



ELSEVIER

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com



Tuning the properties for the self-extinguishing epoxy-amine composites containing copper-coordinated curing agent: Flame tests and physical–mechanical measurements

Helen Lavrenyuk^{a,*}, Ian Hamerton^b, Borys Mykhalichko^a

^a Department of Processes of Burning and General Chemistry, L'viv State University of Life Safety, Ukraine

^b Faculty of Engineering, University of Bristol, United Kingdom

ARTICLE INFO

Keywords:

Self-extinguishing epoxy-amine composites
Fire retardant-hardener
Combustibility
Flame propagation
Physical-mechanical properties

ABSTRACT

An uncomplicated mode of preparing the fire retardant-hardener labeled $DETA-CuSO_4$ ($DETA$ – diethylenetriamine) with its subsequent incorporation into framework of epoxy resin to obtain self-extinguishing epoxy-amine composites possessing the balanced physical-mechanical properties and fire retardancy has been elaborated. The influence of the $DETA-CuSO_4$ complex formation onto the epoxy resin curing processes has been studied by means of data of the rheological, IR spectroscopic and quantum-chemical analyses of the $DGEBA-DETA-CuSO_4$ system ($DGEBA$ – bisphenol A diglycidyl ether). The flammability of the epoxy-amine composites with different content of the fire retardant (0, 5, 16, and 80 mass parts) has been studied. The rate of burning of the epoxy-amine composites ($DGEBA/DETA-CuSO_4$) containing 16 and 80 mass parts of the fire retardant is intensely depressed (their samples do not propagate flame generally), while r_{burn} values for samples of $DGEBA/DETA$ and $DGEBA/DETA-CuSO_4(5)$ are equal 25.2 and 24.0 $mm\cdot min^{-1}$, respectively. The flammability was evaluated by means of UL94 test method and according to all-Union State Standard 12.1.044-89. The smoke-formation is maximal suppressed by fire retardant ($CuSO_4$) in the largest quantities. Physical-mechanical properties were studied by means of the measurements of surface hardness, tensile strength, water absorption, and chemical resistance.

1. Introduction

The wide use of polymer composites in an industry and daily life results in a violent increase of number of fires initiated by ignition of the materials made of polymers [1]. Among a lot of the prevalent polymer materials, the polymers on the base of epoxy resins play a significant role in the technics, as these find wide application in many fields, that is, from electronics to public transport *etc.* [2]. That is why the most rigid conditions concerning fire safety should be put forward to such composites. Unfortunately, epoxy polymers by the nature are combustible substances and at burning they are able to release a great deal of a smoke and toxic products of combustion [3].

Currently, the varied types of the fire retardants are widely used for the effective combustibility lowering of epoxy resins [4]. In this regard, the best fire retardants are the reactive fire retardants. There are several different kinds of reactive fire retardant materials obtained by incorporation of Si, N, B, and P atoms in the monomers [5–9]. Such

monomers can easily undergo various reactions at polymers synthesis. In the latter time, the fire retardants containing *d*-metal complexes (mainly, on the basis of Mn, Co, Ni, Cu, Zn *etc.* salts of organic acids) [10–12] find a wide application. These complexes play a part of both modifiers and curing agents of epoxy resins at the composite materials obtaining. But, the major merits of the using the metal complexes consist in avoidance of the complicated monomer synthesis and the wide variety of choice of the metals and the ligands. Nevertheless, despite ability of these metal complexes to decrease combustibility of the polymer composites, their use results frequently in change of physical-mechanical properties of polymer materials. Therefore, at choosing a fire retardant apart from accessibility, cheapness and desire to attain to the substantial decrease of combustibility for the polymer composites it is necessary to take into consideration fire retardant's influence on the operating characteristics of the materials and to monitor the process-dependent parameters of obtaining and processing the products [13].

* Corresponding author.

Email address: lavrenyuk@ldubgd.edu.ua (H.)

In our previous researches [14–16] the $[\text{Cu}(\text{DETA})(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}$ chelate complex made out of the copper vitriol and diethylenetriamine (DETA) has been structurally characterized. The effectiveness of bonding a combustible DETA (curing agent) with an incombustible inorganic salt – CuSO_4 (fire retardant) in many respects predetermines behavior of the obtained diethylenetriamine copper(II) chelate complex as a fire retardant-hardener of epoxy resins. Exceptional ability of the inorganic cupric salts to complexation has let us foreknow the potentiality of utilizing the dehydrated chelate complex – DETA- CuSO_4 to make the epoxy-amine composite materials with suppressed combustibility. Eventually, we have attained the aim and obtained the polymeric samples of the epoxy-amine composites modified by CuSO_4 as well as investigated their thermal behavior and determined combustibility parameters [16]. The thermic stability and anti-flammability of the elaborated DGEBA/DETA- CuSO_4 composites (DGEBA – bisphenol A diglycidyl ether) were appreciably improved by comparison with unmodified DGEBA/DETA polymer; the maximal combustion temperature of gaseous products for DGEBA/DETA compared to DGEBA/DETA- CuSO_4 has gone down from 867 °C to 640 °C and weight loss has also decreased from 89.0 wt% to 78.6 wt%.

Taking into account the aforesaid, we undertook an attempt to elaborate an uncomplicated mode of the DETA- CuSO_4 fire retardant-hardener preparing and to incorporate this compound into framework of epoxy resin for obtaining several samples of the epoxy-amine composites having the different molar ratio of DGEBA: DETA: CuSO_4 (see Table 1). Thus, begun researches have allowed making the samples of the self-extinguishing epoxy-amine polymers belonging to a new generation of the composite materials. The synthesis and structural characterization (XRPD and FTIR), rheological and quantum-chemical analyses as well as an influence studying of the fire retardant-hardener onto change of the fire hazard indices (flame propagation rate and smoke formation factor) and the tuning the requisite physical-mechanical properties of the epoxy-amine composite materials are reported in the present article.

2. Experimental

2.1. Materials

For synthesis of the fire retardant-hardener (DETA- CuSO_4) and the self-extinguishing epoxy-amine composites (DGEBA/DETA- CuSO_4), the following chemicals were used: the fire retardant – copper(II) sulfate pentahydrate ($\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$) (light blue crystals, $M_r = 249.5$, $\Delta t_{\text{dehydration}} = 90\text{--}280$ °C [17,18]); the curing agent of epoxy resins – diethylenetriamine, $\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$ (DETA) (colorless liquid, $M_r = 103.17$, $d^{20} = 0.955$ g·cm⁻³, $n_D = 1.484$, $t_{\text{boiling}} = 204.1$ °C, $t_{\text{ignition}} = 97$ °C, $t_{\text{self-ignition}} = 350$ °C [19], IR (KBr cuvette, cm⁻¹): 3372, 3254 and 3210 (ν_{NH}); 2934, 2908 and 2790 (ν_{CH}); 1600 (δ_{NH}); 1460 (δ_{CH}); the binder – bisphenol A diglycidyl ether (DGEBA) (colorless resin, ED-20 grade with almost 22% epoxy groups content, value of viscosity from 12 to 18 Pa · s (at 25 °C), $M_r = 390\text{--}430$ (\bar{M}_r

= 410)). All reagents have been purchased through commercial sources and used as-received without further purification.

