

# SYNTHESIS, STRUCTURAL CHARACTERIZATION BY NMR AND IR AND RHEOLOGICAL STUDY OF EPOXY RESIN OCTAFUNCTIONAL

J. EL Azzaoui <sup>(a)\*</sup>, N. EL-Aouni <sup>(a)</sup>, A. EL Harfi <sup>(a)</sup>

<sup>(a)</sup>Laboratory of Agroressources Polymer and Processes Engineering(LAPP), Organic Chemistry and Polymer Team(OCPT), Department of Chemistry, Faculty of Science, University Ibn Tofail, B.P.133, 14000, Kenitra, Morocco.

\*Corresponding author. E-mail : [jililaelazzaoui@gmail.com](mailto:jililaelazzaoui@gmail.com)

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## Abstract

The aim of our work is to synthesize a new epoxy resin octafunctional describing the above characteristics in two steps. In the first step, we synthesized the DGEDDS according to the protocol developed in the laboratory. In the second step, were led to the synthesis of octafunctional resin by condensing the appropriate nucleophilic on DGEDDS. The microscopic structural characterization has been obtained using the Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) <sup>1</sup>H, <sup>13</sup>C. the obtained Octafunctional epoxy resin was studied using rheological analysis.

**Keywords:** octafunctional Epoxy resin, DGEDDS, microscopic characterization and rheological analysis.

## 1. Introduction

Epoxies are widely used in electro-technical and electrical industries [1- 2] for applications such as cable sheathing or coating components. They are also used as adhesives, in aircraft construction [2-3] (car parts and helicopter blades ...) and spatial construction (heat shields rockets, satellites parts and solar panels. The knowledge of rheological properties [4-5] of these thermosetting materials over a wide temperature range is needed for understanding and controlling the storage conditions [6] and linking performances of products quality to conditions' implementation and to material properties. The rheological properties can directly be related to the chemical structure or the degree of conversion of polyepoxy prepolymers [7]. Like any fluid, the resin has a viscosity which reflects its own resistance to its flow. The origin of this molecular arrangement is the viscosity of the fluid. Indeed, the flow is marked by a friction of fluids' molecular layers with each other. In general, the viscosity is a function of temperature, pressure and fluid shear rate [8]. The objective of this work is to synthesize a new octafunctional epoxy resin, the Octaglycidyle dihydrazine 4,4'-diphenyl dipropoxy (OGDHPDS) by chemical modification of the diglycidylethèr 4,4'-dihydroxy diphenyl sulfone (DGEDDS) [9-10 ] according to two phases in the protocol developed in the laboratory [2]. The Microscopic characterization [2,11-15] of the resin obtained by the Fourier Transform Infrared (FTIR) and nuclear magnetic resonance (NMR), and the rheological property of viscosity plays an essential role in the

case of flow of the organic matrix and is mainly based on the influence of temperature and the system of resin / solvent, and by rheometer according to settings: speed / temperature / pressure.

## 2. Materials and methods

### 2.1. Materials Used

The basic products are bisphenol S powder, epichlorohydrin with a purity of 99%, and hydrazine stored at a temperature of 4 to 6 ° C. All these commodities have been provided by the companies Acros Chemical Co. and Aldrich Chemical Co. without any further purification.

### 2.2. Synthesis of epoxy resins

In this study, we present the two steps of the synthesis of new macromolecule epoxy Octaglycidyle dihydrazine 4,4'-diphenyl dipropoxy (OGDHPDS) according to the following scheme:

**Figure 1.** Synthesis of 4,4'-dipropoxy Octaglycidyle dihydrazine diphenylsulfone (OGDHPDS).

#### *First step: preparation Diglycidyl ether 4,4'-dihydroxy diphenyl sulfone (DGEDDS)*

In a two-necked flask fitted with a condenser and a dropping funnel, we introduced  $1.08 \cdot 10^{-3}$  mol of 4,4'-dihydroxy diphenyl sulfone and  $2.16 \cdot 10^{-3}$  mol of epichlorohydrin. After the complete dissolution of the bisphenol S, the mixture is heated to 100 ° C for 3 hours with magnetic stirrings. Then, we have the solution cooled to 60 ° C then added with a dropping funnel  $2.35 \cdot 10^{-3}$  mol of triethylamine. The prepared reactive mixture is stirred for 2 hours (still at 60 ° C) [9-10]. The yield and the physicochemical characteristics of the DGEDDS obtained are recorded in Table 1.

