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Research Article

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Synthesis and structural, microscopic and macroscopic, characterization a new Hexa-functional epoxy resin based on phosphorus trichloride and ethylene dianiline and the study of its viscosimetric behavior

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ABSTRACT

In this work, we present the synthesis of a new epoxy resin based on phosphorus trichloride and ethylene dianiline. The obtained epoxy resin is crosslinked thermally by methylene dianiline (MDA) and deposited on carbon steel. The structural microscopic characterization was conformed using the Fourier Transform Infrared Spectroscopy (FTIR)and Nuclear Magnetic Resonance (NMR) and macroscopy by X-ray diffraction (XRD). The viscosimetric behavior was performed using the capillary viscometer type UBBELOHDE.

Keywords: Epoxy resins, methylene dianiline, carbon steel, coating and viscosimetric behaviour.

INTRODUCTION

Epoxy resins are important thermosets and are widely used in electronic industries (coating of electronic circuits), fireproofing and flame retardant, aging with radioactive adhesive elements, because of their exceptional chemical mechanical properties, and their electrical insulation, etc.[1-6].

However, their storage which is not adapted to the characteristics of the epoxy resins can induce a modification or degradation either in the storage itself or during the subsequent use[7]. So, the knowledge of the rheological properties of these thermosetting materials over a wide temperature range is needed for the understanding and controlling the storage conditions[8].

Thermosetting materials are products which result from chemically transformed functional macromolecular compounds according to the number of epoxy groups (bi, tri, tetra ... and / or Hexafunctional) [9.10] or by the chemical nature of the links between the functions of reactive epoxy among these materials. There are the epoxy resins, which can be phenolic (-OH) based on aromatic amines (- NH_2) ... and / or phosphoric ester [11-19].

The performance and quality of the product can be connected in terms of implementation and the material properties. The rheological properties can be directly related to the chemical structure or the degree of conversion of the prepolymer polyepoxide standard [20].

In this study, we mainly interested in the rheological property of viscosity before the formulation of the standard resin since it plays a crucial role in the flow of macromolecular matrix on the one hand, and the time storage of the latter on the other.

To this end, we synthesized the new phosphorus Hexafunctional epoxy resin. Then, we characterized the synthesized resin by Fourier Transform Infrared Spectroscopy (FTIR) and by the Nuclear Magnetic Resonance

(NMR) .The rheological property of the resin was determined by the UBBELOHDE viscometer. The epoxide resin crosslinked by methylene dianiline (MDA) and coated on carbon steel was analyzed by the X-ray diffraction (XRD).

EXPERIMENTAL SECTION

Experimental materials and methods:

The used products arephosphorus trichloride, ethylene dianiline powder and epichlorohydrin (2, 3-EpoxyChloroPropane1) with a purity of 99%. All these basic chemicals have been provided by the companies AldrichChemical Co and Acros Chemical Co. They were stocked at temperatures between 4 and 7 °C, and used without any further purification.

