Synthesis and physico chemical study of a new hexa and tetra functional epoxy materials based on bis -para-terephthalylidene phosphoric ester.

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Received in 29 Oct 2010, Revised 14 Nov 2010, Accepted 18 Nov 2010.

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Abstract:

The new phosphorus epoxy resins tetraglycidyl of bis-para- terephthalylidene phosphoric ester (TGTEP) and hexaglycidyl of bis -para-terephthal phosphoric ester (HGTEP) were synthesized by condensation of glycedol and new polycholoro organophosphate precursors. The synthesized resins have been characterized by Fourier transform infrared (FTIR), ^{1}H, ^{13}C and ^{31}P NMR analyses. Kinetic of cross linking reactions were carried by the determination of epoxy values, curing behavior and thermal stability was followed by thermogravimetric analysis (TGA). The viscometric study allowed us to determine the thermal of storage conditions of these resins. The results allow verifying the chemical structures of new synthesized products. Thermal analysis reflects the good thermal behavior of new resins. The evolution of viscosity as a function of temperature confirm that the synthesized resins can be stored at temperatures above 45 °C without fear of damaged.

Keywords: Synthesis, Characterization, Epoxy, Viscosity, Phosphorus trichloride, Storage

1. Introduction :

The chemistry of epoxies and the range of commercially available variations allow cure polymers to be produced with a very broad range of properties. The most widely used process for the preparation of these prepolymers, is the glycidation [1]. Often found side reactions [2], during the preparation of a prepolymers epoxy, such as the formation of β-chlorohydrins, the oxirane ring opening homopolymerization and the regenerated resin in the middle reaction. This often leads to a real functionality different to the theoretical functionality one, influencing the reactivity with the hardener and consequently on the characteristics and physicochemical properties of the final product. The most useful methods to determine the structure of epoxy resins are: nuclear magnetic resonance (NMR) and FTIR analyses [3, 4]. To improve some specific characteristics of epoxies, we try to synthesize new formulas (monomers), considering the relation between the physical properties and chemical structures. To improve the thermal properties of epoxy resins we propose to incorporate the phosphorus atom in their structures due to its large contribution to the level of thermal stability [5]. In this aim we propose to synthesize two new epoxies hexa and tetra functional containing phosphorus oxide groups and we study their, reactivity to cross linker agent, thermal stability and viscometric behaviours.

2. Experimental part:

2.1 Materials

Phosphorus oxychloride (99%), Terephtalic acid (98%), Terephtalic aldehyde (98%), 1 hydroxy 2,3 epoxypropane (99%) and 4,4'-diaminodiphenylmethane (DDM) are obtained from Aldrich chemical company. All these materials were stored at 4 to 7°C and used without any further purification.

2.2 Synthesis :

The resins TGTEP and HGTEP were synthesized by the procedures [6, 7, 8].

2.2.1 Synthesis of Tetraglycidyl Terephthal Phosphoric Ester (TGTEP):

The synthesis of tetraglycidyl terephthalylidene bis-p- phosphoric ester (TGTEP), requires two steps (Fig.1). In the first one we mix 0.016 mol of terephthalic acid solution dissolved in methanol and 0.33 mol of phosphorus trichloride, the mixture is stirred rigorously for 8 h at 25 °C using dichloromethane as solvent. A white powder precipitate, which is tetrachloride-bis-para-terephthalylidene phosphoric ester. In the second step we condense 0.011 mol tetrachloride-bis-para-terephthalylidene phosphoric ester and 0.08 mol glycedol (excess) in a solution of 40 ml methanol, in presence of triethylamine, and the mixture is heated at a temperature of 70 ° C for 10 h. The solvent was removed by rotary evaporation, the obtained product then dissolved in trichloromethane, washed with water and dried over sodium bisulfate. A transparent viscous product finally obtained after removal of trichloromethane under vacuum, with a yield of about 70%.

