

# Comparative study of the rheological and thermal properties of the formol phenol novolac epoxy and those of the model resin diglycidylether of bisphenol A (DGEBA).

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## Abstract

The objective of this work is to study the thermal and rheological properties of thermoset polymers, epoxy polymers cases, such as novolac and bisphenol A diglycidylether (BADGE). The macroscopic characterization epoxy resins Diglycidyl ether of bisphenol A and phenol formaldehyde epoxy novolac was made by the method of analysis of the rheological behavior of standard matrices before their cross-linking in order to determine their storage conditions. Both thermosetting matrices showed high mechanical stability in view of temperature, time and constraints. This leads us to assume that they can be stored to standard thermodynamic conditions without fear of cross-linking. The viscosimetric study shows that a good storage of the resin (non-self-cross-linkable) leads to a homogeneous mixture of the composite after the addition of the hardener. Subsequently, these two resins have been an objective of two cross-linking reactive systems in the presence of an aromatic diamine (MDA) Epoxy / Amine (DGEBA / MDA) and epoxy novolac / MDA). Subsequently, we compared their thermal stability. Thermo-gravimetric study shows firstly, that standard resins are thermodynamically stable, and then epoxy novolac systems / MDA and DGEBA / MDA. Furthermore, the thermal behavior of novolac / MDA system is better than the DGEBA / MDA system.

**Keywords:** Comparative study, cross-linked and standard epoxy polymers, novolac / MDA system, DGEBA / MDA system, ATG, viscometer.

## 1. Introduction:

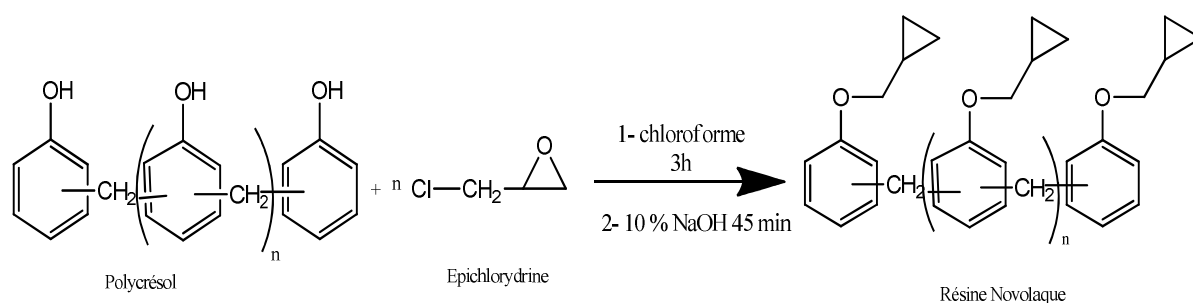
Thermosetting resins, particularly the polyepoxides, constitute binder matrixes of high performance composites by excellence. Many industries make use of thermosetting resins or composites of these materials as cited in the following examples: aerospace industry (aircraft, helicopters ....), car industry (vehicles weight relief by the use of organic matrixes composites), paint industry, varnishes, glues and coating components etc. The various epoxy systems can be manufactured in different chemical compounds to open the epoxy cycle and define the epoxy monomers. Therefore, by the use of aromatic amines as hardening agents [1], various epoxy systems with a wide range of chemical and physical properties can be obtained [1, 2, 3,4]. The thermal properties of such resins depend mainly on their chemical structure, as

provided by their aromatic cycles, and the adhesive strength. The corrosion resistance and the rigidity are provided respectively by the hydroxyl functions and of the cores of Bisphenol A of these types of resins, while their resistance to hydrolysis is due to ether bridges [5]. The properties studied in our work are the rheological properties of the two standard resins and thermal properties of both systems DGEBA / MDA [6,7, 8], novolac / MDA. [9]

## 2. Experimental Methods :

### 2.1. Synthesis of the epoxy novolac resin:

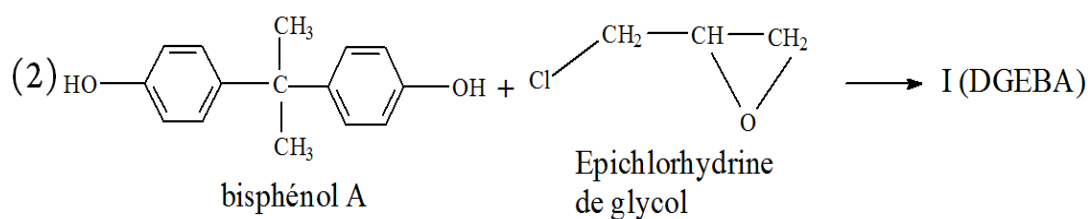
The epoxy novolac resin is prepared by condensing epichlorohydrin and a polycrésol resin (hydroxy novolac) in an alkaline medium [9, 10, 11].