2.2. Characterization

The X-ray powder diffraction (XRPD) pattern (Fig. S1, Supp. Info) of the polycrystalline sample of the $[\text{Cu}(\text{DETA})(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}$ chelate complex – the precursor of the DETA- CuSO_4 fire retardant-hardener was carried out at room temperature on the HZG-4A diffractometer ($\text{Cu } K_\alpha$ -radiation, Bragg-Brentano geometry, angular range $8 \leq 2\theta \leq 50^\circ$ with a step size of 0.02° and exposition time per point 20 s). The profile and structural parameters were refined by the Rietveld method using the package of program FullProf Suite [20]. Indexing of XRPD pattern was fulfilled automatically by means of the method described in [21], using DICVOL91 software package [22]. The structure model was taken from single crystal data [14].

IR absorption spectra (Fig.1) of DETA, $[\text{Cu}(\text{DETA})(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}$, DETA- CuSO_4 , DGEBA/DETA- CuSO_4 and DGEBA/DETA were recorded in the spectral range of 4000–500 cm⁻¹ with a resolution of 2 cm⁻¹ on a Perkin Elmer SpectrumTwo FTIR spectrometer. The IR measurements were performed with a solid sample pressed in spectroscopically pure KBr pellet, or a liquid sample using a KBr cuvette.

The flammability of DGEBA/DETA- CuSO_4 and DGEBA/DETA was evaluated by means of UL94 test method. The flame propagation rate was determined according to IEC 60695-11-10 [23]. Each test piece was mounted horizontally to its long axis and at an angle of 45° to its short axis. The molded samples by 125 mm length, 10 mm width, and 5 mm thickness were exposed to a 20 mm high blue Bunsen burner flame at an angle of 45°. The polymer samples were tested after conditioning for 48 h, at 25 °C and of 50% relative humidity. At a testing result, the time ($\Delta \tau_{\text{burn}}$, s) of the travel of the flame front between two gauge marks was measured and the burning rate (r_{burn} , mm·min⁻¹) of the polymer samples was calculated.

The smoke-formation factor was determined according to all-Union State Standard 12.1.044-89, (the item 4.18). The optical density of the smoke forming at burning or smoldering of the polymers of a certain weight has been measured on the device for the smoke-formation factor determination. The samples assaying were fulfilled at two test mode. At a smoldering mode the sample was exposed solely to a thermal current by density of 35 ± 3.5 kW·m⁻² whereas at a burning mode it was exposed to both a thermal current and a gas burner flame jointly. Smoke-formation factor (D_m , m²·kg⁻¹) was calculated by means of ratio:

$$D_m = \frac{V}{L \cdot m} \ln \frac{T_0}{T_{\min}}$$

where V is a volume of the measuring chamber, 0.343(4) m³; L is a path length of a light beam in a smoke medium, 0.7000(5) m; m is a mass of the sample, kg; T_0 and T_{\min} are values of initial and final transmittance, respectively, %.

Table 1
Stoichiometry of the epoxy-amine composites.

Composite	DGEBA:DETA:CuSO ₄ (molar ratio)	Ingredients (mass p.)		
		DGEBA	DETA	CuSO ₄
DGEBA/DETA	5:2:0	100	10	–
DGEBA/DETA-CuSO ₄ (5)	5:2:0.625	100	10	5
DGEBA/DETA-CuSO ₄ (16)	5:2:2	100	10	16
DGEBA/DETA-CuSO ₄ (80)	5:2:10	100	10	80

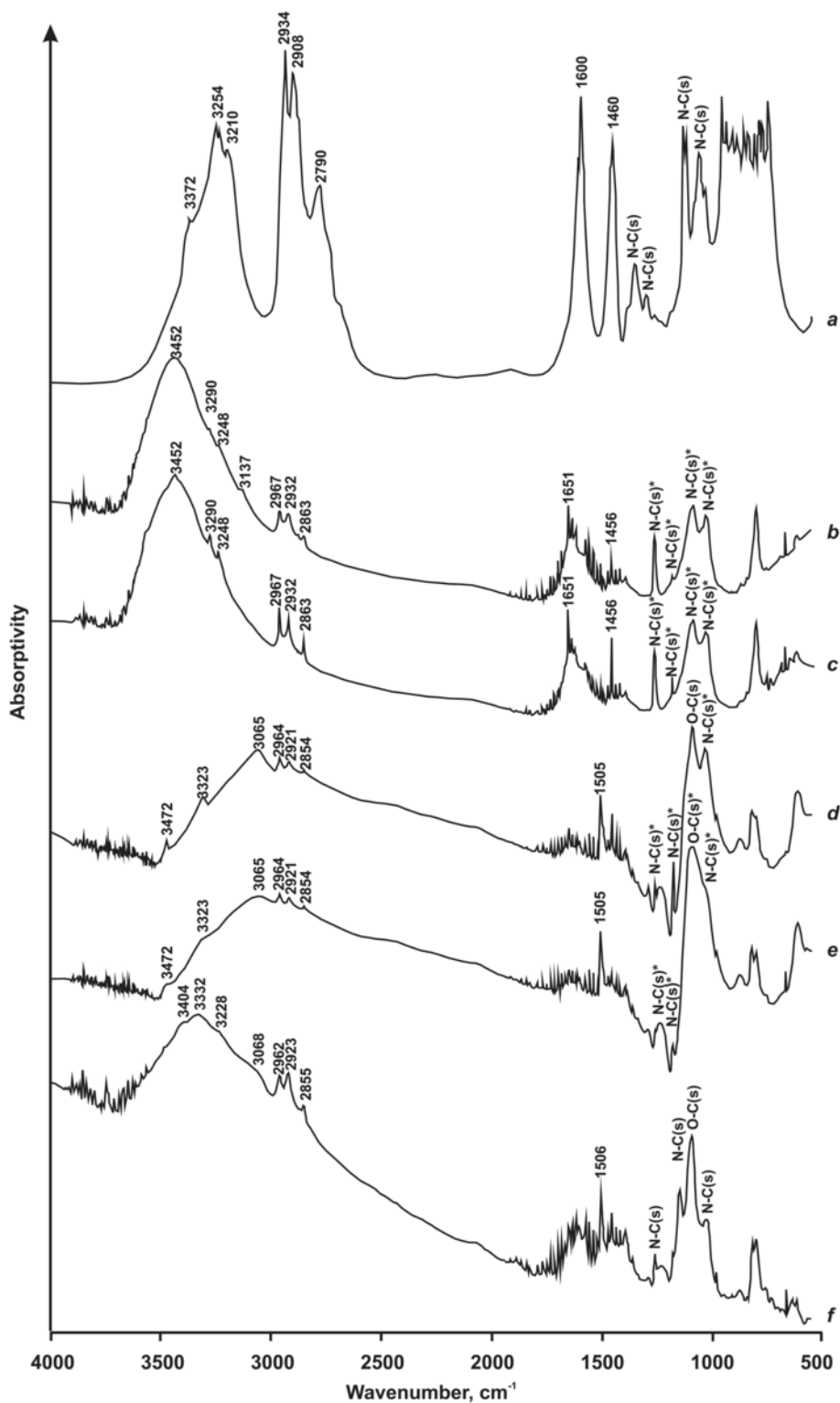


Fig. 1. IR spectra of DETA (a), [Cu(DETA)(H₂O)]SO₄·H₂O (b), DETA-CuSO₄ (c), DGEBA/DETA-CuSO₄(16) (d), DGEBA/DETA-CuSO₄(80) (e), DGEBA/DETA (f).