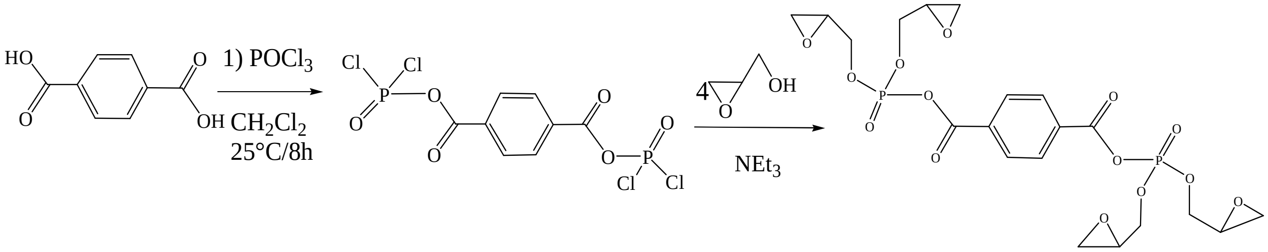

Fig.1. Synthesis of tetraglycidyl of bis-para- terephthalylidene phosphoric ester

2.2.2 Synthesis of Hexaglycidyl Terephthal Phosphoric Ester (HGTEP):

The hexaglycidyle terephthalylidene bis-p-ester phosphoric (HGTEP), is synthesized in two reaction stages (Fig.2). In the first step in 40 ml of dichloromethane is mixed 0.016 mol of a solution of dissolved terephthalaldehyde in methanol and 0.33 mol of phosphorus trichloride, the mixture is stirred rigorously for 12 h at 25 ° C, then evaporated the solvent (dichloromethane), a yellow solution is collected which is a hexa chloro-para-terephthalylidene phosphate ester. In the second step, 0.01 mol of bis-para-hexachloro terephthalylidene phosphate ester has been condensed with 0.15 mol of glycédol (large excess) in a solution of 40 ml of methanol, while adding the triethylamine, the mixture is heated to a temperature of 70 ° C for 24 h, then we follow the same protocol as in the purification resin above.

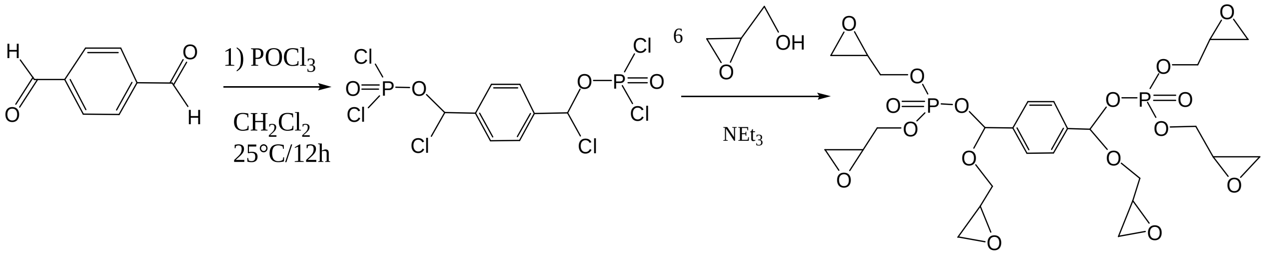

Fig.2. Synthesis of hexaglycidyl of bis-para - terephtalylidene phosphoric ester

Obtained products can be explained by the proposed reaction mechanism presented in Figure 3.

