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Synthesis of novolac matrix and study of a new composite in the presence of tri-sodium phosphate. Characterization and viscometric study, rheological and thermal degradation

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ABSTRACT: The objective of this work is to study the thermosetting composites, the case of polyepoxides based on novolac hydroxide in presence of tri-sodium phosphate loads. Our work is to make three samples of a composite based on synthesized novolac polyepoxide by the polycondensation of a polycrésol resin with the epichlorohydrin in an alkaline medium, adding, on the one hand, methylene dianiline (MDA) as a hardener, and on the other hand, various percentages (0%, 10% and 15%) of tri-sodium phosphate as a load so as to improve the mechanical and thermal properties of the composites obtained. The standard novolac matrix was studied by the viscometer to determine the visco-elastic properties of the matrix. The analysis of thermosetting samples was carried out by Thermogravimetric method (TGM) and Scanning Electron Microscope (SEM).

KEYWORDS: Thermoset composites, novolac resin, tri-sodium phosphate loads.

1 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 reinforcement whose mechanical characteristics are sometimes higher than those of metals. The basic requirement for this definition to be valid is that the cohesion of the whole should be ensured by different types of chemical bonds [3, 4]. The selected components can improve the following properties: stiffness, thermo resistance, fatigue resistance, shock resistance, fire..... etc, and the employment properties required in the industry to the problems of safety and reliability. The ability of a material to resist degradation over time under multiple stresses (mechanical, electrical, chemical ...) is essential. To effectively improve the behavior of these materials and enhance their sustainability, it is essential to analyze each phenomenon keeping a general point of view of all the properties of composites.

Knowledge of the rheological properties of these thermoset materials over a wide temperature range is necessary for the understanding and mastery of storage conditions [5], as well as for the link between the performance [6] and the quality of the product in the conditions of implementation and material properties. The rheological properties can be directly related to the chemical structure or the degree of conversion of the prepolymer polyepoxides [5, 7].

In our work, we have synthesized, studied and formulated the resin based on polycrésol [8, 9 and 10] by the load tri-sodium phosphate to quantify the mechanical, thermal and viscoelastic performance.

2 MATERIALS AND METHODS

2.1 MATERIELS

The basic chemicals are used in this work are the Hardening Methylene Dianiline (MDA) as a crosslink [1], which is a primary aromatic diamine of molecular formula C13H14N2 and which has a functionality equal to four; the tri- sodium phosphate used as a formula load Na3PO4; (The latter is a white granulated product, very soluble in water and widely used in the formulations) the polycrésol; the epichlorydrin with a purity of 99 %; the chloroform; and the sodium hydroxide (NaOH). All these commodities have been provided by the companies Acros Chemical Co. and Aldrich Chemical Co.

2.2 METHODES

The methods used for the study and characterization of materials are:

2.2.1 ANALYSIS INFRARED FOURRIER TRANSFORM (FT-IR)

The spectra of the FTIR spectrometer (BRUKER) were made in transmission by KBr pellets. The light beams pass through the sample to a thickness of about 2 * m. The Analysis of the spectra is carried out between 600cm -1 and 4000cm -1.The area of energy of the vibrational molecules is 2.5 - 25µm.

2.2.2 NUCLEAR MAGNETIC RESONANCE NMR

The NMR (1H) analysis was obtained by means of a device type " BRUKER AVANCE 300MHz " by dissolving the product in DMSO at 60 ° C. Chemical shifts are expressed in ppm, coupling constants in Hz and the following abbreviations have been used: s, d, dd, t, q and m are respectively singlet, doublet, doublet of doublets, triplet, quadruplet and multiplet .

2.2.3 ANALYSIS THERMOGRAVIMETRIC (TGA)

To achieve our study which focuses on the degradation of synthesized epoxy resins, we made a call to the TGA [Thermo Fischer (Versa Thermo HM)] technical. It consists of a spring and a quartz reactive tube in the middle of which is placed the door nacelle sample (platinum) which is suspended on a spring.

- Measurement conditions used by thermo Fischer (Versa Thermo HM).

- Oven: metal resistors.
- Temperature range: ambient to 1100 ° C.
- Ability to scale: 100g.
- Cooling: compressed air.
- Shielding gases: argon.
- Two reaction gases: Nitrogen and / or Air.
- Glass crucibles.
- Software: Acquisition Thermal, thermal analysis [1].

