H. Lavrenyuk, B. Mykhalichko

DFT STUDY ON THERMOCHEMISTRY OF THE COMBUSTION OF SELF-EXTINGUISHING EPOXY-AMINE COMPOSITES MODIFIED BY COPPER(II) SULFATE

Lviv State University of Life Safety, Lviv, Ukraine

The thermochemical parameters (the sum energy of all chemical bonds, the formation enthalpy, and the combustion heat) of burning processes of self-extinguishing epoxy-amine composites modified by copper(II) sulfate occurring in the $DGEBA-deta-CuSO_4-O_2$ system (where DGEBA is bisphenol A diglycidyl ether and deta is diethylenetriamine) have been determined by DFT method. The DFT analysis (the restricted Hartree-Fock (RHF) method with a 6-31G* orbital basis set) was performed at the B3LYP level using HyperChem program (version 8.0.6). The calculations confirmed the experimentally established fact that the incorporation of even a little of anhydrous copper(II) sulfate into the framework of epoxy-amine composites ensures a very efficient decrease of their combustibility. The results of the performed thermochemical calculations are in good agreement with the data of thermogravimetric analysis and experimental determination of ignition point and self-ignition point measured for the $DGEBA/deta-CuSO_4$ polymer composite. Thus, anhydrous $CuSO_4$ is a good flame retardant additive that can efficiently suppress the epoxy-amine polymers combustibility.

Keywords: self-extinguishing epoxy-amine composites, fire retardant-hardener of epoxy resins, DFT calculations, thermochemical parameters of burning.

Introduction

An intensive use of polymer composites in industry and daily life is the reason for a significant increase in the number of fires caused by ignition and self-ignition of materials made of polymers [1]. Among the overwhelming majority of the widely used polymeric materials, epoxy resins play a significant role in engineering since they are utilized in many industries, from electronics to public transport [2]. Because of this, the most rigid fire safety demands should be put forward for such types of polymers. Currently, to efficiently reduce the combustibility of epoxy resins, different types of flame retardant agents are used [3], among which *d*-metals complexes deserve special consideration [4−6]. Copper(II) inorganic salts have a huge prospect of application as flame retardant additives to epoxy resins, because they are able to efficiently inhibit the combustion of various organic amines [7], including epoxy-amine composites [8−10]. To adequately understand the processes accompanying the reduction of the combustibility of epoxy polymers under the influence of copper(II) salts, we have undertaken an attempt to model by DFT-calculations the interaction of diethylenetriamine (*deta*) (the curing agent of epoxy resins) with copper(II) sulfate ($CuSO_4$) (the flame retardant additive to epoxy-amine composites) with the subsequent incorporation of the resulting complex into the binder matrix, *DGEBA* (diglycidyl ethers of bisphenol A). The collected information may be useful to carry out a deep analysis of changes in the energy state of reagents and compounds of the $DGEBA-deta-CuSO_4$ system during the formation of self-extinguishing epoxy-amine composites.

The purpose of the work was to calculate chemical bonds energies by means of DFT method and to perform the thermochemical analysis of the combustion reactions for *deta* molecules in free condition and coordinated state as well as for the epoxy-amine composites (*DGEBA/deta* and *DGEBA/deta-CuSO_4*). It was also necessary to compare the calculation results with the experimental determination of the ignition point (t_{ign}) and self-ignition point ($t_{self-ign}$) as well as the thermal behavior of the

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crystalline complex, *deta*, and modified and unmodified epoxy-amine polymers [8]. These calculations are based on the stoichiometric and stereo-chemical parameters of [Cu(*deta*)H$_2$O)]SO$_4$·H$_2$O complex [4] and free molecules of *deta* and the structural characteristics of the epoxy-amine composites modified by CuSO$_4$ [11]. They will allow discussing in detail the probable mechanism of the influence of complexation processes on the combustibility reduction of epoxy-amine composites, which, in turn, can provide the purposeful search for a new generation of the self-extinguishing epoxy-amine composites.

Computational details

DFT calculations of thermochemical processes occurring in the *DGEBA*−*deta*−CuSO$_4$−O$_2$ system were performed by means of the restricted Hartree-Fock (RHF) method with a 6-31G* orbital basis set at the B3LYP level using the HyperChem program version 8.0.6 [12]. The crystal structure parameters of [Cu(*deta*)(H$_2$O)]SO$_4$·H$_2$O chelate complex (sp. gr. P Ī; a=7.3043(2), b=8.5456(3), c=8.7152(3) Å, α=83.789(3)⁰, β=89.433(5)⁰, γ=85.064(5)⁰; Cu−N 1.997(1)÷2.011(1) Å, Cu−OSO$_3$ 2.421(1) Å) [4] and

data on the structuring processes of epoxy-amine composites modified by CuSO$_4$ [11] were used as starting points for the design of cluster fragments. All calculations were carried out under the hypothesis that corresponding chemical particles are in a vacuum. The DFT calculated values of energies for the constructed particles of *deta*, *deta*-CuSO$_4$, *DGEBA/deta* and *DGEBA/deta*-CuSO$_4$ and their structures are given in Table 1 and Figure, respectively.

