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A new flame retardant on the basis of diethylenetriamine copper(II) sulfate complex for combustibility suppressing of epoxy-amine composites

H. Lavrenyuk^a, V. Kochubei^b, O. Mykhalichko^c, B. Mykhalichko^{a,*}

^a Department of Burning Processes and General Chemistry, Lviv State University of Life Safety, Lviv UA-79007, Ukraine

^b Department of Physical and Colloidal Chemistry, Lviv Polytechnic National University, Lviv UA-79013, Ukraine

^c Chemistry Laboratory, Limited Liability Company "FUCHS Oil Ukraine", Lviv UA-79069, Ukraine

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ABSTRACT

The crystals of diethylenetriamine copper(II) sulfate complex (flame retardant) denoted as DETA-CuSO₄ have been obtained by direct interaction of solid copper(II) sulfate pentahydrate with diethylenetriamine – DETA (hardener of epoxy resins) and characterized by means of X-ray powder diffraction, infrared spectra (IR) and thermal gravimetric analysis (TGA). The results of TGA reveal that the thermal degradation of DETA-CuSO₄ takes place at 290 °C, while the maximal temperature of combustion gaseous products amounts to 520 °C. DETA-CuSO₄ has been used as flame retardant in epoxy-amine polymers (DGEBA/DETA). The thermal behavior and combustibility of modified epoxy-amine composites (DGEBA/DETA-CuSO₄) have been investigated using TGA, method of “ceramic tube” (CT) as well as measurement of ignition point and self-ignition point. TGA data confirms that adding DETA-CuSO₄ to DGEBA (bisphenol A diglycidyl ether) appreciably improve the thermic stability and anti-flammability of DGEBA/DETA-CuSO₄, mainly, owing to chemically interlinking incombustible inorganic salt of copper(II) sulfate with polymeric framework of DGEBA/DETA. Results of CT measurement show that the maximal combustion temperature of gaseous products for DGEBA/DETA in comparison with DGEBA/DETA-CuSO₄ goes down from 867 °C to 640 °C and weight loss decreases from 89.0 wt% to 78.6 wt%.

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1. Introduction

Epoxy resins and materials, elaborated on their basis, because of a unique combination of physical, chemical, mechanical and dielectric properties [1] conquer every time new areas of science and technology, without ceding occupied positions to other materials. Constructional characteristics of these polymeric materials play important role in industry and building [2]. It is necessary to notice that for exploited polymer materials are important not so much mechanical indexes as indexes of resistibility to diffusion or to destruction from aggressive environment. Therefore properties such as anti-flammability and thermic stability should dominate at the employed epoxy polymers. Unfortunately, inherent combustibility of epoxy polymers impedes their wider utilization. Therefore, a search and elaborating of new flame retardants effectively contributing to combustibility decrease of epoxy resins is one of the main problems of fire safety [3,4].

The works related to combustibility decrease of epoxy polymers are put into effect already long since. Currently, assortment

of flame retardants fit for combustibility decrease of epoxy polymers involves an enormous range of diverse substances kinds. Among such substances, the organometallic complexes are the most efficient inhibitors of burning. Therefore, at the producing of incombustible polymeric materials the use of metal-containing retardants is very promising. So, inorganic compounds of metals (oxides, hydroxides or salts as well as complexes of metals in different oxidation states, particularly, chelate complexes [5]) are widely used for the obtaining of polymer composites with decreased combustibility. Among metals salts, copper compounds used as flame retardants, attract special attention. So, in work [6] has been described preparation method of fire-resistant polymeric material on the basis of binders (bisphenol A diglycidyl ether (DGEBA) – ED-16, ED-20 and ED-22 grades) and of hardener (isomethyltetrahydrophthalic anhydride) which additionally has contained nanoparticles of metal copper. Epoxy polymeric composite with the lowered smoke formation containing binder (DGEBA), hardener (monocyanethyldiethylenetriamine), modifier (oligoethertri epoxy oligomer) and flame retardant (monoammonium phosphate with activated basalt scales and copper(II) oxide) has been characterized in [7]. The glue composite with decreased combustibility comprising DGEBA, furfural acetone

* Corresponding author.

E-mail address: mykhalichko@email.ua (B. Mykhalichko).

monomer, inorganic filler, amine hardener as well as copper hydroxychloride and copper-magnesium hydroxychloride (as reactive flame retardant) has been proposed in [8]. In addition, in works [9–16] the great deal of researches are devoted to the study of influence of copper-containing compounds onto hardening, physical-mechanical and thermal properties as well as operating ability of materials founded on epoxy resins.

However in most cases the results set forth in given works are based on the cumulative experimental dependences of influence of chemical composition of epoxy polymers onto their properties. At the same time, in cited works practically have thoroughly been examined neither the mechanism of modifying nor frame of the obtained composites.

Given the above-said, we undertook an attempt to elaborate a new flame retardant on the basis of copper(II) sulfate chelate complex with diethylenetriamine (DETA-CuSO₄) and to incorporate the DETA-CuSO₄ into DGEBA for the obtain of modified epoxy-amine composites (DGEBA/DETA-CuSO₄). The identification by means of infrared spectra (IR) and X-ray powder diffraction as well as the determination of thermal behavior and combustibility of DETA, DETA-CuSO₄, DGEBA/DETA and DGEBA/DETA-CuSO₄ by means of thermic gravimetric analysis (TGA), of “ceramic tube” method (CT) and of measurement of ignition point and self-ignition point are subject of scrutiny in this article.

