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Experimental and theoretical study of the impact of quantum chemistry parameters on the behavior of the thermal degradation of organophosphorus oxide resins inufigeant

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ABSTRACT: In this study, we are interested in the development of a new model "Quantitative Structure Property Relationship" (QSPR). To illustrate the behavior inufigeant of the thermal degradation of resins oxides organophosphate based on the Quantitative Structure-Property Relationship (QSPR) and the quality of the experimental data. Subsequently, we have discussed the influence of the impact of the thermal parameters quantum chemistry on the retardant behavior of degradation of multifunctional resins (DGEBA, TGTEP, HGTEP and HGCP). Self-timer degradation prediction was made by the semi-empirical PM3 and DFT method database software Gaussian 03.

KEYWORDS: QSPR; model; Pm3; DFT; Epoxy resins; Retardant thermal degradation.

1 INTRODUCTION

The development of new materials stands of an extensive experimental work and a large number of tests under different conditions. Synthesis polymer with the desired properties is challenging which implies often much time and resources. The ability to predict the properties of final product of new materials is a large value, a guidance which speeds up the process and the cycle of development. Thermal properties are one of the most important properties of organic polymers and their complexes; they determine temperature ranges for the treatment and employ these materials and conditions front for and understand other properties. There were many methods proposed for predicting the behavior heat systems of polymers. These include empirical equations [1,2], molecular dynamics simulations [3.4], the methods semi-empirical [5] and mathematical tools including neural networks [6.7], the theory of fuzzy sets [8] and chart clues theory [9 , 10]].

In this work, we aim to correlate the electronic properties of some epoxy resins (DGEBA, TGTEP, HGTEP and HGCP) synthesized in the laboratory and hardened by dianilinemethylene (MDA), epoxy resins a certain temperature feature of thermal degradation. Subsequently, we compared the experimental results with the predicted properties for the validation of the theoretical model developed.

2 MATERIALS AND METHODS

2.1 MATERIALS

Our composite materials are formulated from matrices composed of DGEBA resins and new TGTEP, HGTEP HGCP and then cross-linked by dianilinemethylene (MDA), on the one hand, and the load and coupling agents, on the other hand. The formulations contain as charges a powder in the form of very fine particles and the calcium carbonate because of its hydrophobic nature.

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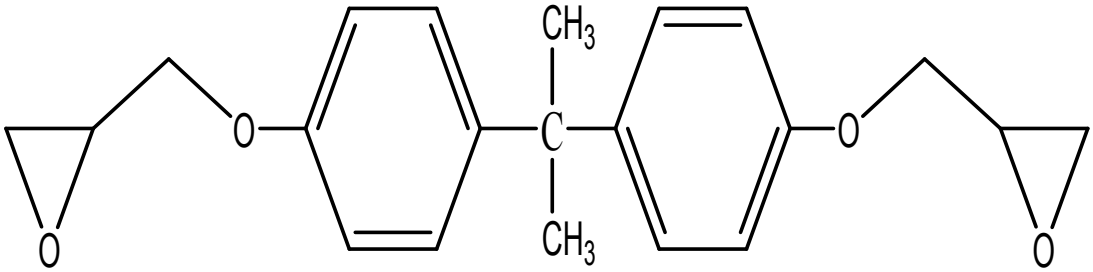


Fig 1: Diglycidyl ether of Bisphenol A (DGEBA)