The ignition point (t_{ign}) and self-ignition point ($t_{\text{self-ign}}$) for DETA, DGEBA/DETA, DETA-CuSO₄, and DGEBA/DETA-CuSO₄ have been measured on a TF devise according to all-Union State Standard 12.1.044-89 (the items 4.7 and 4.9).

Physical-mechanical properties of the composite materials were studied by means of measurement of the following parameters: surface hardness, tensile strength, water absorption, and chemical resistance.

The surface hardness of the samples was measured on the Höppler's consistometer by indentation of a steel cone having angle of 53°08' at weighting in 50 N and duration 60 s.

Uniaxial tensile tests were determined on the epoxy-amine composites according to all-Union State Standard 11262-80 at room temperature using a P-0.5 type tensile testing machine. Rectangular samples with dimensions 250 × 10 × 3 mm³ were used. A displacement

rate of $100 \text{ mm}\cdot\text{min}^{-1}$ was adopted. The tensile properties were averaged from the results obtained from a minimum of three samples.

The water absorption or chemical resistance was studied by gravimetric method; a weight change of the polymer films after their immersion into distilled water or corrosive medium for a certain time was measured.

2.3. Preparation of the fire retardant-hardener

The powdery fire retardant-hardener ($\text{DETA}\cdot\text{CuSO}_4$) suitable to the polymerization has been obtained by dehydration of the $[\text{Cu}(\text{DETA})(\text{H}_2\text{O})]\text{SO}_4\cdot\text{H}_2\text{O}$ chelate complex whose crystals have been synthesized by the direct interaction of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ with DETA [14]. Crystalline $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (25 g, 0.1 mol) was placed into a porcelain mortar, and 11 mL (0.1 mol) of DETA were added. The reaction mixture was triturated till the appearance of a homogeneous blue-violet suspension. It was left for a few days at room temperature; next a blue-violet solid phase of the mentioned complex was crystallized. Yield: 100% (with respect to DETA), $\text{C}_4\text{H}_{17}\text{Cu}_1\text{N}_3\text{O}_6\text{S}_1$ ($M_r = 298.81$). XRPD (P^-1 ; $a = 7.2819(4)$, $b = 8.4669(4)$, $c = 8.7020(3)$ Å, $\alpha = 83.590(3)$, $\beta = 89.620(4)$, $\gamma = 84.946(4)^\circ$); d_{hkl} , Å (hkl): 8.381 (010), 6.385 (011), 5.709 (0 1 $\bar{1}$), 5.548 (101), 5.261 (1 $\bar{1}$ 0), 4.954 (111), 4.646 (1 $\bar{1}$ $\bar{1}$), 4.324 (002), 4.191 (020), 3.948 (021), 3.679 (0 1 $\bar{2}$ 1), 3.627 (200), 3.341 (1 2 $\bar{1}$ 1), 3.227 (2 $\bar{1}$ 0), 3.141 (1 $\bar{2}$ 1), 2.979 (2 $\bar{1}$ 1), 2.824 (0 2 $\bar{2}$), 2.786 (221), 2.094 (1 $\bar{3}$ 2). IR (KBr pellet, cm^{-1}): 3452, 3290 and 3248 (ν_{NH}); 3137 (ν_{OH}); 2967, 2932 and 2863 (ν_{CH}); 1651 (δ_{NH}); 1456 (δ_{CH}).

The obtained chelate complex was placed in a drying oven and left for a day at temperature of 190°C . Under such conditions the blue-violet crystals of the $[\text{Cu}(\text{DETA})(\text{H}_2\text{O})]\text{SO}_4\cdot\text{H}_2\text{O}$ chelate complex turn into the blue-gray powder of the fire retardant-hardener – $\text{DETA}\cdot\text{CuSO}_4$ (IR (KBr pellet, cm^{-1}): 3452, 3290 and 3248 (ν_{NH}); 2967, 2932 and 2863 (ν_{CH}); 1651 (δ_{NH}); 1456 (δ_{CH})) owing to loss, at first, of crystallization water ($90\text{--}130^\circ\text{C}$) and, next, of coordination water ($130\text{--}190^\circ\text{C}$) [16].

2.4. Preparation of the epoxy-amine composites

The indispensable ingredients for synthesis of the epoxy-amine composites in mass parts (mass p.) are given in Table 1. The samples of the epoxy-amine composite with a molar ratio of the $\text{DGEBA}:\text{DETA}:\text{CuSO}_4 = 5:2:2$ can be prepared by two modes. Synthesis of this composite by the first mode supposes a direct participation of the dehydrated chelate complex ($\text{DETA}\cdot\text{CuSO}_4$) in the polymerization. For it 100 g of the binder DGEBA and 26 g of the $\text{DETA}\cdot\text{CuSO}_4$ fire retardant-hardener were placed into the container. Next, the mixture was diligently stirred till formation of homogeneous and aesthetically attractive thick liquid of the ultramarine color. After that, prepared composite material denoted in Table 1 as $\text{DGEBA}/\text{DETA}\cdot\text{CuSO}_4(16)$ (IR (KBr pellet, cm^{-1}): 3472, 3323 and 3065 (ν_{OH}); 2964, 2921 and 2854 (ν_{CH}); 1505 (δ_{CH})) has been poured into the molds and left at room temperature till a total curing.

At the second mode [15], the copper vitriol was preliminarily dried at temperature of $250\text{--}260^\circ\text{C}$ up to full loss of crystal water. The dehydration process is accompanied by conversion of blue crystals of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ into a fine-dispersed white powder of CuSO_4 . Singly, a necessary ratio DGEBA and DETA (see Table 1) is placed into the container and stirred during the 5–10 min. Next, the anhydrous copper(II) sulfate (16 g, 0.1 mol) was added to the epoxy-amine mixture and over again stirred till formation of homogeneous consistence. The obtained sample of the $\text{DGEBA}/\text{DETA}\cdot\text{CuSO}_4(16)$ epoxy-amine composite in a

curing process acquires (as well as in the first mode) an ultramarine color owing to complexing. The rest of samples – $\text{DGEBA}/\text{DETA}\cdot\text{CuSO}_4(5)$ and $\text{DGEBA}/\text{DETA}\cdot\text{CuSO}_4(80)$ (see Table 1) have been prepared by exceptionally second mode.

