Moroccan Journal of Chemistry
ISSN: 2351-812X
http://revues.imist.ma/?journal=morjchem&page=login
El-Aouni & al. / Mor. J. Chem. 6 N°2 (2018) 272-282

Thermal And Rheological Behavior Of A New Hybrid Nanocomposit Based On A New Tetrafonctional Pre-Polymer / Mda / Ntc

N.EL-AOUNI*, 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 IbnTofail, BP 133, 14000, Kenitra, Morocco.

** Corresponding author:* nawal.elaouni@gmail.com
Received 10 Sept 2017, Revised 26 Oct 2017, Accepted 03 Jan 2018.

Abstract

We have synthesized in this work a new tetrafunctional epoxy prepolymer in two steps for the formulation of a new hybrid microcomposite with NTC as a load. In a first step we synthesized the TBDGEBA based on tetrabromo of Bisphenol A for this purpose. In a second step, we proceeded to the chemical modification of this bifunctional pre-polymer precursor of TGEDADPTBBA by aniline as nucleophilic reagent which led to the synthesis of a tetrafunctional epoxy polymer TGEDADPTBBA. This epoxy prepolymer was then thermally crosslinked with methylene dianiline (MDA) in the presence of CNT based load in order to obtain new nano-composite materials at different percentages. The thermal study of these composite composites was studied by thermogravimetric analysis while the rheological characterization of the nanocomposites was carried out through the use of a RHM01-RD HAAKE rheometer.

Keywords: ; New tetrafunctional epoxy prepolyme- Nanocomposites; TBDGEBA; TGEDADPTBBA; Nucleophilic reaction; Nucleophilic reaction; Rheological ; thermogravimetric.

1.Introduction

Polymer nanocomposites reinforced with nanoscale charges have attracted a lot of attention in recently because of their interesting range of applications, as a load for polymeric nanocomposites, carbon nanotubes (CNT), which have Nanometric dimensions. The latter have received a lot of attention as potential materials in many areas because of their outstanding physical, chemical, electrical properties etc. .... [1,2 ,3]. However, their high cost especially that of CNT limits their practical application [4-5]. As a result, a number of recent studies have been carried out on the thermal, electrical and mechanical properties of hybrid nano-composites by using carbon and CNT charges.[6-7].

The rheological behavior of nano-composites which were synthesized in the laboratory was studied with respect to their viscosity, the storage modulus (G') and the loss modulus (G"). Their thermal properties have also been discussed.

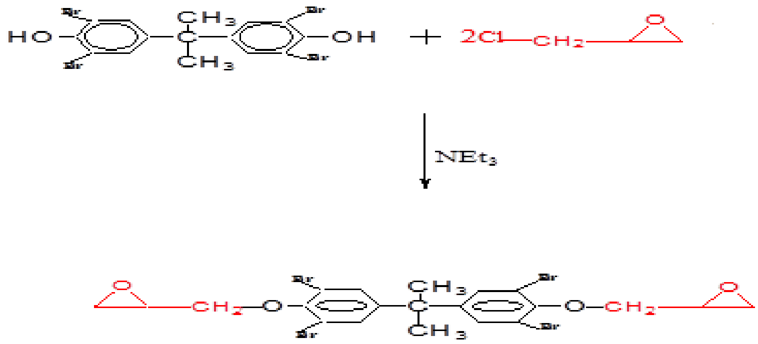
1. Experimental materials and methods

1.1. Materials

The following materials were used in our work: Tetrabromo of bisphenol A, aniline, methanol, epichlorohydrin, and load based on carbon nanotubes (CNT).