Thermochemical simulation

The calculated values of the energy of chemical bonds of *deta* and *deta*-CuSO$_4$, *DGEBA/deta* and *DGEBA/deta*-CuSO$_4$ clusters allow establishing such physicochemical characteristics as the standard formation enthalpy of substances (ΔH_f^0) in the gaseous state, the standard enthalpy of their complete combustion (ΔH_c^0), and the calorific value (Q_c^0) [13]; certain conclusions can also be drawn regarding the role of cupric salts as efficient flame retardants when forming the polymer compositions with decreased combustibility.

According to Hess's law, the formation process of gaseous *deta* (C$_4$N$_3$H$_{13}$) under standard conditions
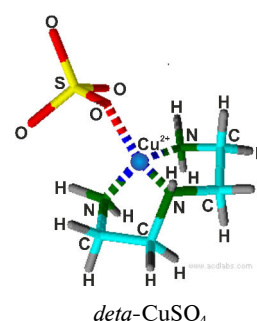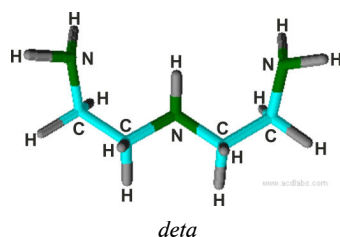
Table 1
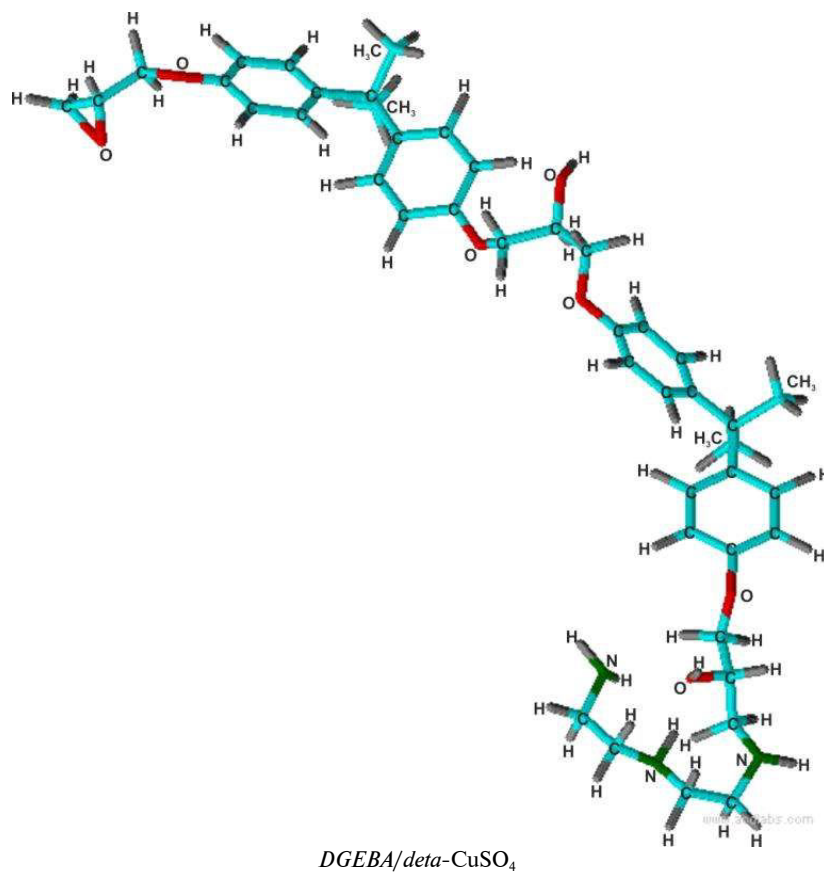
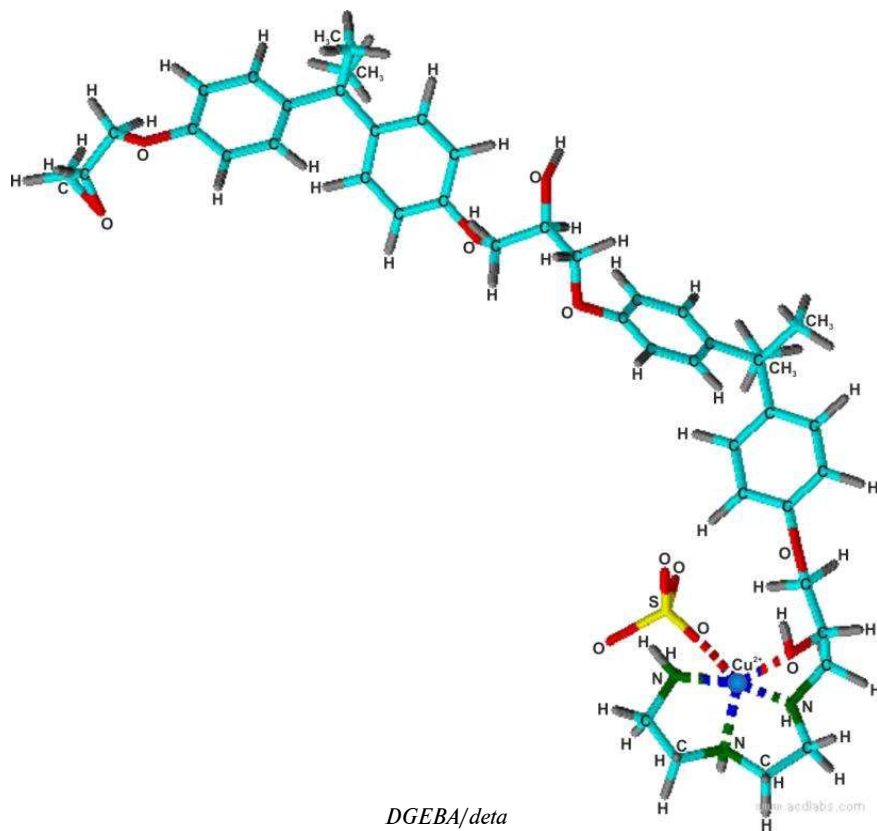**The values of energies calculated by means of DFT method**