2. Experimental

2.1. Materials

The copper vitriol (CuSO₄·5H₂O) was purchased in the company “Industrial and laboratory chemistry” (Ukraine). The bisphenol A diglycidyl ether–DGEBA (epoxy resin) of ED-20 grade with almost 22% epoxy groups content, value of viscosity from 12 to 18 Pa s (at 25 °C) and diethylenetriamine–DETA (epoxy hardener) with not less than 60 minute hardening ability relatively DGEBA and $D^{25} = 1.00(5) \text{ g cm}^{-3}$ were provided by “SphereSeven” company (Ukraine). All chemical reagents were used as-received without further purification.

2.2. Synthesis of DETA-CuSO₄

The flame retardant – DETA-CuSO₄ in solid state has been synthesized by direct interaction of copper(II) sulfate pentahydrate

with diethylenetriamine. Formation of DETA-CuSO₄ is accompanied by simultaneous replacement of three water molecules in CuSO₄·5H₂O by one DETA molecule. This synthesis route is sketched out in Scheme 1. Crystalline CuSO₄·5H₂O (25 g, 0.1 mol) was placed into a porcelain mortar and 10 mL of the DETA was added to it. Content of the mortar was triturated till the appearance of a homogeneous blue–violet suspension. It was left for a few days at the room temperature to obtain blue–violet crystalline phase of the mentioned flame retardant.

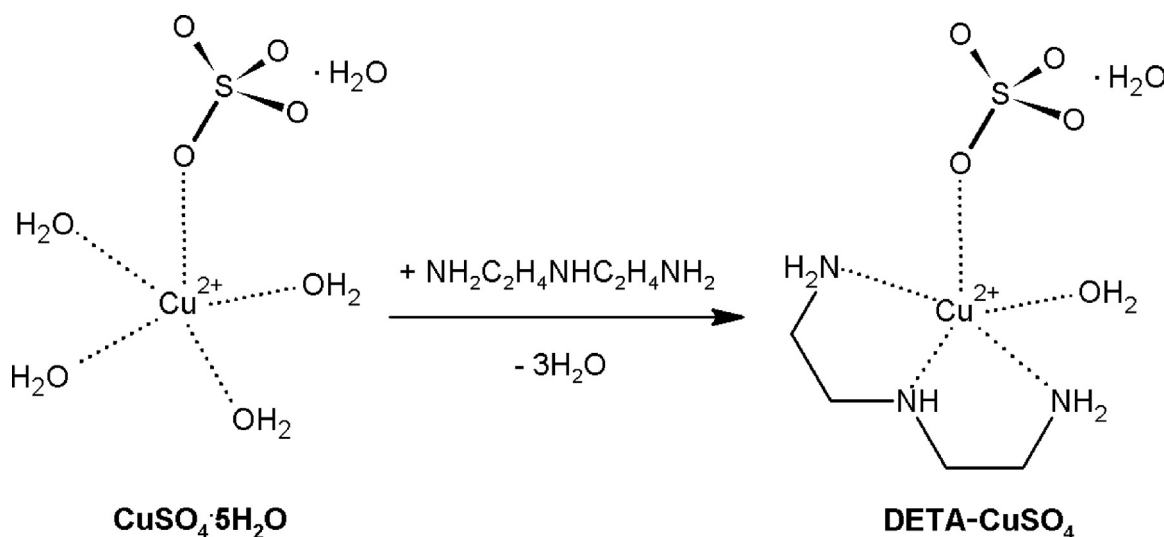
2.3. Preparation of DGEBA/DETA-CuSO₄ composites

Components of the epoxy-amine composites in masses parts (mass. p.) are printed in the Table 1. There are two modes of preparation of modified epoxy-amine compositions. At the first mode [17], copper vitriol was preliminarily dried in oven at temperature of 250–260 °C till full loss of crystal water; dehydration process is accompanied by conversion of blue crystals of CuSO₄·5H₂O into a fine-dispersed white powder of CuSO₄. Then, a necessary ratio (see Table 1) of DGEBA and DETA was placed into the container and mixed within 5–10 minutes. Later, the certain quantity of anhydrous copper(II) sulfate was added continuing, at that, to stir content of container till formation of homogeneous composition which, with time, grows increasingly aesthetic attractive (the composition was dyed in ultramarine after adding of CuSO₄). The prepared composition was packed into forms and was left at room temperature during the day till total solidification. At the other mode, the synthesized previously flame retardant – DETA-CuSO₄ was added to DGEBA and stirred at heating (to 100 °C) to get rid of crystallization water.

2.4. Characterization and measurements

Infrared spectra for samples of DETA, DGEBA/DETA, DETA-CuSO₄ and DGEBA/DETA-CuSO₄ (Fig. 1) were recorded on the spectrometer PerkinElmer Spectrum Two, using KBr pellets or cuvette (for DETA).

The powder X-ray diffraction pattern of DETA-CuSO₄ (Fig. 2) has been obtained for phase identification. The experiment was carried out at room temperature on the DRON-3M diffractometer (Cu K_α-radiation, Bragg–Brentano geometry, angular range $8 \leq 2\theta \leq 50^\circ$, step 0.02° and exposition time per point 20 s). The profile parameters were refined by the Rietveld method using the package of program FullProf Suite [18]. Indexing of powder X-ray



Scheme 1.

Table 1
Stoichiometry of epoxy-amine composites.

