



Novel CuSiF_6 -coordinated epoxy–amine composites with reduced combustibility: Elaboration, thermal-oxidative behavior, and ignition susceptibility

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Abstract

In the *DGEBA*–*PEPA*– CuSiF_6 system (*DGEBA* is diglycidyl ether of bisphenol A, *PEPA* is polyethylenepolyamine), a new flame-retardant hardener for epoxy resins in the form of a chelate complex labeled as *PEPA*– CuSiF_6 was synthesized and incorporated into the framework of *DGEBA* to make a range of CuSiF_6 -containing epoxy–amine composites (*EA*– CuSiF_6) with reduced combustibility. The resulting *EA*– CuSiF_6 composites were characterized using FTIR spectroscopy, thermogravimetric analysis (TGA), and temperatures of ignition and self-ignition measuring. TGA results showed that the thermal decomposition of *PEPA*– CuSiF_6 ends at 368 °C, and after ignition of its organic component, the maximum temperature of the gaseous products of combustion reached 488 °C. TGA of *EA*– CuSiF_6 (22) sample confirms that the incorporation of *PEPA*– CuSiF_6 into *DGEBA* significantly increases the thermal stability and reduces the flammability of the epoxy–amine composites. The combustibility of the epoxy–amine composite samples was investigated using “Ceramic tube” (CT) method. Results of CT measurement reveal that the maximal temperature of combustion gases for *EA*– CuSiF_6 (66) in comparison with unmodified epoxy–amine polymer (EAP) appreciably goes down and relative loss of the mass lessens. The measured ignition and self-ignition temperatures showed that depending on the amount of CuSiF_6 added, t_{ignition} and $t_{\text{self-ignition}}$ for this type of composites increase by 15–34 °C and 25–58 °C, respectively, compared to EAP that does not contain additives.

Keywords Flame-retardant hardener · Copper(ii)-containing epoxy–amine composites · Reduced combustibility · Thermal-oxidative behavior · Ignition susceptibility

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Introduction

It is known that the potential fire hazard of buildings and constructions can be assessed by the level of fire load, that is, by the amount of combustible materials, which are in the premises [1]. One of the main causes of deaths in fires is also known to be acute poisoning as a result of thermal-oxidative destruction of building materials manufactured out of polymers including epoxy polymers [2]. Therefore, the creation of a new generation of polymer materials with reduced combustibility is an extremely important task that requires an urgent solution using the skills of both polymer chemistry and materials science.

Most of the known polymer materials are characterized by a rather low temperature of thermal decomposition, high flame propagation rates, and intense smoke emission containing a large concentration of toxic products [3]. The reason for this is the high content of organic components in polymers, which makes it impossible to obtain completely non-combustible polymers. However, the development of polymer materials with reduced combustibility is a solvable problem.

To reduce the combustibility of polymer materials, including polymers based on epoxy [4–17], flame retardants are used [18–20]. Among them, reactive flame retardants are more in demand than additive flame retardants, the use of which is gradually decreasing. In contrast to additive flame retardants, which are mechanically held in a polymer matrix, reactive flame retardants chemically bond to the polymer at the preparation stage. Moreover, reactive flame retardants are also able to maintain the physical, mechanical, and physicochemical properties of polymers at the proper level.

Among the large number of flame retardants used to reduce the combustibility of epoxy polymers, amino complexes of transition metals deserve special attention. There in particular is a report in [21] about the additives of ammonia, monoethanolamine, and diethanolamine complexes of copper(II) cyanurate and diallyl isocyanurate, improving the fire resistance of epoxy resins.

There is a report in [22] that the macromolecular intumescent flame retardant prepared from formaldehyde, melamine, urea, phosphoric acid, pentaerythritol, and zinc oxide was used to reduce the combustibility of epoxy resins. The presence of this flame retardant in the epoxy–amine composite contributes to a decrease in smoke density, an initial decomposition temperature of the composite, and an increase in the amount of zinc and phosphorus in the residue.

A rather complicated dependence of the limiting oxygen index on the metal content [23] is observed in epoxy polymers modified with triethylenetetramine (*teta*) complexes of various metal salts— $[\text{Ce}(\textit{teta})](\text{CH}_3\text{COO})_3$, $[\text{Ce}(\textit{teta})_2](\text{SO}_4)_3$, $[\text{Co}(\textit{teta})]\text{Cl}_2$, $[\text{Mn}(\textit{teta})]\text{Cl}_2$, $[\text{Ni}_2(\textit{teta})_3]\text{Cl}_4$, $[\text{Ni}_2(\textit{teta})_3](\text{SO}_4)_3$, and $[\text{Cr}(\textit{teta})](\text{CH}_3\text{COO})_3$. In all these cases, the nature of metal and anion determines the nature of this dependence.