1.2. Summaries of DGETBBA, the precursor to the TGEDADPTBBA.

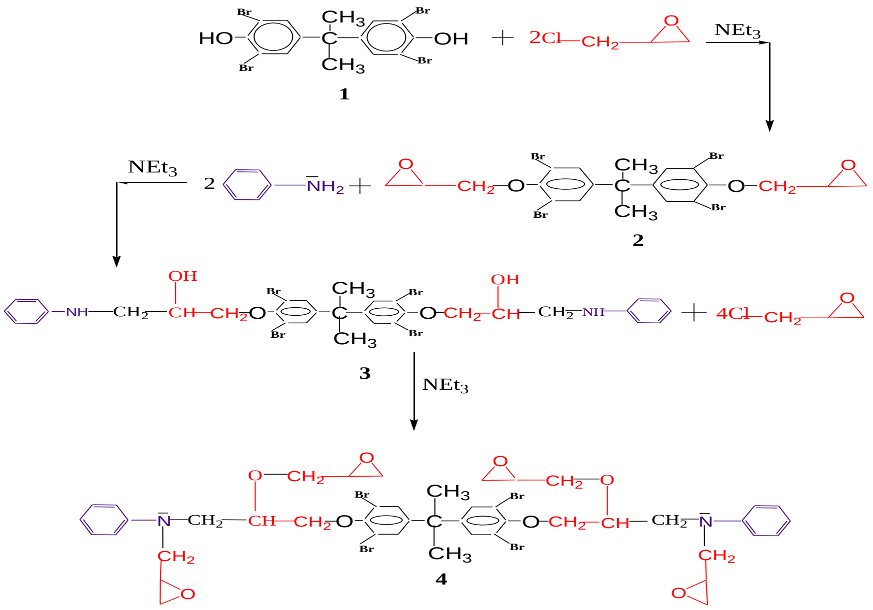
The DGETBBA resin was synthesized according to the procedures of the literature [8, 9, 10, 11].



Schematic 1. The DGETBBA synthesis diagram.

1.3. Synthesis of the TGEDADPTBBA

The tetraglycidyl ether dianilinedipropoxy resin of bisphenolAtetrabromo (TGEDADPTBBA) is synthesized in two reaction steps. We obtained the TBDGEBA by the condensation of the tetrabromo of bisphenolA and the epichlorohydrin in the presence of an NEt3 base in the first step while in the second we synthesized the tetrafunctional resin by the addition of a nucleophile (aniline) to the TBDGEBA[12].



Schematic 2. The TGEDADPTBBA synthesis diagram.

1.4. The hardener

The crosslinking matrix is a primary diamine: methylene dianiline (MDA) is known for its excellent mechanical properties and the good thermal stability which it provides to the final product, compared to the other hardeners [13, 14]. Its structure is given in diagram 3.

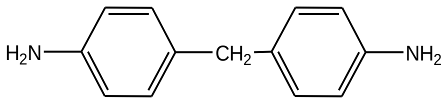


Figure 3. Developed formula of methylene dianiline (MDA).

1.5. The load

We used the multi-carbon nanotube carbon nanotube (CNT) load having the following characteristics in our formulations: outer diameter (10-20 nm), inner diameter (5-10 nm) and length (from 0, 5 to 20 microns). It is evident that the dispersion of the load which leads to a more or less homogeneous mixture of the components is a parameter which influences the physical properties of the composite.

1.6. *Viscosimetric Analysis*

The viscosity measurements were carried out through the use of aUbbelohd viscometer and the measurement conditions which were used are as follows:

- Viscosimeter of size 1b for a dilution series, capillary tube, constant k = 0.051493.
- Measuring temperature in °C: 30; 35, 40, 45, 50, 55, 60 and 65
- Number of measurements: 3 each time
- Solvent: methanol
- Hagenbach correction was calculated according to the formula which is given in DIN 51562 January 1st, 1999 (Measurement of kinematic viscosity by means of the Ubbelohde viscometer).
- the solubilization of the prepolymers of epoxy resin in methanol was carried out with magnetic stirring at 20°C.

1.7. Rheological analysis

The rheological properties of TGEDADPTBBA and the nanocomposites were carried out on a controlled Haake Mars rheometer strain, rheometer system. The samples were pressed less than 15 MPa so as to obtain the disc as samples of 25 mm in diameter and 1.2 mm thickness.

1.8. Thermogravimetric analysis

We used the technique of thermogravimetric analysis (ATG) [16] in order to carry out our study which concerns the degradation of synthesized epoxy resins and the measurements of the degradation kinetics by loss of mass were carried out through the use of SETARAM TAG 24S apparatus. The rise rate of temperature is 10 ° C Min ± and the temperature measurement page is from 0 to 600 ° C. The sensitivity of the balance is 0.5µg, and the masses measurable within ± 200mg.

