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RHEOLOGIC STUDY AND THERMAL BEHAVIOR OF A NEW SULPHURATED AND PHOSPHOROUS TRI-FUNCTIONAL EPOXY RESIN.

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Abstract

In this work, we presented the synthesis of a new sulphurated and phosphorous tri-functional epoxide resin. To reach this result, we proceeded to the synthesis, in a first stage, of a precursor of the epoxide matrix. In the second stage, it would consist in the fictionalization of the precursor by means of the épichloridrine. The microscopic characterization of the synthesized resin was confirmed by the Fourier Transform Infrared (FTIR) and by nuclear magnetic Résonnance (NMR) ^{1}H, ^{13}C, ^{31}P. The epoxy tri-functional polymer was then reticulated thermically by the methyl alcohol dianiline(MDA). Its reactivity towards resin was characterized by a rheologic study. The study of composite material by means of the thermo-gravimetric analysis allowed us to estimate and to estimate the character of the thermal degradation of this new macromolecular chain.

Keywords: *rheologic Study, tri-functional sulphurated and phosphorous epoxide resin, microscopic characterization, thermo-gravimetric Study.*

1. Introduction

Epoxide resins [1, 2] are among the most important materials in the family of thermosetting polymers [3]. They are known to present good electric properties, a chemical resistance and humidity absorption. So they present high properties of thermal resistance with an excellent mechanical resistance. Their application is very diversified in various domains, such as the electronics, the aerospace industry, and the automobile [4-12]. The synthesis of polymers with particular properties is a challenge which involves often a lot of time and resources. The capacity to predict the properties of the final product of these new materials has a considerable value whose manufacturing orientation accelerates the process and the cycle of development.

Before planning and understanding the multiple properties of materials organic the studies of the visco-elastic properties are the most important to determine at the level of polymers in the standard state and their composites in the solid state. They determine the intervals of their use. These epoxide macromolecules present a wide interval of reactivity and a multiple choice of types of hardeners. After saying that, the reticulated epoxy resins with Amines hardeners can present a temperature of a very high and glassy

transition [13, 14]. They also have an excellent thermal stability and a good resistance in chemicals. The variation of the viscosity during their reticulation is closely linked to the reactive mechanism between the epoxy groups and the primary and secondary groups of Amines [15]. In this context, we synthesized a tri-functional resin whose systematic name is the triglycidylether of hydroxydiphénylesulfone bis-para-ester phosphoric (TGEHDSEP). The structural microscopic characterization was obtained by means of the Fourier Transform Infrared (FTIR), and Nuclear Magnetic Resonance (NMR). The macroscopic characterization of our tri-functional resin was made by a rheologic study and the thermo-gravimetric analysis.

2. Materials and methods

2.1. Materials

In our work, we used the following products: bisphenol S, POCl3, methanol, épichlorhydrine. All the basic chemicals were supplied by Aldrich Chemical Company and Acros Chemical Company.

2.2. *Synthesis of the TGEHDSEP*

The resin triglycidylether of hydroxydiphénylsulfone bis - para - ester Phosphoric (TGEHDSEP) was synthesized in two reactive stages [16, 17,18] (figure 1).