It was proposed to use 3(5)-methylpyrazole complexes of transition metal salts as fire retardants for epoxy composites based on diphenylolpropane diglycidyl ether, cured with *n*, *n'*-diaminodiphenylmethane. Epoxy composites containing 2.6–3.1 mass parts of one of the complexes per 100 mass parts of a binder have

not only high fire resistance, but also enhanced physical and mechanical properties. These data also show that composites containing complexes of cobalt and manganese have the greatest fire retardant effect, while nickel complexes have the least [24].

Tris(halogenalkyl)phosphate complexes of metal chlorides and *teta* were used as initiators of curing of epoxy composite prepared from diglycidyl ether of bisphenol A (*DGEBA*), phosphate modifier, and amine hardener [25]. These additives strengthen polymers and give them flame retardant properties. For example, epoxy composites, modified with tris(halogenalkyl)phosphate complexes of SnCl_2 (or TiCl_2), are not able to burn after the flame has been removed.

Inorganic copper(II) salts, whose metal atoms are able to exhibit a high electron-acceptor ability for donor heteroatoms of organic substances such as N, S, and O, can be very efficient fire retardants. The development of new-generation flame-retardant hardeners for epoxy resins in the form of crystalline chelate complexes of inorganic copper(II) salts with polyamines is described in detail in [26–29]. The studies presented in [30–33] confirm the ability of such copper(II) chelate complexes to efficiently suppress burning of the epoxy–amine composites. In particular, it has been shown that epoxy polymers modified with polyamine copper(II) chelate complexes have higher ignition and self-ignition temperatures, lower flame propagation and smoke formation rates, and lower temperatures for gaseous products of combustion in comparison with an epoxy–amine polymer (EAP), which do not contain the polyamine copper(II) chelate complexes. It should be noted that the use of such fire-resistant hardeners does not impair the basic physical and mechanical properties of epoxy–amine composites [34–36].

In view of the above, it has been undertaken an attempt to develop a new type of the polymer material with reduced combustibility, the basis of which is an epoxy–amine composite containing a non-combustible *d*-metal inorganic salt—copper(II) hexafluorosilicate—as a flame retardant. For this, the $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$ chelate complex labeled as *PEPA*– CuSiF_6 [37] (*PEPA* is polyethylenepolyamine containing ethylenediamine (*eda*) and diethylenetriamine (*deta*)) was synthesized and used as a flame-retardant hardener of epoxy resins.

The article reports the development of a new type of epoxy–amine composites modified by CuSiF_6 (EA– CuSiF_6) with reduced combustibility and the study of their thermo-oxidative properties and ignition susceptibility in flame temperature modes.

Experimental part

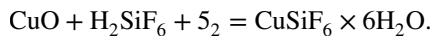
Reagents

To develop EA– CuSiF_6 composites, the following chemicals are required: the flame-retardant agent—copper(II) hexafluorosilicate hexahydrate ($\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$) (light blue crystals, $\Delta t_{\text{dehydration}} = 100$ °C, $\Delta t_{\text{decomposition}} = 174\text{--}446$ °C); the curing agent of epoxy resins—*PEPA* (yellow transparent viscous liquid, $\overline{M}_r = 120$, $d^{20} = 1.011$ g cm⁻³, $n_D = 1.5120$, $t_{\text{boiling}} = 250$ °C, $t_{\text{flash}} = 110$ °C, $t_{\text{ignition}} = 136$ °C, $t_{\text{self-ignition}} = 393$ °C); the binder—*DGEBA* (colorless resin, ED-20 grade with

almost 22% epoxy groups content, viscosity value from 12 to 18 Pa·s (at 25 °C), $M_r = 390\text{--}430$ ($\overline{M}_r = 410$). All reagents have been purchased through commercial sources and used as received without further purification.