Items	DGEBA (mass. p.)	DETA (mass. p.)	CuSO ₄ (mass. p.)
DGEBA/DETA	100	12	1
DGEBA/DETA-CuSO ₄ (5)	100	12	5
DGEBA/DETA-CuSO ₄ (80)	100	12	80

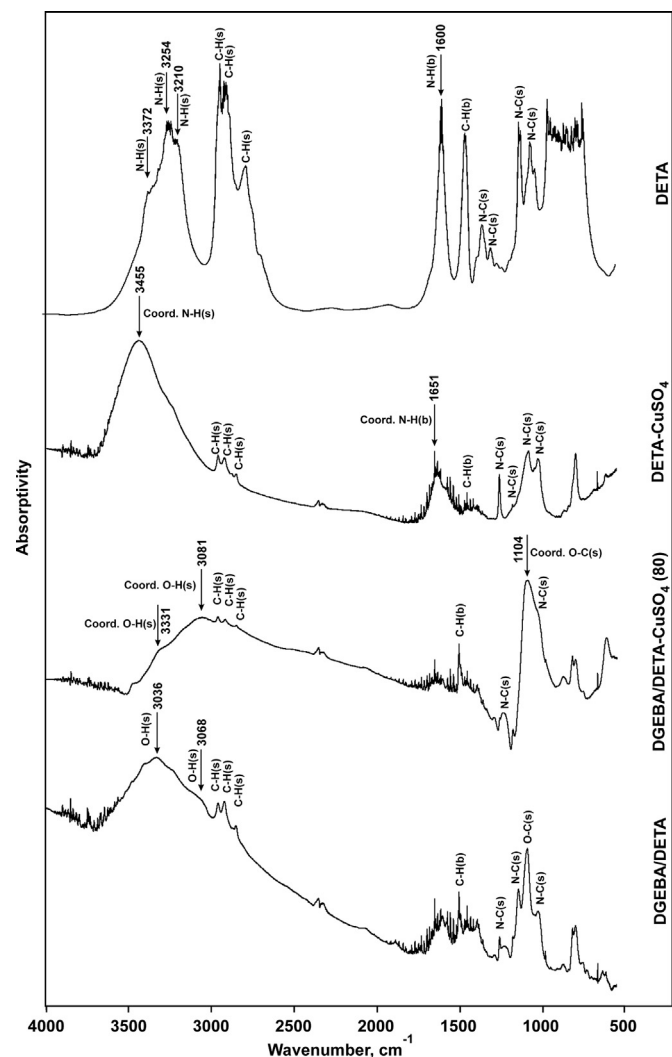


Fig. 1. Infrared spectra of DETA, DETA-CuSO₄, DGEBA/DETA-CuSO₄ and DGEBA/DETA.

diffraction pattern was fulfilled automatically by means of method described in [19], using program DICVOL91 [20].

Thermal gravimetric analysis for samples of CuSO₄ · 5H₂O, DETA and DETA-CuSO₄ as well as DGEBA/DETA and DGEBA/DETA-CuSO₄ was performed on a Q-1500D thermal analyzer (F. Paulik, J. Paulik, L. Erdey system) in the temperature range from 25 to 1000 °C with a heating rate of 5 °C per minute. The researches were carried out at dynamical regime in medium of air. The weight of each sample amounted to 100 mg. Aluminum oxide was used as standard.

The combustibility parameters for DGEBA/DETA and DGEBA/DETA-CuSO₄ composites have been determined according to all-Union State Standard 12.1.044-89 using a method of “ceramic tube”, the gist of which consists in making temperature conditions that can promote burning of these materials. Each sample having dimension of 150 × 60 × 5 mm³ was wrapped in glass

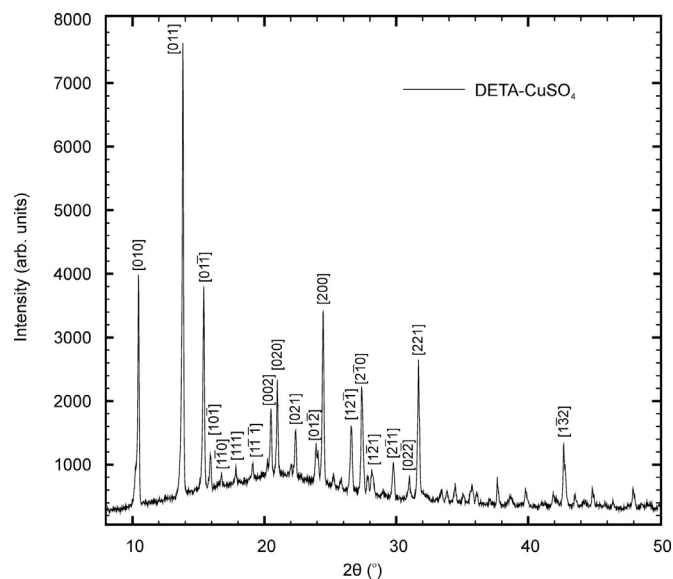


Fig. 2. The powder X-ray diffraction pattern of DETA-CuSO₄.

tissue. The CT measurements were carried out for samples taken in triplicates. The values of three measurements were averaged. All samples before testing were brought to optimal conditions and weighed, whereupon, separately taken samples were placed into ceramic tube which in advance was heated to temperature of 200 °C by means of gas burner flame. The maximal combustion temperature of gaseous products (t_{max}), duration of its reaching ($\Delta\tau$) and loss of the mass (Δm) were determined. The group of combustibility was characterized by values of t_{max} and Δm while the class of inflammable substance was estimated by value of $\Delta\tau$.

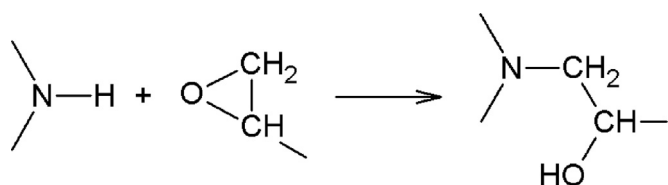
The ignition point (t_{ign}) and self-ignition point ($t_{self-ign}$) for DGEBA/DETA and DGEBA/DETA-CuSO₄ composites were measured on a TF device according to all-Union State Standard 12.1.044-89.

