ЦЕНТР НАУКОВИХ ПУБЛІКАЦІЙ

ЗБІРНИК НАУКОВИХ ПРАЦЬ

"Велес"

ЗА МАТЕРІАЛАМИ V МІЖНАРОДНОЇ КОНФЕРЕНЦІЇ «ВЕСНЯНІ НАУКОВІ ЧИТАННЯ»

1 частина

м.Київ

30 квітня 2020р.

ЦЕНТР НАУКОВИХ ПУБЛІКАЦІЙ
ЗБІРНИК НАУКОВИХ ПУБЛІКАЦІЙ
«ВЕЛЕС»

V МІЖНАРОДНА КОНФЕРЕНЦІЯ «ВЕСНЯНІ НАУКОВІ ЧИТАННЯ»

(м. Київ | 30 квітня 2020р.)

1 частина

м. Київ – 2020

ТЕХНІЧНІ НАУКИ

Cu(II)–(*ПОЛІАМІН*) ХЕЛАТУВАННЯ ЯК ЕФЕКТИВНИЙ СПОСІБ ЗНИЖЕННЯ ГОРЮЧОСТІ ЕПОКСІ-АМІННИХ КОМПОЗИЦІЙ МОДИФІКОВАНИХ НЕОРГАНІЧНИМИ СОЛЯМИ КУПРУМУ(II)

Лавренюк О.,
Михалічко Б.
Кафедра фізики та хімії горіння,
Львівський державний університет безпеки життєдіяльності

Cu(II)–(*POLYAMINE*) CHELATION AS AN EFFICIENT WAY OF REDUCING COMBUSTIBILITY OF EPOXY-AMINE COMPOSITES MODIFIED BY COPPER(II) INORGANIC SALTS

Lavrenyuk H.,
Mykhalichko B.
Department of Physics and Chemistry of Combustion,
L'viv State University of Life Safety

Анотація

Було розроблено технологію виготовлення купрум(II)-координованих епоксі-амінних композитів зі зниженою горючістю, що дозволило сформувати основу нового типу полімеру з підвищеними фізико-хімічними та механічними властивостями. Був запропонований простий спосіб, виготовлення антипіренів-затверджувачів та включення їх в матрицю епоксидної смоли. Останні є продуктами взаємодії поліетиленуполіаміну (*pepa*), що містить етилендіамін (*eda*) та діетилентриамін (*deta*) з неорганічними солями купруму(II) (зокрема $CuSO_4$, $(CuOH)_2CO_3$ та $CuSiF_6$). Горючість отриманих композицій *DGEBA/pepa*, *DGEBA/deta*-$CuSO_4$, *DGEBA/deta*-$CuCO_3$ і *DGEBA/pepa*-$CuSiF_6$ (*DGEBA* – це дигліцидиловий ефір бісфенолу А) досліджували методом керамічної труби. Займистість отриманих зразків оцінювалась за допомогою тестів UL94. Описано вплив неорганічних солей купруму(II) на пожежонебезпечні показники модифікованих епоксі-амінних композитів.

Abstract

Making technology of copper(II)-coordinated epoxy-amine composites with reduced combustibility has been developed that allowed to form the basis of a new type of polymer with enhanced physicochemical and mechanical properties. A proposed simple method allows preparing and incorporating into the epoxy resin matrix the fire retardant-hardeners. These are considered to be the interaction products of the polyethylenepolyamine (pepa) containing ethylenediamine (eda) and diethylenetriamine (deta) with inorganic copper(II) salts (specifically,

$CuSO_4$, $(CuOH)_2CO_3$ and $CuSiF_6$). The combustibility of the DGEBA/pepa, DGEBA/deta-$CuSO_4$, DGEBA/deta-$CuCO_3$ and DGEBA/pepa-$CuSiF_6$ composites obtained (DGEBA is bisphenol A diglycidyl ether) were investigated using ceramic tube method. The flammability of the polymer samples has been evaluated using the UL94 tests. The effects of copper(II) inorganic salts on the fire-hazardous indices of the modified epoxy-amine composites were described.

Ключові слова: купрум(II)-координовані епоксі-амінні композити, антипірен-затвердник, самозгасаючий характер горіння, понижена горючість.

Keywords: copper(II)-coordinated epoxy-amine composites, fire retardant-hardener, self-extinguishing character of burning, reduced combustibility

Polyethylenepolyamine (*pepa*) containing ethylenediamine (*eda*) and diethylenetriamine (*deta*) is known to widely be used as a hardener at the polymerization of epoxy resins. On the other hand, *pepa* (*eda* + *deta*) is a potentially tridentate ligand which can chelate atoms of transition metals, in particular, Cu(II). This behavior feature of *pepa* has allowed us to solve a problem elaborating a new type of polymer materials with reduced combustibility using, at that, the following approach. The flame retardant agent *viz.* $CuSO_4$ [1], $(CuOH)_2CO_3$ [2] and $CuSiF_6$ [3] was added to the epoxy-amine polymer. In this process the chemical interaction between Cu(II) atoms of said inorganic salts and *pepa* (*eda* + *deta*) molecules predetermines lowering combustibility of resulting epoxy-amine composites [4–6]. This can be explained to form virtually non-combustible chelate complexes – $[Cu(deta)H_2O]SO_4 \cdot H_2O$, $[\{Cu(deta)(H_2O)(CO_3)\}_2] \cdot 6H_2O$, and $[Cu(deta)(eda)]SiF_6$ [7–9].