2. Results And Discussion

2.1. Thermogravimetric analysis of nanocomposites: TGEDADPTBBA/NTC/MDA

The thermogravimetric analysis allows the evaluation of the materials' behavior once subjected to the action of temperature, which is an essential tool for testing the heat resistance of polymer materials, and hence the evaluation of their thermal stability. The obtained results for the TGEDADPTBBA / MDA / CNT nanocomposites at different percentages by weight of CNT are shown in figure 1.

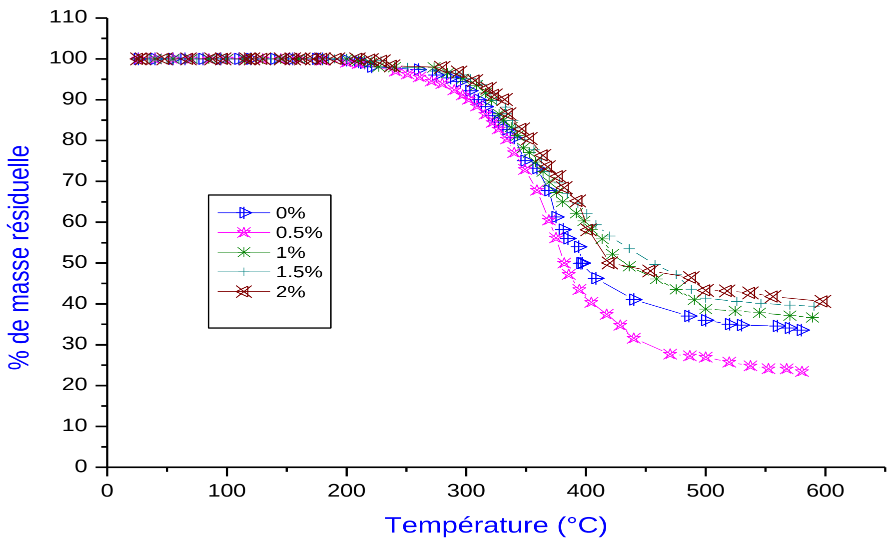


Figure 1 : Thermal behavior of formulations TGEDADPTBBA/ MDA / CNT.

In addition, we have measured the characteristics of these materials, according to conventional standards [16, 17]:

- Td: the starting temperature of degradation which corresponds to the loss of 2% by mass.
- T10: temperature at loss of 10% mass.
- T50: temperature at loss of 50% mass.
- Sdr: the threshold of rapid degradation.
- R500: The residual fraction at 500 ° C.

The main thermal characteristics of the TGEDADPTBBA, which are formulated with the NTC taken from the curves, are given in Table 1:

Table 1: Thermal characteristics of formulations TGEDADPTBBA / MDA / CNT

% Wight of CNT	T_d (°C)	T_{10} (°C)	T_{50} (°C)	S_{dr} (°C)	R_{500}(%)
0	209	301	381.81	350	26.96
0.5	221	310	397	359	36
1	227	316	407	369	38.70
1.5	233	326	413	381	41.4
2	238	332	420	390	43.3

We notice that there is an analogy in these results because the thermal stability increases as the percentage of CNT increases. This improvement, which reaches its maximum of 2% of NTC is probably due to the dispersion of the loading material which occupies the volume of the macromolecular network which is obtained interchain.

The analysis of these results remarkably shows that the use of a charge (NTC) increases the thermal resistance of the formulated materials. According to FIG. 2, the addition of 0.5% NTC indeed increases the start of degradation of the TGEDADPTBBA / MDA / NTC material by 12 ° C. We have also noticed that the thermal stability increases according to the percentage of the added CNT.

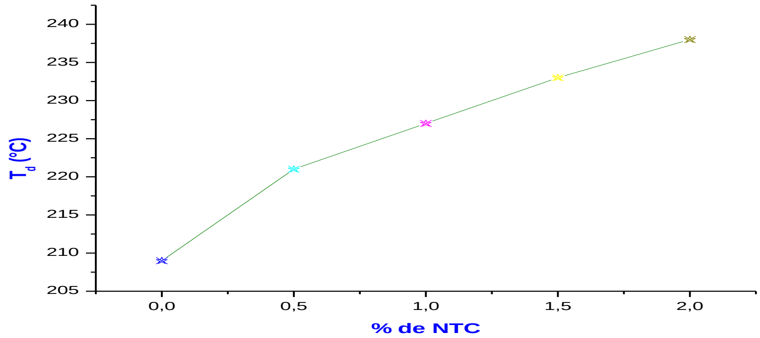


Figure 2: Evolution of Td according to the percentage of NTC

2.2. The rheological behavior

2.2.1. The viscosimetric behavior of the standard pre-polymer analyzed by the Ubbelhod VB-1423 viscometer

The different viscosity curves which are obtained from the synthesized epoxide prepolymer (TGEDADPTBBA) dissolved in methanol are shown in figures 3 and 4.