The usual colorless epoxy resin DGEBA/DETA (IR (KBr pellet, cm^{-1}): 3404, 3332, 3228 and 3068 (ν_{OH}); 2962, 2923 and 2855 (ν_{CH}); 1506 (δ_{CH})) had also been obtained by combination of DGEBA and DETA .

2.5. Rheological measurements

Shelf life tests were carried out on two-component blends (epoxy resins and curing agent), using a viscometer made up of a glass test tube and a metal ball [24]. The graduate test tube was mounted in a socket of holder at an angle 80° and placed at air bath at temperature $20 \pm 2^\circ\text{C}$. Passage time of a metal ball through the two-component blend between two gauge marks at once after mixing (τ_0) and after certain time interval (τ_i) was determined. Relative viscosity is specified by the quotient τ_i/τ_0 . Blend shelf life is estimated by time period when τ_i/τ_0 value equals 1.15 (i.e., when the forming the polymer framework is completed). The results of rheological measurements for the DGEBA/DETA and $\text{DGEBA}/\text{DETA}\cdot\text{CuSO}_4(16)$ is represented in Fig. 2.

2.6. Quantum-chemical calculations

Numerical modeling of the complexing processes in $\text{DGEBA}\text{--}\text{DETA}\text{--}\text{CuSO}_4$ system was carried out by means of quantum-chemical analysis. The *ab initio* quantum-chemical calculations (the restricted Hartree-Fock method with a basis set 6-31*G) were performed using the HyperChem program version 8.0.6 [25,26]. The base crystallographic data concerning the $[\text{Cu}(\text{DETA})(\text{H}_2\text{O})]\text{SO}_4\cdot\text{H}_2\text{O}$ chelate complex [14] and IR spectroscopy data were used for the design of $\text{DETA}\cdot\text{CuSO}_4$ and $\text{DGEBA}/\text{DETA}\cdot\text{CuSO}_4$ discrete clusters as well as for the construction of free DETA and DGEBA molecules and of DGEBA/DETA polymer fragment. Calculation of charge density on atoms for discrete clusters was performed without optimization of the structural fragments whereas the geometry of free molecules was optimized. All calculations were carried out under the hypothesis that the presented clusters (as and the free molecules) are isolated and are in vacuum. The results of the quantum-chemical calculation of the charge density distribution on the atoms in above particles are represented in Fig. 3 while the value of the energy effects is given in Table 2.

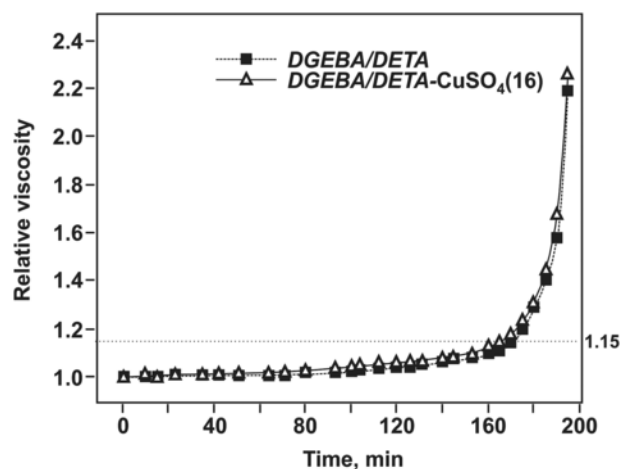


Fig. 2. The relative viscosity of the two-component blends versus time of the curing the epoxy-amine composites.

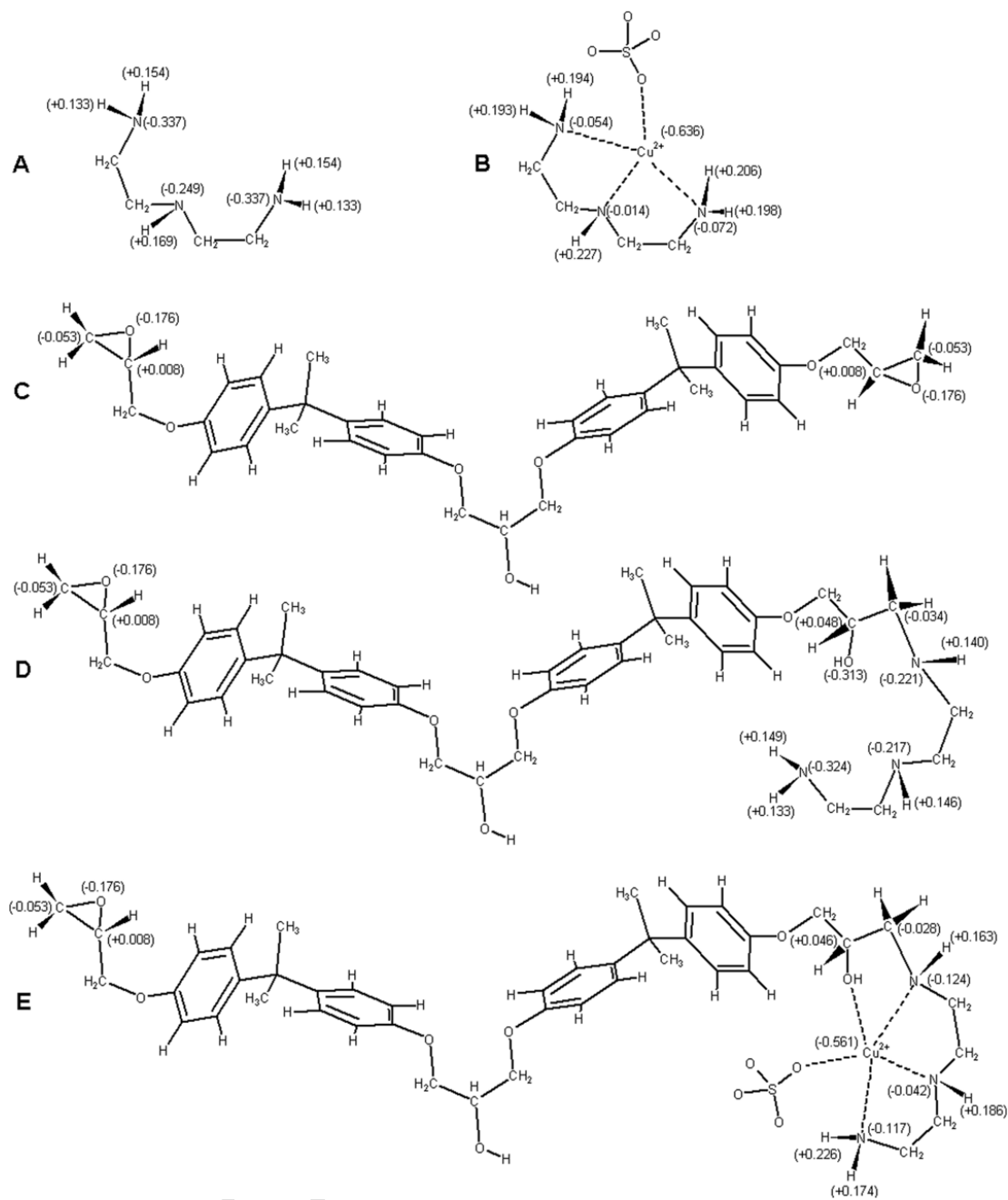


Fig. 3. Charge density ($\pm \delta$, e) distribution on the atoms in the DETA (A), DETA-CuSO₄ (B), DGEBA (C), DGEBA/DETA (D), and DGEBA/DETA-CuSO₄ (E).