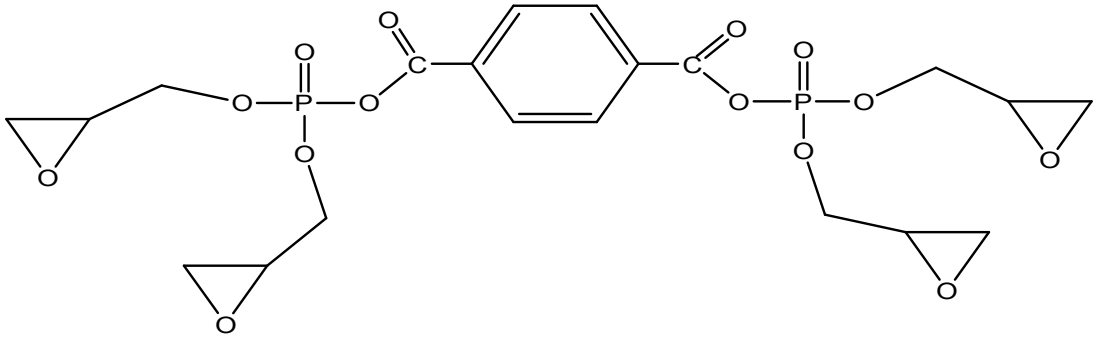


Fig 2: Tetraglycidyle terephtalydiene bias-para-ester phosphoric (TGTEP)

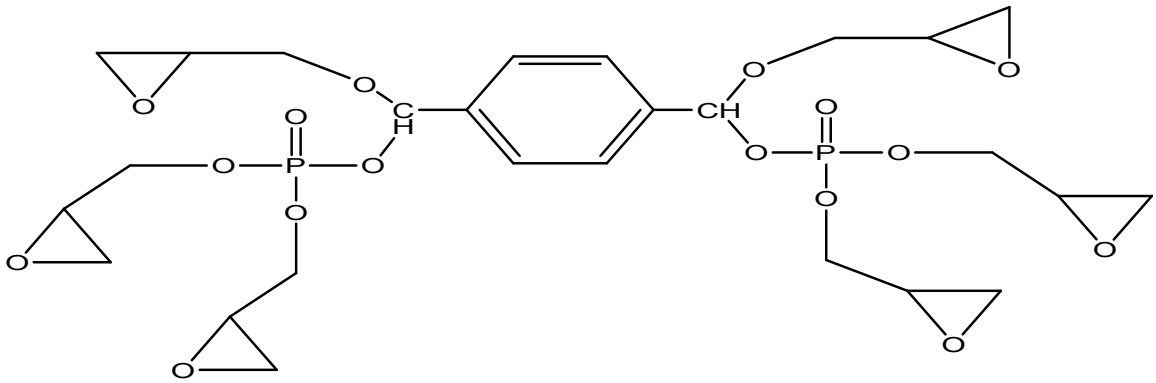


Fig 3: Hexaglycidyle terephtalydiene bias-para-ester phosphoric (HGTEP)

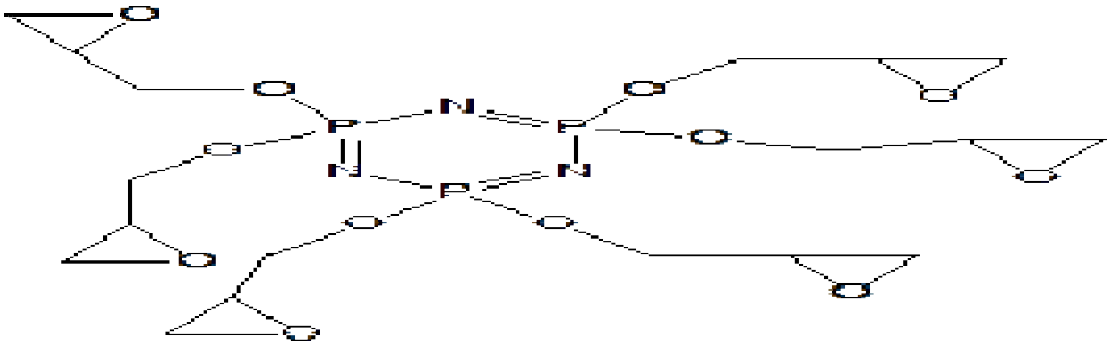


Fig 4: Synthesis of hexaglycidyl Cyclotriphosphazene (HGCP)

2.2 CALCULATION METHODOLOGY

The quantum chemical calculations have been widely used to study the reaction mechanisms [11]. They are also approved to be a very powerful tool for the study of the properties of the molecules [12, 13]. It has been shown that the physical properties may be related to the molecular structure and electronic space.