Synthesis of the flame-retardant hardener

The flame-retardant hardener in the form of the solid $PEPA\text{--}CuSiF_6$ chelate complex was synthesized by direct interaction of anhydrous copper(II) hexafluorosilicate with $PEPA$ [37, 38]. First, copper(II) hexafluorosilicate hexahydrate was synthesized by the reaction:



Black CuO powder (80 g, 1 mol) was dissolved in a 40% aqueous solution of hexafluorosilicate acid (320 g) to obtain a homogeneous dark blue solution. After water evaporation, dark blue hexagonal crystals of $CuSiF_6 \cdot 6H_2O$ appeared. Anhydrous salt ($CuSiF_6$) was obtained by drying $CuSiF_6 \cdot 6H_2O$ at a temperature of 110 °C in an oven until a white powder with a barely perceptible bluish tint formed.

The resulting white $CuSiF_6$ powder (205 g, 1 mol) was placed in a vessel, and $PEPA$ was added in a small excess (178 cm³, 1.5 mol). The mixture was then triturated until a homogeneous, dark blue suspension appeared. This suspension was left for 48 h at room temperature to obtain crystalline $PEPA\text{--}CuSiF_6$. The product yield was 360 g (98%).

Preparation of $EA\text{--}CuSiF_6$ composites

The quantitative ratio of the substances required to obtain $EA\text{--}CuSiF_6$ composites is given in Table 1. Composites can be prepared in two ways. The first way involves direct participation in the epoxy polymerization of the flame-retardant hardener. For this, $PEPA\text{--}CuSiF_6$ (36.8 g) is added to $DGEBA$ (100 g). The resulting mixture is thoroughly stirred until a homogeneous aesthetically attractive dark blue thick mass is formed. The composite material obtained in this way is indicated in Table 1 as $EA\text{--}CuSiF_6(22)$.

Table 1 Stoichiometry of $EA\text{--}CuSiF_6$ composites

Composite	$DGEBA/PEPA/CuSiF_6$	
	Molar ratio	Mass ratio
EAP	2.5:1:0	100:12:0
$EA\text{--}CuSiF_6(11)$	2.5:1:0.5	100:12:11
$EA\text{--}CuSiF_6(22)$	2.5:1:1	100:12:22
$EA\text{--}CuSiF_6(44)$	2.5:1:2	100:12:44
$EA\text{--}CuSiF_6(66)$	2.5:1:3	100:12:66
$EA\text{--}CuSiF_6(88)$	2.5:1:4	100:12:88

However, most composites were obtained in a different way, the essence of which was to mix a certain amount of all three components (Table 1) abiding by the determinate sequence of their addition. In particular, *DGEBA* and *PEPA* are first mixed in a mass ratio of 100:12 and stirred for 15 min. Then, an appropriate amount of anhydrous CuSiF_6 (this is 11, 22, 44, 66, and 88 g) is added to the *DGEBA*–*PEPA* mixture and again thoroughly stirred to a homogeneous consistency formed. The resulting samples of EA– CuSiF_6 composites are assumed dark blue color due to complexation.

The polymer composite that does not contain CuSiF_6 also has been prepared of the binding agent (*DGEBA*) and curing agent (*PEPA*), according to the standard technology; the EAP is light yellow and clear.

Appropriate molds were filled with the resulting mixtures, after which they were left at room temperature for curing. After 24 h, all cured samples were examined.

Characterization

IR spectroscopy

FTIR patterns were made on the PerkinElmer Spectrum Two spectrometer in the spectral range from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1} . FTIR spectra were recorded on solid samples for *PEPA*– CuSiF_6 , EAP, and EA– CuSiF_6 (22) composite pressed into tablets with spectroscopically pure KBr, or on a liquid sample for *PEPA* using KBr cuvette.

Thermogravimetric measurements

Thermal gravimetric analysis (TGA), differential thermogravimetric (DTG) analysis, and differential thermal analysis (DTA) for samples of $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$, *PEPA*, *PEPA*– CuSiF_6 , EAP, and EA– CuSiF_6 were performed on the thermal analyzer Q-1500D (F. Paulik, J. Paulik, L. Erdey system) in the temperature range from 25 to 1000 °C with a heating rate of 5 °C/min.

All measurements were carried out in a dynamic mode in an oxidizing atmosphere of air. The initial weight of each sample was 100 mg. Alumina was used as a standard.

Combustibility tests

Combustibility parameters for samples of EA– CuSiF_6 (66) and EAP (Table 1) were determined according to All-Union State Standard 12.1.044–89 [39] using the “Ceramic tube” apparatus displayed in Fig. 1. The apparatus consists of a rectangular ceramic reaction chamber, the inner surface of which is covered with two layers of aluminum foil. The reaction chamber is placed vertically on a support block, where a gas burner is inbuilt. The position of the sample is fastened in the center of the reaction chamber by a holder. Each sample with 150 mm length, 60 mm width, and 5 mm thickness was wrapped in fiberglass cloth.