Particle	Total energy, kJ·mol⁻¹	Binding energy, kJ·mol⁻¹	Sum energies of all bonds, kJ·mol⁻¹
deta	−180110.01	−24245.80	7105.54
deta-CuSO$_4$	−526631.88	−30850.66	8716.26
DGEBA/deta	−1287979.00	−194408.58	46289.32
DGEBA/deta-CuSO$_4$	−1634501.20	−201014.98	47899.99

Table 2

The reference data on bonds energies and the standard formation enthalpy of substances [14]

Bond	E_b, kJ·mol⁻¹	Process	E_{at}, kJ·mol⁻¹	Substance	ΔH_f^0, kJ·mol⁻¹
E_{H-H}	432.0	C(graphite)→C(g)	715.1	CuO(g)	+320.0
$E_{N≡N}$	941.7	Cu(s)→Cu(g)	337.6	SO$_2$(g)	−296.8
$E_{O=O}$	494.0	S(rhombic)→S(g)	272.8	CO$_2$(g)	−393.5
				H$_2$O(g)	−241.8

deta

deta-CuSO$_4$

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DGEBA/deta

DGEBA/deta-CuSO$_4$

The structures of the particles under consideration

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starting from graphite, molecular hydrogen and molecular nitrogen can be considered as occurring via two following stages:

$$4C(graphite)=4C(g), \ \Delta H_1^0, \quad (1)$$

where $\Delta H_1^0=4E_{at}(graphite)$ (kJ);

$$4C(g)+6.5H_2(g)+1.5N_2(g)=C_4N_3H_{13}(g), \ \Delta H_2^0, \quad (2)$$
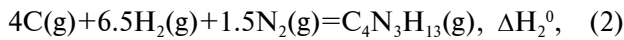
where $\Delta H_2^0=\Delta H_1^0+6.5E_{H-H}+1.5E_{N\equiv N}-\Sigma E_b(C_4N_3H_{13})$ (kJ).

Given the known values of $E_{at}(graphite)$, E_{H-H}, $E_{N\equiv N}$ (Table 2) and calculated values of $\Sigma E_b(C_4N_3H_{13})$ (Table 1), we will have the following: $\Delta H_f^0(C_4N_3H_{13})(g)= \Delta H_2^0$.
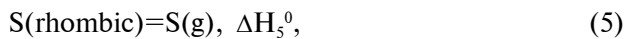
In turn, the formation of *deta*-$CuSO_4$ ($[Cu(C_4N_3H_{13})]SO_4$ complex fragment (Table 1) in the gaseous state proceeds via four stages in which graphite, copper, rhombic sulfur, molecular hydrogen, molecular oxygen and molecular nitrogen participate as follows:
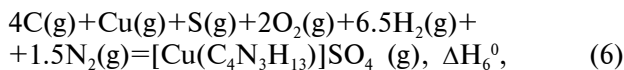
$$4C(graphite)=4C(g), \ \Delta H_3^0, \quad (3)$$

where $\Delta H_3^0=4E_{at}(graphite)$ (kJ);

$$Cu(s)=Cu(g), \ \Delta H_4^0, \quad (4)$$

where $\Delta H_4^0=E_{at}(Cu)$ (kJ);