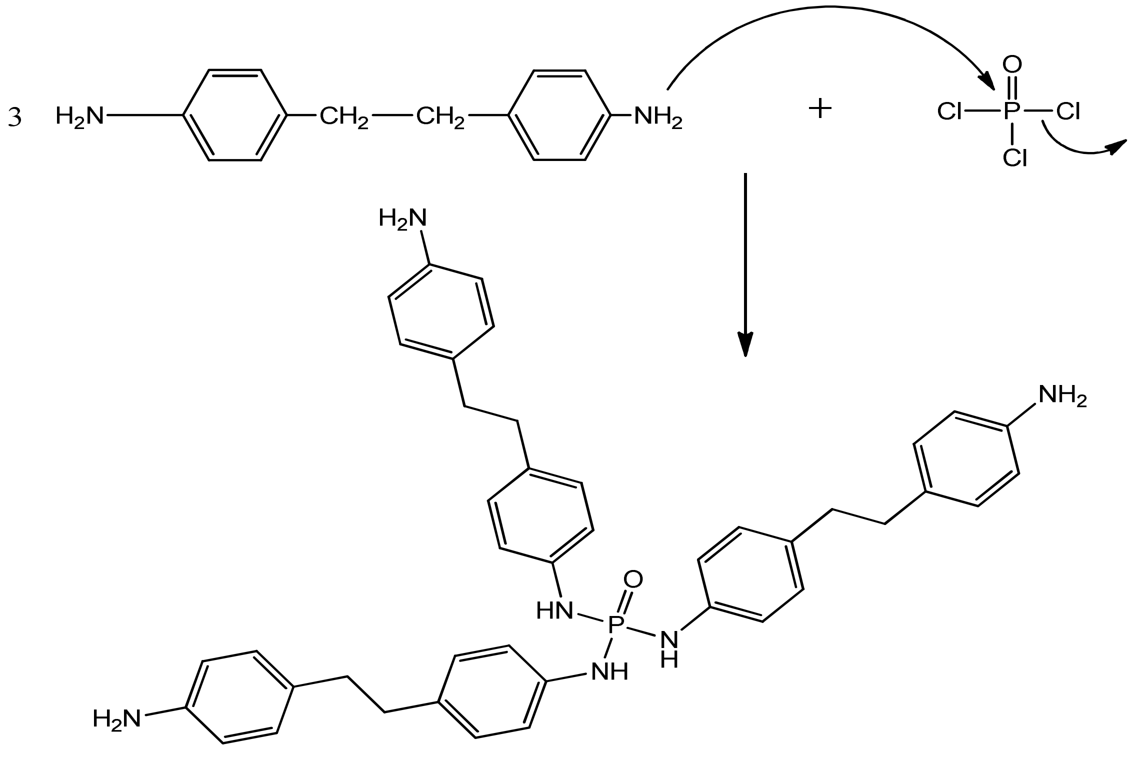
Synthesis of Hexaglycidylethylene dianiline of phosphinetriamine (HGEDAPT):

As we indicated above, this is an epoxy resin, which is homologous to TGEDA, based on ethylene dianiline and phosphorus trichloride ($POCl_3$) and a condensation with epichlorohydrin in order to obtain hexa glycidyl ethylene dianiline of phosphinetriamine (Figure1).

The experimental procedure of the HGEDAPT synthesis:

In a two-necked flask, fitted with a freezer, we deposited 3g of ethylene dianiline and 0.5 cm^3 of phosphorus trichloride was added slowly dropwise, the resulting mixture was stirred vigorously with a magnetic stirrer and heated at room temperature for 72 hours. We then added 2.22cm^3 of epichlorohydrin (excess) with the medium temperature under magnetic stirring maintained for four hours at 80 °C. Then the mixture was cooled at 60 °C and added 4 cm^3 of triethylamine. Then it was left under vigorous stirrings for 3 hours.

The solvent was removed on a rotary evaporator. We obtained a very viscous brown resin, which gives a mass yield of 73%.



