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Quantum Chemical investigation of electronics effect impact on epoxies thermal properties - QSPR model of thermal degradation of some diglycidyl ether bisphenol derivatives / diamine systems.

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Abstract:

In this work we present the development of a new Quantitative Structure Property Relationship (QSPR) model combining the results of solving the time independent Schrodinger equation for the electrons of molecular systems as a function of the positions of the nuclei and thermal properties of some epoxies (*DGEBA, DGDDP, DGETBBA and DGEDDS*) in the objective to predict thermal properties of other similar bifunctional epoxy resins. This computational study is carried through the calculation of quantum parameters linking the electronic effects to properties of studied molecules structures. Subsequently we validate the obtained QSPR model by comparing the predicted theoretical results to experimental of thermal degradation of the studied serial of compounds.

Keywords: QSPR; Model; PM6; DFT; Epoxies; Thermal properties.

1. Introduction :

The development of new materials is synonymous to a vast experimental work and a large number of trials under different conditions. The synthesis of polymers with desired properties is a challenge that often involves considerable time and resources. The ability to predict the properties of the final product of new materials is of great value, a guidance that speeds the process and development cycle.

Thermal properties are one of the most important properties of polymers and composites; they determine the temperature ranges for the treatment and use of these materials and terms prior to predicting and understanding other properties.

There have been many methods proposed for predicting thermal behaviour in polymer systems. These include empirical equations [1–2], molecular dynamic simulations [3–4], semi-empirical methods [5] and mathematical tools including neural

networks [6–7], fuzzy set theory [8] and graph theoretical indices [9, 10].

In this study we propose to correlate the electronic properties of some epoxy resins (*DGEBA, DGDDP, DGETBBA and DGEDDS*) synthesized in the laboratory and cured by methylene dianiline, to some temperatures characteristic of thermal degradation [11]. Subsequently we compare its experimental to predicted properties to ensure the validity of the theoretical developed model.

2. Experimental parts

2.1. Materials

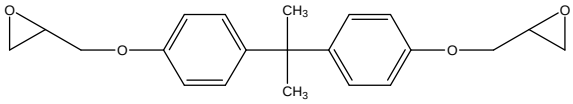
All materials were synthesized in laboratory by glycidylation via condensation of epichlorohydrin and molecules containing hydrogen mobile type polyphenols [12], then are crosslinked by methylene diamine as hardener agent.

The serial of epoxies proposed to invest the quantitative structure-property relationships were the diglycidyl ether of bisphenol A [13], diglycidyl ether of 4,4 '-dihydroxy diphenyl sulfone (DGEDDS) [14], diglycidyl ether dihydroxydiphenyl (DGDDP) [15] and diglycidyl ether of tetra bromo bisphenol A [16]. The chemical structures of synthesized compounds are presented in Table1. All compounds were synthesized according to bibliographies of several works [12-15].

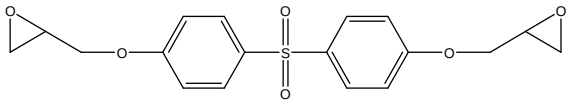
2.2. Sample preparation and characterization

Stoichiometric ratios of epoxy and methylene dianiline were mixed and cured at the cycle of temperature shown in Table 2.

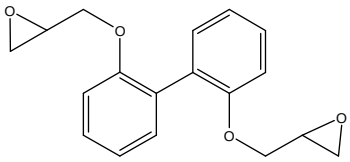
Table 1. Chemical structure of studied epoxies in QSPR model



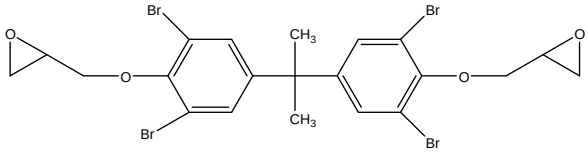
Diglycidyl ether of bis-phenol A
(DGEBA)
Molar weight = 340,413 g/mol



Diglycidyl ether of bis-phenol S
(DGEDDS)
Molar weight = 362,397 g/mol



Diglycidyl ether dihydroxydiphenyl
(DGDDP)
Molar weight = 298,333 g/mol



Diglycidyl ether of tetra bromo bis-phenol A
(DGETBBA)
Molar weight = 655,997 g/mol

Table 2. Curing cycle of prepared samples

Temperatures (°C)	Curing time (min)
120	60
140	30
160	20

The thermal degradation analysis was carried by TG analysis in dynamical mode; the pyrolysis of samples was performed in an inert atmosphere under nitrogen.