#### *Second step: preparing OGDHPDS*

The second step intends to condense  $5.52 \cdot 10^{-3}$  mol of DGEDDS and  $9.29 \cdot 10^{-3}$  mol of hydrazine in a solution of 17 ml of methanol. The mixture is then heated to a temperature of 100 ° C for 4 hours. Furthermore, we

cooled the solution to 80 ° C, then we added it to the reactive mixture  $8.64 \cdot 10^{-3}$  mol of epichlorohydrin (in excess) while adding triethylamine ( $\text{NEt}_3$ ). The mixture is brought to a temperature of 80 ° C for 3h. The Performance and the physicochemical characteristics of the OGDHDPDS are summarized in Table 1.

**Table 1.** Performance and physico-chemical characteristics and DGEDDS OGDHDPDS

Product Aspect	brute Formula	molar Mass (g/mol)	performance (%)
DGEDDS whitish viscous	C18H18O6S	362-364	82%
OGDHDPDS Brown viscous	C45H64N4O12	874-876	92%

### 2.3. Analytical methods

#### 2.3.1. Fourier Transform Infrared (FTIR)

The used IR spectrometer is an infrared spectroscopy Fourier Transformed (FTIR) BRUKER. The tapes were obtained in transmission on the total attenuated reflection (ATR Total Attenuated Reflectance). The spectral range corresponding to the molecules vibrating energies are situated between 2.5 and 25 microns. The analysis was done between  $600\text{cm}^{-1}$  and  $4000\text{cm}^{-1}$ .

#### 2.3.2. Nuclear Magnetic Resonance (NMR)

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  analyzes were obtained using a device of Bruker AVANCE 300 MHz, by dissolving the product in DMSO. Chemical shifts are expressed in ppm and coupling constants in Hz. The following abbreviations have been used: s, d, dd, t, q and m respectively mean singlet, doublet, doubled doublet, triplet, quadruplet and multiplet.

#### 2.3.3. Rheological Analysis

##### 2.3.3.1 Viscosimetric Analysis by UBBELOHDE

The reactivity of the epoxy storage systems was monitored using a viscometer of UBBELOHDE VB-1423 type (Figure 2). The selected measurement conditions are:

- Viscometer of 1B size for a series of dilution, capillary tube diameter of 0.46 mm, constant  $k = 0.051493$ ;
- Measuring temperature in ° C: 25 to 55;
- Number of measurement: 5 each time;
- Solvent: Methanol;
- Hagenbach correction was calculated using the formula specified in DIN 1999 standard 51562-1Janvier (Measurement of kinematic-viscosity by means clustering of the Ubbelohde viscometer)
- Solubilization of epoxy resin prepolymers in methanol was carried out under magnetic stirring at 20° C.



**Figure 2.** Device of viscosimetric measures.

### 2.3.3.2 Analysis Viscometer Rheometer

Rheometers are mainly used in research and development, such as adhesives formulation, oils, bitumen, paints, cosmetics, or the monitoring of a thermosetting resin cross-linking (a measure of the minimum viscosity, the freezing weather). The viscosity was obtained using a rotational rheometer Thermo Scientific HAAKE MARS type III, Rheometer rotation in the constant stream of test mode and the parallel plane-plane geometry (Figure 3).

The substantial parameters for a plate-plate rheometer are: a controlled scanning shear around 0.1 and 100  $\text{s}^{-1}$  was applied at a temperature of 30 to 200 ° C. The distance between these two planes is between 0.2 to 3 mm, and the diameter of the two planes is between 20 and 60 mm.