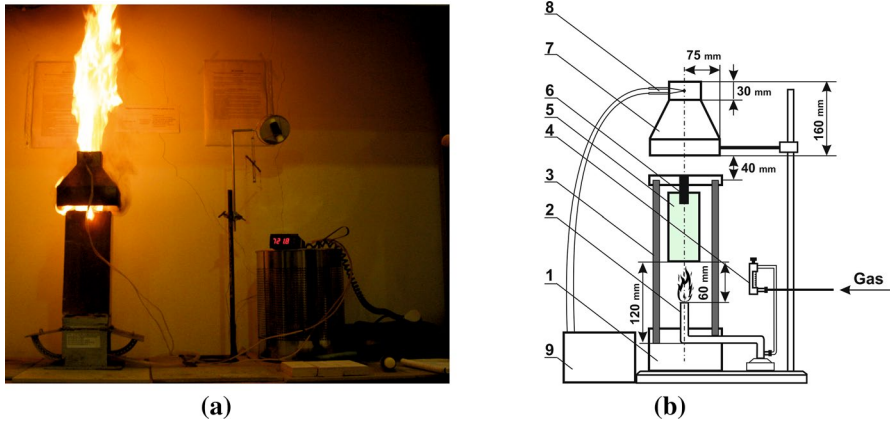


Fig. 1 **a** Photograph of combustibility test chamber (the ceramic tube method); **b** schematic of the “Ceramic tube” apparatus: 1—supporting block; 2—gas burner; 3—ceramic tube; 4—gas flowmeter; 5—test sample; 6—sample holder; 7—funnel cover; 8—thermocouple; 9—potentiometer

The measurements were carried out on samples taken in triplicate. The values obtained at least from three measurements were averaged. Samples before testing were air-conditioned and weighed; next, these were placed into ceramic tube that in advance was heated to temperature of 200 °C by means of gas burner flame. The maximal temperature of the combustion gases (T_{\max}) and time of T_{\max} reaching ($\Delta\tau$, s) were experimentally measured. The maximal increment of temperature (ΔT_{\max} , °C) and relative loss of the mass (Δm , %) have been determined as

$$\Delta T_{\max} = T_{\max} - 200;$$

$$\Delta m = \frac{m_0 - m_b}{m_0} \cdot 100\% ,$$

where m_0 and m_b are mass (g) of sample up to and after testing, respectively.

The combustibility group of the substances was specified by means of the ΔT_{\max} and Δm values, while the flammability of the substances was assessed by the value of $\Delta\tau$.

Flammability tests

The ignition (t_{ignition}) and self-ignition ($t_{\text{self-ignition}}$) temperatures for samples of EAP, EA-CuSiF₆(11), EA-CuSiF₆(22), EA-CuSiF₆(44), EA-CuSiF₆(66), and EA-CuSiF₆(88) composites (Table 1), as well as PEPA and PEPA-CuSiF₆, were measured on the TF device in accordance with ASTM D1929-16 [40]. Three specimens were tested from each group of composites; the resulting values were averaged.

Results and discussion

Epoxy–amine polymerization in the DGEBA–PEPA–CuSiF₆ system

A distinguishing feature of epoxy–amine polymerization running in the DGEBA–PEPA–CuSiF₆ system is that the curing agent is PEPA coordinated with CuSiF₆, which has flame retardant properties. A flame-retardant hardener in the form of the PEPA–CuSiF₆ complex was isolated from this system and characterized with FTIR (Fig. 2) [37]. Cu(II)–amine bonding can be detected by the shift of the vibration frequencies of N–H bonds. Figure 2a shows the FTIR pattern of PEPA before bonding to CuSiF₆. The appearance of absorption bands in the high-frequency region (3372 and 3254 cm⁻¹) is due to the N–H stretching of –NH₂ groups, and the band at 3210 cm⁻¹ is associated with the N–H stretching of the –NH– group. The bending frequency of N–H bonds appears at 1600 cm⁻¹ [41].