2.3. *Computational methodology*

Quantum chemical calculations have been widely used to study reaction mechanisms [17]. They have also been proved to be a very powerful tool for studying properties of molecules [18-19]. It has been found that the physical properties can be related to its electronic and spatial molecular structure [20-21]. In this study, the relationship between quantum chemical parameters and thermal behaviour of some epoxies derivative bisphenol was investigated. The quantum chemical parameters were computed by the semi empircial method for five different hamiltonians, namely, parametric method 6 (PM6) [22] and DFT [23, 24] method of three-parameter compound of Becke (B3LYP) using the 6-31G basis, all calculations were carried out by the Gaussian 03 [25] and Mopac softwares [26].

3. Results and discussion :

3.1.Synthesis of epoxies

The derivatives epoxy compounds (1-4) were prepared from the reaction of epychlorhidryne with the corresponding bisphenol compound (diglycidyl ether of bisphenol A, diglycidyl ether of bisphenol S, diglycidyl ether of dihydroxydiphenyl, and diglycidyl ether of tetra bromo bisphenol A) in the presence of 10% wt sodium hydroxide in a solution of ethanol [27] as shown in Figure 1. The solvent was removed by rotary evaporation; the obtained product is dissolved in trichloromethane, washed with water and dried over sodium bisulfate. Viscous products finally obtained after removal of trichloromethane under vacuum.