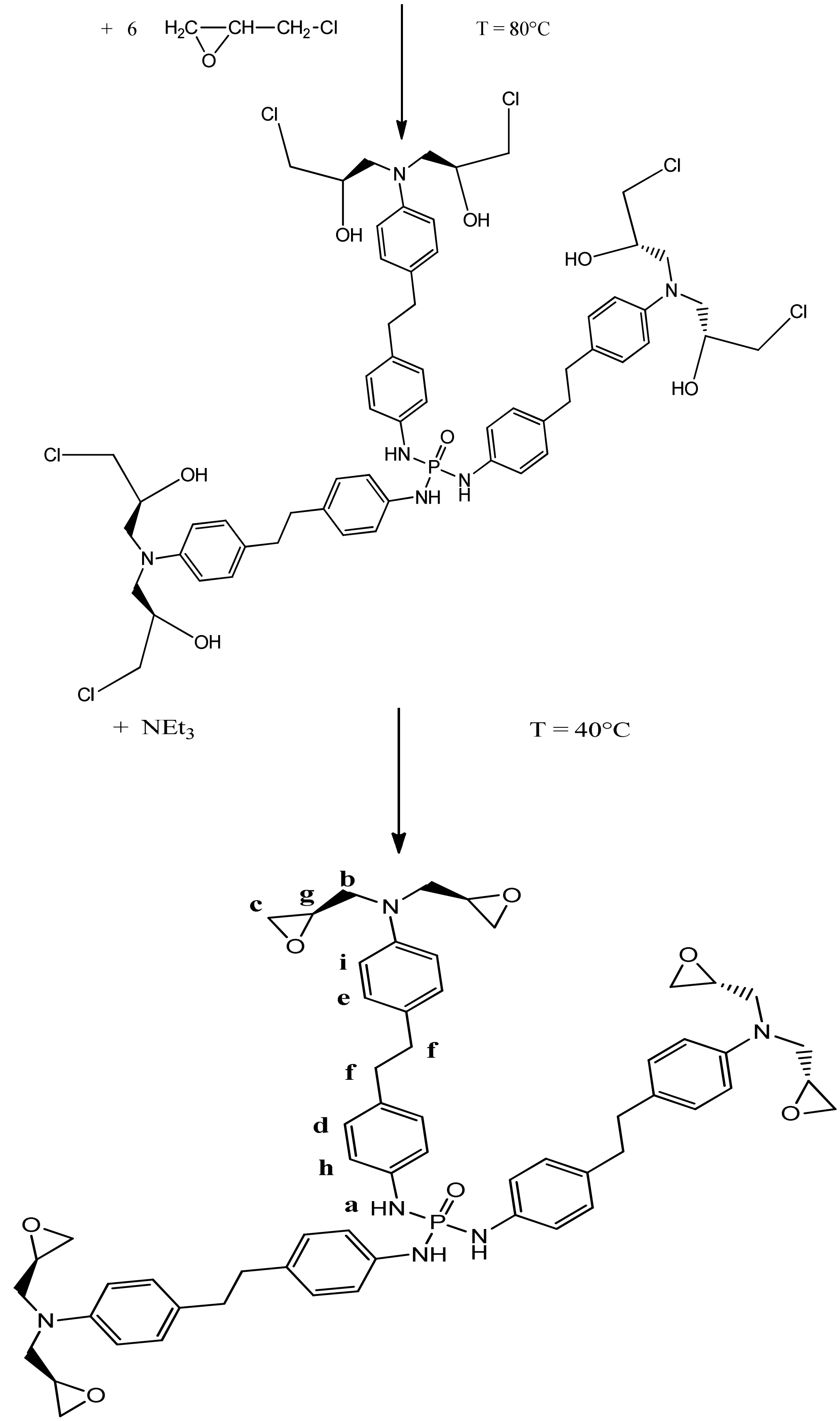
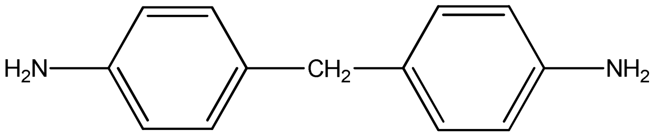


Fig 1: Schematic synthesis of Hexa glycidyl ethylene dianiline of phosphinetriamine

Hardening of Hexa glycidyl ethylene dianiline of phosphine triamine:

Epoxy resins can be processed into thermally cured polymers through many chemical compounds acting as bypassing agents or curing agent during the implementation[21].

Among the curing polyepoxide systems, there are two broad classes: the amines and acid anhydrides. We limited ourselves to one hardener class: aromatic diamine. By their chemical structure, thearomatic compounds provide an excellent thermal stability and a good mechanical property to the resin. Therefore, they are often used for high-tech applications. The hardener that we used is methylene dianiline (MDA) whose chemical formula is as follows [22-23]:



The reaction between epoxide and diamine is a reacting bimolecular addition of primary amine functions on the epoxide cycles by the opening of the oxirane cycles. Polymer networks are formed thanks to functional precursors by reactions between their functional groups resulting in bond formation. The crosslinked-ramified structures are formed generally by this method. The system consisting of a tetra functional epoxy and a bi-functional diamine remain a typical example. Primary amine sites in this system act as chain extenders while secondary amines produce the branches.