After the formation of Cu(II)–N coordination bonds, the shift of the corresponding absorption bands is observed (Fig. 2b). Due to complexation, one of the frequencies, caused by the N–H stretching of –NH₂ groups, appears at 3416 cm⁻¹, and the other two bands are shifted to the region of lower frequencies (3238 and

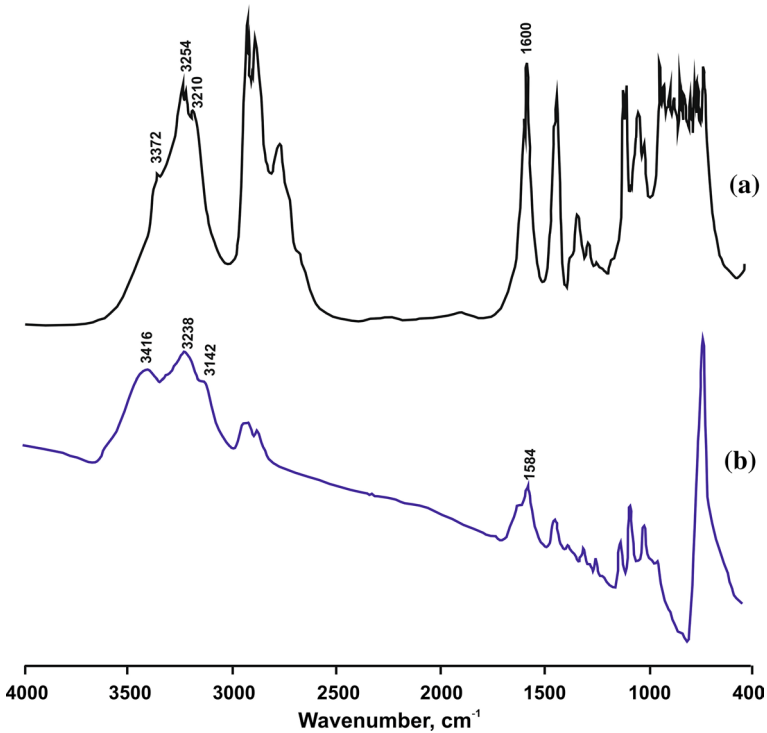


Fig. 2 FTIR pattern of PEPA (a) and PEPA–CuSiF₆ (b)

3142 cm^{-1}); the absorption band at 1548 cm^{-1} , associated the N–H bending, is also shifted to low-frequency region.

To prove the involvement of *PEPA*– CuSiF_6 in the formation of the epoxy polymer framework, FTIR spectra were recorded for both EAP and EA– $\text{CuSiF}_6(22)$ (Fig. 3).

It is known that epoxy–amine polymerization is accompanied by the disappearance of N–H bonds, the formation of N–C bonds, and the appearance of new O–H bonds. Figure 3a shows FTIR spectra recorded for EAP, where, in addition to the frequencies characteristic for *DGEBA* [42], there is an absorption band (3332 cm^{-1}) responsible for stretching of O–H bond [43, 44]. Thus, the curing of epoxy polymers with *PEPA* is the result of cross-linking of the amino groups of the hardener and the epoxy groups of the binder (see Scheme 1).

However, the FTIR spectra of EA– $\text{CuSiF}_6(22)$ (Fig. 3b) clearly show that the absorption band (3323 cm^{-1}) related to the O–H stretching is noticeably weakened due to Cu(II)–O bonding. This can be explained by the involvement of an additional oxygen atom in the coordination sphere of the chelated Cu^{2+} ion due to the Cu(II)–OH coordination [45], as shown in Scheme 2.

An analysis of the FTIR spectra showed that the polymerization proceeding in the *DGEBA*–*PEPA*– CuSiF_6 system results in the formation of copper(II)-coordinated epoxy–amine composites. It is accompanied by the interlinking of CuSiF_6 and *PEPA*