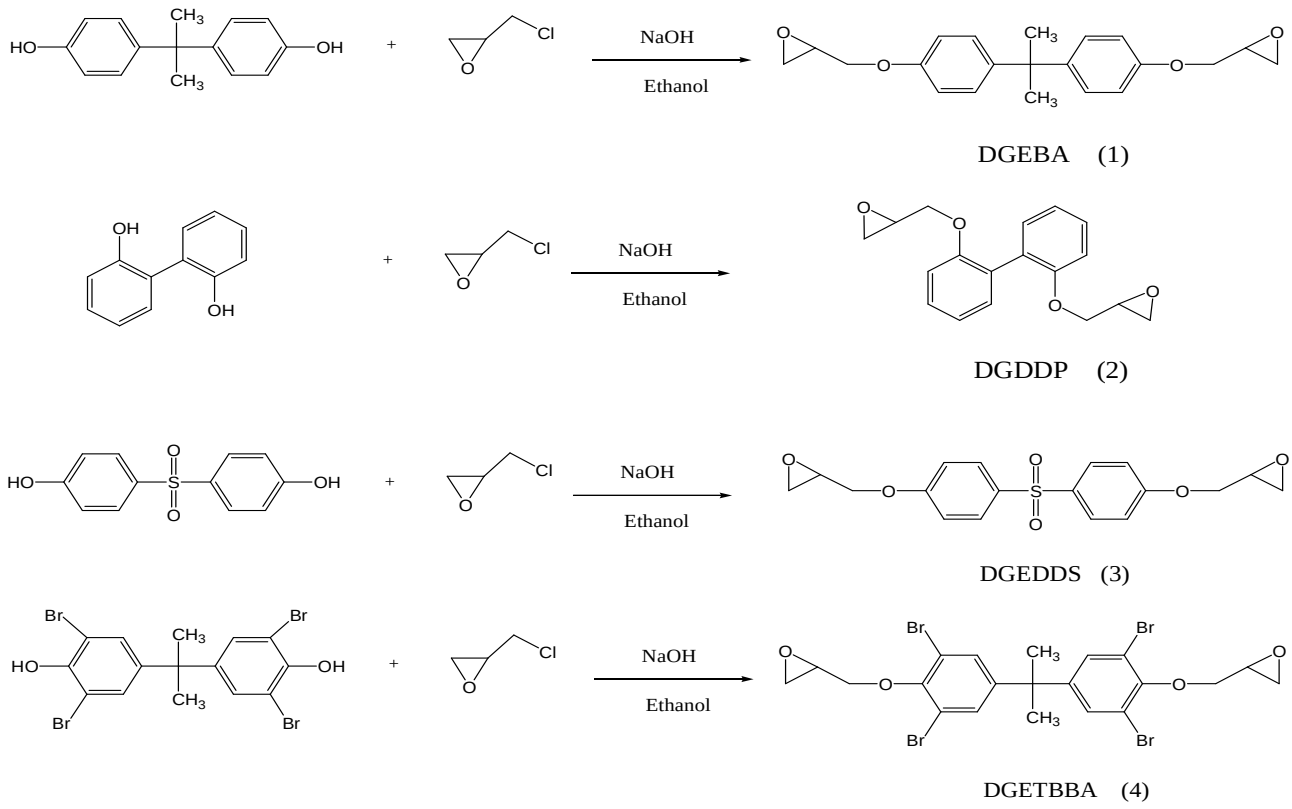


Figure 1. Synthesis scheme of derivatives bisphenol epoxy resins

3.2. Experimental results:

To find the correlation between the thermosta bility in terms of use, and electronic properties we have hardened our epoxy resins by means of a diamine hardener. The studied serial consists of four difunctional epoxy resins: D GEBA, as resin model and the DGEDDP, DGEDDS and DGETBBA.

We have classified the main thermal characteristics of resins extracted from the curves of Figure 2 in Table 3, in accordance with co nventio nal standar ds [28]:

- ♦ The onse temperature T_d composition corresponding to a mass loss of 2%
- ♦ The temperature at 10% mass loss T_{10}
- ♦ The temperature at 50% mass loss T_{50}
- ♦ The fraction of the residue at 500 ° C R_{500}
- ♦ The threshold of rapid decomposition $S_{dr.}$

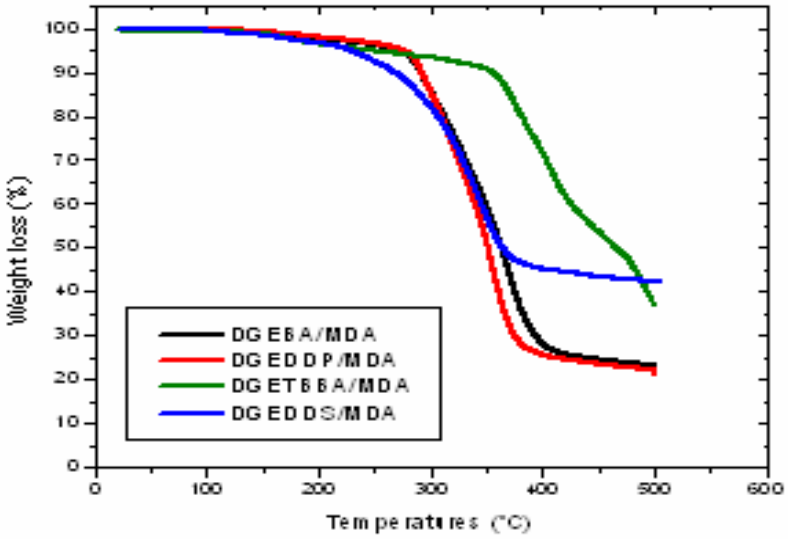


Figure 2. TG analysis curves of derivatives bisphenol pyrolysis

Table 3. TG characteristics of epoxies –diamine pyrolysis

Product	T_d (°C)	T_{10} (°C)	T_{50} (°C)	S_{dr} (°C)	R_{500} (%)
DGEBA/MDA	153	288	361,5	271,6	23,1
DGDDP/MDA	145	281	347,7	268,5	20,1
DGEDDS/MDA	185	361	468,1	358,2	37,6
DGETBBA/MDA	161	304	381,5	238,1	41,1

3.3. Theoretical results

To perform the computational investigation of epoxy resins derivatives from bisphenol we propose to study several descriptors based on electronic steric and thermodynamic effect. The calculation of the various descriptors was done by two different methods, the first semi-empirical (PM6) using the MOPAC software and a second based on electron densities (DFT) using the Gaussian 03 [25] software. The main results of this study are summarized in Table 4.

