., *Ann. Chim. Sci. Mat.*, 33 (2009) 479.
15. Hsissou R., Rafik M., Hegazi S. E., El Harfi A., *Ar. J. Ch. Env. Res.*, 3 (1) (2016) 35-50.
16. El Azzaoui J., EL-Aouni N., A. Bekhta, El Harfi A., *Mor. J. Chem.* 3 (2) (2015) 338-345.
17. Hsissou R. and El Harfi A., *Mor. J. Chem.* 4 (2) (2016) 315-323.
18. Ziraoui R., Meghraoui H., Rami N., Cherkaoui O., Choukri A., Hakam O., El Harfi A., *Ann. Chim. Sci. Mat.*,37 (2012) 85-96.
19. Raskin A., Salomon J. P., Sabbagh J., *Les rés.comp.: Classif. et évol.. Conc.clin.. Edit. SNPMD, Paris.* (2007)7-21.
20. Meghraoui H., Rami N., Grich M., Echchelh A., El Harfi A., *Ann. Chim. Sci. Mat.* 34 (3) (2009) 141-153.
21. Rami N., Meghraoui H., Grich M., Fetouaki S., Elharfi A., *Ann. Chim. Sci. Mat.* 33(6) (2008) 479-492.
22. Bacon S.L., Daugulis A.J., Parent J.S., *Chemical Engineering Journal*, 299 (2016) 56-62
23. krasovskii A.N., Novikov D.V., Filippov V.N., *Zh. Prikl. Khim.* 77 (8) (2004) 2382-2388.

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