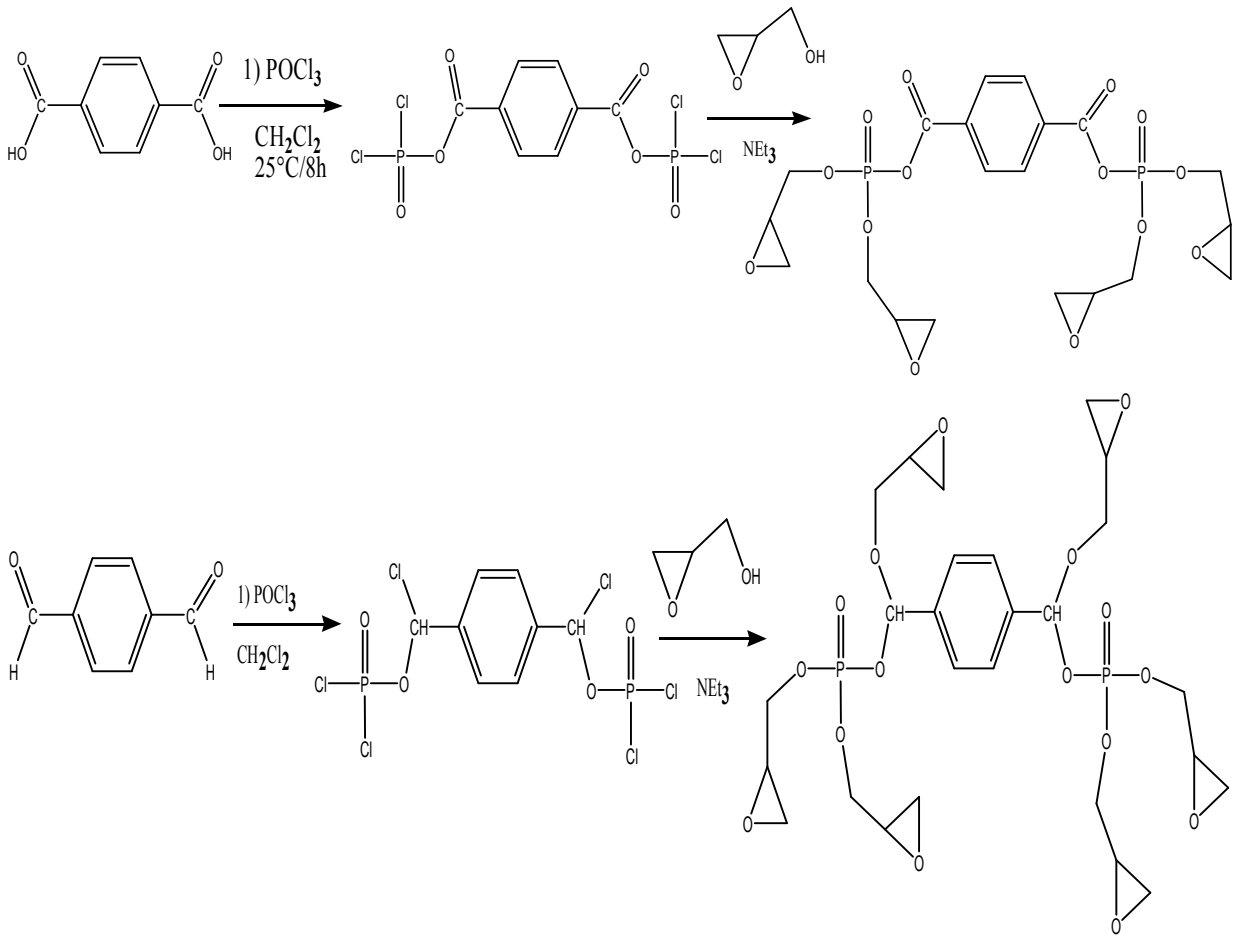
In this study, we studied the relationship between the parameters of the quantum chemistry and self-timer degradation behavior heat some epoxy resins organophosphorus synthesized in the laboratory [14, 15, 16]. The quantum chemical parameters were calculated by the semi-empirical method namely, the parametric method (PM3 and DFT), the three compounds method of Becke parameter (B3LYP) has been used on the basis of (6-31 G), all the calculations were performed by Gaussian 03.