2.2.4 ANALYSIS VISCOSIMETRIC:

The viscometric analysis of the standard matrix was followed by a capillary tube viscometer Ubbelohd VB- 1423 as well as a rheometer type RHM01 -RD (HAAKE MARS) in liquid , paste and solid samples .

- The measurement conditions obtained by a capillary viscometer tube Ubbelohd VB- 1423 are as follows:

- Viscometer 1B size for a series of dilution, capillary tube diameter of 0.46 mm, constant k = 0.051493.
- Temperature measurement in ° C: 30 up to 45 ;
- Number of measurement: 4 each time.
- Solvent: Chloroform.
- The Hagenbach correction was calculated using the formula given in the norm DIN 51562 - 1Janvier 1999 (Measurement of kinematic viscosity by means clustering of the Ubbelohd of viscometer).
- Prepolymers Solubilization of epoxy resin in methanol was conducted at 20 ° C under magnetic stirring.

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

- Oven: 150 ° C to 600 ° C.
- Speed mode CR: 10-8 0 1500 rpm.
- Speed mode CS: 10-7 at 1500 rpm.
- Frequency: 10-5 to 100 Hz.
- Force: 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 THE NOVOLAC EPOXY RESIN

Mono or multifunctional epoxy resins are generally synthesized in two ways; the first is based on two stages and the second is on one.

- **THE FIRST WAY:**

The novolac epoxy resin obtained in this case passes through two ways.

- ***Stage 1 :***

Novolacs are prepared with an excess of phenol with formaldehyde until being exhausted under acidic conditions (Figure 1). A methylene glycol is protonated with an acid from the reactional medium, which in turn releases water to form a hydroxymethyl cation (step 1 of Figure 1). This ion hydroxyazoïc phenol by electrophilic aromatic substitution. The step which determines the rate of the sequence occurs in the 2nd step in Figure 1, where a pair of electrons from an electrophilic attack phenol ring forms an intermediate carbocation. The methyl group of hydroxy - methylene phenol is unstable in the presence of acid and water to form an easily lost benzyl carbonium ion (Step 3of FIG 1). This ion reacts further with another phenol to form a methylene bridge in other substitution explained in step 4 of Figure 1. [10]

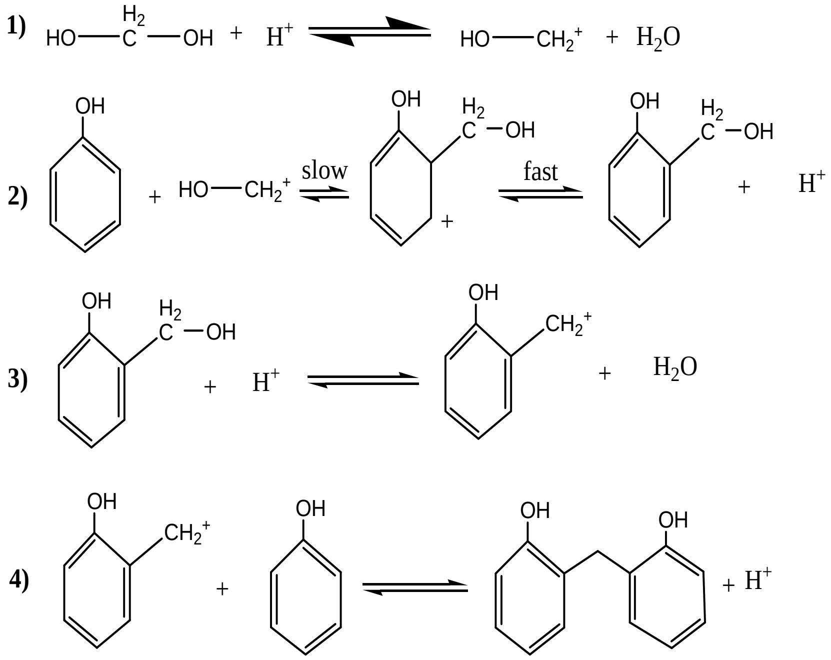


Fig. 1. Mechanism of hydroxy novolac synthesis by electrophilic aromatic substitution.