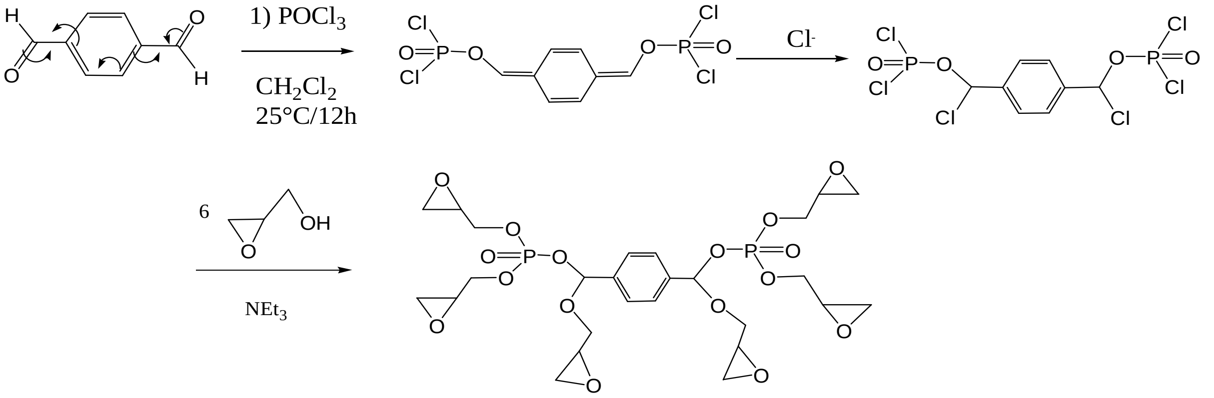

Fig.3. Mechanism of synthesis of the hexaglycidyl of bis-para - terephtalylidene phosphoric ester.

2.3 Measurement :

Fourier transform infrared (FTIR) spectra were recorded on Brucker FTIR spectrophotometer using ATR technique; Vibrational transition frequencies are reported in wave number (cm^{-1}). ^1H, ^{13}C and ^{31}P NMR spectra were obtained on a Brucker Avance 300 NMR Spectrometer using $CDCl_3$ as solvent. The epoxy values of HGTEP and TGTEP were determined according to the method reported by Korshak and Vinogradova [9]. The extent of reaction *P* is defined as the fraction of epoxy groups at reaction time *t*. This is calculated from the epoxy value of the resins, which is a measure of the concentration of epoxy groups, using the following equation:

$$P\ (\%) = 100.\ (M_0 - M) / M_0.$$

where M_0 and M are respectivly the molecular masses of epoxy at t_0 and the instant t of glycidation .

Thermal degradation was carried by TGA in dynamic mode. Pyrolysis of samples was performed in an inert atmosphere under nitrogen. The viscosity measurements were made using a viscometer Ubbelohde.

The measuring conditions were as follows:

-Size 0c Viscometer for dilution series, capillary diameter 0.46 mm, constant k = 0.003
-Measuring temperature: 25, 30, 35, 40 and 45°C.
-Number of measurement: 3 each.
-Solvent: chloroform
-The starting concentration: 1.00 g resin 100ml chloroforme. -The Hagenbach correction was calculated using the formula given in DIN 51562.
-Solubilization of epoxy resin prepolymers in chloroform was carried out at 20 °C with magnetic stirring.

3. Results and discussion

We performed the synthesis of the TGTEP and HGTEP through glycidylation via the condensation of glycedol with structures containing chlore, this pathway is used for the introduction of the oxirane group to a variety of industrial epoxy resin precursors. During the synthesis of epoxy prepolymers, some secondary reactions can take place, such as: the polycondensation of glycedol, the formation reaction medium. These reactions are important insofar as the real functionality is lower than the theoretical functionality and responsiveness of the product is thus amended, which does not happen without major influence on final product characteristics : openness regeneration cycles and the homopolymerization of oxirane prepolymer [10,11].

3.1 Spectral characterization:

Chemical structural compounds was confirmed by FTIR spectroscopy, ^1H, ^{13}C and ^{31}P NMR.

3.1.1. Spectral characterization of TGTEP:

Tetrachloride-bis-para-terephthalylidene phosphoric ester: RMN ^{1}H (ppm) : 7,9 (s, 4 H aromatic). RMN ^{13}C (ppm): 134 (s, C aromatic) ; 140 (s, C tertiaire aromatic); 171,5 (s**,** C of phosphoric ester). RMN ^{31}P (ppm) **:** 13,9 (s, R-P(O)Cl_2).