3 RESULTS AND DISCUSSIONS

3.1 SYNTHESIS OF EPOXY RESINS

The fig (5) recollects the different phosphorus epoxy resin synthesized in the laboratory with the D GEBA as a model.

The homologs of epoxy polymer represented by fig (2 and 3) have been prepared from the reaction of the epychloridrine with the compound of terephthalaldehyde [14] as mentioned in the following reaction scheme while the DGEBA fig (1) and the hexaglycidyl cyclotriphosphazene (HGCP), fig (4) were obtained by condensation of the epychloridrine respectively on Bisphenol A and the cyclotriphosphazene hexaglycidyl.



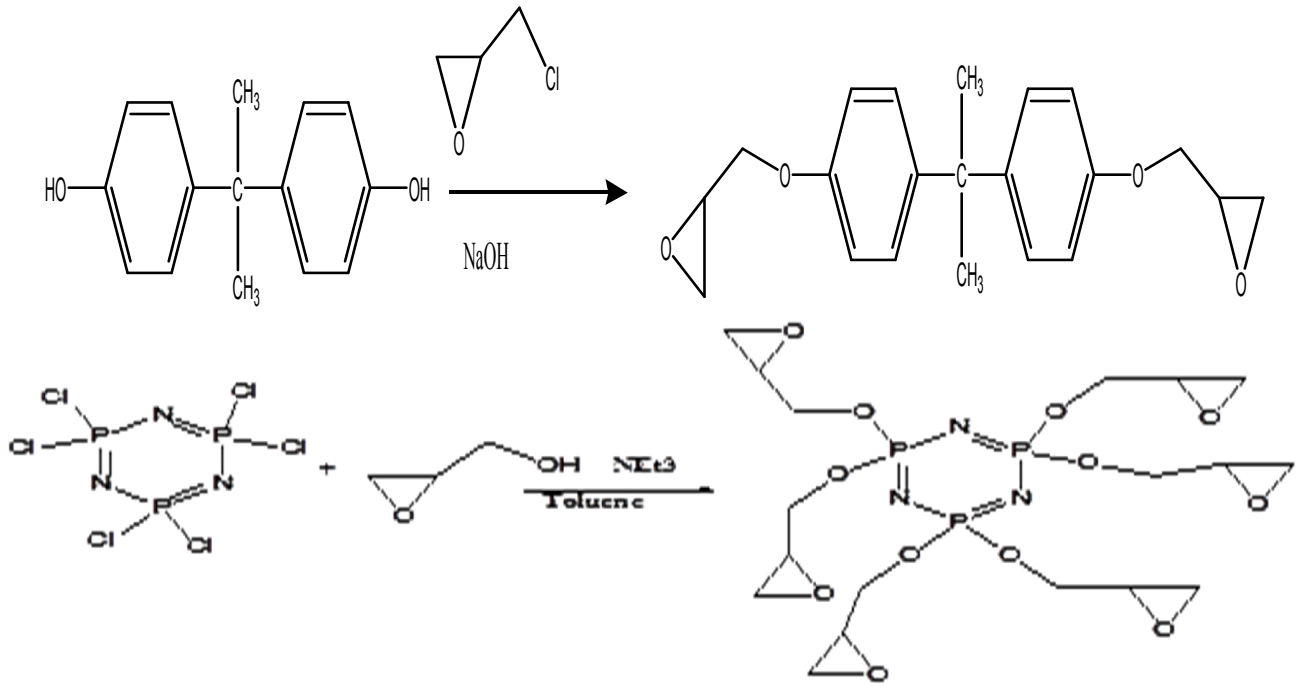


Fig 5: derivatives epoxy compound (DGEBA, HGTEP, TGTEP and HGCP)

Thermogravimetric analysis shows monocomponent composite developed as temperature, from which the degradation takes a steeper shape, is substantially identical for all three materials. Then, we classified the main features according to conventional standards,With:

Td: start temperature of decomposition (mass loss of 2%)

T 10: temperature 10% of mass loss

T 50: temperature at 50% of mass loss

Table1: Main characteristics of paralysis of one composite sample

Sample	T d ° C	T 10 ° C	T 50 ° C
DGEBA	164,34	291,79	350,44
TGTEP	205,09	391,12	430,08
HGTEP	213,18	391,11	480,66
HGCP	250,22	344,54	375,12

3.2 THEORETICAL RESULTS

To search for calculating epoxy resins organophosphorus we propose to study several descriptors on electronic and steric basis thermodynamic effect.