The impact of methylene dianiline on the epoxide is described by the following reaction [24-25]:

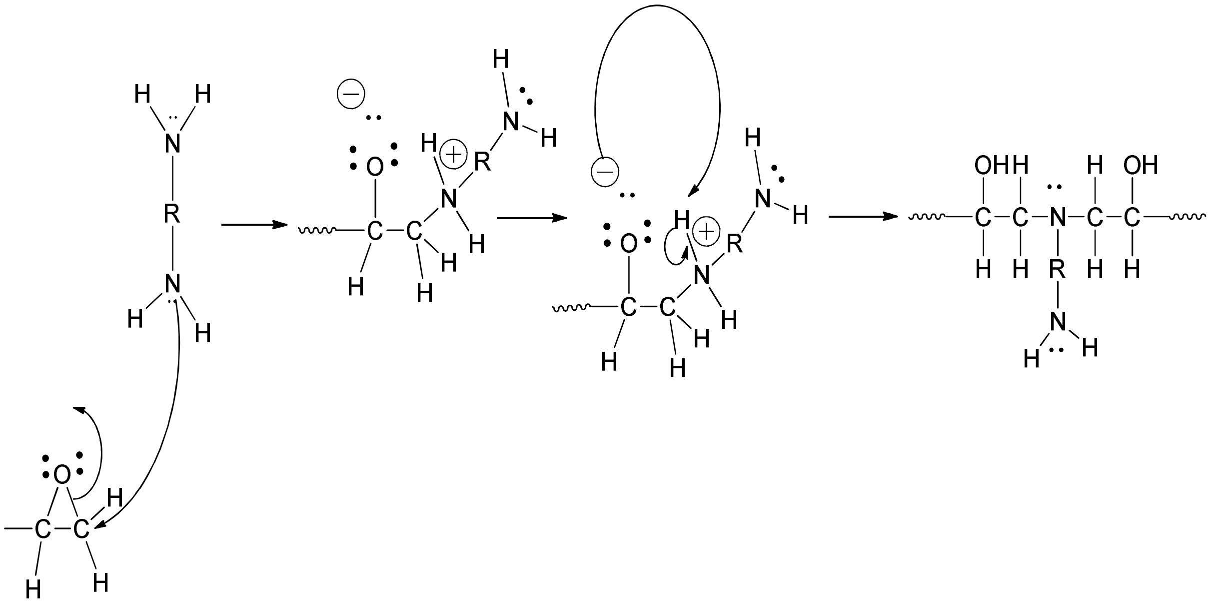


Fig 2: The proposed mechanism for the reaction of an epoxy resin and a primary amine as hardeners

Metallic coating of carbon steel by HGEDAPT:

The metal material was cut into plates of 4cm x 1cm x 0.25 cm dimensions. To obtain reliable and reproducible results, each plate before each test undergoes a surface polishing with an abrasive paper of the finest grain size: 1200/800/600/360/220/120 and after it is rinsed with distilled water, defatted in ethanol and finally dried in pulsed air.

The used experimental procedure includes the following steps:

a) Adding an amount of HGEDAPT and the curing agent (MDA) in the presence of an epichlorohydrin solvent.

b) Maintaining the stirring for about one hour to evaporate the solvent existing in our sample.

The formulation was applied to carbon steel using a wand which produces a film of a controlled thickness (170 ± 10 microns). This coated plate was allowed to air for 5 hours prior to its thermal treatment to avoid a serious contraction of the polymer film which may be caused by the evaporation of residual solvent. Indeed, this contraction may induce a phenomenon of heterogeneity of the film. This coated plate was then placed in an oven for 12 hours to remove the solvent and to crosslink, the resin deposited on the substrate (Figure 3).