3. Results and discussion

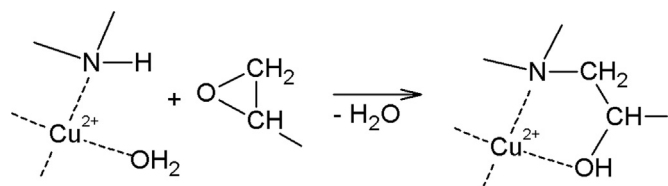
3.1. Structural identification of DETA-CuSO₄ phase

The interaction of DETA (a hardener) with noncombustible salt (copper(II) sulfate) in many respects predetermines the properties of DETA-CuSO₄ as flame retardant. The fact that Cu²⁺ ion is linked with DETA into chelate complex can be seen on IR spectra recorded for DETA and DETA-CuSO₄ (see Fig. 1a and b). Although a detailed assignment of all the bands is difficult, the most important attribution mode is their comparison with typical compounds [21]. It is to be noted that for DETA 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 stretching of NH. The observed at 1600 cm⁻¹ is attributed to the bending of N-H bonds. After fastening of DETA through Cu(II)-N bonds and forming DETA-CuSO₄ chelate complex, three bands that have been concerned with the stretching of NH₂ and NH is merged into one wide band and shifted to high-frequency region observed at 3455 cm⁻¹; the observed wavenumber at 1652 cm⁻¹, related to the bending of N-H bonds, is shifted too (see Fig. 1b). IR spectra depicted in Fig. 1c and d represent the modified (DGEBA/DETA-CuSO₄) and ordinary (DGEBA/DETA) epoxy-amine polymers, respectively. In the course of polymerization of DETA with DGEBA, N-H bonds practically disappear and instead of them are formed N-C bonds and arisen new O-H bonds (Scheme 2).

In Fig. 1d (IR spectrum of DGEBA/DETA), besides the bands that are characteristic for DGEBA [22], the widened band observed at



Scheme 2.



Scheme 3.

3336 cm^{-1} is related to stretching of OH. However, for DGEBA/DETA-CuSO₄ (see Fig. 1c) the same band observed at 3331 cm^{-1} is materially weakened owing to Cu(II)-OH coordination (Scheme 3).

The phase identification of polycrystalline sample of DETA-CuSO₄ has been carried out by means of the X-ray diffraction analysis. All reflexes from atomic planes of crystal lattice (see the powder X-ray diffraction pattern in Fig. 2) have been indexed and refined with such the unit cell parameters: $a=7.3043(2)$, $b=8.5456(3)$, $c=8.7152(3)\text{ \AA}$, $\alpha=83.789(3)$, $\beta=89.433(5)$, $\gamma=85.064(5)^\circ$, space group $P\bar{1}$. Hence, the flame retardant DETA-CuSO₄ is $[\text{Cu}(\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$ chelate

complex whose crystal structure as early as has been studied [23]. The structural formula of this chelate complex is displayed in Scheme 1.

3.2. Flame retardancy properties of DETA-CuSO₄

The flame retardancy properties of DETA-CuSO₄ chelate complex were studied by means of thermal gravimetric analysis fulfilled in atmosphere of air. The curves of thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) are displayed in Fig. 3. The detailed data of thermal degradation for DETA-CuSO₄, DETA, CuSO₄·5H₂O as well as for DGEBA/DETA and DGEBA/DETA-CuSO₄ is given in Table 2.

As shown in Fig. 3a, the TG curve of thermal degradation for DETA-CuSO₄ can be divided into five stages. The first stage of the thermal degradation involves the temperature range from 20 to 190 °C. It is accompanied with weight loss at 12.6 wt% and by appearance of extreme peak on respective portion of DTA curve (see Fig. 3c). At this temperature interval (DTA curve) arises endothermic effect with extremal value of temperature at 120 °C. This portion of curve is related to the process of dehydration of crystallization water and, next, of coordinated water (Scheme 4).

The second stage of the thermal degradation occurs in the temperature range from 190 to 260 °C and is accompanied by appearance of pronounced exothermic effect (DTA curve) with maximum at 240 °C. The loss of weight on this stage amounts to 4.1 wt%. In indicated temperature interval takes place the partial decomposition on the metallic center of the coordinated DETA with a concurrent dehydrogenization and formation of dicyanomethylamine [24,25] (Scheme 5). Hydrogen *in statu nascendi*