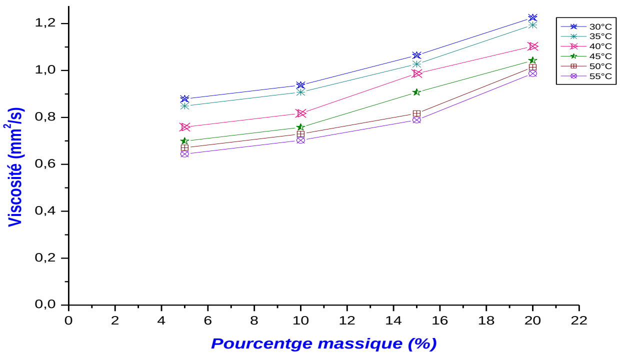


Figure 3: Variation of the viscosity of the standard prepolymer according to percentage by mass at different temperatures.

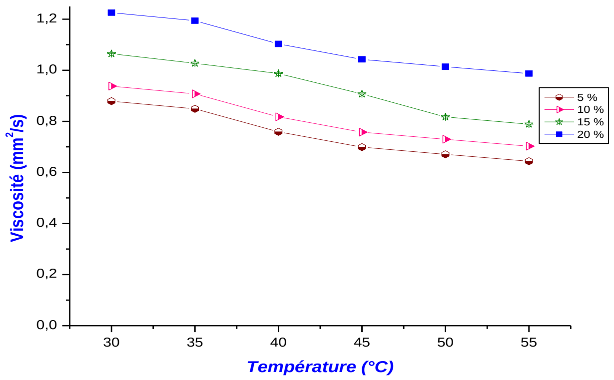


Figure 4 : Variation of the viscosity of the standard prepolymer according to temperature at different concentrations.

We have concluded from these figures that the viscosity values increase as the pre-polymer mass concentration increases, which 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 [18-19-20-21]. This increase in temperature indeed implies that the prepolymer TGEDADPTBBA passes from a viscous state to a liquid state, which explains the drop in the observed viscosity (Figure 4) [22]. According to this study, the synthesized resin (TGEDADPTBBA) could be conserved / stored under optimum conditions before any industrial use.

2.2.2. ***Viscoelastic behavior of the prepolymer (TGEDADPTBBA) analyzed by the RHM01-RD HAAKE type rehometer***.

The rheology is related to the study of the flow, the deformation, the elasticity and the viscosity of the material in question but we have been interested in the visco-elastic behavior of the prepolymer (TGEDADPTBBA) since it plays a major role in the flow phenomena of the macromolecular matrix. Our rheological study of the standard matrix based on epoxy prepolymer (TGEDADPTBBA) gives the viscosity under the effect of rotation constraint and under a controlled atmosphere according to temperature. The Figure 5 shows the characteristics of the rheological behavior of the tetrafunctional resin as a function of temperature. We observe in this figure that the gel time decreases with increasing temperature [23-24] while the heat supplied accelerates the process of depolymerization of the resin. We also notice a viscoelastic diagram of four phases in our case, namely:

Vitreous state: molecular mobility is high at low temperature and reduced viscosity.

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

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

Flowing state: the viscosity is reduced at high temperature and totally free molecular mobility.

The viscosity strongly depends on temperature in order to maintain a sense of the measure in which we specify the temperature at which it was made. The viscosity decreases rapidly according to temperature in a liquid. This result allowed us to confirm the study of the viscosimetric behavior of Ubbelhod type.