Table 4. Computational results

Product	Method	E_{Homo} (ev)	E_{Lumo} (ev)	ΔE (ev)	μ (Debye)	Log P	Mol. area ($A°^2$)	Mol. volume ($A°^3$)
DGEBA	PM6	- 9,32	- 0,18	9,14	24,09	3,84	340,16	288,61
	DFT	- 9,68	0 ,05	9,73				
DGDDP	PM6	- 8,72	- 0,35	8,36	4,18	2,62	273,81	242,99
	DFT	- 9,30	0,10	9,41				
DGEDDS	PM6	- 10,31	- 1,31	9 ,00	8,25	1,83	319,41	265,01
	DFT	- 8,89	0,54	9,43				
DGETBBA	PM6	- 9,76	- 0,53	9,23	14,86	7,15	409,13	366,50
	DFT	- 8,51	0,02	8,54				

3.4. Quantitative Structure - Property Relationships (QSPR)

To establish a mathematical model connecting the experimental temperatures characteristic of thermograms to values obtained by quantum study of proposed descriptors (QSPR), we were asked to calculate the correlation between each descriptor and each property. Values of correlation coefficients of R^2 are given in the Table 5.

Table 5. Correlation between degradation temperatures characteristic and QSPR descriptors

	T(°C)	E_{Homo} (ev)	E_{Lumo} (ev)	ΔE (ev)	μ (Debye)	Log P	Mol. Area ($A°^2$)	Mol. Volume ($A°^3$)
PM6	T_d	0,91	0,88	0,19	0,01	0,05	0,03	0,00
	T_{10}	0,82	0,95	0,10	0,06	0,11	0,00	0,00
	T_{50}	0,82	0,94	0,10	0,05	0,12	0,00	0,00
DFT	T_d	0,84	0,72	0,00	0,01	0,05	0,03	0,00
	T_{10}	0,91	0,82	0,00	0,06	0,11	0,00	0,00
	T_{50}	0,98	0,95	0,82	0,02	0,86	0,76	0,88

The values of correlations coefficient show clearly the influence of the electronic properties on the thermal properties of epoxy resins studied. The QSPR mathematical models consist of multiple regressions taking into account only the influential descriptors.

Using the linear model, multiple regressions were performed between some characteristic temperatures of degradation and some quantum chemical parameters/descriptors. The solutions of the above multiple linear regressions (MLR) are given by equations 1 to 3 for PM6, and 4 to 6 for DFT. The corresponding correlation coefficients R^2 were determinant in the choice of parameters. Values of T_d, T_{10} and T_{50} calculated from Equations 1 to 6 are presented in Table 6.

PM6:

$$\begin{cases} T_d = -14{,}2 * E_{HOMO} - 16{,}8 * E_{LUMO} + 15{,}6 & R^2 = 0{,}98 \quad (1) \\ T_{10} = -64{,}1 * E_{HOMO} - 46{,}5 * E_{LUMO} - 347{,}9 & R^2 = 0{,}96 \quad (2) \\ T_{50} = -27{,}3 * E_{HOMO} - 74{,}5 * E_{LUMO} + 84{,}9 & R^2 = 0{,}97 \quad (3) \end{cases}$$

DFT

$$\begin{cases} T_d = 11{,}3 * E_{HOMO} + 56{,}9 * E_{LUMO} + 253{,}5 & R^2 = 0{,}86 \quad (4) \\ T_{10} = -17{,}3 * E_{HOMO} - 51{,}6 * E_{LUMO} + 112{,}1 & R^2 = 0{,}98 \quad (5) \\ T_{50} = 28{,}8 * E_{HOMO} - 193{,}7 * E_{LUMO} + 616{,}5 & R^2 = 0{,}92 \quad (6) \end{cases}$$

Table 6. Theoretical results

	Product	T_d (°C)	T_{10} (°C)	T_{50} (°C)
DFT	DGEBA/MDA	146,9	275,1	348,1
	DGDDP/MDA	154,5	253,4	369,5
	DGEDDS/MDA	183,9	247,5	465,7
	DGETBBA/MDA	158,8	199,1	376,5
PM6	DGEBA/MDA	135,4	268,5	286,5
	DGDDP/MDA	129,8	264,5	281,9
	DGEDDS/MDA	168,6	246,3	379,7
	DGETBBA/MDA	147,7	196,5	306,5

Figure 3 shows the variation of experimental and theoretical temperatures of degradation with theoretical values for DGEBA, DGDDP, DGEDDS and DGETBBA us a function of weight loss. From the plots, it is evident that there is a strong relationship between the theoretical and experimental values, indicating that these models can be used to predict the thermal properties of new precursors that are structurally related to the studied epoxies.