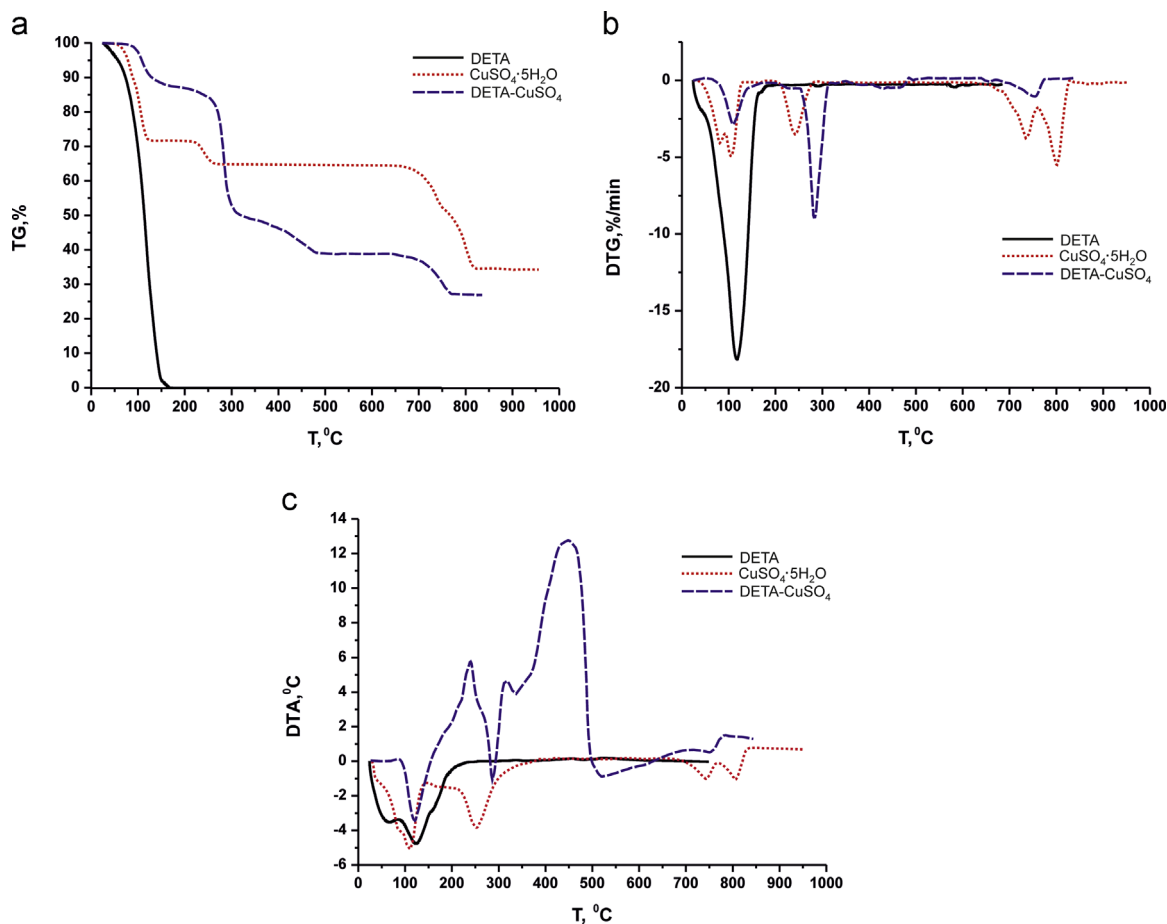


Fig. 3. TG (a), DTG (b) and DTA (c) curves for, DETA, CuSO₄·5H₂O and DETA-CuSO₄.

Table 2
The thermal degradation results of the samples.

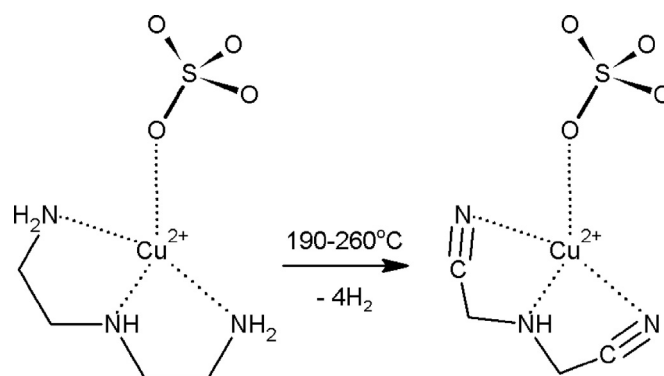
Sample	Stage	Temperature range (°C)	Weight loss (wt%)
DETA	I	20–170	100
CuSO ₄ · 5H ₂ O	I	20–92	11.1
	II	92–130	17.4
	III	200–280	6.7
	IV	640–762	13.8
	V	762–828	18.2
DETA-CuSO ₄	I	20–190	12.6
	II	190–260	4.1
	III	260–318	33.0
	IV	318–520	10.4
	V	520–780	11.9
DGEBA/DETA	I	20–180	3.1
	II	180–360	32.0
	III	360–460	12.1
	IV	460–900	52.0
DGEBA/DETA-CuSO ₄ (80)	I	20–175	16.0
	II	175–245	4.2
	III	245–300	8.3
	IV	300–400	28.0
	V	400–535	20.1
	VI	535–660	6.3

instantly combusts and it is cause of heat-evolution. The third stage of thermal degradation happens in the temperature range from 260 to 318 °C. It is concerned with complete decomposition of aminonitrile complex of copper(II) on N≡CCH₂NHCH₂C≡N and CuSO₄. This phenomenon is accompanied by appearance of endothermic peak on DTA curve with extremal value of temperature at 290 °C. The loss of weight on third stage amounts to 33 wt%.

The fourth stage occurs in the temperature range from 318 to 520 °C; it is responsible for combustion process of destruction products of organic aminonitrile. The weight loss on this stage amounts to 10.4 wt%. There is exothermic peak on DTA curve with maximum at 450 °C.

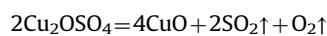
The final, fifth stage of combustion of pyrolytic residue of organic component of sample happens in the temperature range from 520 to 780 °C. This stage is completed by thermal degradation of copper(II) sulfate. The weight loss on this stage amounts to 11.9 wt%.

Unlike DETA-CuSO₄, full loss of weight for DETA occurs in the temperature range from 20 to 170 °C with clear-cut endothermic peak on DTA curve (see Fig. 3). It corresponds to total volatilizing of liquid DETA [26]. In contrast to it, thermal decomposition of CuSO₄ · 5H₂O happens in wider temperature range. At the beginning of process in the temperature range from 20 to 92 °C the



Scheme 5.