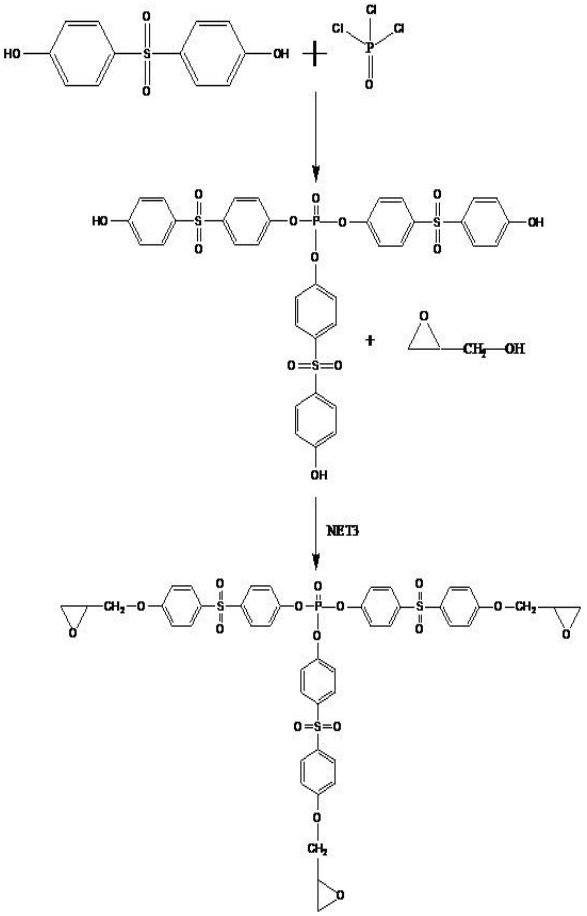


Figure1. Plan of synthesis of the triglycidylether of hydroxydiphénylesulfone bis - para - ester Phosphoric (TGEHDSEP)

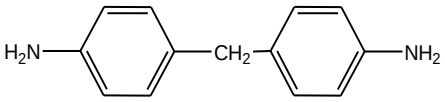
2.3. *Experimental protocol of synthesis of the new epoxy resin triglycidylether of hydroxydiphénylesulfone bis - para - ester phosphoric (TGEHDSEP)*

The TGEHDSEP resin is synthesized in two reactive stages. In the first stage, we mixed 12.10^{-3} mol of bisphenol S, dissolved in the methanol and 4.10^{-3} mol of phosphorus trichloride, under strong agitation of the mixture for 48 hours in a temperature of 25 °. The second stage consists in condensing 12.10^{-3} mol of épichlorhydrine with the obtained product in the first stage while adding the triéthylamine. The mixture is held in a temperature of 60°C during 24 hours. We added then some water and extracted the organic phase by means of the chloroform; then we dried on Na_2SO_4 and evaporated with vacuum. We obtained, at the end, a viscous product of a brown color.

2.4. The Hardening of the synthesized epoxy resin

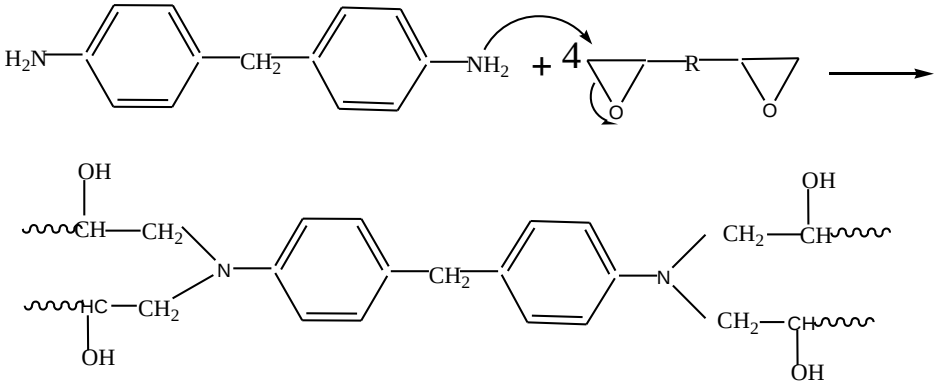
The synthesis of an epoxide polymer is a reaction of reticulation between the epoxy functional sites and the anhydride function or the hardener's Amine.

In our case, the reticulation was realized by means of a hardener of primary diamine type, the methyl alcohol dianiline (MDA), whose chemical formula is the following one:



This hardener has a function equal to four, which means that during the reaction of reticulation with multifunctional resins, both Amines react in theory with the epoxide functions when they are in stœchiometric proportions [19, 20]. The final product is thus a bridged chemical three-dimensional network resulting from the

following reaction:



2.5. The Preparation of the thermosetting material with the synthesized epoxy resin:

For our later study, we synthesized a new reticulated material with the new synthesized epoxide resin, with the stœchiométric quantities with the hardener MDA.