Table 2

Results of the quantum-chemical calculation of the energy effects.

Particle	Total energy (kJ·mol ⁻¹)	Binding energy (kJ·mol ⁻¹)	Summary energy of all bonds (kJ·mol ⁻¹)
DETA	-180,110.01	-24,245.80	7105.54
DGEBA	-1,104,897.80	-167,191.51	40,855.78
DGEBA/DETA	-1,287,979.00	-194,408.58	46,289.32
DETA-CuSO ₄	-526,631.88	-30,850.66	8716.26
DGEBA/DETA-CuSO ₄	-1,634,501.20	-201,014.98	47,899.99

3. Results and discussion

3.1. Influence of a chelation in system DGEBA-DETA-CuSO₄ onto the epoxy-amine composite curing

The interaction of DETA (a curing agent) with CuSO₄ (fire retardant) in many respects predetermines the properties of DETA-CuSO₄ as fire retardant-hardener. The fact that Cu²⁺ ion is bonded with DETA into chelate complex can be seen on XRPD of the [Cu(DETA)(H₂O)]SO₄·H₂O (Fig.S1, Supp. Info) as well as on IR spectra recorded for DETA, [Cu(DETA)(H₂O)]SO₄·H₂O, DETA-CuSO₄, DGEBA/DETA-CuSO₄(16), DGEBA/DETA-CuSO₄(80) and DGEBA/DETA (Fig. 1). The peaks of the simulated diffraction image for the [Cu(DETA)(H₂O)]SO₄·H₂O chelate complex are in good agreement with the experimental XRPD pattern peak positions, indicating that the polycrystalline sample and the single crystals [14] are the same compound. Besides, the [Cu(DETA)(H₂O)]SO₄·H₂O and its dehydrated form DETA-CuSO₄ were identified by IR spectroscopy (see Fig. 1). Absorption bands caused by stretching and bending of NH₂ and NH groups of the coordinated and free DETA molecule will interest us primarily [27,28]. For free DETA (Fig. 1a) the high-frequency region 3372 and 3254 cm⁻¹ is related to the stretching of —NH₂ whereas the band observed at 3210 cm⁻¹ is ascribed to the stretching of —NH—; the observed oscillation frequency at 1600 cm⁻¹ is attributed to the bending of N—H bonds. After bonding of the DETA with copper(II) sulfate into [Cu(DETA)(H₂O)]SO₄·H₂O complex (Fig. 1b), all three the N—H absorption bands are merged into one wide band and shifted to high-frequency region observed at 3452, 3290 and 3248 cm⁻¹; here is also observed O—H absorption band at 3137 cm⁻¹ from the coordinated H₂O molecule. The observed wavenumber at 1651 cm⁻¹, related to the bending of N—H bonds, is also shifted. It is important to note that oscillations frequencies values caused by a stretching and bending of NH₂ and NH groups of the coordinated DETA molecule are practically equal in the [Cu(DETA)(H₂O)]SO₄·H₂O and DETA-CuSO₄ complexes (see Fig. 1b and c). IR spectra depicted in Fig. 1d-f represent the modified (DGEBA/DETA-CuSO₄(16) and DGEBA/DETA-CuSO₄(80) and ordinary (DGEBA/DETA) epoxy-amine polymers. The polymerization of epoxy composite cured by DETA or DETA-CuSO₄ is accompanied by disappearance of N—H bonds, N—C bonds forming and arising of new O—H bonds [29]. In Fig. 1f (IR spectrum of DGEBA/DETA), besides the absorption bands that are characteristic for DGEBA [30], the widened band observed in range of 3404–3068 cm⁻¹ is related to O—H stretching. However, for DGEBA/DETA-CuSO₄ (see Fig. 1d and e) the same band observed in range of 3472–3065 cm⁻¹ is more widened and materially weakened. It can be explained by complement of the coordination sphere of the chelated Cu²⁺ ion by oxygen atom through the Cu(II)–OH interlinking, as shown in Fig. 3E.

In this subsection, we would like to briefly discuss the influence of the coordinated hardener in comparison with uncoordinated one onto

the epoxy resin curing processes. Rheological measurements (see Fig. 2) have revealed that viscosity increasing rates for epoxy composites cured by DETA and DETA-CuSO₄ are very close; shelf life time of modified and unmodified epoxy-amine composite is 165 and 171 min, respectively. Such close behavior at the curing the DGEBA – DETA-CuSO₄ and DGEBA – DETA blends indirectly indicates onto identity of the polymerization mechanisms of two epoxy-amine composites. One must attract the results of the quantum-chemical analysis (Fig. 3) to better understand the curing mechanism taking place in the DGEBA – DETA – CuSO₄ system. The fulfilled calculations reveal that the electron density of the N atoms within coordination core efficiently shifts to the central Cu atom owing to a chelate effect. So, the values of charge density (δ) on N atoms of uncoordinated DETA molecule are -0.337 , -0.337 and $-0.249 e$ for two primary amino groups and secondary amino group, respectively (Fig. 3 A). However, the electron density on the N atoms of coordinated DETA molecule is greatly lowered owing to chelation of the DETA-CuSO₄ (the δ value are -0.054 , -0.072 and $-0.014 e$ for two primary amino groups and secondary amino group, respectively); herewith, the electron density on the copper atom, contrariwise, is strongly increased (δ value is $-0.636 e$) (Fig. 3B). As a result of such redistribution of the electron density in the coordination core, the positive charge on the H atoms of coordinated amino groups is also increased in comparison with uncoordinated ones (the δ values are ranged from $+0.193$ to $+0.226 e$) (compare Fig. 3A and B). Thus, the Cu(II)–(H₂NC₂H₄NHC₂H₄NH₂) interlinking causes the N—H bonds polarization and, as consequence of it, increases electrophilic ability of the H atoms in amino groups. It in the best way possible facilitates the electrophilic addition of the H atom to the O atom of the oxirane ring and, concurrently, promotes the nucleophilic attack of the N atom onto one of two C atoms of the epoxy group, which has smaller number of alkyl-substituents (Fig. 4). The presented mechanism of curing the epoxy amine composites modified by CuSO₄ is in a good agreement with the mechanism of the oxyrane ring opening at the conditions of electrophilic attack on the oxygen atom leading to epoxy resin polymerization [13,29,31,32].