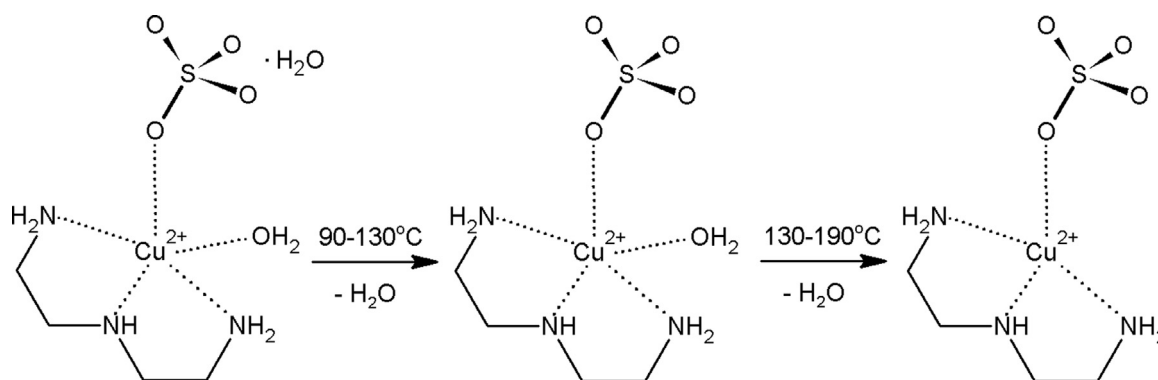
weight loss amounts to 11.1 wt%. It is accompanied by crystallization water loss. At the temperature range from 92 to 130 °C the weight loss ($\Delta m=17.4$ wt%) conforms with evolution of three molecules of coordinated water. There is endothermic peak on DTA curve (Fig. 3c) with extremal value of temperature at 109 °C. Final dehydration of copper vitriol happens in the temperature range from 200 to 280 °C ($\Delta m=6.7$ wt%) with endothermic extremum at 251 °C. Subsequent endothermic effects are observed in temperature ranges from 740 to 762 °C ($\Delta m=13.8$ wt%) and from 762 to 828 °C ($\Delta m=18.2$ wt%) with extremal temperature values at 740 °C and 800 °C, respectively. The thermal-oxidative breakdown of the anhydrous copper(II) sulfate take place in these temperature intervals [27]:



Thereupon, it is interesting to compare the ignition points (self-ignition points) measured for DETA and DETA-CuSO₄. So, if uncombined DETA inflames (or spontaneously inflames) at 97 °C (or 350 °C) [26], then chelate complex does not inflame generally. Thus, performed experiments clearly reveal that combustible DETA after interlinking with cupric sulfate turns into practically incombustible substance. The cause of it is in the forming chemical bonds between cupric sulfate and DETA (hardener of epoxy resins) in the course of chelation. These strong coordination bonds are responsible for the combustibility suppressing of the epoxy-amine composites.

3.3. Thermal behavior of DGEBA/DETA-CuSO₄ composites

Incorporation of the flame retardant DETA-CuSO₄ to DGEBA results in forming the polymeric composite DGEBA/DETA-CuSO₄ with suppressed combustibility. The thermograms recorded for DGEBA/DETA and DGEBA/DETA-CuSO₄ are represented in Fig. 4.



Scheme 4.