Tetraglycidyl terephthalylidene bis-p- phosphoric ester : RMN ^{1}H (ppm) : 2,23 (dd, 2H, CH_2 oxirane) ; 2,7- 2,9 (m, 1H, CH oxirane) ; 3,8 et 4,3 (dd, 2H, CH_2 ester) ; 7,9 (s, 4H, aromatic). RMN ^{13}C (ppm): 41,2 (s, CH_2 oxirane); 52,4 (s, CH oxirane); 69,8 (s, P-O-CH_2); 128,7 (s, CH, aromatic); 139,6 (s, C-C aromatic); 171,3 (s, carbonyl). RMN ^{31}P (ppm): 11,2 (s, R-P(O)Cl_2); 2,3 (s, O=P-(OR)$_3$). FTIR (cm^{-1}) : 913, 93 (epoxy) ; 2877,39 - 2977 (elongation of C-H) 1030,13 (γ of P(O)-O-C).

3.1.2 Spectral characterization of HGTEP:

Hexachloride bis-para-terephthalylidene phosphoric ester: RMN ^{1}H (ppm): 6,1 (s, 1H, HC-O-P); 6,8 (s, 4H aromatic). RMN ^{13}C (ppm): 71, 5 (s, C-OH); 128,2 (s, CH aromatic), 149,6 (s, C tertiairy aromatic). RMN ^{31}P (ppm) : 26,3 (s, C_2P(O)Cl,) ;13,6(s, R-PO(Cl)$_2$).

Hexaglycidyl terephthalylidene bis- para- phosphoric ester (HGTEP) RMN ^{1}H (ppm) : 2,1 (dd, 2H, CH_2 oxirane) ; 2,4 (m, 1H, CH oxirane) ; 4,3 et 4,5 (dd, 2H, OCH_2); 3,1 et 3,4 (dd, 2H, CH_2 ether), 5,5 (m, 1H, CH-O-P); 6,81 (s, 4H Aromatic). RMN ^{13}C (ppm): 40,7 (s, CH_2 oxirane of ether); 41,9 (s, CH_2 oxirane of phosphoric ester) ; 49,1 (s, CH oxirane of ether) ; 50,5 (s, CH oxirane); 69,3 (s, $POCH_2$) ; 67,2 (s, CH_2O ether) ; 105,5 (s, CH-O-P); 128,12 (s, CH, Aromatic) ; 138,7 (s, C-C aromatic). RMN ^{31}P (ppm) : 26,3 (s, C_2P(O)Cl) ; 13,6 (s, R-PO(Cl)$_2$), 2,1 (s, C-O-PO(OR)$_2$). FTIR (cm^{-1}) : 931, 56 (oxirane) ; 2921,14 – 2983,04 (elongation of C-H); 1019,94 (γP(O)-O-C); 1190,61 (γP(O)-C).

3.2. Conversion rate:

The change of epoxy values as a function cross-linking reactions time of TGTEP and HGTEP monomers (condensation step) are presented in (Fig.4). We note decreases in epoxy index at curing.

Initially, the variation of the index of epoxy remain almost linear, this is due to a greater concentration of reactive sites (functions antagonists).The second part of the curves shows a reduction in the kinetics of crosslinking that can be explained by the low concentration of antagonistic functions and the large size of macromolecular chains, which makes the reactions between the amine hardener and epoxies more difficult.