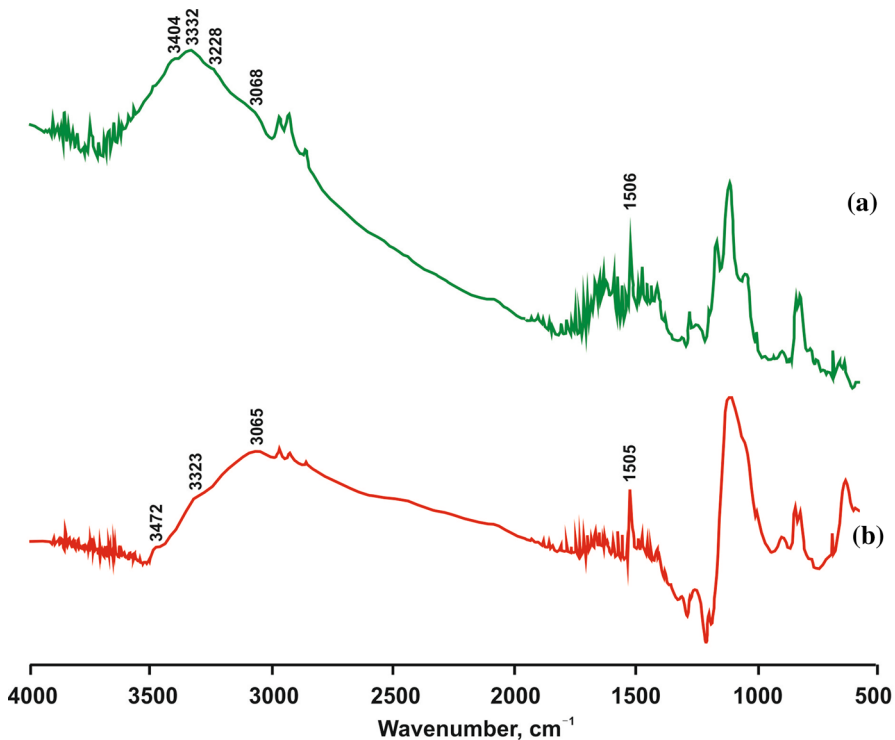
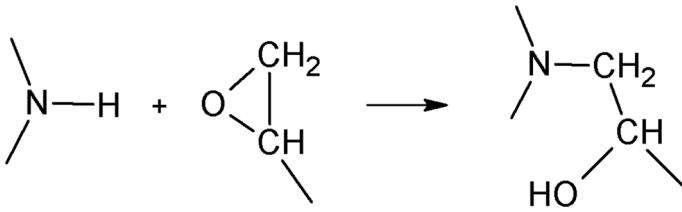
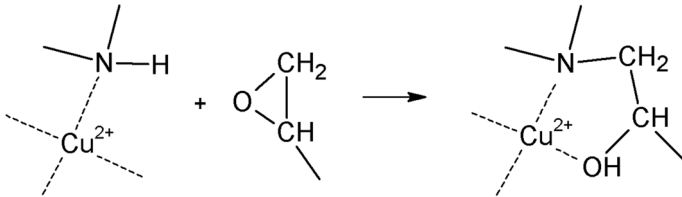


Fig. 3 FTIR pattern of EAP (a) and EA– $\text{CuSiF}_6(22)$ (b)

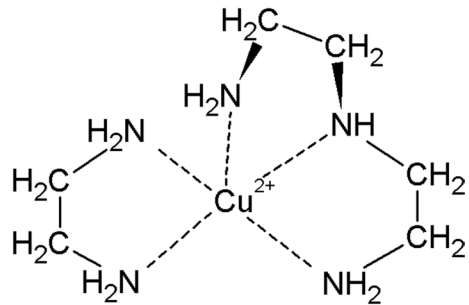


Scheme 1 Curing of epoxy polymers with *PEPA*



Scheme 2 Curing of epoxy polymers with *PEPA*- CuSiF_6

Scheme 3 $[\text{Cu}(\text{eda})$
 $(\text{deta})]^{2+}$ complex cation of
PEPA- CuSiF_6



into *PEPA*- CuSiF_6 chelate complex [37] (see Scheme 3), which has the properties of both flame retardant and hardener of epoxy resins.

Thermal decomposition of *PEPA*- CuSiF_6

To determine the effectiveness of the flame-retardant hardener, a comparative assessment of the thermal behavior of the traditional hardener of epoxy resins (*PEPA*) with developed (*PEPA*- CuSiF_6) was carried out. Since thermal decomposition is a main prerequisite to flame any substance in a condensed state, the thermo-oxidative destruction of *PEPA*, CuSiF_6 , and *PEPA*- CuSiF_6 was studied in the first place.

The results of the TGA presented in Fig. 4 show that *PEPA* completely evaporates in the temperature range from 20 to 170 °C; this process is endothermic (see DTA curve).