**Figure 3.** Thermo Scientific HAAKE MARS III device.

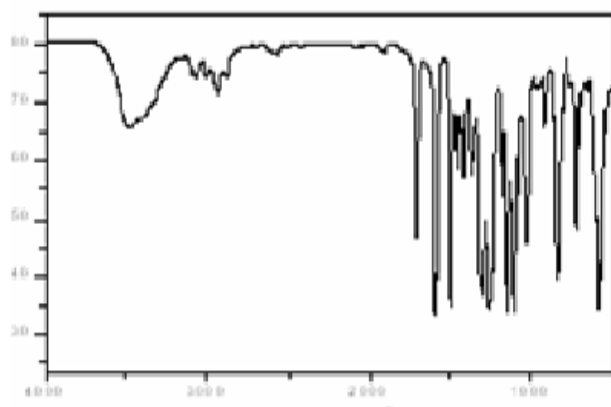
## 3. Results and Discussions

### 3.1. Spectral characterization of the synthesized epoxy resins

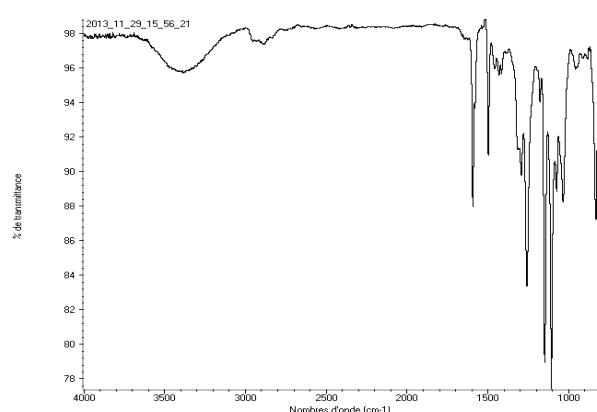
We performed the structural analysis of the obtained products by means of nuclear magnetic resonance of the proton ( $^1\text{H}$  NMR), carbon ( $^{13}\text{C}$  NMR) on the one hand, then the analysis by the Transformed infrared spectroscopy Fourier (FTIR) on the other. The results of structural analyzes, given below, have indeed confirmed the synthesized epoxy resin structure.

#### 3.1.1. Structural study by FTIR

The FTIR spectra of DGEDDS OGDHDPDS and the synthesized products are illustrated in Figures 4, 5. The results of the examination of FTIR spectra are summarized in Tables 2.



**Figure 4.** IR spectrum of DGEDDS.



**Figure 5.** IR spectrum of OGDHDPDS.

**Table 2.** the powers of the IR spectrum of resins and DGEDDS OGDHDPDS.

OGDHDPDS	DGEDDS [10]	Attributions
3500	3300-3600	$\nu$ OH
--	3090	$\nu_{\text{asym}}$ CH <sub>2</sub> epoxy
--	3050	$\nu$ C-H <sub>ar</sub>
--	3004	$\nu_{\text{sym}}$ CH <sub>2</sub> epoxy
2890	2932-2950	$\nu_{\text{asym}}$ CH <sub>2</sub> ether of methylene
2820	2850	$\nu_{\text{sym}}$ CH <sub>2</sub> ether of methylene
-	1800-2000	Harmonical of aromatic cycle
1600	1600	$\nu$ C <sub>ar</sub> =C <sub>ar</sub> aromatic benzene cycle
1465	1470	the aromatic bisphenyl
1450	1450	$\delta_{\text{C-H}}$ epoxy $\delta_{\text{CH}_2}$ or methylene linked to the oxirane cycle and the aromatic cycle
1420-430	1410	$\delta_{\text{C-H}}$ epoxy/ether
-	1360	$\delta_{\text{C-H}}$ ether of methylene
-	1345	$\delta_{\text{C-H}}$ methylene of the epoxide
1310-1240	1336, 1164	$\nu_{\text{asym}}$ and $\nu_{\text{sym}}$ of sulfone (Ar-SO <sub>2</sub> -Ar)
1250-1260	1258	$\nu_{\text{Car-O-Alkyl}}$ : ether aromatic and $\nu_{\text{C-O-C}}$ epoxy
1190-1195	--	$\nu_{\text{sym}}$ C-N
1100-1110	1170	$\delta_{\text{C-Har}}$ deformation in the plane of the aromatic cycle
1070-1080	1028, 1104	$\nu_{\text{C-O-Ar}}$ ether alkyl-aromatic and $\delta_{\text{C-Har}}$
930	916	Asymmetrical deformation of the epoxide cycle
870	850	Symmetrical deformation of the epoxide cycle
830	815	$\delta_{\text{C-Har}}$ deformation out of the plane of the para substituted aromatic cycle
-	740	Rocking skeleton CH <sub>2</sub>