- ***Stage 2 :***

  Synthesis of the epoxy novolac resin from hydroxy novolac (polycresol)

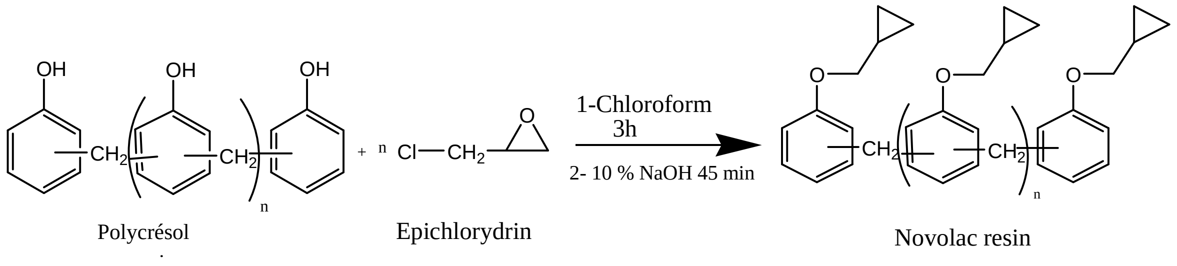


Fig. 2. Synthesis of the novolac epoxy resin by polycondensation [11, 12]

- **THE SECOND WAY:**

The epoxy novolac resin was directly prepared by condensing the epichlorohydrin and a resin polycrésol (hydroxy novolac) in an alkaline medium [3].

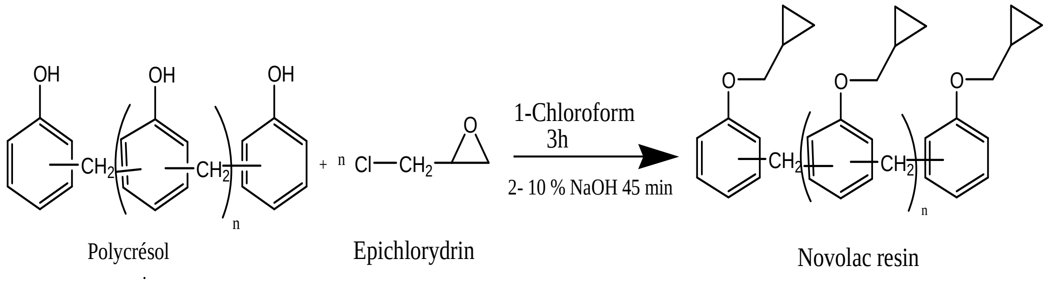


Fig. 3. The reactional scheme of the epoxy novolac resin synthesis

In our work we have carried out the synthesis of epoxy novolac by the second track.

2.3.2 PROCECURE

In a round bottom flask, we mixed a solution of 5 g of the hydroxyl novolac epoxy resin diluted in 40 ml of dimethyl sulfoxide and a stoichiometric amount of epichlorohydrin. Then, we heated it for 3 hours at a temperature of 80 ° C to promote the condensation of epichlorydrin and hydroxyl functions novolac.

The reaction is continued by adding any subsequently a solution of a massive concentration of 10 % sodium hydroxide to the reactive mixture to obtain the closure of the oxirane cycle.

The reactive system at 60 ° C is reduced under magnetic stirring for 45 minutes.

The novolac epoxy matrix is extracted with chloroform, followed by washing with water. The final product is obtained after dissolution in chloroform followed by the evaporation method.

2.4 SAMPLE PREPARATION

The bringing together of the epoxy resin and MDA produces a hardening of the resin after the cross-linking reaction. The protocol is that adopted by Fetouaki et al. It consists of a preheating of the stoichiometric amounts of both the resin and the hardener [13].

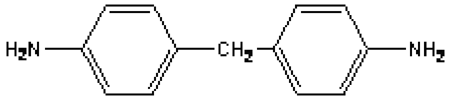
The methylene dianiline (MDA), crystallized at room temperature, is placed in an oven at 120 ° C (a temperature above its melting point), while the resin is heated to 60 ° C. When molten, the MDA is mixed with the resin to give a single fluid phase, being then at 70 ° C.