The diagrammatic sketch of the fragment of polymer framework of the DGEBA/DETA-CuSO₄ produced out of coordinated DETA and DGEBA molecules is exemplified in Fig. 3E.

3.2. The fire hazard index of the epoxy-amine composites

From our experiments, one can draw an unambiguous conclusion that the first cause of combustibility lowering of the epoxy-amine composites is effective interlinking the curing agent (DETA) with incombustible inorganic salt (CuSO₄) that, in turn, results in forming the DETA-CuSO₄ chelate complex acting as a fire retardant-hardener in epoxy-amine polymerization process. For example, DETA which essentially is inflammable liquid [14], after bonding to copper(II) sulfate becomes a virtually incombustible substance (the DETA molecule interlinked into the DETA-CuSO₄ chelate complex does not inflame gen-

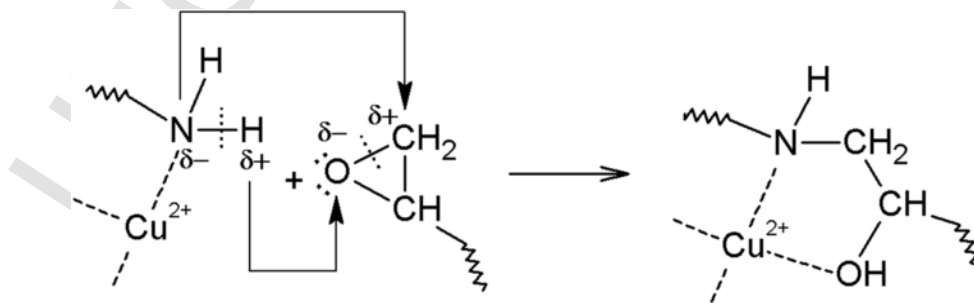


Fig. 4. Schematic representation of the proposed mechanism of the curing the epoxy-amine composites in DGEBA-DETA-CuSO₄ system.

erally). A similar tendency is also observed in case of the epoxy-amine composites. So, the ignition point of epoxy-amine polymer after adding CuSO_4 (e.g. 80 mass p.) increases from 320 °C to 358 °C (Table 3). It is mainly related to the extra chemical bonds that have been formed in the course of epoxy-amine polymerization with participation of the cupric salt. As revealed in the quantum-chemical calculations, the summary energy of all Cu—N and Cu—O bonds in the coordination core (see Fig. 1E) equals 337.32 kJ·mol⁻¹. After addition of the *DETA*- CuSO_4 chelate complex to the epoxy oligomer (*DGEBA*) the coordinated *DETA* enters into a polymerization. As a result of this, the polymeric framework which forms within this composite matrix contains the chemically connected incombustible inorganic salt (CuSO_4). The coordination bonds that arise between Cu(II) atom of inorganic salt and N atoms of the curing agent are responsible for the combustibility lowering of the epoxy-amine composite.

The flame propagation rate over the surface of a sample is one more a fire hazard index characterizing the combustibility of the polymer materials; the value of this rate is determined by a generation velocity of combustible mixture which, in turn, depends on chemical composition of the composite material. So, the experimental results (Table 3) reveal that addition of a small number of the copper(II) sulfate (5 mass p.) to the epoxy-amine composite has a little influence on the flame propagation rate over the surface of a sample placed horizontally. The polymer samples containing 5 mass p. of the fire retardant and even without fire retardant do not cease to burn as far as moment of forced extinguishing whereas polymer composites with 16 and, *a fortiori*, 80 mass p. of the fire retardant do not propagate flame at all; the flame will itself have been extinguished up to reaching a zero gauge mark. (The duration of a free burning for the composite *DGEBA/DETA-CuSO*₄(80) does not exceed 60 s). Since flame propagation rate over the horizontal surface for the *DGEBA/DETA-CuSO*₄(5) or *DGEBA/DETA* samples does not exceed 40 mm·min⁻¹ hence such samples are subsumed a PH. However, in case of the composite *DGEBA/DETA-CuSO*₄(80) the burning rate of the horizontally fastened sample is impossible to determine, consequently the highest category of the resistance at burning, *viz.* PV-1 category, is attributed to this polymer material.

The measurements of the smoke-formation factor for the epoxy-amine composites at the smoldering have revealed that these materials possess high-level smoke-formation ability. However, the fire retardant inclusion to the polymer composite in a quantity of 80 mass p. lowers the smoke-formation factor nearly in two times. The same tendency is typical for the smoke-formation factor measured during epoxy-amine composites burning. Decreasing the smoke-formation ability at increasing the content of CuSO_4 in the epoxy-amine composites can be explained in the following way. It is known that thermal decomposition of copper(II) sulfate is accompanied by formation of the copper(II) oxide [18]. On the other hand, benzene and its homologs is a major smoke-forming component part of the pyrolysis of polymers [33]. There are data [34] concerning the influence of different quan-

ties of CuO onto decreasing the benzene concentration in destruction products of epoxy-amine composites.

3.3. The physical-mechanical properties of the epoxy-amine composites

In order to impart the required operating characteristics to the developed epoxy-amine composites as well as to attain the optimal technological parameters of an obtaining and processing of the products made out of them it is necessary to have a reliable information about their physical-mechanical properties [35]. As criteria of assessment of the operating characteristics of the epoxy-amine composites, we have decided on such physical-mechanical properties as the surface hardness, tensile stretch, water absorption, and chemical resistance. The option significance of aforementioned parameters consists in the fact that these might become a base for the subsequent optimization of the quantitative content of the fire retardant in the composite materials.

It has been found experimentally that incorporation into the polymer framework of a bit cupric salt (5 mass p.) results in the some worsening of the surface hardness of the testing sample *DGEBA/DETA-CuSO*₄(5) (Fig. 5). Contrariwise, the composite with the fire retardant content in 80 mass p. is characterized by the largest value of the surface hardness. The surface hardness value for *DGEBA/DETA-CuSO*₄(80) composite is increased on 36,04 MN·m⁻² in comparison with the original *DGEBA/DETA* epoxy-amine polymer.

The measurements of the tensile strength (Fig. 6) have also revealed that if CuSO_4 content is in the range of 16 to 80 mass p. (12.7–42.1 wt%), the tensile strength of the epoxy-amine composites is characterized by the maximal values.

Thus, the mechanical properties of the epoxy-amine composites depending on content of CuSO_4 rank as 80 > 16 > 0 > 5. Decreased surface hardness and tensile strength for *DGEBA/DETA-CuSO*₄(5) compared to *DGEBA/DETA*, apparently, are related with the certain defectiveness of the polymer framework caused by partial incorporation of the *DETA-CuSO*₄ chelate core into the polymer matrix, *i.e.* due to the unequal molar ratio between CuSO_4 and *DETA*. It is not difficult to surmise that cause of the maximal values mechanical properties for the *DGEBA/DETA-CuSO*₄(80) and *DGEBA/DETA-CuSO*₄(16) composites consists in forming the more compact polymer framework [36] in which the nitrogen-containing hardener is rigidly fastened by the copper(II) sulfate. The excess amount of CuSO_4 in *DGEBA/DETA-CuSO*₄(80) compared to *DGEBA/DETA-CuSO*₄(16) plays a part of the active filling agent which can be coordinated by numerous -OH groups of *DGEBA*. It results in more profound cross bonding and forming the even more compact polymer framework. That is why the CuSO_4 excess augments the mechanical strength of *DGEBA/DETA-CuSO*₄(80) composite.