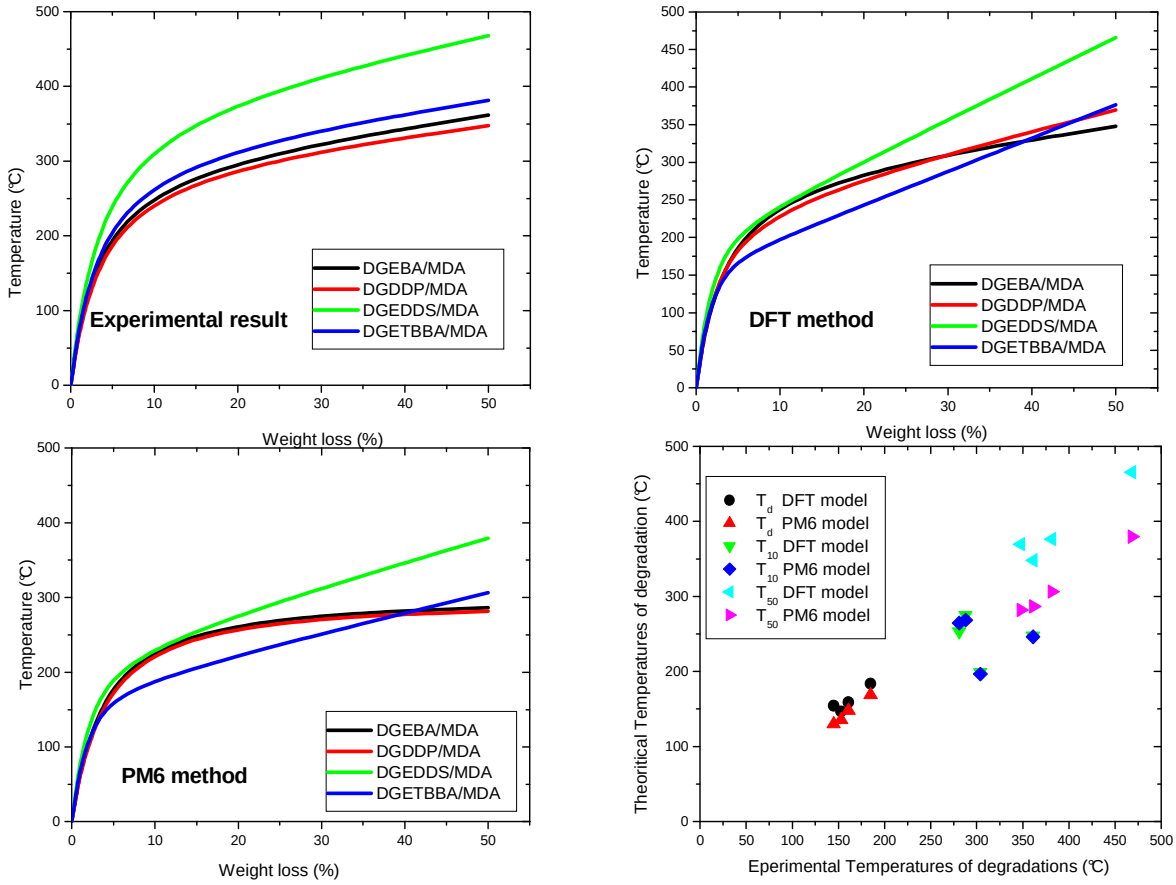
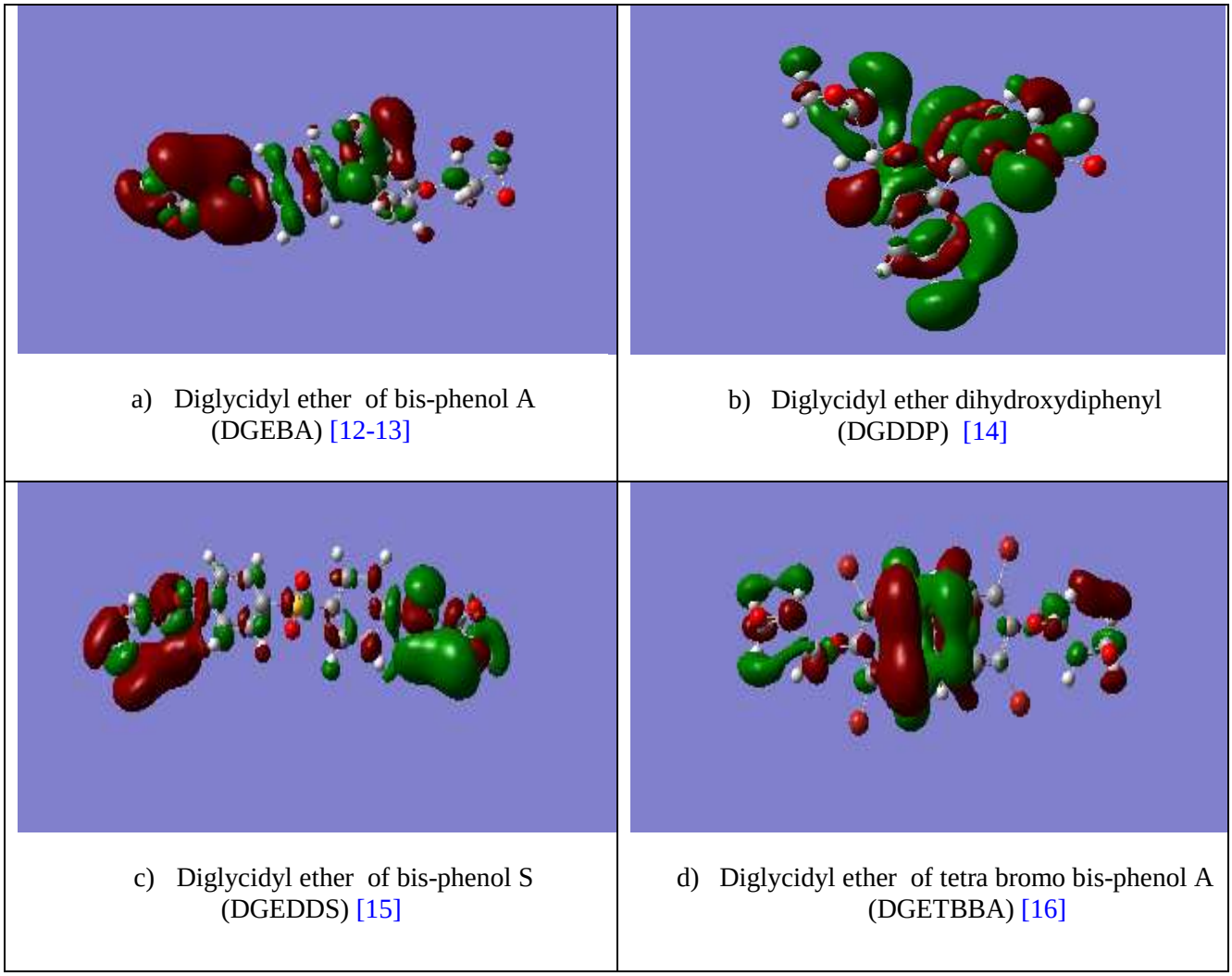