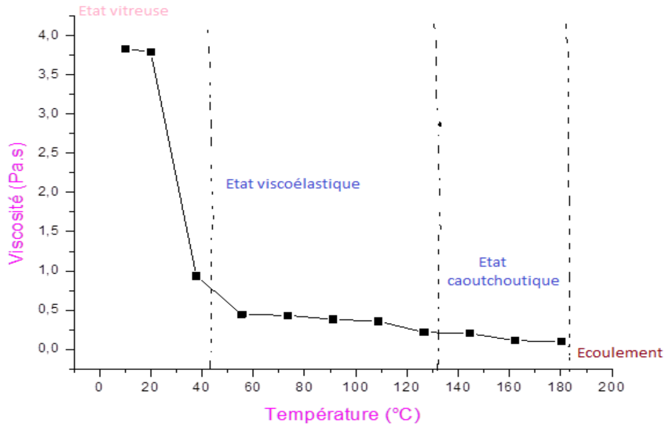


Figure 5: the different states of the viscoselastic η of the prepolymer according to temperature T.

2.2.3. Behavior of the viscosity of the crosslinked and formulated prepolymer.

We have shown the influence of temperature and the CNT content on the viscosity behavior of the cross-linked prepolymer in figure 6.

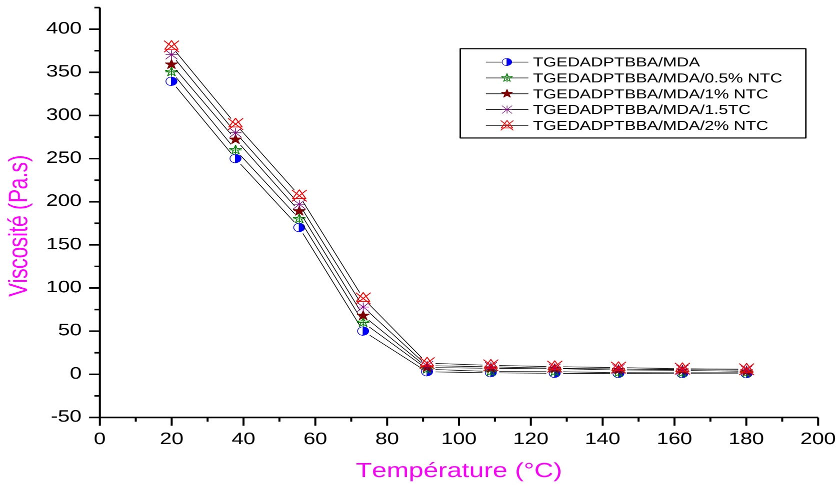


Figure 6 : Variation of viscosity according to temperature

This figure shows the flow curve which is obtained for TGEDADPTBBA / MDA and TGEDADPTBBA / MDA containing different levels of NTC at different temperatures. The viscosity of the prepared preparations based on the prepared prepolymer (TGEDADPTBBA) increases, in fact, once the CNT content increases. The addition of a low CNT content (0.5% by weight) induces a slight increase in viscosity.

2.2.4. *Elastic rheological behavior (storage or stock modulus G') and vitreous (loss modulus G'') of the cross-linked and formulated pre-polymer.*

The rheological behavior of nanocomposites literature (viscoelastic behavior) often shows that the latter leads to a better understanding of the structures and relations responsible for the reinforcement of polymers by CNT. This technique is most often the key to understanding and improving the implementation. We concentrated in this part on the study of the rheological behavior of nanocomposites made up of a dispersion of CNT particles in an epoxy matrix (TGEDADPTBBA). We sought to establish a link at least qualitatively between the thermal properties which are

obtained for nanomaterials and their rheological behavior. The rheological analyzes of the nanocomposites TGEDADPTBBA / MDA / CNT were carried out at 80 ° C and with a frequency ranging from 0.1 to 100 rad / s.

2.2.4.1. Evaluation of the elastic G' and vitreous G'' behavior according to the frequency and the angular velocity of the crosslinked and formulated prepolymer.

Figures 7 and 8 show the storage or stock module G ' and the loss modulus G". They shows, on the one hand, the increase of the latter according to the frequency and that the variation in elastic behavior G' and vitreous behavior G" increases with the percentage of the charge of NTC incorporated in the epoxy matrix on the other hand. This may explain that the formulation of the composite (TGEDADPTBBA / MDA / CNT) is well cured.