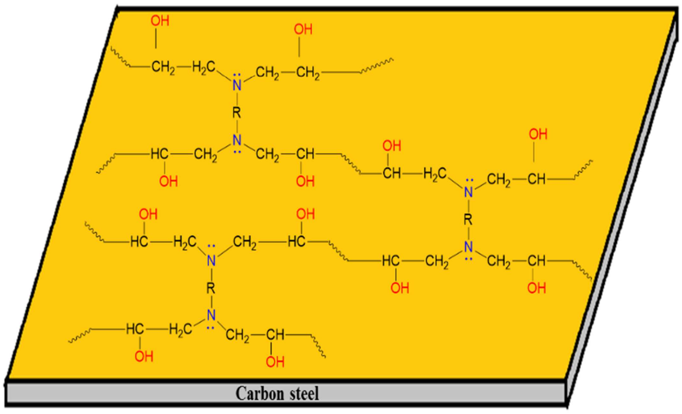


Fig 3:Idealized structure of crosslinked epoxy-amines resins deposited on carbon steel

Analytical method:

Fourier Transform Infrared Spectroscopy (FTIR)

The used infrared spectrum is a Fourier Transform Spectrometer (FTIR) BRUKER; the resin is deposited on a KBr pellet and placed in the FTIR spectrometer. The analysis is performed between 4500 cm^{-1} and 400 cm^{-1}.

Nuclear magnetic resonance (NMR).

The NMR analyses ^1H and ^{31}P were obtained by using the BRUKER AVANCE 300MHz device, and by dissolving the product in $CDCl_3$. The chemical shifts are expressed in ppm.

Viscosimetric analysis

Viscosity measurements were made by using the UBBELOHDE viscometer. The used measurement conditions are as follow:

- The viscometer of 0 B size for a series of dilutions, capillary tube of 0.46 mm diameter, constant k = 0.0047187.
- Measuring temperature over the range 298 K to 318 K.
- Solvent: Methanol

X-ray diffraction (XRD):

The used apparatus is an XPERT-3 diffractometer with a copper anticathode bombarded by electrons accelerated at a voltage of 45 kV and generating a wavelength of radiation λ ($K\alpha_1$) = 1.5405980 nm and λ ($K\alpha_2$) = 1, 5,444,260 nm. The equipment is provided with a back monochromator selecting $K\alpha_1$-$K\alpha_2$ doublet. The sample has the form of a film coated on a flat ordinary steel support: the incident beam continuously irradiates the flat surface of the sample according to angle θ. The sensor detects the radiation diffracted at an angle 2θ. The various diffraction patterns are stored in vector mode where the angles θ and 2θ are coupled in an angular range in 2θ ranging from 10 ° to 90 ° with a step of 0.04 ° and a count time of 2 sec.

RESULTS AND DISCUSSION

Spectral characterization of the new synthesized Hexafunctional epoxy resin:

We performed the structural analysis of the obtained product by means of the proton's nuclear magnetic resonance (^1H NMR) and phosphate (^{31}P NMR) and thus confirmed the results by the Fourier Transform Infrared Spectroscopy (FTIR).

Structural study by FTIR

Figure 4 represents the FTIR's spectrum performed on the synthesized HGEDAPT:

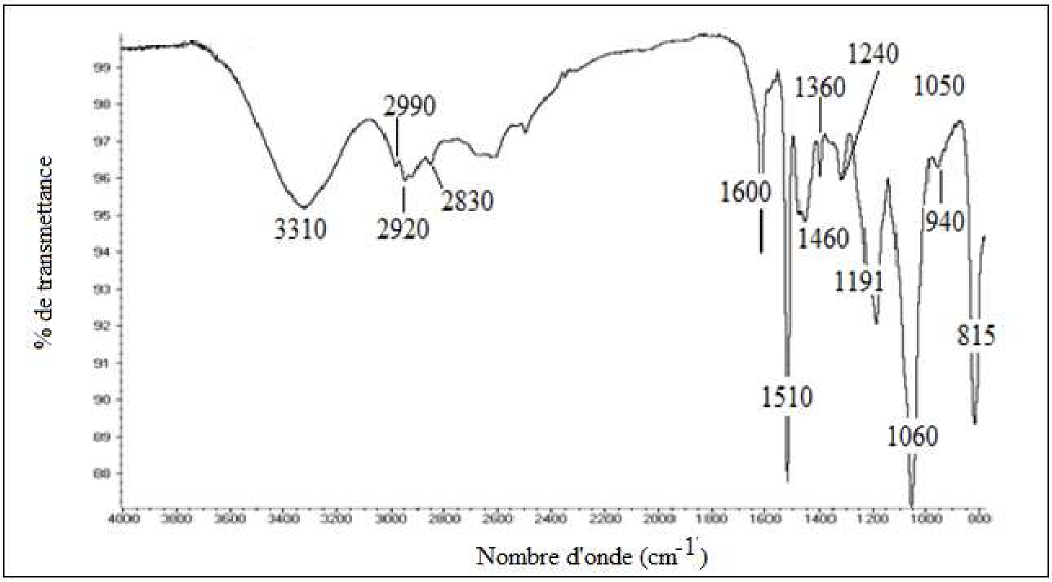


Fig 4 :IR spectrum of the synthesized HGEDAPT resin

The attributions of the different bands of absorbance of the FTIR spectrum formed on the resin are placed in Table 1.

Table 1: Data of FTIR spectrum of HGEDAPT

Frequency ν (cm^{-1})	Attributions
-815 ; 940 ; 1240	vibration of deformation of the epoxide cycle
1060	asymmetric vibrations of P-N group
1191	asymmetric vibration of the group $NP(O)N_2$
-1360 ; 1460 ; 1510 ; 3310	Amines
-1600	$\nu_{C=C}$aromatic of benzene cycle
-2830	$\nu_{s\ C-H}$at CH_2
-2920	ν_{asC-H}at CH_2
-2990	$\nu_{C-H}$of epoxy

Structural NMR study

The HGEDAPT's structure was confirmed by the proton's spectroscopy (Figure 5), and that of phosphorus (Figure 6):