The crystalline copper(II) hexafluorosilicate hexahydrate ($\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$) decomposes in two stages (Fig. 5). The temperature range of the first stage of thermolysis is

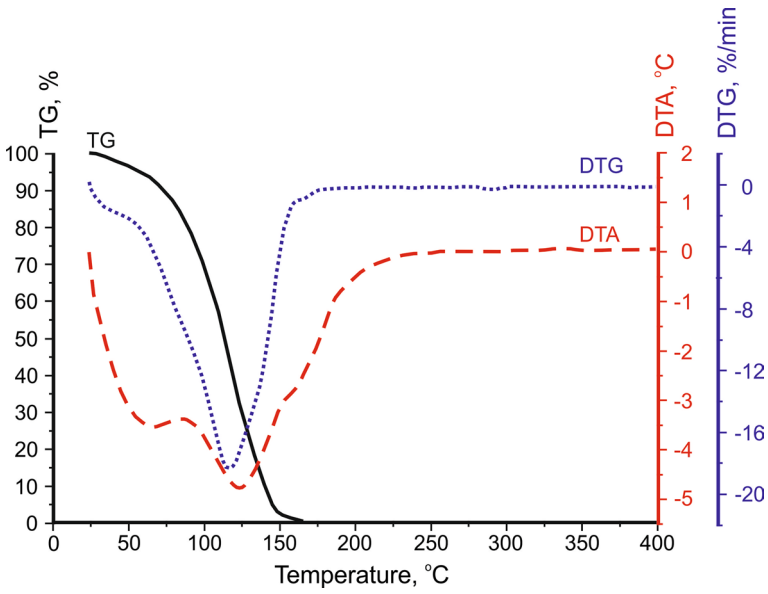


Fig. 4 TG, DTG, and DTA curves of PEPA

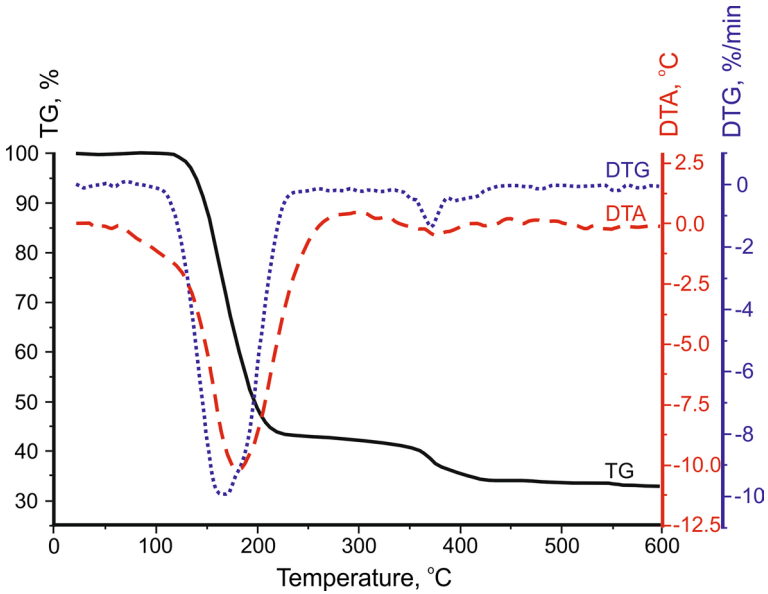


Fig. 5 TG, DTG, and DTA curves of $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$

Table 2 Thermal decomposition of $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$

Sample	Stage	Temperature range, °C	Experimental weight loss, wt%	Calculated weight loss, wt%
$\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$	I	20–174	34.0	34.4
	II	174–446	32.8	33.1

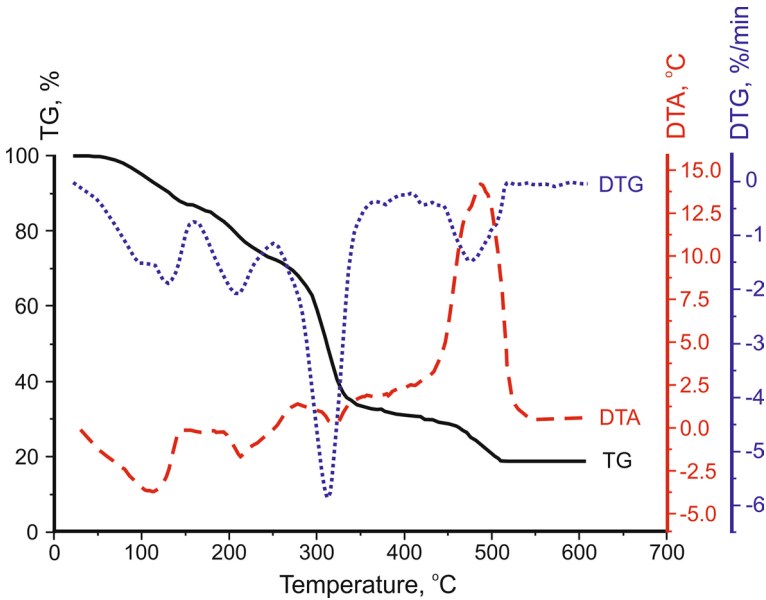
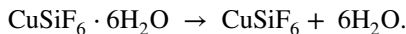