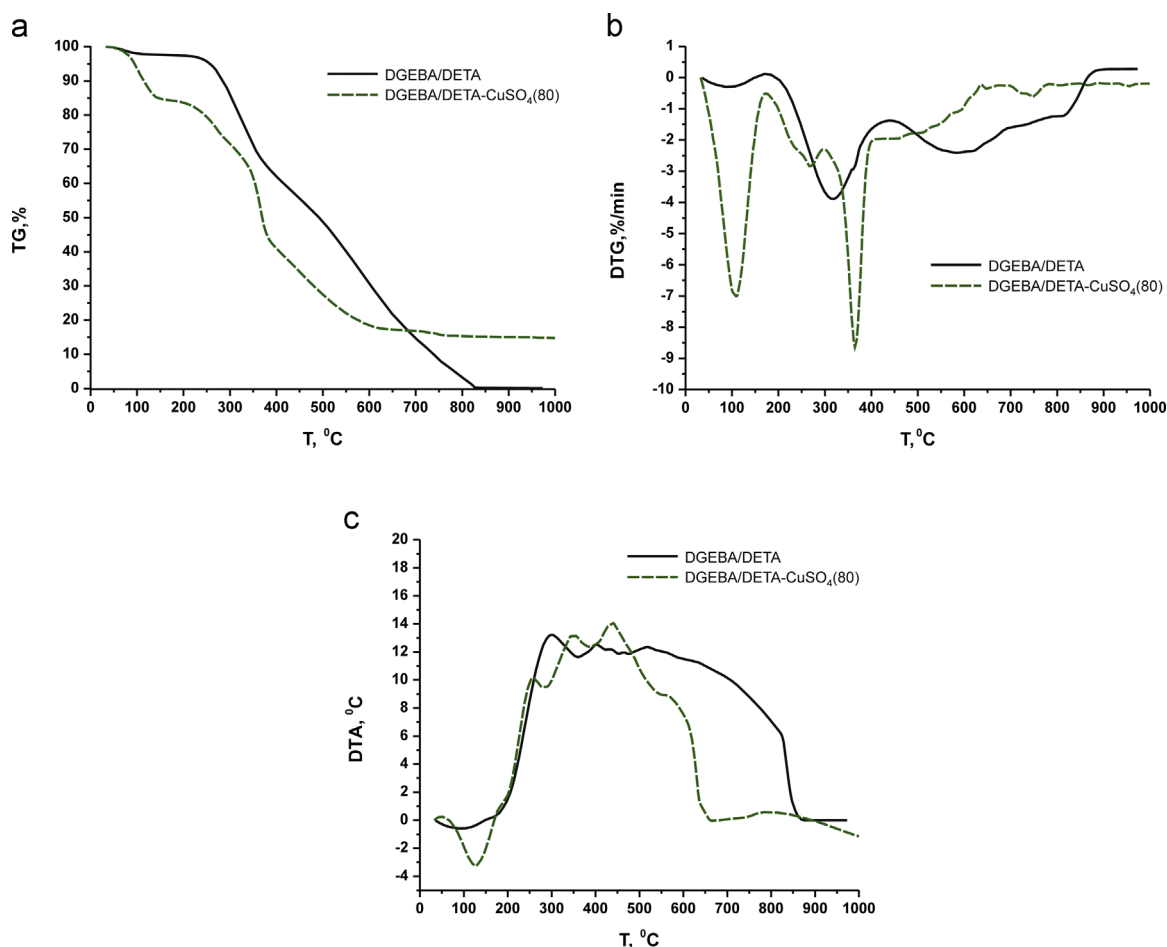


Fig. 4. TG (a), DTG (b) and DTA (c) curves for DGEBA/DETA and DGEBA/DETA-CuSO₄ (80) samples.

Table 3

The combustibility group indexes of epoxy-amine composites.

Sample	TC (°C)	MT (°C)	$\Delta\tau$ (s)	WL (wt%)	CG
DGEBA/DETA	200	667	150	89.0	CA
DGEBA/DETA-CuSO ₄ (5)	200	491	160	79.2	MA
DGEBA/DETA-CuSO ₄ (80)	200	440	215	78.6	MA

Note: TC, the temperature of ceramic chamber before sample bringing; MT, the maximum increment of temperature; $\Delta\tau$, the duration of flame action; WL, the weight loss of sample; CG, the combustibility group (CA—combustion agent, MA—moderately inflammable agent)

The TG curve (Fig. 4a) of thermal degradation of epoxy-amine polymer-DGEBA/DETA is divided into four stages. The first stage happening in temperature range from 20 to 180 °C is accompanied by an appearance of the endothermic effect at the respective portion of DTA curve (see Fig. 4c) which is in good accord with emission of the volatile substances uncombined into framework of polymer. The weight loss at this stage amounts to 3.1 wt%. The second stage occurs in the temperature range from 180 to 360 °C ($\Delta m=32$ wt%). At this stage arisen exothermic effect with maximum at 300 °C belongs to the thermal-oxidative breakdown of DGEBA/DETA polymer. The mechanism of this process is free-radical with participation of alkyl particles ($\cdot R$) and peroxide particles ($\cdot O-OR$) and with formation of hydroperoxides (HO-OR) [28,29]. The combustion of thermal degradation products of organic component of polymer takes place at the third stage in temperature range from 360 to 460 °C ($\Delta m=12.1$ wt%). On this portion of DTA curve is appeared exothermic maximum at 400 °C. Complete combustion of pyrolytic residue of DGEBA/DETA

happens at the fourth stage of thermolysis in temperature range from 460 to 900 °C ($\Delta m=52$ wt%) with exothermic effect.

However, the thermal degradation of modified epoxy-amine composite (DGEBA/DETA-CuSO₄ (80)) is more complicated and divided into six stages (see Fig. 4a). The first stage occurs in temperature range from 20 to 175 °C; it is accompanied by an appearance of the endothermic effect at DTA curve with extreme peak at 132 °C (see Fig. 4c). At this stage happens a removal of coordinated water and emission of the volatile substances uncombined into framework of polymer ($\Delta m=16$ wt%). At second stage occurring in temperature range from 175 to 245 °C takes place the partial decomposition of fastened DETA molecule with simultaneous dehydrogenization. This is exothermic process and as in the event of DETA-CuSO₄ the weight loss at this stage amounts to 4.2 wt%. In temperature range from 245 to 300 °C (the third stage) happens the thermal breakdown of coordination bonds that is complicated by thermal-oxidative destruction of organic constituent part of DGEBA/DETA-CuSO₄ (80) polymer sample ($\Delta m=8.3$ wt%). On this portion of DTA curve arises exothermic effect with maximum at 258 °C. It should be noted that little weight loss for sample of DGEBA/DETA-CuSO₄ (80) at II and III stage of thermolysis in temperature range from 175 to 300 °C in comparison with DGEBA/DETA in the same temperature range can be explained by more firm structure of polymer which arises from additional interlinking of CuSO₄ with DETA. It is the reason of increase in thermal stability of the given sample. The fourth stage covers the temperature range from 300 to 400 °C where the thermal-oxidative destruction of organic constituent part of sample takes place. It is accompanied by considerable weight loss

