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Morphological, Viscosimetric and Rheological Behavior of Epoxy Resin NGTHTPTBAE and their composite (NGTHTPTBAE/MDA/TSP)

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Abstract: This work presents the elaboration, formulation, morphological, viscosimetric and rheological behaviors of epoxy resin NGTHTPTBAE and its composite (NGTHTPTBAE/MDA/TSP). Furthermore, we studied the viscosimetric behavior of epoxy resin NGTHTPTBAE. Then, the rheological behavior of prepared composites (NGTHTPTBAE/MDA/TSP) crosslinked by methylene dianiline (MDA) as hardened and formulated by trisodium phosphate (TSP) as filler at different percentages. Thus, the conservation modulus G' and loss modulus G'' (or tanδ = G''/G') are established according to temperature. From these dependencies, we determined the glass transition temperature or tanδ maximum. Moreover, tan δ > 1 for liquid-like materials and it becomes lower than unity for solid-like materials. Finally, the dispersion of the trisodium phosphate incorporated into various prepared composite (NGTHTPTBAE/MDA/TSP) was determined using the scanning electron microscope (SEM).

Keywords: Elaboration, formulation, viscosity, rheology, NGTHTPTBAE, composite, SEM.

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INTRODUCTION

Composite polymers are new and more developed hybrid structures (1-2). These reinforced composites contain a single reinforcing phase in the single polymeric matrix, however the hybrid composites can have more than one reinforcing phase and a single matrix phase or a single reinforcing phase with several matrix phases (3-4). Indeed, the hybrid composites can have natural or synthetic fillers. The natural fillers have superior rheological properties such as rigidity, flexibility etc. Their main advantages are low cost, easy production and friendly to the environment. However, the addition of nano-scale synthetic fillers in nanoparticles can improve the viscosity and rheological properties of the polymer (5-6). Furthermore, the hybrid composite materials can generate high rheological properties such as specific strength, rigidity and processing (7-8).

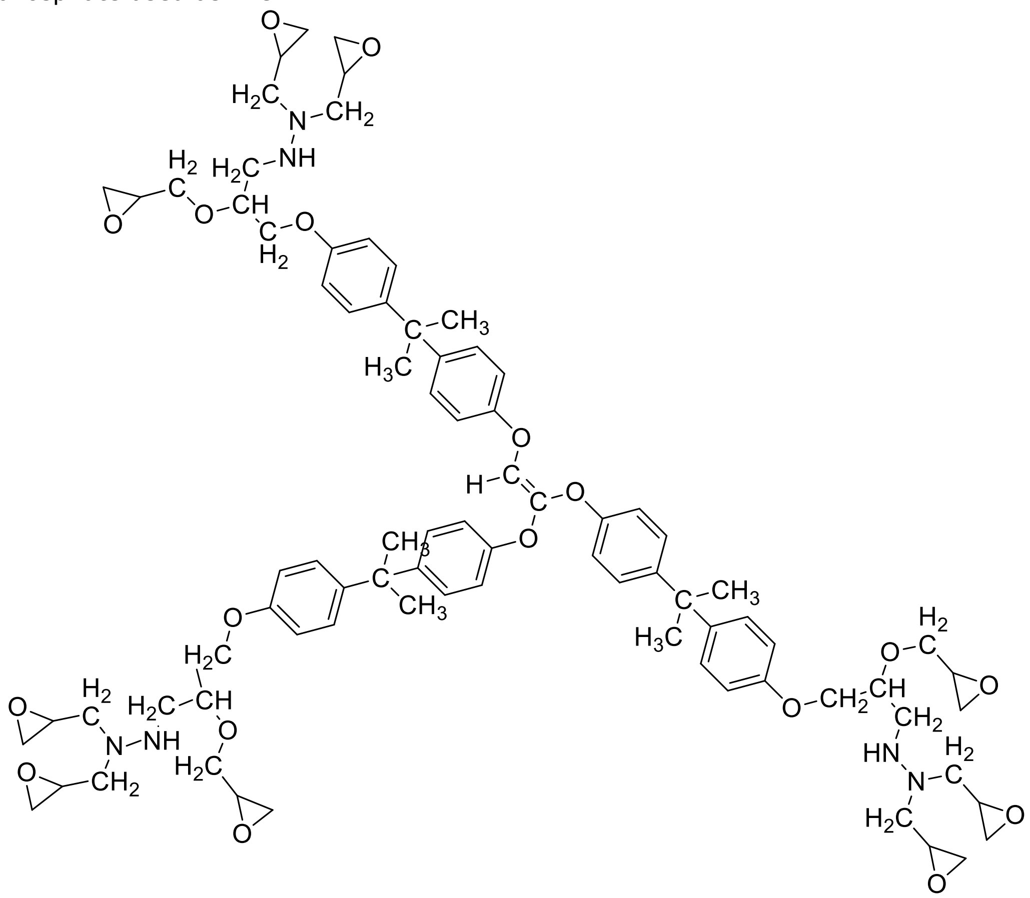
The goal of this work is based on the elaboration, formulation, morphological, viscosity and rheological behaviors of the nanofunctional epoxy resin NGTHTPTBAE and their composite (NGTHTPTBAE/MDA/TSP). The presence of the trisodium phosphate dispersed in the epoxy matrix is used to improve the rheological properties of the composite (NGTHTPTBAE/MDA/TSP) (9-10). Finally, the dispersion of the charge in the macromolecular epoxy resin NGTHTPTBAE was monitored using a scanning electron microscope.