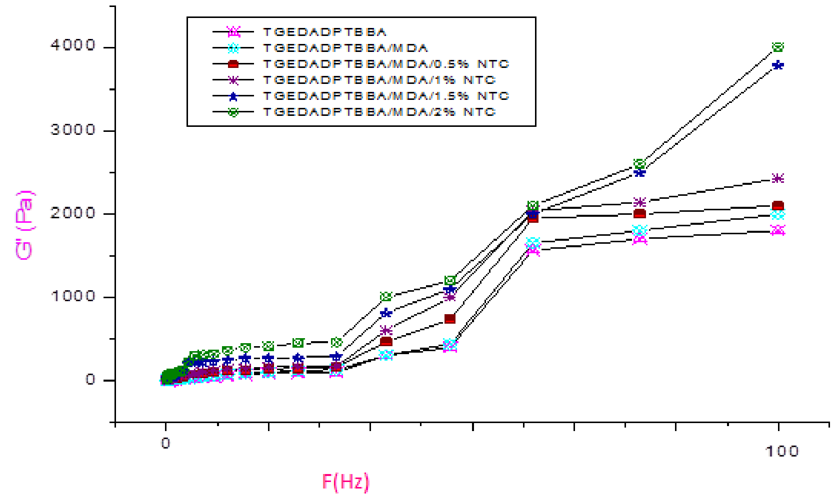


Figure 7 : Variation of the elastic behavior G " according to the frequency of the formulations (TGEDADPTBBA / MDA / CNT)

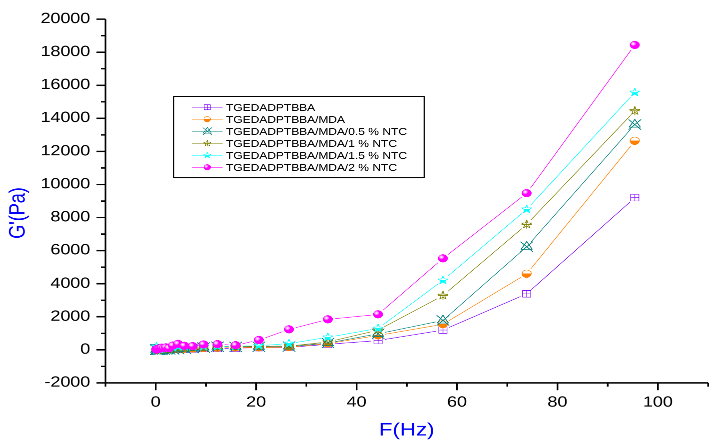


Figure 8 : Variation of the elastic behavior G 'according to the frequency of the formulations (TGEDADPTBBA / MDA / CNT)

Figures 9 and 10 which show the storage or stock module G ' and the loss modulus G' ' clearly show once again the increase in the latter according to the angular velocity. We observed on the one hand a regular increase in the elastic behavior G ' and the low-frequency of glassy behavior G' ', reflecting the progressive reorganization of the structure. However, we observed on the other hand that the variation of elastic behavior G ' and vitreous behavior G' ' increases

with the percentage of the charge NTC incorporated in the epoxy matrix. These results for the studies of the elastic behavior G ' and the vitreous behavior G' ' according to the angular velocity, which confirm the previous results. Therefore, they confirm that an epoxy system loaded with a CNT charge exhibits a strong interaction between the epoxy resin and the carbon nanotube charges. [25-26].

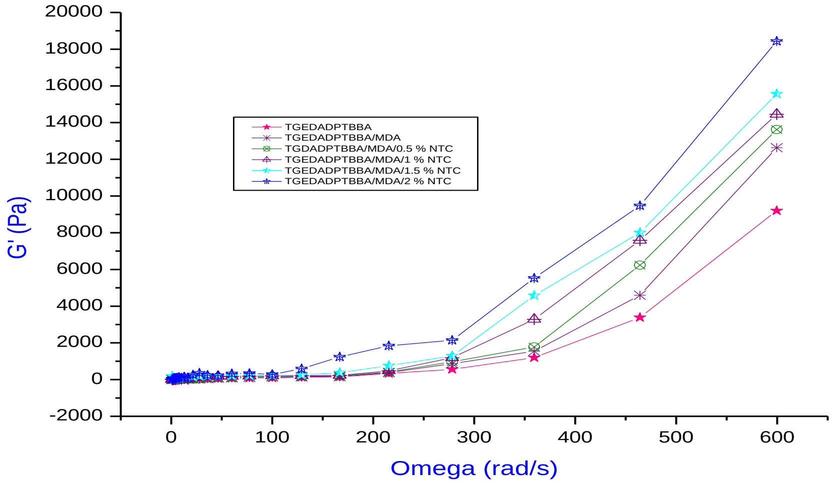


Figure 9 : Variation of the elastic behavior G ' according to the angular velocity of the formulations (TGEDADPTBBA / MDA / CNT).