2.6. Methods of analysis

2.6.1. Fourier Transform Infrared (FTIR)

The used spectrometer IR is the one used in Fourier Transform Infrared (IRTF) BRUKER. Specters were realized in transmission on pastilles of KBr. The beam of light crosses the sample on a thickness of 2 µm approximately. The analysis is realized between 4000 cm^{-1} and 600 cm^{-1}

2.6.2. Nuclear magnetic resonance (NMR)

The analysis of NMR ^{1}H, ^{13}C and ^{31}P was obtained by means of a device of type MOVED FORWARD 300 Bruker. The chemical displacements are expressed in ppm. The letters, d, t, q and m respectively mean singulet, doublet, triplet, quadruplet and multiplet.

2.6.3. Viscosimètric Analysis :

The reactivity of epoxy resin was followed by a viscosi-meter of type Searle ContravesRheomat 115 in a variable temperature.

2.6.4. Thermo-gravimétric Analysis

To realize our study, which concerns the degradation of synthesized epoxide resins, we called on to the technique of thermogravimétric analysis (ATG) [21]. The measures of kinetics of degradation by loss of mass were realized by means of a device SETARAM tag 24S. The speed of rise in temperature is of 10°C min^{-1}, the page of measure of temperature 0 in 600°C, the sensibility of the balance is of 0,5µg and the measurable masses in a range of ±200mg.

3. Results and Discussions

3.1. Spectral characterizations of synthesized epoxide resin

We proceeded to the structural analysis of the synthesized resin on one hand, by the spectroscopy of Fourier transform infrared (FTIR); and on the others hand, by the nuclear magnetic resonance NMR (^{1}H, ^{13}C and ^{31}P). The results of the structural analyses, given below, confirmed the structure of tri-functional synthesized epoxy resin.

3.1.1. Characterization by IRTF

Figure 3 represents the peaks abounding in TFIR of the synthesized resin TGEHDSEP.

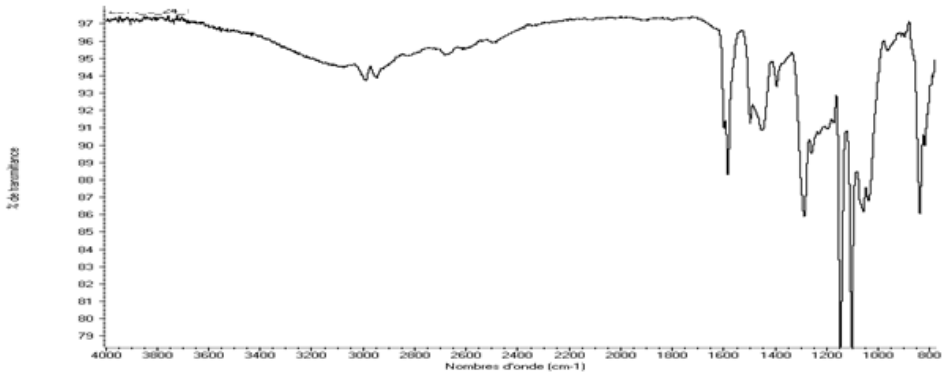


Figure 3. IR spectre of TGEHDSEP

FTIR (cm-1) : 3100 : νas CH2 epoxyde, 3050 : ν C-Har , 2700 : νas CH2 methylene ether , 1700 : Harmonious of the aromatic cycle, 1600 : ν Car=Car Aromatic of the cycle benzene, 1480 : δ C-H epoxydeou δCH2 some methylene to the cycle oxirane and in the aromatic cycle, 1400 : δ C-H epoxyde/ether, 1336-1160 : νas and νs ofsulfone (Ar-SO2-Ar), 1100 : νC-O-Ar ether alkyl-aromatic and δ C-Har, 900 : Deformation asym of the cycle of the epoxide, 810 : δ C-HarDeformation outside the plan.

3.1.2. Characterization by NMR ^{1}H and ^{13}C and ^{31}P

In this study, we strengthened the results obtained by the Infra-Rouge technique (IR) while using the spectroscopic method RMN 1 hour and 13C 31P. Figures 1, 2 and 3 respectively represent the spectres of NMR ^{1}H, ^{13}C and of ^{31}P of the synthesized resin (TGEHDSEP).