MATERIALS AND METHODS

Used products

During this work, we used the epoxy resin named nanoglycidyl trihydrazine 4.4.4-tripropoxy tribisphenol A of ethylene (NGTHTPTBAE) (11)

(Scheme 1), methylene dianiline as hardened and trisodium phosphate used as filler.



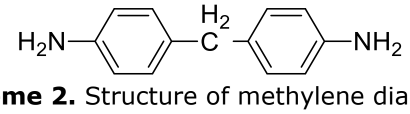
Scheme 1. The structure of the epoxy resin NGTHTPTBAE.

Rheological analysis

The viscosimetric and rheological behaviors of epoxy resin and its composite were followed by using a RHM01-RD HAAKE type of rheometer. The measurement conditions used by a RHM01-RD HAAKE rheometer are as follows:
Temperature in °C: 80 °C;
Rotation speed CR mode: 10-8 0 1500 rpm;
Frequency: 10^{-5} to 100 Hz.

Preparations of the samples analyzed by the rheometer

We used methylene dianiline as a hardener to crosslink the epoxy resin. The methylene dianiline has good thermal stability and good mechanical properties. It is often used for high-tech applications in the implementation in the desired form (12-13).The chemical structure of methylene dianiline is shown in Scheme 2.



Scheme 2. Structure of methylene dianiline.

The procedure consists of preheating the stoichiometric amounts of both the hardener and the epoxy resin. The methylene dianiline is placed in an oven at 120 °C while the resin is heated to 60 °C. Once molten, the methylene dianiline is mixed with the resin to give a single fluid phase. We applied the same protocol to the crosslinking reaction in the presence of trisodium phosphate at various percentages (0%, 5%, 10% and 15%) as a filler.

Scanning electron microscopy

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

Calculation of stoichiometric coefficients

In order to obtain optimum properties when we cure the nanofunctional epoxy polymer in the presence of hardener, it is desirable to make the polymer and the curing agent react to approximately stoichiometric amounts (14-15). The equivalent epoxy weight and the amine hydrogen equivalent weight are calculated according to equations 1 and 2. Furthermore, the ratio by weight of the hardener relative to the epoxy resin is calculated in the majority of cases per 100 parts of the resins or parts per hundred parts of resin (PHR) (equation 3). Thus, the amount of the desired charge is calculated using equation 4.

$$EEW = \frac{M_w(NGTHTPTBAE)}{f} \quad \text{(Eq. 1)}$$

$$AHEW = \frac{M_W(MDA)}{f} \quad \text{(Eq. 2)}$$

$$PHR = \frac{AHEW}{EEW} \quad \text{(Eq. 3)}$$

$$y\% = \frac{x}{resin+MDA+x} \quad \text{(Eq. 4)}$$

Where *f* is the functionality of the epoxy resin, x is the amount of the NGTHTPTBAE and y is the amount of the trisodium phosphate load.