$$S(rhombic)=S(g), \ \Delta H_5^0, \quad (5)$$

where $\Delta H_5^0=E_{at}(S)$ (kJ);

$$4C(g)+Cu(g)+S(g)+2O_2(g)+6.5H_2(g)+ \\ +1.5N_2(g)=[Cu(C_4N_3H_{13})]SO_4 \ (g), \ \Delta H_6^0, \quad (6)$$
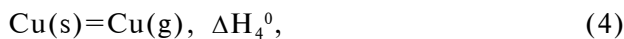
where $\Delta H_6^0=\Delta H_3^0+\Delta H_4^0+\Delta DH_5^0+2E_{O=O}+6.5E_{H-H}+ \\ +1.5E_{N\equiv N}-\Sigma E_b([Cu(C_4N_3H_{13})]SO_4)$ (kJ).

Since $E_{at}(graphite)$, $E_{at}(Cu)$, $E_{at}(S)$, $E_{O=O}$ E_{H-H}, $E_{N\equiv N}$ and $\Sigma E_b([Cu(C_4N_3H_{13})]SO_4)$ are known (Table 1 and 2), then $\Delta H_f^0([Cu(C_4N_3H_{13})]SO_4)(g)=\Delta H_6^0$.

Further, the formation process of epoxy-amine polymer fragment, *DGEBA/deta* ($C_{39}O_7H_{44}/C_4N_3H_{13}$) (Table 1), in the gaseous state occurs via two stages from graphite, molecular hydrogen, molecular oxygen and molecular nitrogen:

$$43C(graphite)=43C(g), \ \Delta H_7^0, \quad (7)$$

where $\Delta H_7^0=43E_{at}(graphite)$ (kJ);

$$43C(g)+3.5O_2(g)+28.5H_2(g)+1.5N_2(g)=$$

$$=C_{39}O_7H_{44}/C_4N_3H_{13} \ (g), \ \Delta H_8^0, \quad (8)$$
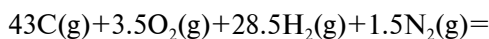
where $\Delta H_8^0=\Delta H_7^0+3.5E_{O=O}+28.5E_{H-H}+1.5E_{N\equiv N}- \\ -\Sigma E_b(C_{39}O_7H_{44}/C_4N_3H_{13})$ (kJ).

Taking into account the known values $E_{at}(graphite)$, $E_{O=O}$ E_{H-H}, $E_{N\equiv N}$ and $\Sigma E_b(C_{39}O_7H_{44}/C_4N_3H_{13})$ given in Tables 1 and 2, we obtain $\Delta H_f^0 (C_{39}O_7H_{44}/C_4N_3H_{13})(g)= =\Delta H_8^0$.
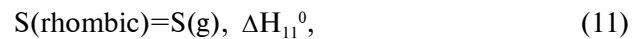
Finally, the formation of *DGEBA/deta*-$CuSO_4$ ($C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4$) gaseous fragment was calculated based on four following step-by-step reactions starting from graphite, copper, rhombic sulfur, molecular hydrogen, molecular oxygen and molecular nitrogen:
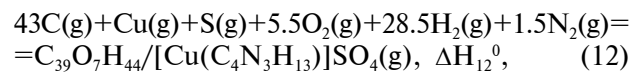
$$43C(graphite)=43C(g), \ \Delta H_9^0, \quad (9)$$

where $\Delta H_9^0=43E_{at}(graphite)$ (kJ);

$$Cu(s)=Cu(g), \ \Delta H_{10}^0, \quad (10)$$

where $\Delta H_{10}^0=E_{at}(Cu)$ (kJ);

$$S(rhombic)=S(g), \ \Delta H_{11}^0, \quad (11)$$

where $\Delta H_{11}^0=E_{at}(S)$ (kJ);

$$43C(g)+Cu(g)+S(g)+5.5O_2(g)+28.5H_2(g)+1.5N_2(g)= \\ =C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4(g), \ \Delta H_{12}^0, \quad (12)$$

where $\Delta H_{12}^0=\Delta H_9^0+\Delta H_{10}^0+\Delta H_{11}^0+5.5E_{O=O}+28.5E_{H-H}+ \\ +1.5E_{N\equiv N}-\Sigma E_b(C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4)$ (kJ).