The samples thus prepared were sealed in the mold and subjected to the following curing cycle:

- Twelve hours at 70 ° C and one hour at 140 ° C.

- After demoulding, the sample is put into the targeted geometric shape.

Our crosslinks are formed by a primary diamine, methylene dianiline (MDA) [13], known for its excellent mechanical properties and the good thermal stability it provides to the final product, compared with other hardeners. Its structure is given in the figure below. Formula of methylene dianiline (MDA):



This hardener has a functionality of four, which means that during the reaction with a bi-functional cross-linking resin (e.g., BADGE), the two amine functions theoretically react with four functions of epoxides when in stoichiometric proportions [14, 15]. The final product is a three-dimensional network chemically bridged. After the chemical reaction, the crosslinked materials are hard, infusible and insoluble.

By applying the previous protocol in cross-linking the resin charged with tri-sodium phosphate at different percentages, we obtain samples with well dispersed charges in the base matrix after a significant mixing.

3 RESULTS AND DISCUSSIONS

3.1 STRUCTURAL STUDIES OF THE STANDARD EPOXY NOVOLAC:

We performed structural analysis of the epoxy resin obtained by infrared spectroscopy Fourier transform, and confirmed the results by nuclear magnetic resonance of proton (1 H NMR).

3.1.1 MICROSTRUCTURAL CHARACTERIZATION BY INFRARED FOURRIER TRANSFORMATION:

Novolac epoxy resin was characterized by means of infrared analysis of Fourrier transformation. The resin was exposed in its viscous state to infrared radiation in ATR mode.

The results obtained are illustrated in Figure 4 of the following spectrum.

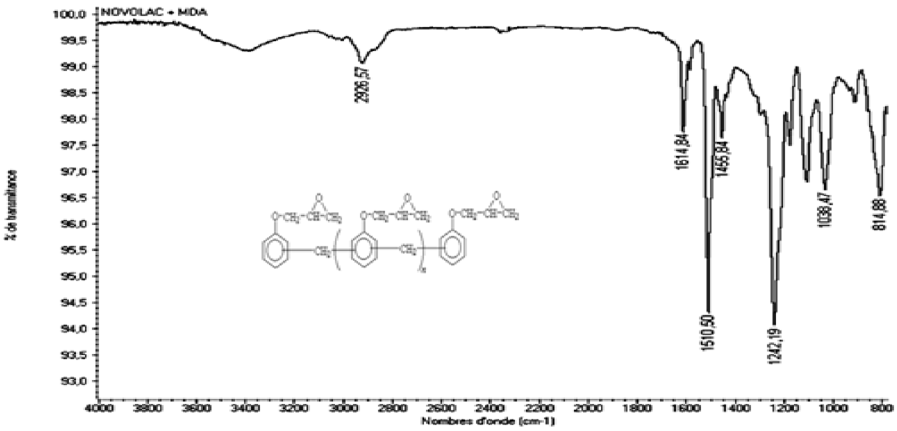


Fig. 4. Analysis of Novolac epoxy resin by FTIR.

The attribution of the different peaks obtained through the mode ATR infrared analysis is given in Table 1 below:

Table 1. Infrared analysis in ATR mode novolac resin

υ Band (cm-1)	**Attributions**
3450	residual O-H
2926 ; 1614	Substituted aromatic cycle
1242	aromatic C-O (Ar-O)
1038	alcohols and ethers C-O
815	Epoxy

3.1.2 DETERMINATION OF THE MICROSTRUCTURE BY NMR

The compounds (epoxy novolac) were analyzed by the magnetic nuclear resonance of the proton

The results of the analysis and the attributions of the peaks in the spectra are given below.