RESULTS & DISCUSSION

Viscosity

The viscosity concerns the study of deformation, elasticity, flow and implementation of material considered. Moreover, we were interested in the viscosity of the epoxy resin (NGTHTPTBAE) because it plays an important role in the flow and implementation phenomena. The viscosity of the matrix according to temperature is presented in Figure 1, which shows the viscosity of the nanofunctional epoxy resin NGTHTPTBAE as a function of temperature. The viscosity diminished with increasing temperature, this indicates that the molecular mobility of the nanofunctional epoxy resin NGTHTPTBAE is high. This means by the heat provided by the device that speeds up the process of depolymerization of the nanofunctional epoxy resin NGTHTPTBAE (16-17).

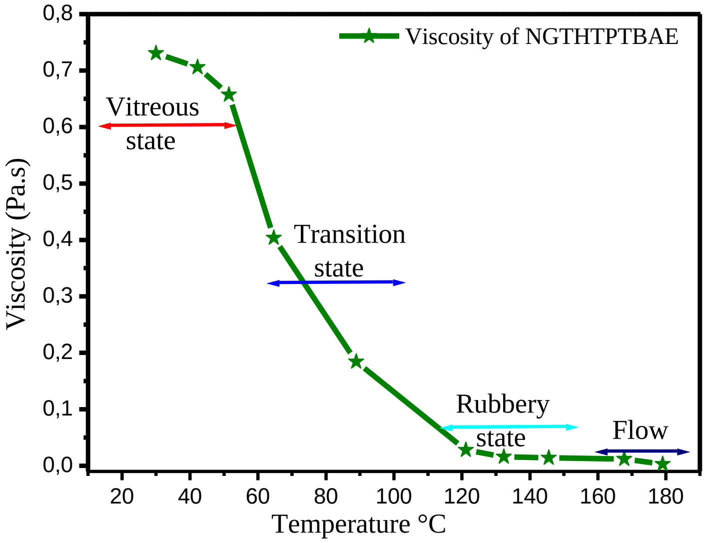


Figure1. Viscosity of the epoxy resin NGTHTPTBAE according to the temperature.

Complex viscosity

Figure 2 present the complex viscosity of the epoxy resin (NGTHTPTBAE) according to frequency. Moreover, the complex viscosity in Figure 4 shows that the complex viscosity decreases with increasing frequency. Then, the increase in the frequency implies that the epoxy resin NGTHTPTBAE passes from a viscous state to a liquid state, which explains the drop in the observed viscosity (18). This result confirms that of the viscosity according to temperature. Therefore, it is necessary to store the synthesized epoxy resin (NGTHTPTBAE) at low frequency and at low temperature.

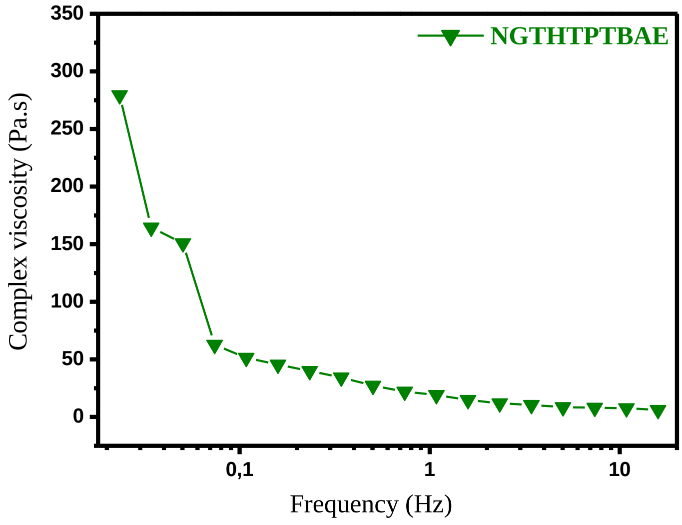


Figure 2. Complex viscosity of the epoxy resin NGTHTPTBAE according to frequency.