The presence of the epoxide in the ether of glycidyl bisphenol S was confirmed by referring to the work of the literature [10,1619]. The appearance of characteristic bands of the oxirane at 3090 and 3004  $\text{cm}^{-1}$  corresponds to  $\nu_{\text{asym}}\text{CH}_2$  valence vibrations and  $\nu_{\text{sym}}\text{CH}_2$  epoxide; 1258  $\text{cm}^{-1}$  to the pulsation of the epoxide cycle (breathing) (1255 or 1201  $\text{cm}^{-1}$  according to Shukla et al., 2008) in the DGEDDS [20] and 1250 to 1260  $\text{cm}^{-1}$  in OGDHDPDS, and finally the deformation of oxirane cycles  $\delta_{\text{asym}}\text{CH}_2$  and  $\delta_{\text{sym}}\text{CH}_2$  appear at 916 and 850  $\text{cm}^{-1}$  in 930 and then DGEDDS 870  $\text{cm}^{-1}$  OGDHDPDS. The signal at 1450  $\text{cm}^{-1}$  is according to  $\delta\text{CH}_2$  of shear (scissoring) of methylene linked to oxirane cycle; 1190-1195  $\text{cm}^{-1}$  corresponds to the symmetric vibration of atoms linked to nitrogen [2].

### 3.1.2 Structural study by NMR

#### 3.1.2.1 Diglycidylether of bisphenol S (DGEDDS)

**Figure 6.** Schema of DGEDDS structure.

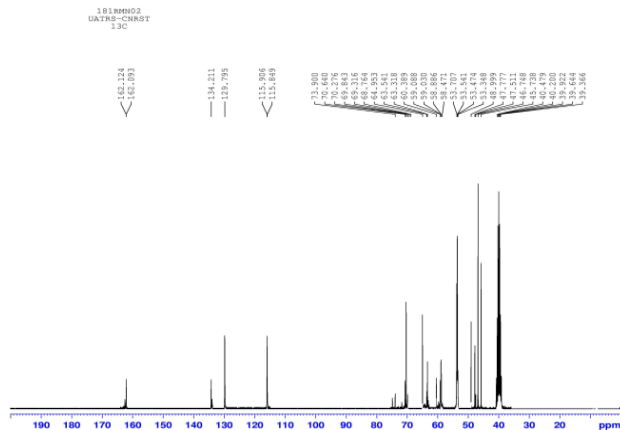
**$^1\text{H}$  NMR (ppm):** 2.7 (dd, 2H<sub>1</sub>, oxirane CH<sub>2</sub>); 3.3 (m, 1H<sub>2</sub>, oxirane CH) 4.1 (dd, 2H<sub>3</sub>, OCH 2); 6.94 (dd, 1H<sub>5</sub>, aromatic CH); 7.79 (dd, 1H<sub>6</sub>, aromatic CH).

**$^{13}\text{C}$  NMR (ppm):** 44.2 (s, CH<sub>2/1</sub> epoxide); 50 (s, CH<sub>2</sub> epoxy); 69.5 (s, CH<sub>2/3</sub> ether); 128.9 (s, C<sub>4</sub> aromatic tertiary linked to oxygen); 115.4 (s, CH<sub>5</sub> aromatic); 133 (s, CH<sub>6</sub> aromatic); 162.6 (s, C<sub>7</sub> aromatic tertiary linked to sulfur) [9].

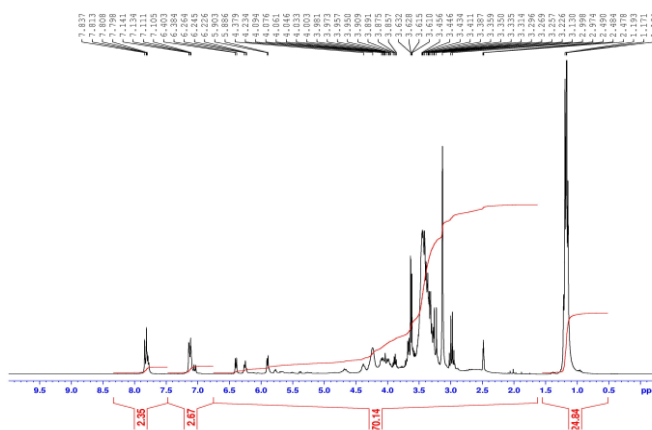
#### 3.1.2.2 Octaglycidyle dihydrazine 4,4'-dipropoxy diphenylsulfone (OGDHDPDS)

Figures 8 and 9 respectively show the spectra of the proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) of the resin Octaglycidyle dihydrazine diphenylsulfone 4,4'-dipropoxy (OGDHDPDS) obtained by NMR whose attribution is described below:

**Figure 7.** Diagram of the structure of the OGDHDPDS.



**Figure 8.**  $^{13}\text{C}$  NMR spectrum of the OGDHDPDS.



**Figure 9.**  $^1\text{H}$  NMR spectrum of the OGDHDPDS.

**$^1\text{H}$  NMR (ppm):** 2.54 (dd,  $2\text{H}_{13}$ , oxirane  $\text{CH}_2$ ); 2.97 (dd,  $2\text{H}_9$ , oxirane  $\text{CH}_2$ ); 3.13 (m,  $\text{H}_{12}$ , CH oxirane); 3.29 (m,  $\text{H}_8$ , oxirane CH); 3.35 (m,  $1\text{H}_6$ , CH); 3.45 (dd,  $2\text{H}_{11}$ ,  $\text{CH}_2$  linked to nitrogen); 3.63 (dd,  $2\text{H}_{10}$ ,  $\text{CH}_2$  linked to nitrogen); 5.78 (dd,  $2\text{H}_7$ ,  $\text{OCH}_2$  epoxy); 4.23 (dd,  $2\text{H}_5$ ,  $\text{CH}_2$  linked to oxygen); 7, 81 (d,  $1\text{H}_2$ , aromatic CH); 6.94 (d,  $1\text{H}_3$ , aromatic CH).

**$^{13}\text{C}$  NMR (ppm):** 47.60 (s,  $\text{CH}_{2/13}$  oxirane- $\text{CH}_2$ -N); 45.51 (s,  $\text{CH}_{2/9}$  oxirane- $\text{CH}_2$ -O); 60.38 (s,  $\text{CH}_{2/11}$  linked to nitrogen and epoxide cycle); 64.95 (s,  $\text{CH}_{2/10}$  linked to nitrogen ether and CH); 66.76 (s,  $\text{CH}_{12}$  oxirane linked to nitrogen); 70.27 (s,  $\text{CH}_{2/5}$  linked to the oxygen-aromatic); 73.80 (s,  $\text{CH}_8$  oxirane  $\text{CH}_2$  O); 70.64 (s,  $\text{CH}_{2/7}$  linked to oxygen and epoxide cycle); 58.47 (s,  $\text{CH}_6$  ether linked to oxygen); 129.79 (s,  $\text{CH}_2$  aromatic); 115.84 (s,  $\text{CH}_3$  aromatic); 162.12 (s, aromatic tertiary  $\text{C}_1$  linked to sulfur); 134.21 (s, aromatic tertiary  $\text{C}_4$  linked to oxygen).

### 3.2. Study of the viscosimetric of OGDHDPDS

#### 3.2.1. Effect of the mass concentration on the viscosity OGDHDPDS

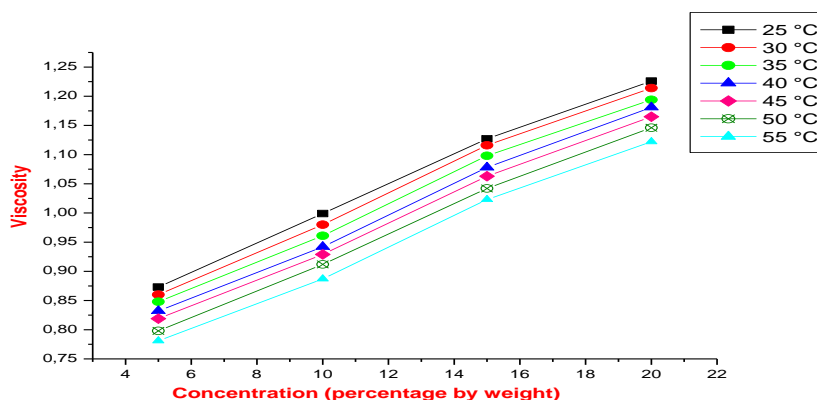
The rheological properties can directly be related to the chemical structure or the degree of conversion of the reactant system [2-10-14-21- 22]. To determine the viscosimetric behavior [23-24-25-26-27] of the OGDHDPDS standard, we dissolved this resin in methanol at different concentrations of 5%, 10%, 15% and 20% and a temperature variations of 25 °C to 55 °C. Figure 10 shows the study of the effect of the mass concentration on the viscosity OGDHDPDS / methanol of resin octaglycidyle dihydrazine diphenylsulfone 4,4'-dipropoxy (OGDHDPDS):

Concerning the different viscosity curves of the octafunctional phenolic resin in the methanol, we noticed that the viscosity values increase with the concentration of the octafunctional resin. This showed the progress of the reaction of homopolymerization since the viscosity increases with increase of the molecular mass of the solute.