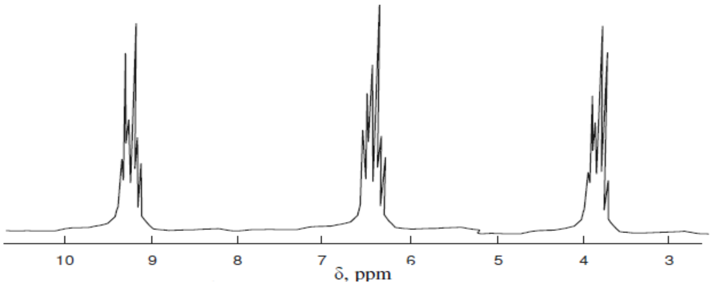


Fig. 5. Magnetic nuclear resonance of the cresol resin proton

The attributions of the peaks of the observed cresol resin are as follows:

Table 2. The proton NMR analysis of the novolac resin

ppm	**Protons and interpretations**
between3,4 and 4,2	The aliphatic protons of the cresol resin (m)
between 6,2 and 6,8	The aromatic protons (m)
between 9,1 and 9,7	hydrogen groups of the alcohols (m)

After condensing the epichlorohydrin and the cresol resin, we obtain the following proton spectrum:

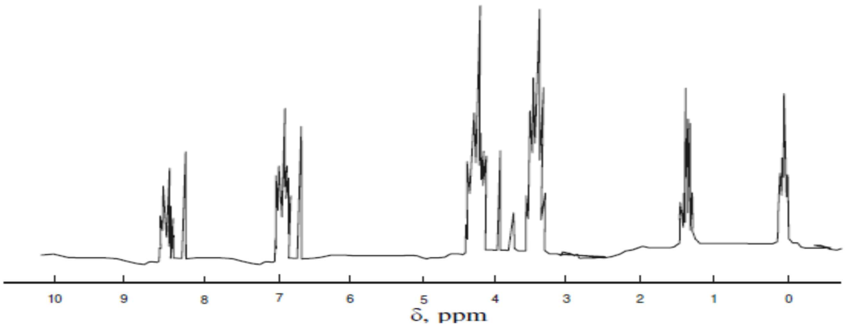


Fig. 6. The magnetic nuclear resonance of the novolac epoxy resin proton

The attributions of the observed peaks in the novolac resin are as follows:

Table 3. The NMR analysis of the novolac resin proton.

ppm	Protons and interpretations
2,39-2,91	CH2 of oxirane (m)
3,08-3,33	CH of oxirane (m)
From 3,39 to 3,43	CH2 ethers as well as aliphatic CH2 protons between the benzenic cycles (m)
6,61 to 7,45	Representing the aromatic protons of the novolac epoxy resin (m)

Both NMR 1 H and FTIR analyzes confirm the structure of the synthesized novolac resin.

3.2 VISCOMETRIC BEHAVIOR OF NOVOLAC EPOXY RESIN

3.2.1 THE VISCOSITY DEPENDING ON THE TEMPERATURE

As we mentioned previously, the rheological properties can be directly related to the chemical structure or the degree of conversion of the reactive system [7, 9and 10].

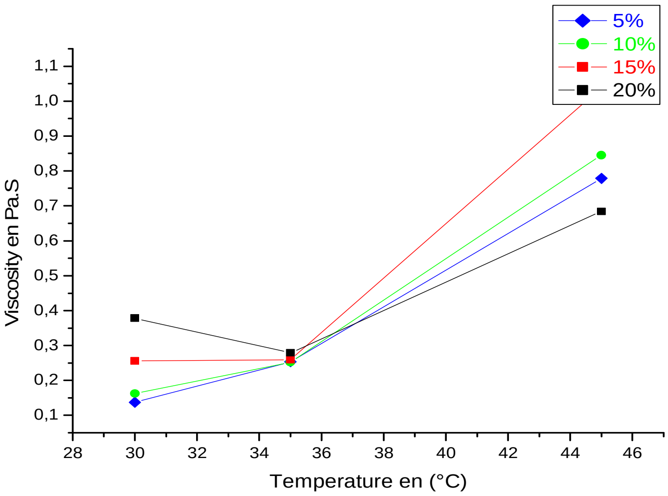


Fig. 7. The viscosimetric variation in different temperatures

The different speeds of viscosity obtained from the novolac epoxy resin in the Chloroform at different percentages of novolac/Chloroform system have all the same curves regardless of the temperature between 30 and 45 C. So, for this system we found that the viscosity values increase with temperature.

- We can conclude that:

This demonstrates the progress of the reaction of the homopolymerization since the viscosity increases with increasing molecular weight of the solute.

This may be due to chemical changes undergone by the resin [2, 16].