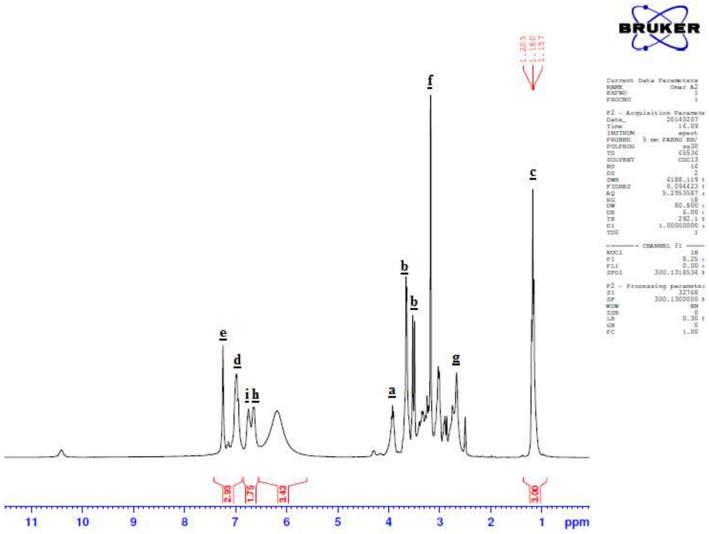


Fig 5 :Spectrum of NMR ^{1}H of HGEDAPT

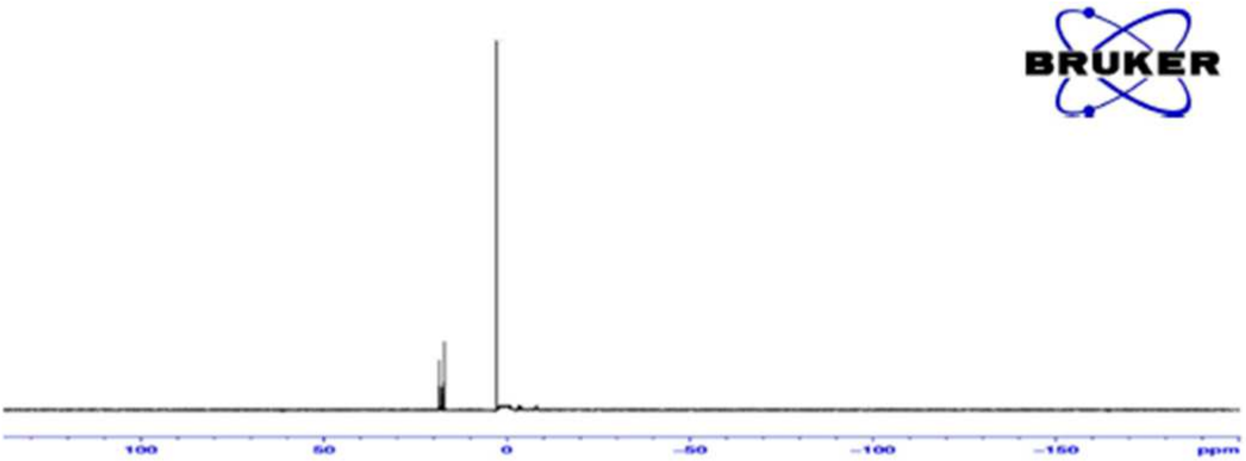


Fig 6 : Spectrum of NMR ^{31}P of HGEDAPT

The NMR spectrum of the proton shows several peaks whose displacements are shown in Table 2.

Table 2: Data of NMR ^{1}H of HGEDAPT

Reference	δ (ppm)
f	3.35
d	7,04
c	1.35
e	7,11
b	3,61
a	4.00
g	2.82
h	6.58
i	6.71

In the end, the NMR spectrum of phosphorus (Figure 6) shows two peaks whose displacements are shown in Table 3.

Table 3:Data of NMR^{31}P of HGEDAPT

Attribution	δ (ppm)
P=O	2, 30
P-N	17,8

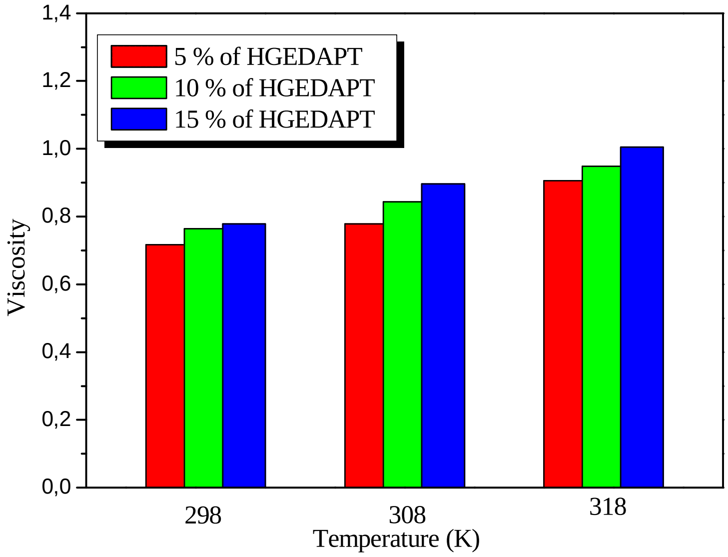


Fig 7: Effect of mass concentration on the viscosity prepolymers / methanol: HGEDAPT / methanol

Viscosimetric behavior of HGEDAPT:

As we mentioned previously, the rheological properties can be directly related to the chemical structure and / or the degree of conversion of the reagent system. To determine the viscosimetric behavior of the HGEDAPT, we dissolved this resin in methanol at the concentrations of 5%, 10% and 15% according to the varying temperatures going from 298 K to 318 K.

Figure 7 shows the study of the effect of the mass concentration on the viscosity HGEDAPT / methanol.

Through the obtained viscosity curves, we found that the viscosity values increase according to the concentration. This demonstrates the progress of the reaction of homopolymerization since the viscosity increases with the increase of molecular mass of the solute. This may be due to the chemical changes undergone by the resin [26-27].

One might suspect the following causes:

The addition of the epichlorohydrin was not complete because of the steric hindrance of the NH_2 groups;

1) The intervention of the reactions of the opening of the regenerated epoxide cycles;

2) An abnormality of adding the epichlorohydrin to the amine which can be represented schematically by the following reaction:

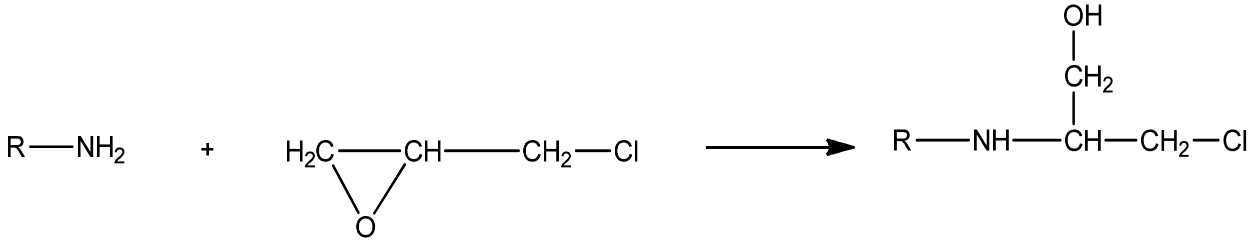


Fig 8 :The addition of epichlorohydrin to the amine

All these factors, therefore, can influence the functionality of the obtained product. So, we have obtained some residual amines and some hydroxyls which have labile protons, which may be responsible to a self-crosslinking of the prepolymer by acting as a hardener.

X-rays diffraction

The resulting diagram was recorded at room temperature in a wide angular range ($10° \leq 2\theta \leq 90°$); with a step of 0.04 ° and a count time of 2 sec. Figure 9 shows the diffraction pattern of X-rays of the HGEDAPT on the carbon steel after crosslinking.

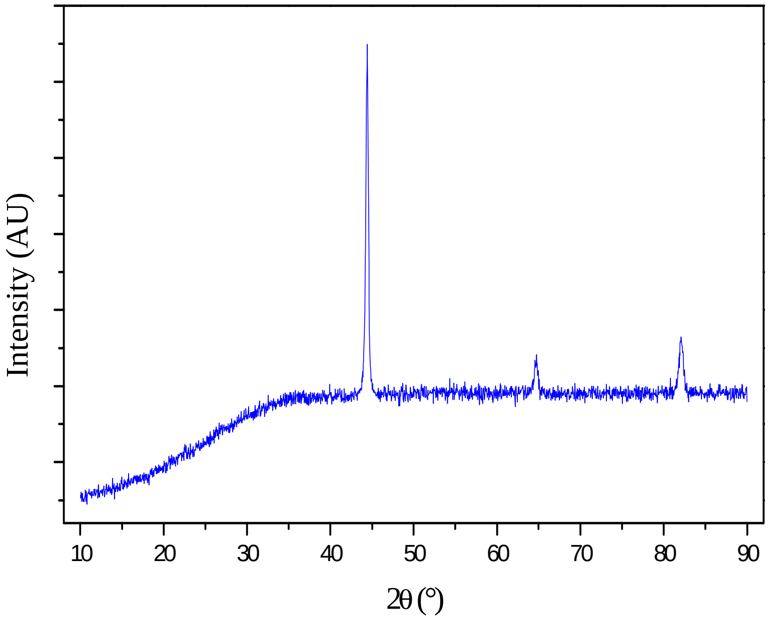


Fig 9 :XRD diffractogramof the standard formulation after the coated crosslinking on carbon steel

The film HGEDAPT / MDA coated on carbon steel exhibits no peaks of XDR characteristics due to the amorphous nature of the polymers [28], and we notice that there is a presence of three lines which are those characterizing the iron and corresponding to the positions 2θ = 44.4348 ° , 64.6574 ° and 82.1170 °. This is generally observed for amorphous polymers on steel.

CONCLUSION

In this work, we presented the synthesis of a new Hexafunctional epoxy resin Hexaglycidyl of ethylene dianiline phosphinetriamine (HGEDAPT) based on phosphorus trichloride and ethylene dianiline.

- The structure of this resin was confirmed and characterized by the conventional spectroscopy FTIR, NMR^{1}H and ^{31}P.
- The viscosimetric study has shown that the Hexafunctional prepolymer based on HGEDAPT aromatic diamine has the drawback of self-crosslinking because of the aforementioned factors manifested by an increase in viscosity. Even if all the amine groups have completely reacted with epichlorohydrin, there would be formed some tertiary amines which are capable of initiating reactions of homopolymerization of the epoxy resins. This obliged us to store the HGEDAPT resin at low temperatures in order to overcome this drawback.
- The characterization of the film coated on carbon steel by the protective matrix HGEDAPT / MDA by X-rays diffraction indicates the amorphous film nature.

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