The calculation of descriptors has been done by two different methods. The first semi-empirical (PM3) using the MM2 and a second method based on the electron density (DFT) using the Gaussian program 03. The main results of this study are summarized in table 2.

Table2: Quantitative Structure-property of different descriptors

Molecule	Method	EHOMO (eV)	ELUMO (eV)	ΔE	M (Debye)	Log P
DGEBA	DFT	-9,68	0,05	9,73		
	PM3	-9,338	-0,167	9,171	24,09	3,835
TGTEP	DFT	-3,1926	-1,6396	1,553		
	PM3	-9,411	-1,737	7,674	8,25	2,52
HGTEP	DFT	-3,37	-1,79	1,58		
	PM3	-9,86	-0,53	9,33	13,71	13,71
HGCP	DFT	-9,52	-3,6789	5,8411		
	PM3	-5,243	-1,67	3,573		

3.3 RELATIONSHIP - PROPERTY (QSPR)

To establish a mathematical model relating the experimental temperature characteristical of thermo grams with values obtained from the study of quantum descriptors available (QSPR), we need to calculate the correlation between each descriptor and each property in the table to model parameters and their equations.

3.4 GENERAL MODEL

$$\mathbf{Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2}$$

Table 3: Model parameters

	TD		T10		T50	
	PM3	DFT	PM3	DFT	PM3	DFT
β_0	253,556	170,191	7,824	0.451	-20,338	22,663
β_1	242,483	402,436	7,440	11,360	-47,944	-13,729
β_2	280,206	491,682	14,646	14,393	-4,792	-5,175

3.4.1 CASE 1 DFT METHOD

$T_d(C°)$ **= 170, 191 + 0, 451 * E_{HOMO}+ 22, 663 * E_{LUMO}** R^2= **0.969** Equation 1

$T_{10}(C°)$ = **402, 436 + 11, 360 * E_{HOMO} -13,729 * $_{ELUMO}$** R^2= **0.998** Equation 2

$T_{50}(C°)$ = **491, 682 + 14, 393 * $_{EHOMO}$ -5, 175 * E_{LUMO}** R^2= **0.863** Equation 3

3.4.2 CASE 2 PM3 METHOD

$T_d(C°)$ = **253, 556 + 7, 824 * E_{HOMO} -20,338 * $_{ELUMO}$** R^2= **0.685** Equation 4

$T_{10}(C°)$ = **242, 483-7, 440 * $_{EHOMO}$ -47, 944 * E_{LUMO}** R^2= **0.465** Equation 5

$T_{50}(C°)$ = **280, 206-14, 646 * $_{EHOMO}$ -4,792 * $_{ELUMO}$** R^2= **0,260** Equation 6

The results of theoretical calculation which is represented in table 4

Table 4: Theoretical calculation

Method	Molecule	TD ° C	T10 ° C	T50 ° C
PM6	DGEBA	183,890282	319,965685	417,773461
	TGTEP	215,250897	395,781767	426,367269
	HGTEP	187,188955	341,253275	427,15856
	HGCP	246,499866	361,559274	365,00071
DFT	DGEBA	164,688403	291,7799	352,094321
	TGTEP	212,959691	393,309345	456,291958
	HGTEP	205,910121	388,677367	454,216139
	HGCP	249,271785	344,793388	373,697582

The Fig (6, 7, 8 and 9), show the variation of temperatures in experimental and theoretical degradation of resins studied (DGEBA, TGTEP, HGTEP and HGCP). They are obvious that there is a strong relationship between experimental and theoretical values, indicating that these models can be used to predict the thermal flame-retardant properties of news precursors which are structurally related to epoxy resins studied.