**Figure 1:** reaction scheme of the synthesis of the novolac epoxy resin [9]

### 2.2. Synthetic resin DGEBA:

DGEBA resin based on two condensation reactions:



**Figure 2:** reaction scheme of the synthesis of the DGEBA resin [4.11]

### 2.3. Samples preparation:

The presence of the epoxy resin and the MDA produces a hardening of the resin due to the cross-linking reaction. The protocol is the one adopted by Fetouaki et al. It consists of a pre-heating of stoichio-metric amounts of the resin and the hardener [10]. 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. Once melted, MDA is mixed with the resin to provide a single fluid phase being then at 70 ° C. The samples, thus prepared, were sealed in molds and underwent the following heating cycle:

- Twelve hours at 70 ° C and one hour at 140 ° C [10, 12, 13,14, 15, 16].
- After demoulding, the sample is brought into the desired geometric shape.

## 3. Results and discussion:

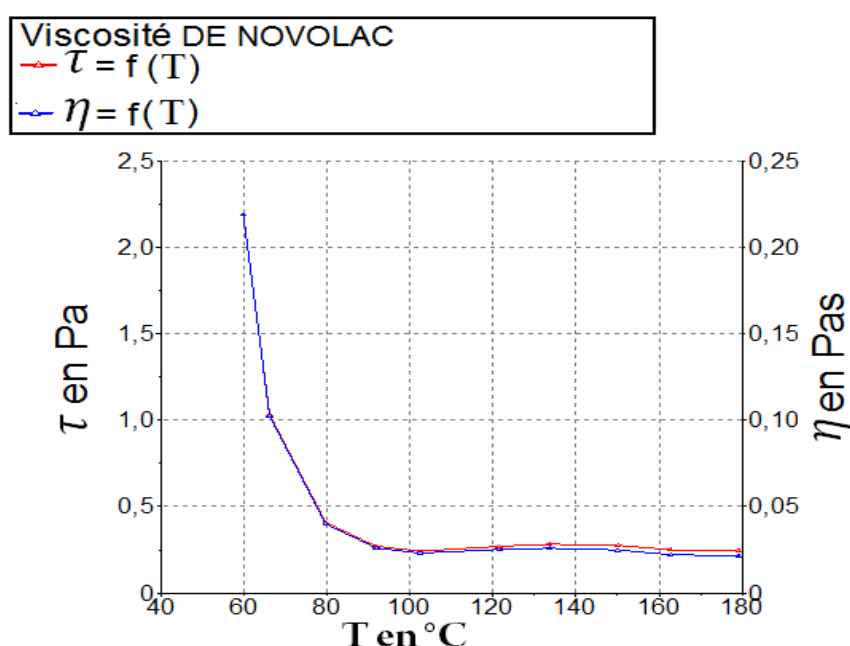
### 3.1. Physical properties of the two epoxy resins:

Rheology refers to the study of the flow, deformation, elasticity and viscosity of the material in question. We are primarily interested in the viscosity as long as it plays a key role in the phenomena of flow of the organic matrix, more generally the viscosity of the material under the effect of an applied stress. It also determines the macroscopic mechanical properties from a study based on micro or nano-scopal structure of the material. Our rheological study of standard matrixes are respectively the novolac epoxy resin and DGEBA resin giving the viscosity under the rotational effect of stress and under an atmosphere controlled with respect to time and temperature.

### 3.1.1. Rheological Study standard novolac epoxy resin:

#### 3.1.1.1. Viscosity and constraint in view of the temperature ° C

In Figure 3, we varied the viscosity of the Novolac under the effect of constraint in view of temperature with the fixing speed.