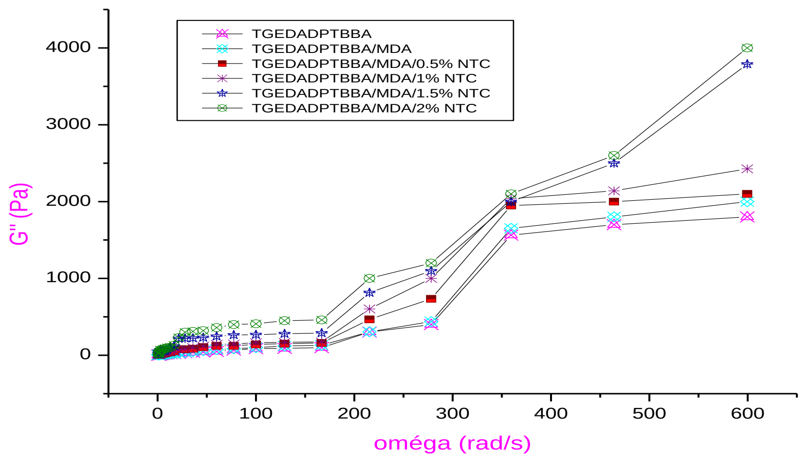


Figure10: Variation of the glassy behavior G " according to the angular velocity of the formulations (TGEDADPTBBA/MDA/CNT)

2.2.4.2. The variation of the elastic G' and the vitreous G'' behavior of the pre-polymer cross-linked and formulated according to temperature.

The figure11 presents the elastic behavior G ' (frequency is 1 Hz and a stress is 0.1 Pa) according to the nano-composites' temperature with different content of the CNT.

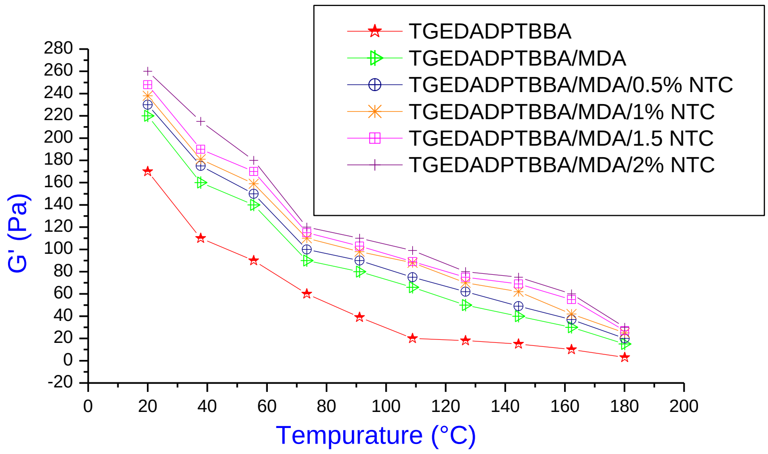


Figure 11: Variation of the elastic behavior G ' according to the formulations' temperature (TGEDADPTBBA/MDA/CNT)

According to the latter:

- We observed that the storage (stock) modules G' vary according to the increase in temperature.
- We also notice that the increase in the tenure of the NTC improves the storage modulus G
- The rheological results are synonymous to improve the physical properties of our formulated materials. We find that there is a correlation between the optimization of the rheological and thermal properties due to the increase of the CNT in the matrix, which is in agreement with the thermo-gravimetric results.

4. Conclusion

In fact, the rheological study of nanocomposites (TGEDADPTBBA/MDA/NTC) exhibit a better behavior in the nano-composites formulas based on the NTC. Their thermal properties were increased by the addition of CNTs. They are synonymous with the stability of the heterogeneous network in three dimensions (matrix - charge) and can also have a positive impact on the mechanical strength of the material since the rheological analyzes show a certain analogy between the thermal and rheological behavior.

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