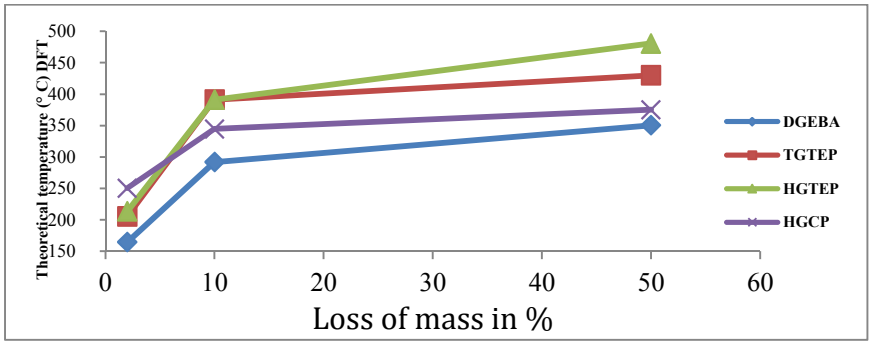


Fig 6 : Variation of Theoretical temperature DFT based on% loss

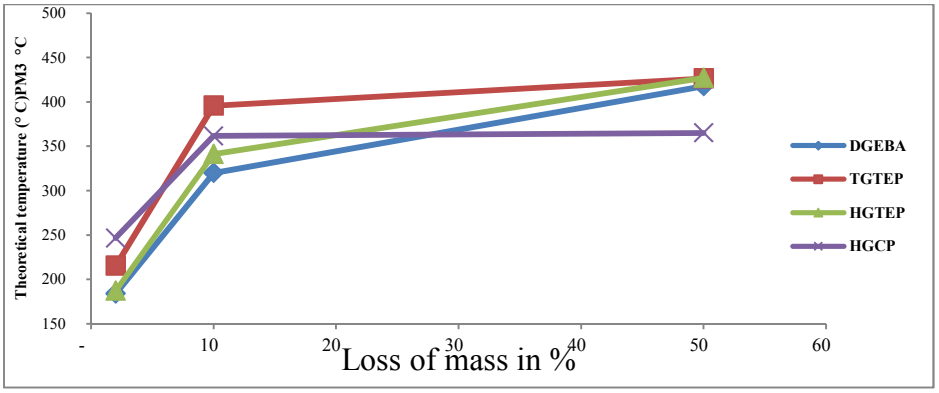


Fig 7: Change in Theoretical temperature PM3 depending % loss

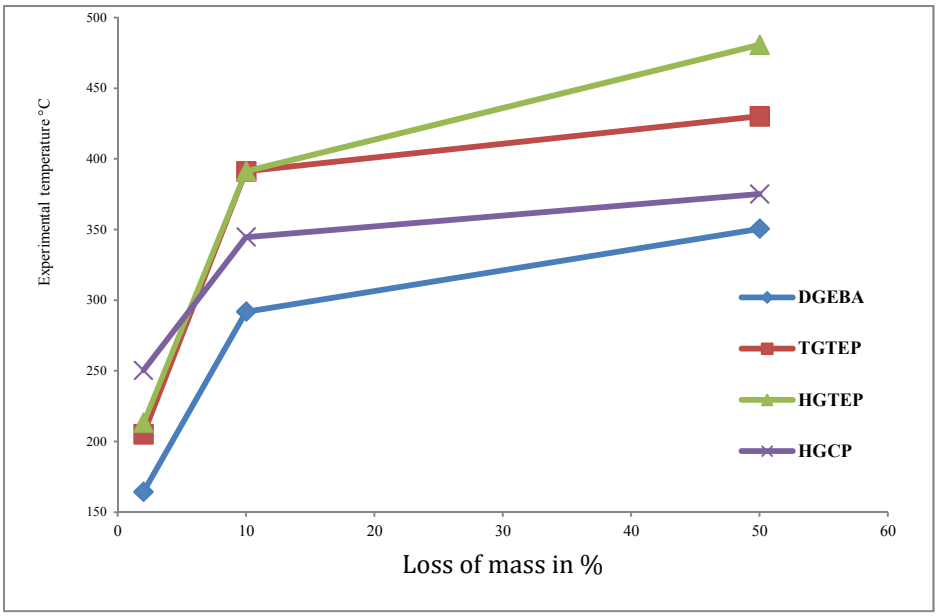


Fig 8: Change in Temperature Experimental based mass loss in %