**Figure 3:** Rheogram of viscosity  $\eta$  and constraint  $\tau$  in view of temperature

#### 3.1.1.2. Viscosity and constraint in view of speed (1 / S) :

In the study relating to figure 4, we varied the viscosity of novolac under the effect of constraint in view of speed at the fixing temperature. The velocity gradient values  $\gamma'$  obtained after the corresponding equation is:

$$\tau = \eta \gamma'$$

Where  $\tau$  is the constraint (measured in Pa in the International System (IS) of measurement),  $\gamma'$  is the velocity gradient in the thickness (measured in s<sup>-1</sup>), and  $\eta$  is the dynamic viscosity (measured in Pa). The unit of dynamic viscosity is sometimes called 'Poiseuille' (1 Poiseuille = 1 Pa = 1 kg m<sup>-1</sup>.s<sup>-1</sup>). This assumption formula is made according to [Newton, 1687].

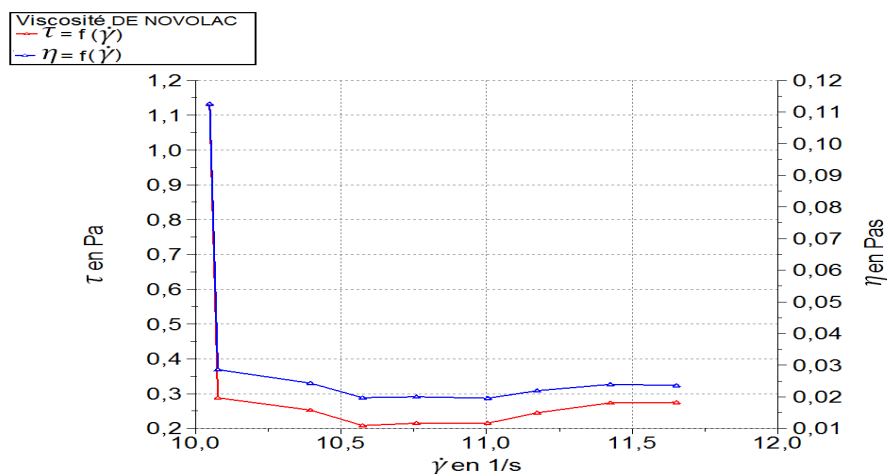


Figure 4: Rheogram of viscosity  $\eta$  and constraint  $\tau$  according to the speed  $\gamma$  (1 / s).

### 3.1.2. Rheological study of DGEBA standard resin:

#### 3.1.2.1. Viscosity and constraint according to the temperature ° C:

Figure 5 shows the variation of the viscosity of the DGEBA under the effect of constraint according to temperature with the fixing speed.