3.3 PHYSICAL PROPERTIES OF THE STANDARD NOVOLAC EPOXY RESIN

Rheology refers to the study of the flow, deformation, elasticity and viscosity of the material in question. We are mainly interested in the viscosity since it plays an important role in the flow phenomena of the organic matrix, and generally the viscosity of the material under the effect of an applied stress. It also helps determine the macroscopic mechanical properties from a study based on the micro or nanoscale structure of the material.

Our rheological study of the standard matrix based on the novolac epoxy resin gives the viscosity under the constraint effect of rotation and at a controlled atmosphere in view of time and temperature. The obtained results may also be presented as the curves seen in Figures 8, 9 below:

3.3.1 VISCOSITY AND CONSTRAINT IN VIEW OF TEMPERATURE °C:

In this study we have varied the viscosity under the effect of constraint according to the temperature with the fixation of speed.

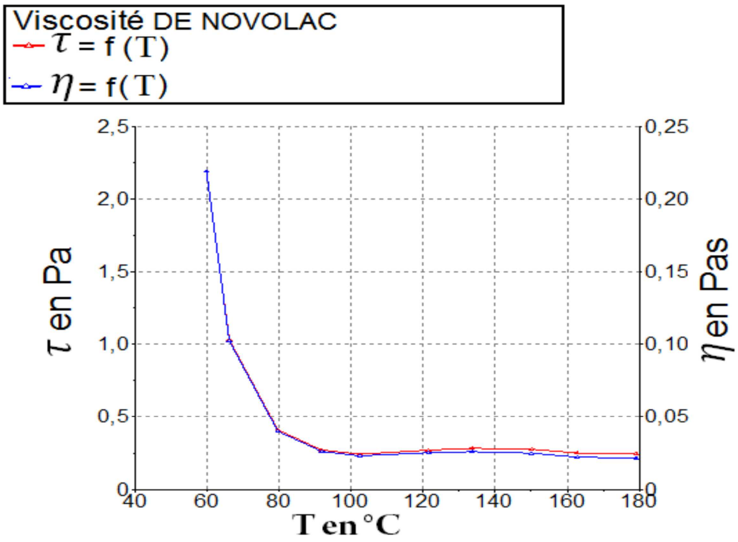


Fig. 8. Rheogram viscosity η and constraint τ according to temperature

3.3.2 VISCOSITY AND CONSTRAINT ACCORDING TO SPEED (1/S)

In this study we have varied the viscosity under the effect of constraint according to the speed with the fixation of temperature. The gradient values of $\dot{\gamma}$ speed obtained from the corresponding equation are written as:

$$\tau = \eta \dot{\gamma}$$

Where τ is the constraint (measured in Pa in the International System (IS) of measurement), $\dot{\gamma}$ is the velocity gradient in the thickness (measured in s -1), and η is the dynamic viscosity (measured in Pa.s). The unit of dynamic viscosity is sometimes called « Poiseuille » (Poiseuille 1 = 1 Pa = 1 kg.m - 1.s -1). The formula of this assumption is made according to [Newton, 1687].

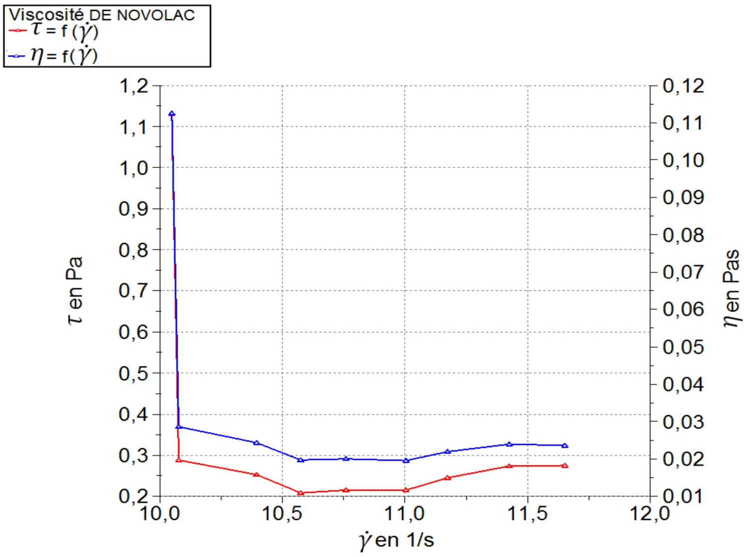


Fig. 9. Rheogram viscosity η constraint τ in terms of speed γ (1/s)

We concluded from these rheogram that the increase of the temperature in (°C) and of the speed in (1/s) results in the reduction of the constraint and the viscosity **η**.