Considering already known reference data on $E_{at}(graphite)$, $E_{at}(Cu)$, $E_{at}(S)$, $E_{O=O}$, E_{H-H}, $E_{N\equiv N}$ and $\Sigma E_b(C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4)$ (Tables 1 and 2), we will have the following:

$$\Delta H_f^0 (C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4)(g)=\Delta H_{12}^0.$$

Now, there are all facilities for reliable thermochemical calculations of *deta*, *deta*-$CuSO_4$, *DGEBA/deta* and *DGEBA/deta*-$CuSO_4$ complete combustion. The most probable course of these processes is described by the following equations:

$$C_4N_3H_{13}(g)+7.25O_2(g)= \\ =4CO_2(g)+6.5H_2O(g)+1.5N_2(g), \ \Delta H_{13}^0, \quad (13)$$
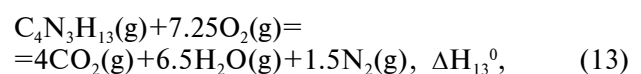
where $\Delta H_{13}^0=4\Delta H_f^0(CO_2(g))+6.5\Delta H_f^0(H_2O(g))- \\ -\Delta H_f^0(C_4N_3H_{13}(g));$

$$[Cu(C_4N_3H_{13})]SO_4(g)+8.75O_2(g)= \\ CuO(g)+SO_2(g)+4CO_2(g)+6.5H_2O(g)+ \\ +1.5N_2(g), \ \Delta H_{14}^0, \quad (14)$$
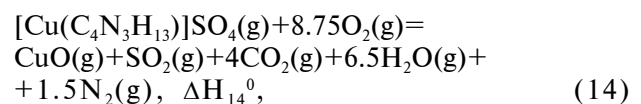
where
$$\Delta H_{14}^0 = \Delta H_f^0(CuO(g)) + \Delta H_f^0(SO_2(g)) + \\ + 4\Delta H_f^0(CO_2(g)) + 6.5\Delta H_f^0(H_2O(g)) - \\ - \Delta H_f^0([Cu(C_4N_3H_{13})]SO_4(g));$$

$$C_{39}O_7H_{44}/C_4N_3H_{13}(g) + 53.75O_2(g) = \\ = 43CO_2(g) + 28.5H_2O(g) + 1.5N_2(g), \ \Delta H_{15}^0, \quad (15)$$

where $\Delta H_{15}^0 = 43\Delta H_f^0(CO_2(g)) + 28.5\Delta H_f^0(H_2O(g)) - \\ - \Delta H_f^0(C_{39}O_7H_{44}/C_4N_3H_{13}(g));$

$$C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4(g) + 53.25O_2(g) = \\ = CuO(g) + SO_2(g) + 43CO_2(g) + 28.5H_2O(g) + \\ + 1.5N_2(g), \ \Delta H_{16}^0, \quad (16)$$

where
$$\Delta H_{16}^0 = \Delta H_f^0(CuO(g)) + \Delta H_f^0(SO_2(g)) + \\ + 43\Delta H_f^0(CO_2(g)) + 28.5\Delta H_f^0(H_2O(g)) - \\ - \Delta H_f^0(C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4(g)).$$

Based on the ΔH_f^0 values of $CuO(g)$, $SO_2(g)$, $CO_2(g)$ and $H_2O(g)$ [14] (see Table 2) and the calculated values of $\Delta H_f^0(C_4N_3H_{13}(g))$, $\Delta H_f^0([Cu(C_4N_3H_{13})]SO_4(g))$, $\Delta H_f^0(C_{39}O_7H_{44}/C_4N_3H_{13}(g))$ and $\Delta H_f^0(C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4(g))$, the ΔH_f and Q_c^0 values for reactions (13)−(16) were calculated. Then we have:

$$\Delta H_c^0(C_4N_3H_{13}(g)) = \Delta H_{13}^0;$$

$$\Delta H_c^0([Cu(C_4N_3H_{13})]SO_4(g)) = \Delta H_{14}^0;$$

$$\Delta H_c^0(C_{39}O_7H_{44}/C_4N_3H_{13}(g)) = \Delta H_{15}^0;$$

$$\Delta H_c^0(C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4(g)) = \Delta H_{16}^0.$$

Results and discussion

The results of thermochemical calculations performed for *deta*, *deta*-CuSO$_4$, *DGEBA/deta* and *DGEBA/deta*-CuSO$_4$ are summarized in Table 3. As one can see, the complexation processes occurring in the *DGEBA*−*deta*−CuSO$_4$ system are accompanied by an energy release due to the appearance of additional coordination bonds of the Cu(II)−N type (the DFT calculated energy of Cu(II) chelating by means of the tridentate molecule of *deta* amounts to 338.5 kJ).

The observed changes in the energy state of *deta* after bonding with Cu(II) and the influence of chelating on the combustibility reducing of both the coordinated *deta* and the modified polymer composite are in good agreement with the experimental results. In particular, thermochemical calculations showed that the calorific value of gaseous chelate complex *deta*-CuSO$_4$ is almost three times less than that of free *deta* molecules in gaseous state.

The experimental determination of t_{ign} and $t_{self-ign}$, which was carried out for crystals of [Cu(*deta*)(H$_2$O)]SO$_4$·H$_2$O chelate complex [4], indicates that the bonded *deta* becomes practically noncombustible. So, neither ignition nor self-ignition of coordinated *deta* was observed, although t_{ign} and $t_{self-ign}$ for free molecules of *deta* are $96(2)^0C$ and $350(2)^0C$, respectively.