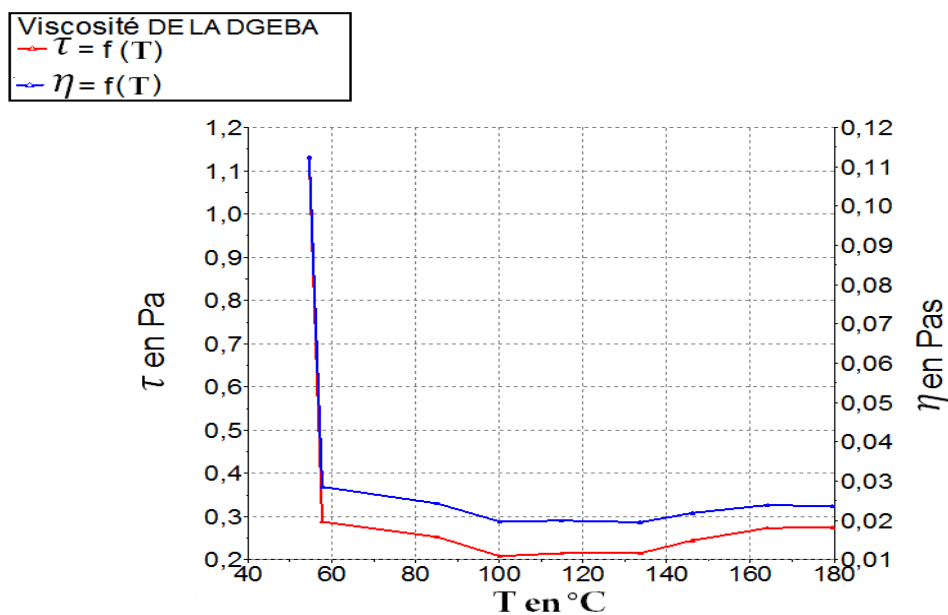
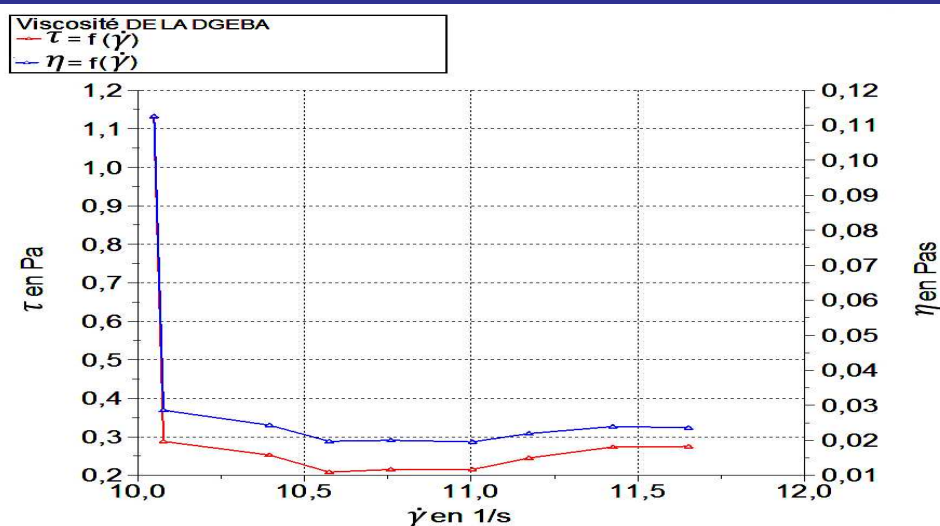


Figure5: Rheogram of viscosity  $\eta$  and constraint  $\tau$  in view of temperature ° C.

#### 3.1.2.2. Viscosity and constraint in view of the speed $\gamma$ (1 / S):

In the following study, we varied the viscosity of DGEBA under the effect of constraint in view of speed with the fixing temperature (Figure 6).



**Figure 6:** Rheogram of constraint  $\tau$  and  $\tan \delta$  in view of speed (1 / s).

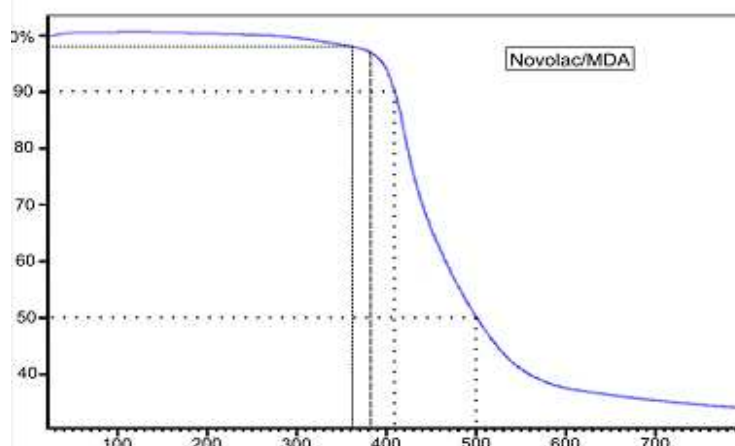
In these rheo-grams, we noticed that the increase of temperature ( $^{\circ}\text{C}$ ) and speed (1 / s) results in the reduction of constraint and viscosity  $\eta$  for the two molecular matrices. The knowledge of the rheological properties of these thermosetting materials over a wide temperature range is needed for the understanding and control of storage conditions and also to link the performance and the product quality with the implementing conditions and the material properties. The rheological properties can be directly related to the chemical structure or the degree of the polyepoxide prepolymer conversion. In this study, we were mainly interested in the viscosity since it plays a crucial role in the flow phenomena of the organic matrix.

### 3.1. Thermal properties of the two epoxy resins:

We followed, through thermo-gravimetric techniques, the mass loss of the two cross-linked systems with MDA: the novolak epoxy resin and DGEBA resin, depending on the temperature when subjected to a heat treatment.