3.4 THERMOGRAVIMETRIC BEHAVIOR

3.4.1 THERMAL BEHAVIOR OF THE CROSSLINKED NOVOLAC RESIN

We followed by thermogravimetric technical [3] the loss in mass of the crosslinked MDA/epoxy novolac system in terms of the temperature when subjected to a thermal treatment.

The following figure shows the thermal behavior of the crosslinked epoxy novolac by MDA.

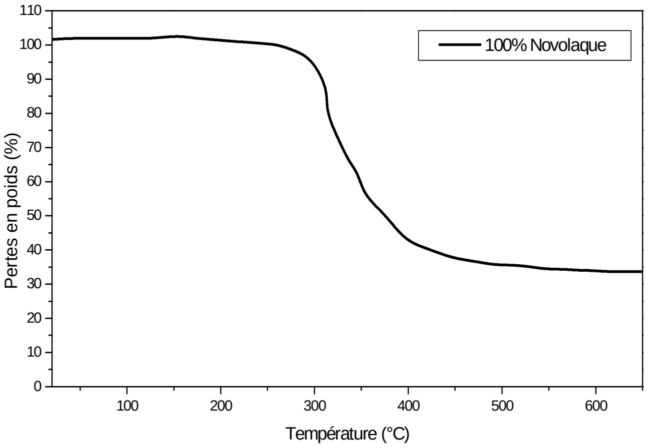


Fig. 10. TGA of the novolac/MDA system

We have classified the main thermal characteristics of novolac epoxy resin extracted from the thermo-gram curve in the following table:

- Td: temperature of the starting decomposition (loss of weight of 2 %).
- T10: temperature at 10 % of mass loss;
- T50: temperature at 50 % of mass loss;
- Sdr: threshold of rapid decomposition;
- R500: fraction of the residue at 500 °C.

Table 4. The key features of products

Epoxides	Td (°C)	T10 (°C)	T50 (°C)	Sdr (°C)	R500 (%)
Novolac Resin	310	410	450	325	45%

These results show that this resin is thermally stable compared to the Diglycidyl ether bisphenol A (DGEBA) having Td = 110 °C. This stability is influenced by a chemical structure of the agent of the novolac resin (aromatic cycle) and the MDA hardener (aromatic cycle).

3.4.2 IMPROVED THERMAL BEHAVIOR OF NOVOLAC EPOXY RESIN MADE BY CHARGING A REINFORCEMENT OF TRI- SODIUM PHOSPHATE

In this study we have directly incorporated the tri-sodium phosphate into the mixture of epoxy resin and the hardener prior to the crosslinking, then we have achieved the polymerization according to the cooking cycle previously adopted.

The study of the thermal stability of the products obtained was carried out by thermogravimetric analysis under the same conditions of the previous sample. The results of the pyrolysis of all formulations at different mass percentages (15% and 10 Na_3PO_4) are presented in the following figures:

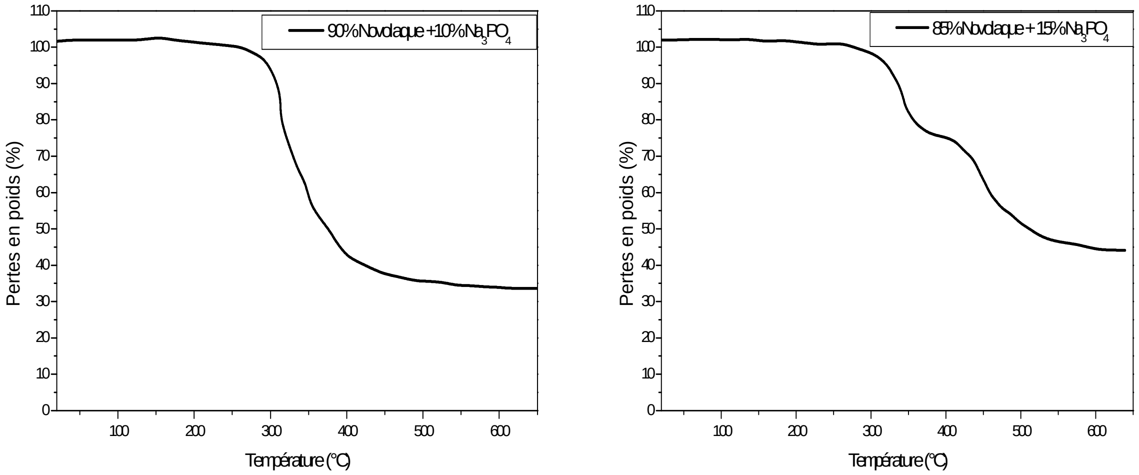


Fig. 11. TGA of the Novolac/MDA/10 system and 15% of Na_3PO_4

These curves have similar rates. The only difference is that the degradation occurs at different rates. All these results show the influence of the rate of phosphate particles on the thermal behavior of composites studied. It is apparent that the incorporation of the mineral charge in this macromolecular matrix improves the thermal stability since the Td rises up to 331 ° C (Table 6).

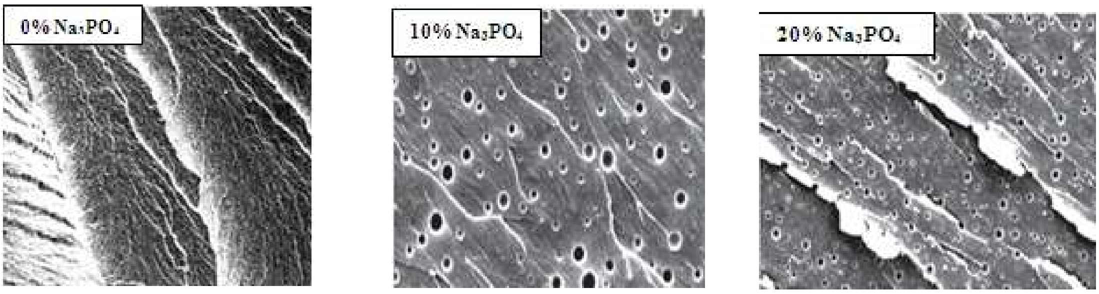
Table 5. Main characteristics of the products

% of the mineral charge	Td (°C)	T10 (°C)	T50 (°C)	Sdr (°C)	R500 (%)
10% Na3PO4	306	340	415	321	45
15% Na3PO4	331	365	485	355	52

3.5 THE SCANNING ELECTRON MICROSCOPY(SEM)

The study of the dispersion of the charge was conducted in novolac epoxy resin matrix to see the dispersion of that charge (Na2 PO 4).

Our composite materials were analyzed by scanning electron microscopy. The results obtained are respectively shown below:



(a) (b) (C)

Fig. 12. The microscope Resin Epoxy Novolac crosslinked by MDA to 0 % (a), 10 % (b) and 15% (c) tri-sodium phosphate load (Na_3PO_4).

According to the observations by SEM , the composites developed based on novolac / Na3PO4/MDA , have clearly shown the appearance of spherical charges of tri- sodium phosphate well dispersed on the analyzed surfaces according to Figure 12.

4 CONCLUSION

In this work, we synthesized, characterized and formulated new composite materials based on novolac epoxy matrix. The hardener used is the methylene diphenylamine in the presence of a load based on tri-sodium phosphate with 0 %, 10 % and 15% percentages. The thermal behavior of these materials has been studied by means of thermogravimetric analysis. It emerges that increasing mass percentage of the load clearly improves the thermal properties of the formulated materials. The knowledge of the rheological properties of these thermoset materials over a wide temperature range is necessary for understanding and controlling the storage conditions, as well as connecting the performance and quality of the product to implementation conditions and the material properties. The rheological properties can be directly related to the chemical structure and / or the degree of conversion of the prepolymer polyepoxy novolac. In this study we are mainly interested in the viscometric and thermal study of this standard novolac resin, crosslinked and formulated by nano-filler based on tri-sodium phosphate, according to its subsequent use in the coating of radioactive wastes.

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