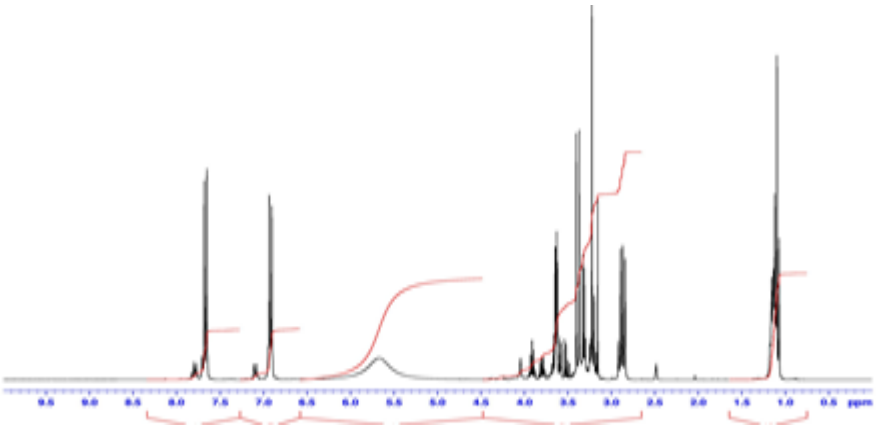


Figure 4. spectre NMR ^{1}H of TGEHDSEP.

NMR 1H (ppm) : 2,38 (d, 6H, CH2epoxyde) ; 2.63 (d, 6 H, CH2 Dregs with the epoxide); 3,4 (m, 3H, CH epoxyde); 6,90-7,80 (m, 24H, CH benzene).

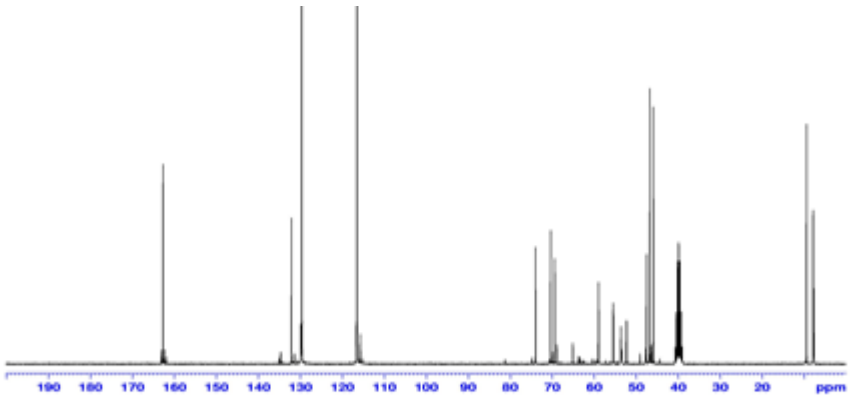


Figure 5. Spectre NMR ^{13}C of TGEHDSEP

NMR ^{13}C (ppm) : 44.2 (S,**C**H_2-epoxyde) ; 50,01 (S, O-**C**H-CH2); 69,5(S,**C**H-CH_2-O); 115,4-129,7(S,**C**H aromatic) 133-162(S, **C** aromatic).

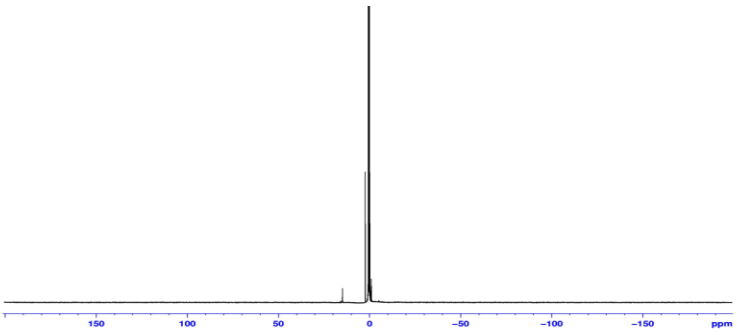


Figure 6. Spectre NMR ^{31}P of TGEHDSEP

NMR ^{31}P (ppm): 2,157 (PO (OR) $_3$).