The reason is the additional chemical bonds that arise between combustible *deta* and non-combustible CuSO$_4$. To wholly break the Cu(II)←N coordination bonds, it is necessary to spend a considerable part of the heat energy coming from the flame. We believe that the coordination bonds are responsible for combustibility reducing of the metal-coordinated epoxy-amine polymers. Thus, in the system *DGEBA*−*deta*−CuSO$_4$, efficient Cu(II)−*deta* bonding gives rise to the formation of *deta*-CuSO$_4$ chelate complex which acts as the flame retardant under the condition of the epoxy-amine polymerization. The values of ignition point and self-ignition point determined for epoxy resins hardened by *deta* (*DGEBA/deta*) are 320^0C and 545^0C, respectively. But after adding the flame retardant (CuSO$_4$) to the *DGEBA/deta*, those temperature values for *DGEBA/deta*-CuSO$_4$ increase to 356^0C and 569^0C, respectively. Incidentally, it well correlates with the caloricity values calculated for the *DGEBA/deta* and *DGEBA/deta*-CuSO$_4$ composites (see Table 3). In addition, the results of thermographic study [9] show that the final combustion of the pyrolytic residue of the *DGEBA/deta*-CuSO$_4$ epoxy-amine composite, that was cured by *deta*-CuSO$_4$, ends at 660^0C, whereas the same process for *DGEBA/deta* is completed at a significantly higher temperature (900^0C). And one more thing: the maximum of the exothermic effect

Table 3

The results of thermochemical calculation

Substance	ΔH_f^0, kJ·mol^{-1}	ΔH_c^0, kJ·mol^{-1}	Q_c^0, kJ·kg^{-1}
$C_4N_3H_{13}(g)$	−24.6	−3121.1	30301.9
$[Cu(C_4N_3H_{13})]SO_4(g)$	−37.0	−3085.2	11753.1
$C_{39}O_7H_{44}/C_4N_3H_{13}(g)$	−86.5	−23725.3	32634.5
$C_{39}O_7H_{44}/[Cu(C_4N_3H_{13})]SO_4(g)$	−98.8	−23689.8	26722.8

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responsible for the thermal-oxidative destruction of the organic component of *DGEBA/deta*-CuSO$_4$ (345°C) is shifted to a higher temperature region compared with the largest extremum for that of *DGEBA/deta* (300⁰C); this indicates a slightly higher thermal stability of CuSO$_4$-containing epoxy-amine polymers. That is why inorganic salt (CuSO$_4$) should be considered as a very efficient flame retardant additive to epoxy resins which can significantly reduce combustibility of epoxy-amine composite materials.

Conclusions

The results of performed DFT computations and thermochemical analysis of the complexation process showed that the formation of *deta*-CuSO$_4$ chelate complex in the *DGEBA−deta−*CuSO$_4$ system is accompanied by a change in the energy state of chemically bound *deta* in relation to its free molecules. In addition, the binding process of non-combustible inorganic salts with combustible organic substances into the chelate complex provides a decrease in combustibility of both *deta* molecules coordinated with the metallic center and the epoxy-amine composites hardened by *deta*-CuSO$_4$. These issues are crucial to understand the manner in which *d*-metal salts can affect the combustibility of epoxy-amine polymers. That is why copper(II) salts, in particular CuSO$_4$, can be successfully used as flame retardant additives which are able to efficiently reduce the epoxy-amine polymers combustibility.

REFERENCES

1. *Mouritz A.P., Gibson A.G.* Fire properties of polymer composite materials. − Dordrecht: Springer. − 2006. − 401 p.

2. *Ratna D.* Handbook of thermoset resins. − London: Smithers Rapra Publishing. − 2009. − 422 p.

3. *Lu S.-Y., Hamerton I.* Recent developments in the chemistry of halogen-free flame retardant polymers // Progr. Polym. Sci. − 2002. − Vol.27. − P.1661-1712.

4. *A new* copper(II) chelate complex with tridentate ligand: synthesis, crystal and molecular electronic structure of aqua-(diethylenetriamine-N,N',N'')-copper(II) sulfate monohydrate and its fire retardant properties / Lavrenyuk H., Mykhalichko O., Zarychta B., Olijnyk V., Mykhalichko B. // J. Molec. Struct. − 2015. − Vol.1095. − P.34-41.

5. *Synthesis*, structural, and thermal characterization of a new binuclear copper(II) chelate complex bearing an amine-hardener for epoxy resins / Lavrenyuk H., Mykhalichko O., Zarychta B., Olijnyk V., Mykhalichko B. // J. Coord. Chem. − 2016. − Vol.69. − P.2666-2676.

6. *Hamerton I., Howlin B., Jepson P.* Metals and coordination compounds as modifiers for epoxy resins // Coord. Chem. Rev. − 2002. − Vol.224. − P.67-85.