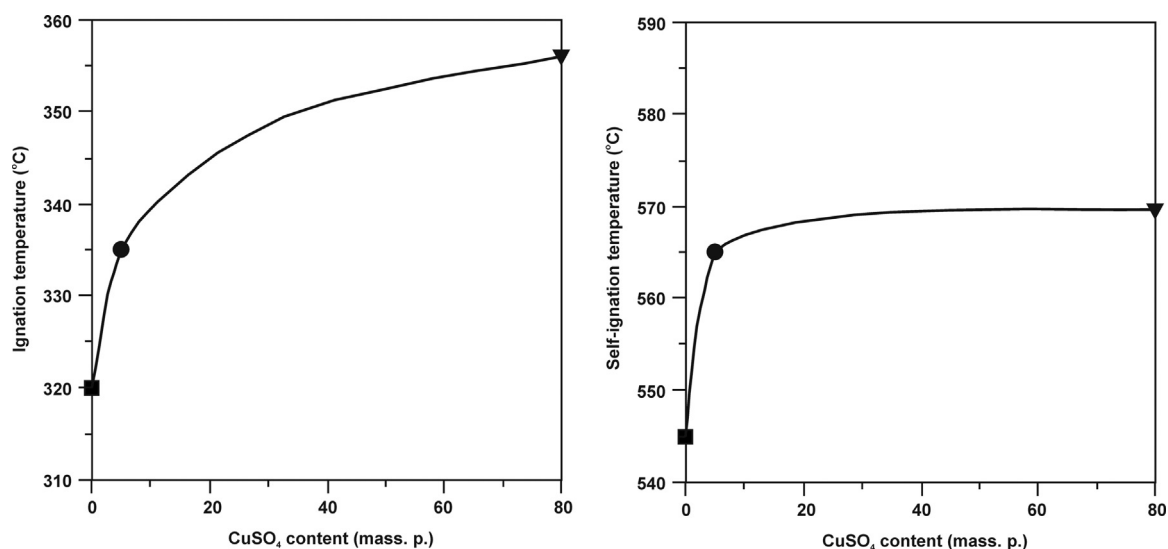


Fig. 5. Ignition point (a) and self-ignition point (b) of epoxy-amine composites (■—DGEBA/DETA, ●—DGEBA/DETA-CuSO₄ (5) and ▼—DGEBA/DETA-CuSO₄ (80)).

($\Delta m=28$ wt%) and appearance of exothermic effect (see curve of DTA, Fig. 4c) with maximum at 353 °C. The combustion of the thermal degradation residue of DGEBA/DETA-CuSO₄ (80) happens at the fifth stage of thermolysis in temperature range from 400 to 535 °C ($\Delta m=20.1$ wt%) with perceptible exothermic maximum at 437 °C. The final combustion of pyrolytic residue of this sample occurs at the sixth stage in temperature range from 535 to 660 °C ($\Delta m=6.3$ wt%).

Comparative analysis of DTA curves obtained at studying of the thermal degradation of DGEBA/DETA and DGEBA/DETA-CuSO₄ (80) is displayed in Fig. 4c. The maximum of exothermic effect that is responsible for thermal-oxidative destruction of organic constituent part for DGEBA/DETA-CuSO₄ (80) (350 °C) in comparison with DGEBA/DETA (300 °C) is shifted into area of higher temperatures. It testifies the increased thermal stability of modified epoxy-amine composite. Furthermore, combustion of pyrolytic residue of organic constituent part of DGEBA/DETA-CuSO₄ (80) occurs in more restricted temperature interval than it is for DGEBA/DETA. So, if combustion of pyrolytic residue in case of DGEBA/DETA is completed at 900 °C, then combustion of DGEBA/DETA-CuSO₄ (80) ceases at 660 °C. The cause of it consists in strong interlinking of noncombustible inorganic salt with organic constituent of epoxy-amine polymer. This specifies structure of polymeric materials with suppressed combustibility.

The combustibility group for modified epoxy-amine composites has been determined by “ceramic tube” method. The measurement results of filled epoxy-amine polymers depending on CuSO₄ content are given in Table 3. The obtained data reveals that combustibility of modified epoxy-amine polymers even with minor content of copper(II) sulfate (5 mass. p. of CuSO₄ per 100 mass. p. of DGEBA) is considerably suppressed in comparison with unmodified composites. Maximum increment of temperature exceeds 60 °C while weight loss amounts to 60% for all samples. Duration of reaching of maximal combustion temperature of gaseous products is in the range of 0.5–4 min. It means that studied polymer composites belong to class of substances with moderate inflammability. Besides, the maximal temperature of gases combustion depends on modifier content (CuSO₄). Temperature in filled epoxy-amine composites versus ordinary epoxy-amine polymers lowers by 176 and 227 °C for 5 mass. p. and 80 mass. p. CuSO₄, respectively. At the same time, the weight loss of sample at addition of modifier decreases by 9.8% and 10.4 wt%.

The measurement results of t_{ign} and $t_{\text{self-ign}}$ of epoxy-amine composites as well as influence of additional quantity of modifier

onto values of respective temperatures are represented in Fig. 5. The values of ignition point and self-ignition point for ordinary (unmodified) epoxy-amine polymer amount to 320 and 545 °C, respectively. The t_{ign} (or $t_{\text{self-ign}}$) increases to 356 °C (or 569 °C) with the addition of copper(II) sulfate (80 mass. p.). Thus, obtained data once again confirms that combustibility of epoxy-amine polymers is appreciably suppressed at their filling by anhydrous copper(II) sulfate.

4. Conclusions

Thus, the study of processes relating to polymerization in system DETA (hardener) – DGEBA (binder) – CuSO₄ (modifier) has revealed that noncombustible inorganic salts, in particular, anhydrous copper(II) sulfate, can effectively lower combustibility of modified epoxy-amine composites (DGEBA/DETA-CuSO₄). Here, the effectiveness of combustibility suppressing of epoxy-amine polymers depend on CuSO₄ interlinking strength with amine-hardener (DETA-CuSO₄ chelation) that is accompanied by formation of Cu–N bonds within framework of polymeric composite. Therefore, in the course of burning, the considerable amount of thermal energy outgoing from flame should be expended mainly onto destroying of these chelate bonds. TGA data obtained for DETA-CuSO₄, DGEBA/DETA and DGEBA/DETA-CuSO₄ in atmosphere of air and results of CT measurement are better evidence of it. Thus, DETA-CuSO₄ chelate complex can be used as the flame retardant at elaborating of polymeric materials with suppressed combustibility.

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