3.2. viscosimetric Study

In figure 7, we represented the influence of the temperature on the Viscosimètric behavior of the resin TGEHDSEP. According to the results of the viscosimétric analysis of epoxy resin TGEHDSEP, we notice clearly that the viscosimétric behavior decreases according to the increase of temperature.

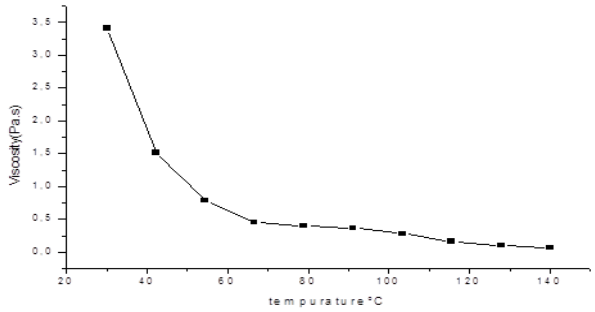


Figure 7. Effect of the temperature on the viscosity of one Prepolymer: TGEHDSEP.

3.3. Thermal properties of the synthesized resin

The thermal behavior of mono-composing material formulated with the synthesized resin and with the hardener diamine methyl alcohol (MDA) was estimated by means of the thermo-gravimetry. The obtained result is described by the curve of the figure 8. The thermogravimetric analysis of elaborate mono-composing composites shows that the temperature, from which the degradation takes a more pronounced look, begins from 300c. Then, we classified the main thermal characteristics of the studied resin, extracted from thermo-grams, in the picture I [22, 23, 24], according to the conventional standards, with:

- Td: the temperature of the beginning of degradation which corresponds to the 2 % mass loss.
- T10: the temperature in the loss de10 % of mass.
- T50: the temperature in the loss of 50 % of mass.
- Sdr: the threshold of fast degradation.
- R500: the residual fraction in 500 °C.

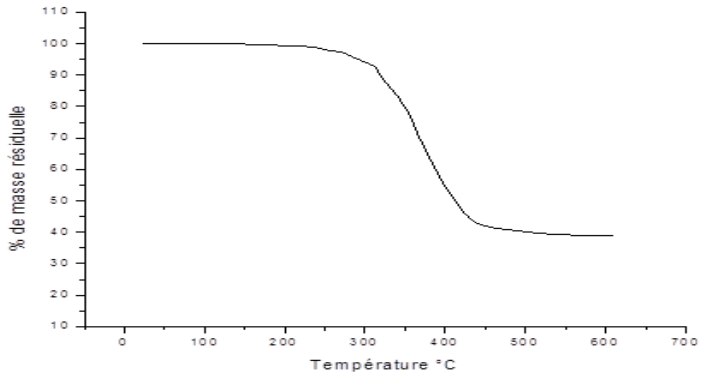


Figure 8. Thermo-gravimetric analysis of synthesized epoxy/MDA system.

The analysis of these results shows that the new tri-functional organophosphate resin TGEHDSP presents a better thermal behavior.

Table 1: main thermal characteristics of mono-composing sample TGEHDSEP / MDA.

Sample	**T_d (°C)**	**T_{10} (°C)**	**T_{50}(°C)**	**S_{dr} (°C)**	**R_{500} (%)**
TGEHDSEP	195	374	478	371	39.5

4. Conclusion

In this work, we have synthesized a new tri-functional resin the triglycidylether of hydroxydiphénylesulfone bis - para - ester phosphoric (TGEHDSEP) with bisphenol S and the trichloride of oxide of phosphor. The latter was obtained with a good yield. The structure of the resin TGEHDSP was confirmed and characterized by the usual spectroscopic methods of the Fourier Transform Infrared (IRTF) and Nuclear Magnetic Resonance (NMR) ^{1}H, ^{13}C and ^{31}P. Their Viscosimètric study was estimated by viscosimètric dynamics. This resin was thermically reticulated with the MDA hardener. The result of thermogravimétric analysis was able to highlight the good behavior and the good thermal stability of a new phosphorous tri-functional epoxy resin.

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