Conservation modulus G' and loss modulus G'' according to temperature

Figure 3 present the conservation modulus G' and the loss modulus G'' of epoxy resin (NGTHTPTBAE) according to temperature, respectively. From Figure 5, we observed that the conservation modulus and loss modulus of epoxy resin (NGTHTPTBAE) increases with the increase in the temperature. From the phase transition temperature the conservation modulus and loss modulus are seen to diminish. Moreover, at the temperature below of the glass transition temperature, the response of the rheological behaviors is the gel type. However, at the temperature superior the glass transition temperature, the response of the rheological behaviors is the liquid type (19). Then, the glass transition temperature of the conservation modulus G' and the loss modulus G'' are equal to 114 °C and 128 °C, respectively. Moreover, the variation of tanδ as a function of temperature is presented in Figure 4. From Figure 4 we noticed, up to 76 °C, the response of the material is of the gel type. Starting at 76 °C the answer is of the liquid type. This is explained by the polymerization of the nanofunctional epoxy resin (NGTHTPTBAE).

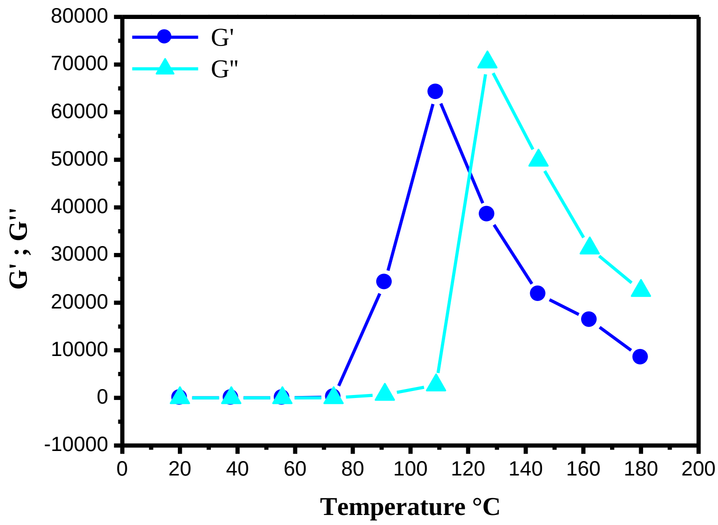


Figure 3. Conservation modulus and loss modulus according to the temperature.

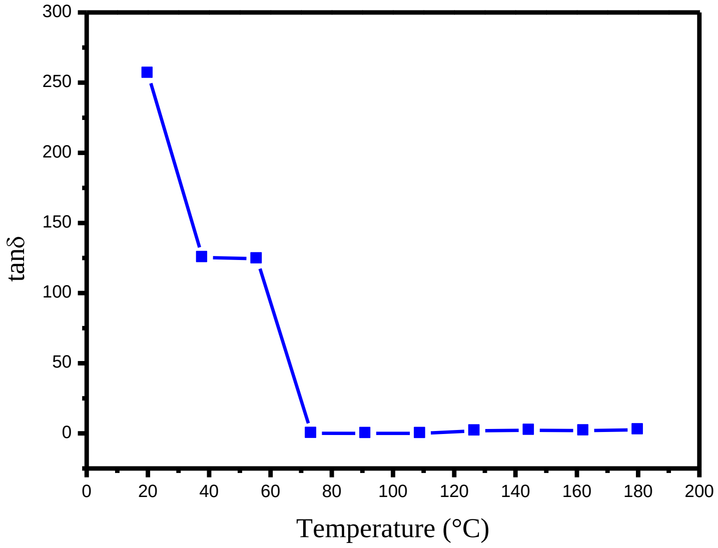


Figure 4. tan δ according to temperature.