The resistance to water erosion or corrosive medium is one more important parameter that cannot be ignored when the operating characteristics for the polymer composite materials need tuning. Fig. 7 plots

Table 3
The fire hazard index of the epoxy polymers.

Species	$t_{\text{ign.}}$, °C	$t_{\text{self-ign.}}$, °C	$r_{\text{burn.}}$, mm·min ⁻¹	$\Delta t_{\text{burn.}}$, s	FC	D_m , m ² ·kg ⁻¹	
						S	B
<i>DETA</i>	97	350			C		
<i>DETA-CuSO</i> ₄	–	–			I		
<i>DGEBA/DETA</i>	320	545	25.2	a	PH	1100	421
<i>DGEBA/DETA-CuSO</i> ₄ (5)	335	565	24.0	a	PH	1139	937
<i>DGEBA/DETA-CuSO</i> ₄ (16)	350	567	b	76	PV-2	987	513
<i>DGEBA/DETA-CuSO</i> ₄ (80)	356	570	b	60	PV-1	537	244

Note: FC, Flammability Category (C – Combustible, I – Incombustible, PH – to Propagate Horizontally, PV – to Propagate Vertically); S, Smoldering; B, Burning.

a Samples are on fire as far as moment of forced extinguishing.

b Flame does not propagate, it has been self-extinguished up to reaching a zero gauge mark

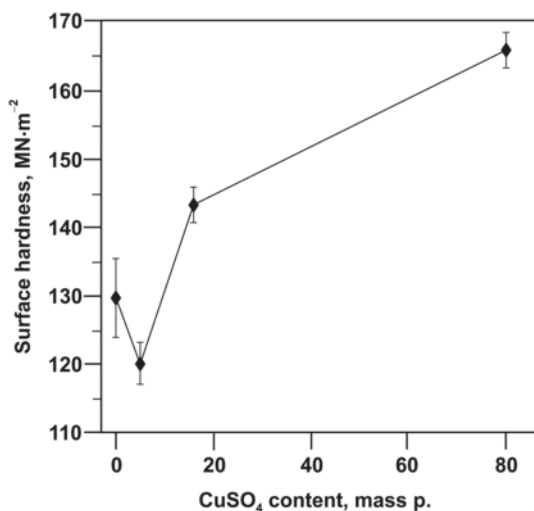


Fig. 5. A dependence plot of the surface hardness from the content of the fire retardant in epoxy-amine composites.

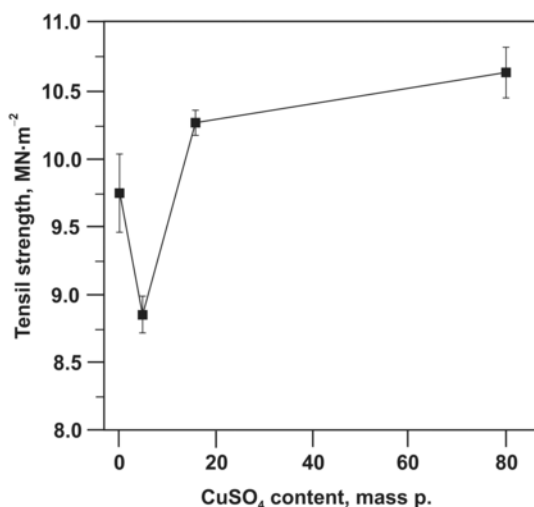


Fig. 6. A dependence plot of the tensile strength from the content of the fire retardant in epoxy-amine composites.

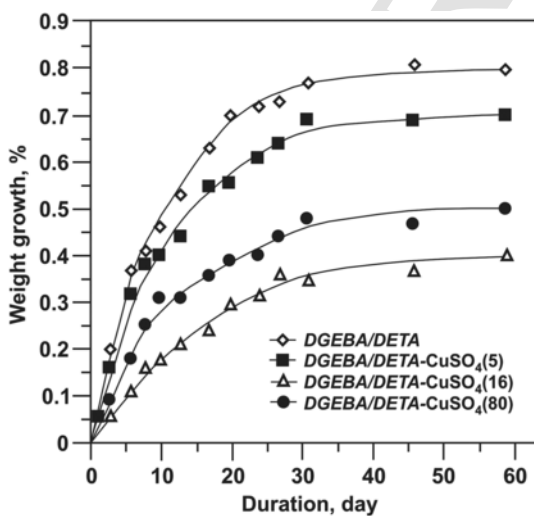


Fig. 7. Water absorption of the epoxy-amine composites versus the course of time.

a water absorption kinetics for the four epoxy-amine composites – *DGEBA/DETA*, *DGEBA/DETA-CuSO₄(5)*, *DGEBA/DETA-CuSO₄(16)*, and *DGEBA/DETA-CuSO₄(80)*. This plot demonstrates how the polymeric samples swell in the course of time after their immersion into water. So, over a three-day initial period of the water exposure, the weight growth did not exceed 0.2% per day. During next 10–20 days a sorption rate of water by films made out of epoxy-amine composites is decelerated up to 0.04–0.07% per day. The same systems after 25–30 days of an exposure arrives at an equilibrium; that is, when quantity of absorbed and desorbed water become equal. Thus, a water absorption by films made out of modified epoxy-amine composites is one-stage process what testifies homogeneity of the system.

The incorporation of the copper(II) sulfate into the epoxy polymers decreases absorption ability of epoxy-amine composites both in water and in aqueous solutions of alkalis or acids (Table 4). Such attenuation of a diffusion permeability of the samples, apparently, can be explained by drop of defectiveness caused by internal stress decreasing [37,38]. The additional coordinated bonds arising between Cu^{2+} ion and three N atoms of *DETA* molecule play a decisive role in the structuring of the epoxy-amine composite and, in the best way possible, limit a permeability of particles of the corrosive medium through films. The results of sorption study of the polymer films reveal that formation of the more compact framework of the epoxy-amine composites is in progress under the influence of copper(II) sulfate.