#### 3.1.1. Thermo-gravimetric analysis of novolak epoxy resin:

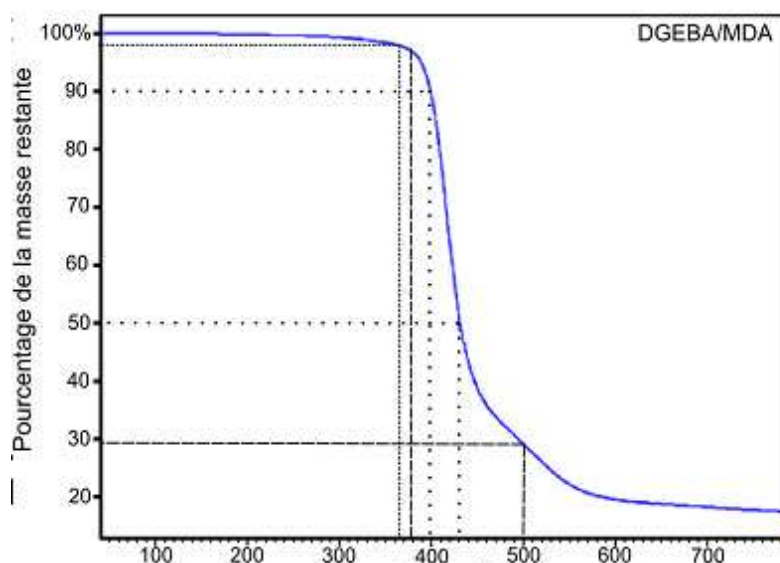
Figure 7 explains the mass variation of the hardened novolak with (MDA) according to the temperature.



**Figure 7:** Evolution of the percentage of the remaining mass in view of temperature  $^{\circ}\text{C}$  (epoxy novolak / MDA)

### 3.1.2. Thermogravimetric analysis of the DGEBA resin:

Figure 8 shows the evolution of mass degradation of DGEBA cross-linked with MDA.



**Figure 8:** Evolution of the percentage of the remaining mass in view of temperature ° C (DGEBA / MDA).

**Table 1:** Main characteristics of the products:

Resin	Td (°C)	T10 (°C)	T50 (°C)	Sdr (°C)	R500 (%)
<b>DGEBA/MDA</b>	<b>365</b>	<b>400</b>	<b>430</b>	<b>378</b>	<b>29</b>
<b>Novolac / MDA</b>	<b>362</b>	<b>410</b>	<b>500</b>	<b>382</b>	<b>50</b>

Given all this, we subsequently rated the main thermal characteristics of the studied resins, extracted from the thermo-grams curves in the following table, in accordance with the conventional standards according to M-td: The decomposition starting temperature corresponding to a weight loss of 2%. T10: The temperature at 10% of mass loss.-T50: The temperature at 50% of mass loss.-Sdr: Rapid decomposition threshold.-R500: The fraction of the residue at 500 ° C. These results show that our resins are thermally stable. This stability is influenced by the chemical structure of the hardening agent and the resin in the case of hardening by the MDA. The cross-linked resins are thermally more stable due to the presence of aromatic cycles. The epoxy novolac resin / MDA shows a thermal behavior better than that of DGEBA / MDA system. This basically amounts to the number of aromatic cycle and glycidyl ether branches which facilitate the connection of polymers with more stable and hard tri-dimensional networks.

## 4. Conclusion:

In this work, we have studied two epoxy resins which are the Diglycidyl ether of bisphenol A (DGEBA) and epoxy novolac by the viscosimetry following the rheological properties of the standard matrices without the use of the cross-linking agent I order to fully determine their storage conditions. The resins showed high mechanical stability in view of temperature, time and constraint, in which we have assumed that these can be stored in the standard thermodynamic conditions without fear of cross-linking.

Subsequently, these two resins have been subjects to two reactive systems epoxy / amine (DGEBA / MDA and Epoxy Novolac / MDA). After being cross-linked in the presence of an aromatic diamine (MDA), we investigated by thermo-gravimetry (TGA) their thermal stabilities. He concludes in this study that the system DGEBA / MDA is less stable than that of the epoxy novolac / MDA. This result can be explained by the number of aromatic and epoxy branches which are largely higher in the novolac epoxy compared to the bifunctional DGEBA.

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