7. *Lavrenyuk H.I., Mykhalichko B.M., Parhomenko V.-P.O.* Quantum-chemical simulation of the behavior of [Cu(H$_2$NC$_2$H$_4$NH$_2$)(H$_2$NC$_2$H$_4$NHC$_2$H$_4$NH$_2$)]SiF$_6$ chelate complex, a fire retardant-hardener of epoxy resins, under the conditions of burning // Voprosy Khimii i Khimicheskoi Tekhnologii. − 2018. − No. 3. − P.31-36.

8. *A new* flame retardant on the basis of diethylenetriamine copper(II) sulfate complex for combustibility suppressing of epoxy-amine composites / Lavrenyuk H., Kochubei V., Mykhalichko O., Mykhalichko B. // Fire Saf. J. − 2016. − Vol.80. − P.30-37.

9. *Metal-coordinated* epoxy polymers with suppressed combustibility. Preparation technology, thermal degradation, and combustibility test of new epoxy-amine polymers containing the curing agent with chelated copper(II) carbonate / Lavrenyuk H., Kochubei V., Mykhalichko O., Mykhalichko B. // Fire Mater. − 2018. − Vol.42. − P.266-277.

10. *Lavrenyuk H., Hamerton I., Mykhalichko B.* Tuning the properties for the self-extinguishing epoxy-amine composites containing copper-coordinated curing agent: flame tests and physical-mechanical measurements // React. Funct. Polym. − 2018. − Vol.129. − P.95-102.

11. *Lavrenyuk O.I., Mykhalichko B.M.* X-ray powder diffraction and infra-red spectroscopic analysis of the structuring process of modified epoxy-amine composites with the participation of flame retardant [Cu(diethylenetriamine)H$_2$O]SO$_4$·H$_2$O // Voprosy Khimii i Khimicheskoi Tekhnologii. − 2016. − No. 5-6. − P.73-77.

12. *HyperChem*: molecular modeling system, Hypercube, Inc., release 8.0.6. Florida, USA, − 2009.

13. *Hurley M.J.* SFPE Handbook of fire protection engineering. − Springer. − 2016. − 3493 p.

14. *Thermodynamic* properties of individual substances / Gurvich L.V., Veyts I.V., Medvedev V.A., Khachkuruzov G.A. − Moscow: Nauka. − 1978. − 3664 p.

DFT ДОСЛІДЖЕННЯ ТЕРМОХІМІЇ ГОРІННЯ САМОЗГАСАЮЧИХ ЕПОКСІАМІННИХ КОМПОЗИЦІЙ, МОДИФІКОВАНИХ КУПРУМ(II) СУЛЬФАТОМ

О.І. Лавренюк, Б.М. Михалічко

В роботі DFT методом були визначені термохімічні параметри (сумарна енергія всіх хімічних зв'язків, ентальпії утворення, теплоти згоряння) процесу горіння самозгасаючих епоксіамінних композицій модифікованих купрум(II) сульфатом, що відбувається у системі DGEBA−deta−CuSO$_4$−O$_2$ (DGEBA − диглідиловий етер бісфенолу А; deta − діетилентриамін). DFT аналіз здійснювали з використанням обмеженого методу Гартрі-Фока з базисним набором орбіталей 6-31G (B3LYP рівень), за допомогою програми HyperChem professional version 8.0.6. Обчислення підтвердили експериментально встановлений факт, що інкорпорування навіть невеликої кількості безводної солі купрум(II) сульфату в епоксіамінну композицію забезпечує доволі ефективне зниження їх горючості. Результати термохімічних обчислень добре узгоджуються з даними термогравіметричного аналізу та експериментально виміряними темпе-*

ратурами займання і самозаймання полімерної композиції DGEBA/deta-CuSO₄. Отже, безводний CuSO₄ виявився чудовою антипіреновою добавкою, здатною ефективно пригнічувати горючі властивості епоксіамінових полімерів.

Ключові слова: самогасаючі епоксіамінні композиції, антипірен-затвердник епоксидних смол, DFT обчислення, термохімічні параметри горіння.

DFT STUDY ON THERMOCHEMISTRY OF THE COMBUSTION OF SELF-EXTINGUISHING EPOXY-AMINE COMPOSITES MODIFIED BY COPPER(II) SULFATE

H. Lavrenyuk, B. Mykhalichko
Lviv State University of Life Safety, Lviv, Ukraine

The thermochemical parameters (the sum energy of all chemical bonds, the formation enthalpy, and the combustion heat) of burning processes of self-extinguishing epoxy-amine composites modified by copper(II) sulfate occurring in the DGEBA−deta−CuSO₄−O₂ system (where DGEBA is bisphenol A diglycidyl ether and deta is diethylenetriamine) have been determined by DFT method. The DFT analysis (the restricted Hartree-Fock (RHF) method with a 6-31G* orbital basis set) was performed at the B3LYP level using HyperChem program (version 8.0.6). The calculations confirmed the experimentally established fact that the incorporation of even a little of anhydrous copper(II) sulfate into the framework of epoxy-amine composites ensures a very efficient decrease of their combustibility. The results of the performed thermochemical calculations are in good agreement with the data of thermogravimetric analysis and experimental determination of ignition point and self-ignition point measured for the DGEBA/deta-CuSO₄ polymer composite. Thus, anhydrous CuSO₄ is a good flame retardant additive that can efficiently suppress the epoxy-amine polymers combustibility.