This may be related to the chemical transformations undergone by the resin [2-10-28-29]. Therefore we could provide the following actions: the addition of epichlorohydrin was not complete because of the steric hindrance of  $\text{NH}_2$  groups of the hydrazine, the reactivity of the tertiary amine vis-a-vis the epoxide function under the effect of the temperature and the intervention of the opening reactions of the regenerated epoxide cycles.



All these factors can influence the functionality of the obtained product, thus, we will have residual and hydroxyl amines containing labile protons which could be responsible for a self-crosslinking of the prepolymer by acting as the hardener agent [2-10-23].



**Figure 10.** Effect of mass concentration on the viscosity OGDHDPDS / methanol.

### 3.2.2. The effect of temperature on the visco-elastic property of the OGDHDPDS

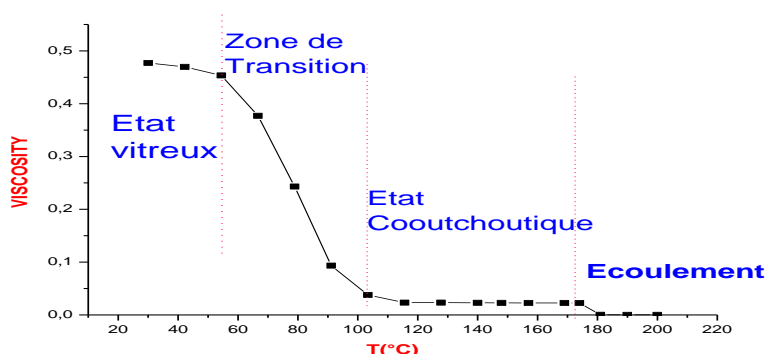
In the Haake March III rheometer, a cylindrical container is rotated about its axis of rotation. It contains the viscous liquid and a solid cylinder. This cylinder, which is movable on its axis of rotation, is driven by the fluid. A spring is attached to the cylinder which holds the balance.

It is shown that the dynamic viscosity is proportional to the rotation angle:

$$\eta = K \alpha$$

The angle  $\alpha$  is even greater when the viscosity of the liquid placed between the two cylinders is greater.

The molecular mobility of polymer chains is very closely linked to the temperature. A conformational equilibrium corresponds to each temperature; this balance can be changed particularly through the rotation around simple bonds which are present in the polymer chain.



**Figure 11.** Effect of Temperature on the OGDHDPBS viscosity.

The Figure 11 represents the characteristics of the rheological behavior of a octafunctional resin depending on the temperature. The jellification time for different temperatures decreases with an increase in temperature because the supplied heat accelerates the depolymerization process of the resin [Kenny, 1996; Gorovaya, 1996]. The gelling time decreases exponentially with the temperature. In this figure we notice that:



- **Vitreous State:** At low temperature and reduced viscosity, the molecular mobility is high.
- **Transitory State:** A small increase in temperature can induce a significant increase in molecular mobility and decrease in viscosity.
- **Rubbery State:** At higher temperature and a higher molecular mobility, the viscosity is not limited. it is flexible but has no flow.
- **Flow state:** At high temperature and a totally free molecular mobility, the viscosity is reduced.
- The viscosity strongly depends on temperature to maintain a sense of measuring in which we specify the temperature at which it was made. In a liquid, the viscosity rapidly decreases according to temperature.

#### 4. Conclusion

The objective of this work is to present the synthesis and structural characterization of the new epoxy resin "the Octaglycidyle dihydrazine 4,4'-diphenyl dipropoxy (OGDHPDS)." The synthesis of this macromolecular matrix has been obtained by a chemical modification of the DGEDDS using hydrazine with a good yield. The structure of this resin was confirmed and characterized by the usual spectroscopic methods FTIR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

The viscosimetric study of the octafunctional resin was formed to have a clear idea of its rheological properties according to the temperature increase during its implementation. Yet, it must be noted that the rheological characterization of multifunctional epoxy resins is made difficult by the reactive chemical structure of these prepolymers.

The octafunctional prepolymer based on DGEDDS and the synthesized hydrazine, can give the drawback of self-crosslinking because of factors mentioned above and which are manifested by an increase in viscosity: even if all amine groups have completely reacted with the epichlorohydrin, there would be some formed tertiary amines which are capable of initiating some reactions of homopolymerization of the epoxy resins. This led us to the obligation of storing the resin at low temperatures in order to overcome this drawback.

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