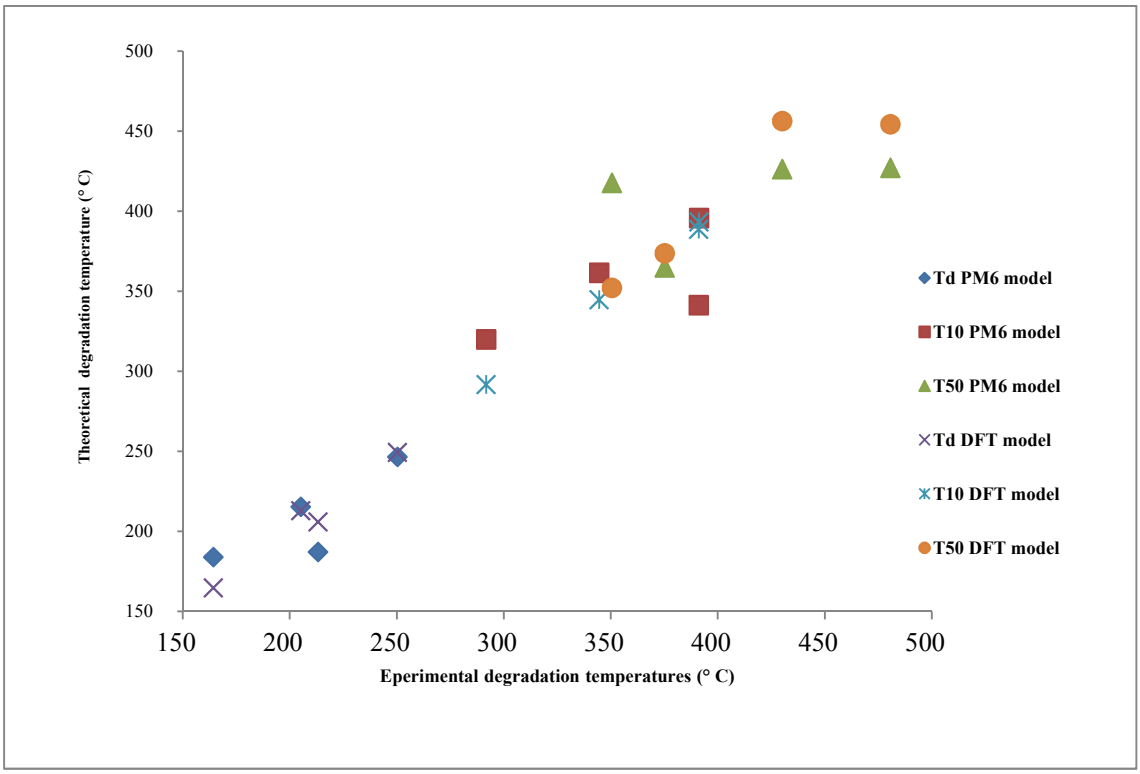


Fig 9: Variation of temperature versus theoretical, experimental temperature

The HOMO and LUMO orbitals of resins organophosphorus derivatives are presented in fig (10-13). This shows clearly that the effect of the electronic regulating the thermal phenomenon on the epoxy-dimmine systems studied.