Keywords: self-extinguishing epoxy-amine composites; fire retardant-hardener of epoxy resins; DFT calculations; thermochemical parameters of burning.

REFERENCES

1. Mouritz A.P., Gibson A.G., *Fire properties of polymer composite materials.* Springer, Dordrecht, 2006. 401 p.

2. Ratna D., *Handbook of thermoset resins.* Smithers Rapra Publishing, London, 2009. 422 p.

3. Lu S.-Y., Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. *Progress in Polymer Science*, 2002, vol. 27, pp. 1661-1712.

4. Lavrenyuk H., Mykhalichko O., Zarychta B., Olijnyk V., Mykhalichko B. A new copper(II) chelate complex with tridentate ligand: synthesis, crystal and molecular electronic structure of aqua-(diethylenetriamine-N,N',N'')-copper(II) sulfate monohydrate and its fire retardant properties. *Journal of Molecular Structure*, 2015, vol. 1095, pp. 34-41.

5. Lavrenyuk H., Mykhalichko O., Zarychta B., Olijnyk V., Mykhalichko B. Synthesis, structural, and thermal characterization of a new binuclear copper(II) chelate complex bearing an amine-hardener for epoxy resins. *Journal of Coordination Chemistry*, 2016, vol. 69, pp. 2666-2676.

6. Hamerton I., Howlin B.J., Jepson P. Metals and coordination compounds as modifiers for epoxy resins. *Coordination Chemistry Reviews*, 2002, vol. 224, pp. 67-85.

7. Lavrenyuk H.I., Mykhalichko B.M., Parhomenko V.-P.O. Kvantovo-khimichne model'yuvann'ya povedinky khelatnogo kompleksu [Cu(H₂NC₂H₄NH₂)(H₂NC₂H₄NHC₂H₄NH₂)]SiF₆ − antypirenu-zatverdnyka epoksydnykh smol v umovakh gorinn'ya [Quantum-chemical simulation of the behavior of [Cu(H₂NC₂H₄NH₂)(H₂NC₂H₄NHC₂H₄NH₂)]SiF₆ chelate complex, a fire retardant-hardener of epoxy resins, under the conditions of burning]. *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2018, no. 3, pp. 31-36. (*in Ukrainian*).

8. Lavrenyuk H., Kochubei V., Mykhalichko O., Mykhalichko B. A new flame retardant on the basis of diethylenetriamine copper(II) sulfate complex for combustibility suppressing of epoxy-amine composites. *Fire Safety Journal*, 2016, vol. 80, pp. 30-37.

9. Lavrenyuk H., Kochubei V., Mykhalichko O., Mykhalichko B. Metal-coordinated epoxy polymers with suppressed combustibility. Preparation technology, thermal degradation, and combustibility test of new epoxy-amine polymers containing the curing agent with chelated copper(II) carbonate. *Fire and Materials*, 2018, vol. 42, pp. 266-277.

10. Lavrenyuk H., Hamerton I., Mykhalichko B. Tuning the properties for the self-extinguishing epoxy-amine composites containing copper-coordinated curing agent: flame tests and physical-mechanical measurements. *Reactive and Functional Polymers*, 2018, vol. 129, pp. 95-102.

11. Lavrenyuk O.I., Mykhalichko B.M. Rentgenofazovyi ta ICh-spektroskopichnyi analiz protsesu strukturuvannia modyfikovanykh epoksyaminnykh kompozytsii za uchastiu antypirenu [Cu(*diethylenetriamine*)H₂O]SO₄·H₂O [X-ray powder diffraction and infra-red spectroscopic analysis of structuring process of modified epoxy-amine composites with flame retardant participation of [Cu(*diethylenetriamine*)H₂O]SO₄·H₂O]. *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2016, no. 5-6, pp. 73-77. (*in Ukrainian*).

12. *HyperChem: molecular modeling system, Hypercube, Inc., release 8.0.6.* Florida, USA, 2009.

13. Hurley M.J., *SFPE Handbook of fire protection engineering.* Springer, 2016. 3493 p.

14. Gurvich L.V., Veyts I.V., Medvedev V.A., Khachkuruzov G.A. *Termodinamicheskie svoistva individual'nykh veshchestv* [Thermodynamic properties of individual substances]. Nauka, Moscow, 1978. 3664 p. (*in Russian*).