Conservation modulus G' and loss modulus G'' according to the frequency

The conservation modulus *G'* and loss modulus G'' of composite (NGTHTPTBAE/MDA/TSP) is illustrated in Figures 5 and 6. From figures 5 and 6, we observed that the conservation modulus and loss modulus of elaborated composite (NGTHTPTBAE/MDA/TSP) increase with increasing frequency (20). In addition, we noticed that the conservation modulus and loss modulus increased with the percentage of the load of the trisodium phosphate incorporated in the composite (NGTHTPTBAE/MDA/TSP) (21-23). This can be explained by the charge of the trisodium phosphate incorporated in the different composites is well formulated.

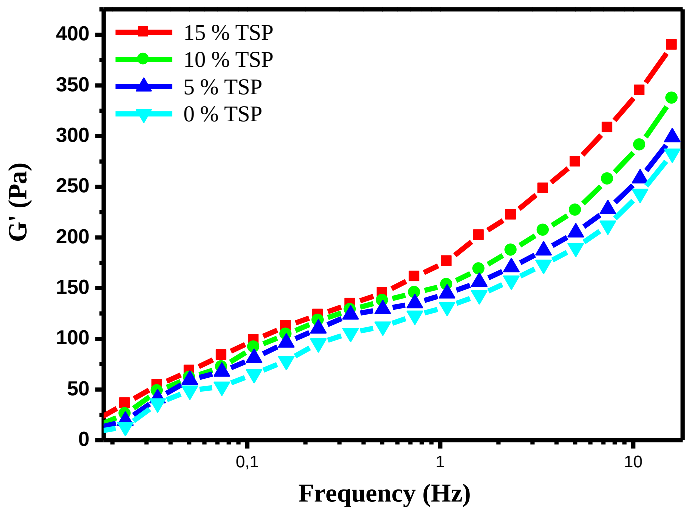


Figure 5. Conservation modulus G' of composite (NGTHTPTBAE/MDA/TSP) according to frequency.

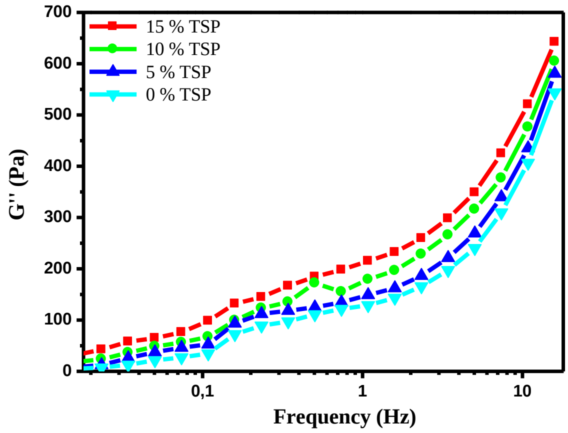


Figure 6. Loss modulus G'' of composite (NGTHTPTBAE/MDA/TSP) according to frequency.

Scanning Electron Microscopy

The morphology of different composites (NGTHTPTBAE/MDA/TSP) prepared in the absence and in the presence of trisodium phosphate is shown in Figure 7. This morphology was determined by the scanning electron microscope. In addition, the morphology of different composites (NGTHTPTBAE/MDA/TSP) crosslinked by methylene dianiline and formulated by trisodium phosphate was observed by the scanning electron microscope. The comparison of the different morphologies based on four different formulations showed that the type of formulation is a key factor in controlling the morphology of the composite. The morphology of the thermosetting composite varied with the different percentages of the trisodium phosphate (TSP) load (24-26). According to these observations of the morphology (Figure 7), we showed the good dispersion of the trisodium phosphate in the composite.