The *ab initio* quantum-chemical calculations of charge density distribution on atoms and the bonding energy carried out for *pepa* in coordinated and uncoordinated state reveal that Cu(II)–(*pepa*) chelation is accompanied by some changes in the electronic parameters for coordinated *pepa* in comparison with uncoordinated *pepa* [10–14]. So, the electron density of all N atoms within coordination chelate-core efficiently shifts to the central atom of Cu(II) due to chelation effect. At that, a lone-electron pair of each N atom of amino-groups more efficiently overlap with the four of six unoccupied hybrid $sp^3d_{x^2-y^2}d_{z^2}$ AOs of the central Cu(II) atom. At the same time, the total energy of three Cu–N bonds which belong to the square-pyramidal coordination core is 237.39 kJ·mol^{-1}. The initial octahedral surrounding of the Cu(II) atom is strongly distorted and acquires the shape of the extended square pyramid. As a result, the square-pyramidal field of the ligands simultaneously with chelate effect eliminates the degeneracy of the 3*d*-AOs of Cu^{2+} ion. Thus, the geometrical parameters of the square-pyramidal polyhedron of Cu(II) atom are in good agreement with the Jahn-Teller principle and are the result of the mutual strengthening of two individual effects (of square-pyramidal crystal field effect and chelate effect). This synergism causes the splitting of the

degenerate 3*d*-AOs of the Cu^{2+} ion onto four sets of the energy levels (d_{xy} < twice degenerate d_{xz} and d_{yz} < d_{z^2} < $d_{x^2-y^2}$).

In summary, the strong coordination bonds that arise between Cu(II) atoms of incombustible inorganic salts and N atoms of the amine hardener as well as formation of stable chelate complexes in solid state are responsible for the combustibility suppression of the epoxy-amine composites modified by copper(II) inorganic salts.

References

1. 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 // J. Mol. Struct. – 2015. – Vol. 1095. – P. 34–41. DOI: 10.1016/j.molstruc.2015.03.039
2. 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 // J. Coord. Chem. – 2016. – Vol. 69(18). – P. 2666–2676. DOI: 10.1080/00958972.2016.1212340
3. Lavrenyuk H., Mykhalichko B., Dziuk B., Olijnyk V., Mykhalichko O. A new copper(II) chelate complex with polyamines as fire retardant and epoxy hardener: Synthesis, crystal and electronic structure, and thermal behavior of (ethylenediamine-N,N′)-(diethylenetriamine-N,N′,N″)-copper(II) hexafluorido-silicate // Arabian J. Chem. – 2020. – Vol. 13(1). – P. 3060–3069. DOI: 10.1016/j.arabjc.2018.08.014
4. Lavrenyuk H., Mykhalichko B. Epoxy composite with lowered combustibility. Patent No 109187 UA, 2015 (in Ukraine).
5. Lavrenyuk H., Mykhalichko B., Pastuhov P. Self-extinguishing epoxy composition with reduced smoke formation. Epoxy composite with lowered combustibility. Patent No 114557 UA, 2017 (in Ukraine).
6. Lavrenyuk H., Mykhalichko B., Parhomenko V.-P. Flame retardant-hardener for epoxy resins and self-extinguishing epoxy-amine composition. Patent No 118709 UA, 2019 (in Ukraine).
7. 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 Saf. J. – 2016. – Vol. 80. – P. 30–37. DOI: 10.1016/j.firesaf.2016.01.001
8. 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. – P. 266–277. DOI:10.1002/fam.2489

9. Lavrenyuk H., Parhomenko V.-P., Mykhalichko B. The effect of preparation technology and the complexing on the service properties of self-extinguishing copper(II) coordinated epoxy-amine composites for pouring polymer floors // Int. J. Tech. – 2019. – Vol. 10(2). – P. 290–299. DOI: 10.14716/ijtech.v10i2.66

10. Lavrenyuk H, Mykhalichko B. DFT study on thermochemistry of the combustion of self-extinguishing epoxy-amine composites modified by copper(II) sulfate // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2018. – Vol. 6. – P. 42–48. DOI: 10.32434/0321-4095-2018-121-6-42-48

11. Lavrenyuk H.I., Mykhalichko B.M., Parhomenko V.-P.O. Quantum-chemical simulation of the behavior of $[Cu(H_2NC_2H_4NH_2)(H_2NC_2H_4NHC_2H_4NH_2)]SiF_6$ chelate complex, a fire retardant-hardener of epoxy resins, under the conditions of burning // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2018. – Vol. 3. – P. 31–36. (in Ukraine)

12. Lavrenyuk H., Mykhalichko B., Pastuhov P. Applying of copper(II) carbonate as a decrease mode of a fire hazard of epoxy-amine // ScienceRise. – 2016. – Vol. 22(5/2). – P. 25–29. DOI: 10.15587/2313-8416.2016.69601

13. 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 Funct. Polym. – 2018. – Vol. 129. – P. 95–102. DOI: 10.1016/j.reactfunctpolym.2017.10.013

14. Lavrenyuk H., Mykhalichko B. Principles of controlled effects of performance properties of self-extinguishing epoxy-amine composites modified by copper(II) carbonate // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2019. – Vol. 5. – P. 58–64. DOI: 10.32434/0321-4095-2019-126-5-58-64