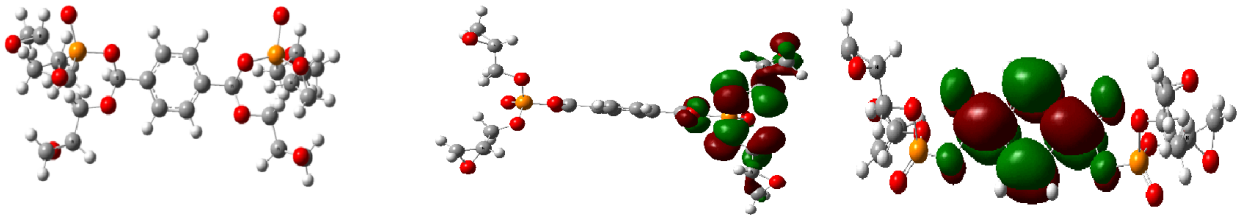


Fig 10: HGTEP

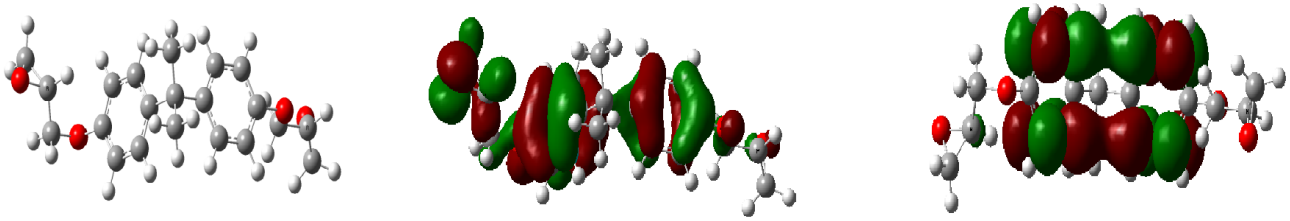


Fig 11 : DGEPA

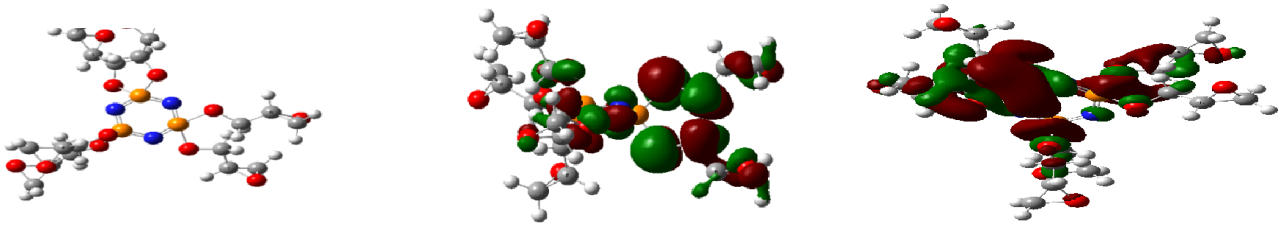


Fig 12 : HGCP

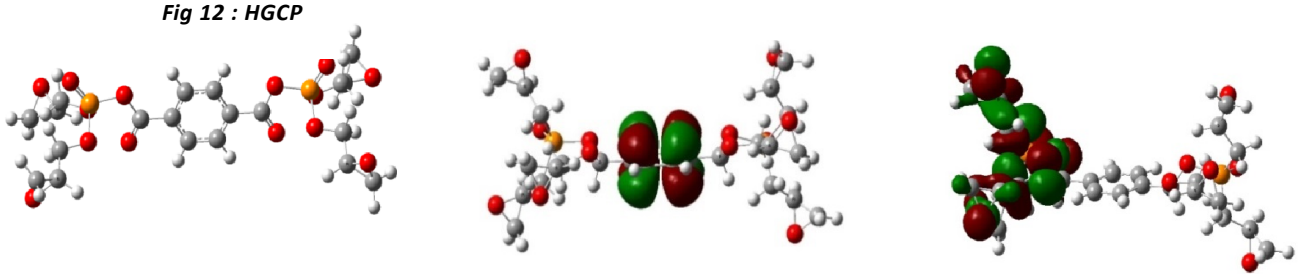


Fig 13 : TGTEP

4 CONCLUSION

In this work, we have studied the impact effect of electronics on the retardant behavior property heat a classy variety of epoxy resins organophosphorous. This calculation allows QSPR models to calculate the values of certain characteristical temperatures of the retardant behavior of thermal degradation involving a number of quantum parameters (descriptors). All theoretical results obtained coincide with the experimental results The distribution of electron density of the influence on properties of the behavior retardant epoxy resins range studied where the strong correlation between the phenomenon and the electronic effect of thermal degradation are linked.

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