4. Conclusions

An uncomplicated and commercially-viable mode of preparing the polymer composites of *DGEBA* epoxy resin with different CuSO_4 content has been developed; the fire hazard indices and the physical-mechanical properties have been improved. The curing process of the epoxy-amine composites of the *DGEBA-DETA-CuSO₄* system has been studied by means of the rheological, IR spectroscopic and quantum-chemical analyses. It has been elicited that an electronic density within coordination core of the *DETA-CuSO₄* chelate complex acting as a fire retardant-hardener is appreciably redistributed. It in the best way possible contributes to the epoxy-amine composites curing. The self-extinguishing epoxy-amine composites (*DGEBA/DETA-CuSO₄*) consisting of the fire retardant-hardener (*DETA-CuSO₄*) incorporated in the framework of epoxy resin have been elaborated. The prepared in such a way the polymers exhibit a good homogeneity. From this point of view, the obtained *DGEBA/DETA-CuSO₄* composites have to be considered as individual chemical substances, not as mixtures (especially if the CuSO_4 content amounts to 16 mass p.). It results in significant decrease of the combustibility, viz. of the flame propagation rate, the smoke-formation factor and the values of ignition point or self-ignition point. The physical-mechanical properties such as surface hardness, tensile strength, water absorption and chemical resistance were enhanced mainly because of the additional coordinated bonds (Cu(II)-N) arising in the *DGEBA/DETA-CuSO₄* polymer framework.

Table 4
Sorption properties of polymer films based on the epoxy-amine composites.

Species	WAD, %	EWA, %	ES _o , %	ES _b , %
<i>DGEBA/DETA</i>	0.026	0.8	1.2	1.4
<i>DGEBA/DETA-CuSO₄(5)</i>	0.022	0.7	1.2	1.4
<i>DGEBA/DETA-CuSO₄(16)</i>	0.015	0.4	0.9	1.0
<i>DGEBA/DETA-CuSO₄(80)</i>	0.017	0.5	1.1	1.2

Note: WAD, Water Absorption for Day; EWA, Equilibrium Water Absorption; ES_o, Equilibrium Swelling in 10% H_2SO_4 ; ES_b, Equilibrium Swelling in 10% NaOH.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.reactfunctpolym.2017.10.013>.

References

- [1] A.P. Mouritz, A.G. Gibson, *Fire Properties of Polymer Composite Materials*, Springer, Dordrecht, 2006.
- [2] D. Ratna, *Handbook of Thermoset Resins*, Smithers Rapra, London, 2009.
- [3] D. Ratna, *Epoxy Composites: Impact Resistance and Flame Retardancy*, Rapra Technology Ltd., Shawbury, 2006.
- [4] S.-Y. Lu, I. Hamerton, *Prog. Polym. Sci.* 27 (2002) 1661–1712.
- [5] G.H. Hsiue, W.J. Wang, F.C. Chang, *J. Appl. Polym. Sci.* 73 (1999) 1231–1238.
- [6] H. Horacek, W. Grabner, *Makromol. Chem. Macromol. Symp.* 74 (1993) 271–276.
- [7] H. Yang, X. Wang, B. Yu, L. Song, Yu. Hu, R.K. Yuen, *Thermochim. Acta* 535 (2012) 71–78.
- [8] W. Liu, R.J. Varley, G.P. Simon, *J. Appl. Polym. Sci.* 92 (2004) 2093–2100.
- [9] W. Liu, R.J. Varley, G.P. Simon, *Polymer* 47 (2006) 2091–2098.
- [10] J.M. Barton, G.J. Buist, I. Hamerton, B.J. Howlin, J.R. Jones, S. Liu, *J. Mater. Chem.* 4 (3) (1994) 379–384.
- [11] J. Brown, I. Hamerton, B.J. Howlin, *J. Appl. Polym. Sci.* 75 (2000) 201–217.
- [12] J.M. Barton, I. Hamerton, B.J. Howlin, J.R. Jones, S. Liu, *Polymer* 39 (10) (1998) 1929–1937.
- [13] I. Hamerton, B. Howlin, P. Jepson, *Coord. Chem. Rev.* 224 (2002) 67–85.
- [14] H. Lavrenyuk, O. Mykhalichko, B. Zarychta, V. Olijnyk, B. Mykhalichko, *J. Mol. Struct.* 1095 (2015) 34–41.
- [15] H. Lavrenyuk, B. Mykhalichko, *Epoxy composite with lowered combustibility*, In: Patent No 109187 UA, 2015, (in Ukraine).
- [16] H. Lavrenyuk, V. Kochubei, O. Mykhalichko, B. Mykhalichko, *Fire Saf. J.* 80 (2016) 30–37.
- [17] J.N. Varghese, E.N. Maslen, *Acta Cryst B41* (1985) 184–190.
- [18] A.K. Galwey, M.E. Brown, *Thermal Decomposition of Ionic Solids*, Elsevier Science B. V, Amsterdam, 1999.
- [19] A.N. Baratov, A. Ya, Korolchenko, *Fire and Explosion Risk of Substances and Materials and Means of their Extinguishing: Reference Book. Part 1*, Khimia, Moscow, 1990, (in Russian).
- [20] J. Rodríguez-Carvajal, *IUCr. Newsl.* 26 (2001) 12–19.
- [21] D. Louër, M. Louër, *J. Appl. Crystallogr.* 5 (1972) 271–275.
- [22] A. Boulitif, D. Louër, *J. Appl. Crystallogr.* 24 (1991) 987–993.
- [23] IEC 60695–11–10. *Fire Hazard Testing-Part-10: Test Flames- 50W horizontal and vertical flame test methods*.
- [24] M.I. Kariakin, *Tests of Paint-and-Lacquer Materials and Paint Coats*, Khimia, Moscow, 1988, (in Russian).
- [25] HyperChem: Molecular Modeling System, Hypercube, Inc., Release 8.0.6, Florida, USA, 1995–2009.
- [26] L.P. Frank, *Elementary Quantum Chemistry*, McGraw-Hill Inc., New York, 1990.
- [27] A.J. Gordon, R.A. Ford, *The chemist's Companion. A Handbook of Practical Data, Techniques and References*, Wiley-Interscience Publication, New York, 1972.
- [28] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1997.
- [29] H. Lee, K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
- [30] I. Hamerton, *Recent developments in epoxy resins*, *RAPRA Rev. Rep.* 8 (91) (1996) 1–176.
- [31] B. Ellis, *Chemistry and Technology of Epoxy Resins*, Springer Science & Business Media, Dordrecht, 2012.
- [32] L.G. Netchitailo, M.Z. Reznikova, I.M. Shologon, M.K. Pakter, *IR-Spectroscopy of Epoxy Resins*, NIITEKIM, Moscow, 1988, (in Russian).
- [33] M.T. Bryk, *Destruction of the Filled Polymers*, Khimia, Moscow, 1989, (in Russian).
- [34] Y.V. Popov, O.M. Grigorenko, V.O. Ponomarev, *Probl. Fire Saf.* 31 (2012) 155–159.
- [35] A.V. Kurnoskin, *Polym.-Plast. Technol. Eng.* 31 (5–6) (1992) 505–525.
- [36] V.G. Hozin, *The Strengthening of Epoxy Polymer*, PIK Dom Pechati, Kazan, 2004, (in Russian).
- [37] C.F. Rogers, in: E. Baer (Ed.), *Permeability and Chemical Resistance in Engineering Design for Plastic*, Van Nostrand Reinhold, London, 1964.
- [38] M. Shimbo, M. Ochi, K. Arai, *J. Coatings Technol.* 57 (728) (1985) 93–99.