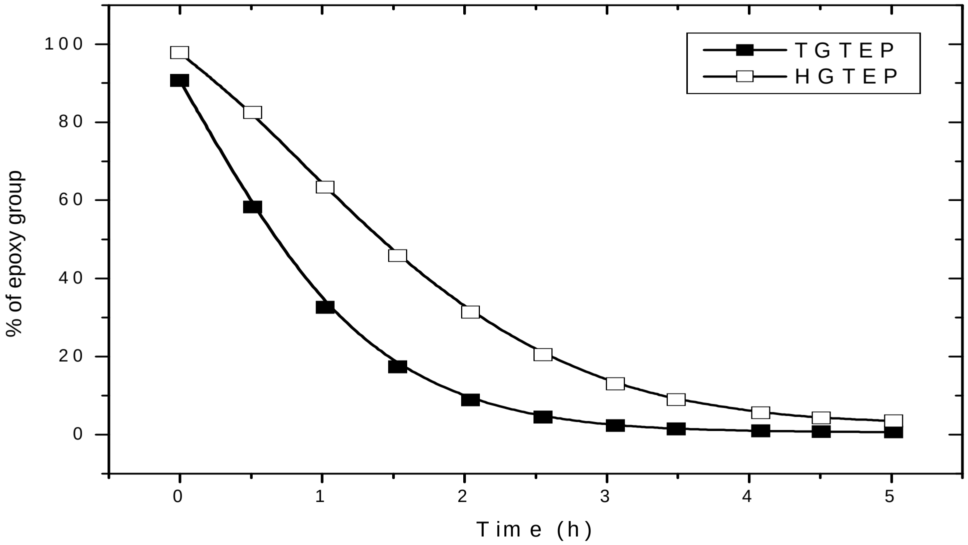

Fig.4. Evolution of epoxy group versus reaction time

We note that, kinetic of cross linking reaction is a function of a regioselectivity, the tetra functional resin TGTEP reacts easily than hexa functional resin (HGTEP).

3.3 Thermal stability of the new epoxy resins:

The presence of epoxies and DDM (4.4-diaminodiphenylmethan as a curing agent) produces a hardening of the resins due to the crosslinking reaction. The main thermal characteristics of the studied resins, extracted from thermograms (fig.5), according to the conventional standards [12, 13], are classified in Table1.

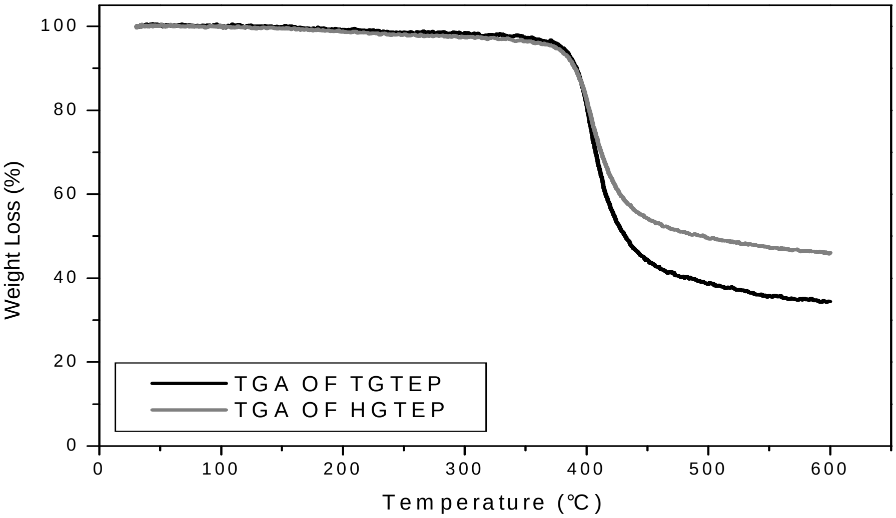

Fig.5. TGA curves of TGTEP and HGTEP epoxy resins

Table 1. Main characteristics of the epoxies samples pyrolysis.