Figure 3. Validation of the Quantitative Structure – Property Relationship model

The HOMO and LUMO orbitals of derivatives bisphenol resins are presented in figure 4. This clearly reveals that electronics effect governs the thermal phenomenone on the studied epoxy-diamine systems.



a) Diglycidyl ether of bis-phenol A (DGEBA) [12-13]

b) Diglycidyl ether dihydroxydiphenyl (DGDDP) [14]

c) Diglycidyl ether of bis-phenol S (DGEDDS) [15]

d) Diglycidyl ether of tetra bromo bis-phenol A (DGETBBA) [16]

Figure 4. Molecular orbitals of the studied epoxies showing the HOMO and LUMO.

The results show that the distribution of electron density influence on the thermal properties of the studied epoxy resins. More electron densities are distributed equivalently over the different atoms constituting the molecule, more thermal properties are of great interest. Thus DGETBBA and DGEDDS resins represent values of thermal resistance better than DGEBA and DGDDP.

Conclusion

In this work we have study the impact of electronics effect on the thermal properties of a variety of epoxy resins derived from bisphenol. This needs to establish a QSPR model to calculate values of some characteristic temperatures of thermal degradation involving a few quantum parameters (descriptors). All theoretical results are consistent with experimental results, the distribution of electron density influence on the thermal properties of studied range of epoxies where the high correlation between electronic and effect phenomenon of thermal degradation.

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