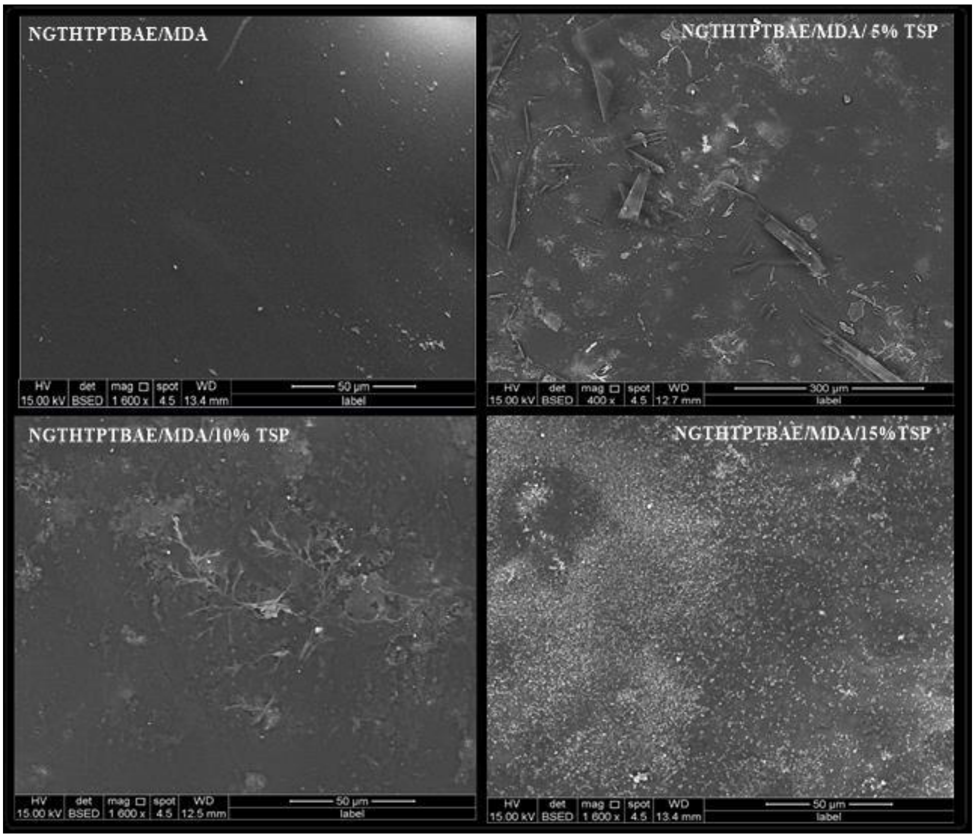


Figure 7. Morphology of different composite (NGTHTPTBAE/MDA/TSP) crosslinked by methylene dianiline and formulated by trisodium phosphate.

CONCLUSION

In this work, we elaborated and formulated a nanofunctional epoxy resin NGTHTPTBAE. Then, we prepared the composite (NGTHTPTBAE/MDA/TSP) crosslinked with methylene dianiline and formulated by trisodium phosphate. Furthermore, we proceeded to the viscosimetric and rheological properties of the epoxy resin (NGTHTPTBAE) and its composite (NGTHTPTBAE/MDA/TSP), respectively. On the one hand, we deduced the different viscosity states of the epoxy resin as a function of temperature. This allowed us to notice that the variation of the complex viscosity decreases according to frequency. On the other hand, we studied the conservation modulus and loss modulus according to the temperature and the frequency. Indeed, the study of the composite (NGTHTPTBAE/MDA/TSP) with different formulations showed us that the conservation modulus and loss modulus increase according to the frequency. Finally, we followed the dispersion of the trisodium phosphate load incorporated in the composite (NGTHTPTBAE/MDA/TSP), using a scanning electron microscope.

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