Epoxies	T_d (°C)	T_{10} (°C)	T_{50} (°C)	S_{dr} (°C)	R_{500} (%)
TGTEP	205,09	391,12	430,08	386,93	38,64
HGTEP	213,18	391,11	480,66	82,89	49,33

The TGA curves show that decomposition of TGTEP and HGTEP thermoset with DDM starts respectively at 205° C and 213°C, the residues at 500°C of the both resins are 38 and 49%. Compared with a several [6,10,12,13] studies of the most useful epoxy resin DGEBA cured with DDM which has a starting degradation temperature of 167°C and an residue at 500°C of 22%, it means that the new synthesized resins are more stable. All this results reflects the low kinetic of the thermal degradation of the TGTEP and HGTEP epoxy resins.

3.4 Determination of the storage temperature:

The viscometric properties can be directly related to the chemical structure or the degree of conversion of reactive system [14;15]. The viscometric behaviors of prepared resins were studied at different ranges of temperature (Fig.6). The curves present the effect of temperature on the viscosity of the new resins diluted in chloroform, the both resins are almost the same behaviour whatever system temperature resin /solvent. The viscosity increases by increasing the percentage of resin, which can be explained by the progress of the reaction of homopolymerization. The viscosity increases with increasing molecular weight of the solute. Viscosities of each ratio remain constant as functions of temperature. It appears from this analysis that the synthesized prepolymers based phosphate esters have a thermostability of avoiding self crosslinking during storage. We can therefore confirm that our synthesized resins can be stored at temperatures above 45°C without fear of damaged.

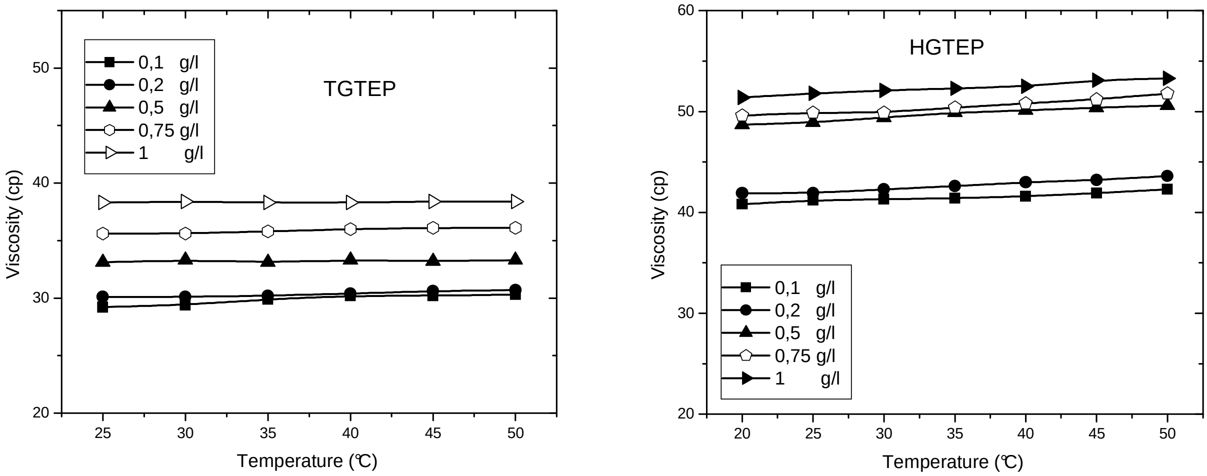

Fig.6. Temperature effect on viscosities of synthesized epoxies.

4. Conclusion

Two new epoxies hexa and tetra functional have been synthesized and characterized by ^{1}H, ^{13}C, ^{31}P NMR and FTIR. The results confirmed the structure of our resins. The epoxy resins were further cured with diamine curing agents, 4,4-diaminodiphenylmethane (DDM), to obtain the corresponding epoxy polymers.

The thermal stability was confirmed by thermogravimetric analysis, the results prove the good thermal properties and stability of TGTEP and HGTEP resins. The viscometric study confirms that the packaging of resins can take place at room temperature without fear of self-crosslinking.

5. References

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