Fig. 6 TG, DTG, and DTA curves of *PEPA*– CuSiF_6

from 20 to 174 °C; the weight loss is 34.0 wt%. The endothermic effect is observed on the DTA curve of this temperature range. This correlates well with the loss of six molecules of crystallization water:



The second stage of decomposition of the already dehydrated CuSiF_6 occurs in the temperature range from 174 to 446 °C and is accompanied by the release of gaseous SiF_4 :



Weight loss on this stage is 32.8 wt%. The endothermic effect appears on the DTA curve. The resulting experimental data are in good agreement with the calculation results (Table 2).

Thermal-oxidative destruction of *PEPA*– CuSiF_6 is more complex and consists of four stages (Fig. 6). Thermolysis in the first stage occurs in the temperature range

from 20 to 160 °C, and the weight loss is 13.4 wt%. The DTA curve indicates the endothermic nature of thermolysis in the first stage with an extremum at 112 °C. The temperature range of the second stage is 160–253 °C. At this stage, weight loss is 14.3 wt%, and on the DTA curve the endothermic minimum is observed at a temperature of 212 °C. It is assumed that gaseous silicon fluoride is released at this stage. The third stage of thermolysis has a temperature range of 253–368 °C. Here, weight loss reaches its highest value of 39.9 wt%. This once more confirms that the third stage is responsible for the partial destruction of the amine component of the chelate complex. The *PEPA*–CuSiF₆ destruction process itself consists of several consecutive thermal-oxidative reactions, which appear on the DTA curve in the form of exothermic and endothermic extrema. The fourth stage (368–544 °C) corresponds to the complete combustion of the decomposition products of the organic components of *PEPA*–CuSiF₆. This is evidenced by the pronounced exothermic effect observed on the DTA curve with a maximum at 488 °C. Weight loss at this final stage is 15.3 wt% (Table 3).

It is known that *PEPA* molecules are kept in a condensed state only due to weak hydrogen bonds. Consequently, liquid *PEPA* is very easily converted to a vapor state, and at a suitable concentration of its vapors in air, it is highly flammable. In contrast, in the *PEPA*–CuSiF₆ chelate complex, *PEPA* molecules are strongly bonded to CuSiF₆ by Cu–N coordination bonds. This makes difficulties for the evaporation and then ignition of *PEPA*. All of the above is in good agreement with experimental data.

Thermal degradation of epoxy composites

In this section, we will consider the thermal behavior of polymer composites based on epoxy resins cured by both *PEPA* and *PEPA*–CuSiF₆ (Table 4).

The thermal degradation of EAP can be divided into four stages (Fig. 7). The first stage takes place in the temperature range from 20 to 180 °C. At this stage of thermal degradation, weight loss of the sample was not great and was 3.1 wt%. However, the endothermic effect was greatest at this stage (see DTA curve). As a result of the partial destruction of the polymer framework of the EAP, which apparently started at this stage, volatile particles are formed. The second stage includes temperatures of 180–360 °C. At that, weight loss is 32.0 wt%. This stage is characterized by the greatest exothermic effect at 300 °C that can be caused by the thermal-oxidative reactions. During the thermal degradation of EAP, free-radical particles

Table 3 Thermal decomposition of *PEPA*–CuSiF₆

Sample	Stage	Temperature range, °C	Weight loss, wt%
<i>PEPA</i> –CuSiF ₆	I	20–160	13.4
	II	160–253	14.3
	III	253–368	39.9
	IV	368–544	15.3

Table 4 Thermal degradation of EAP and EA–CuSiF₆(22)

Sample	Stage	Temperature range, °C	Weight loss, wt%
EAP	I	20–180	3.1
	II	180–360	32.0
	III	360–460	12.1
	IV	460–900	52.0
EA–CuSiF ₆ (22)	I	20–127	6.4
	II	127–320	21.2
	III	320–580	65.1

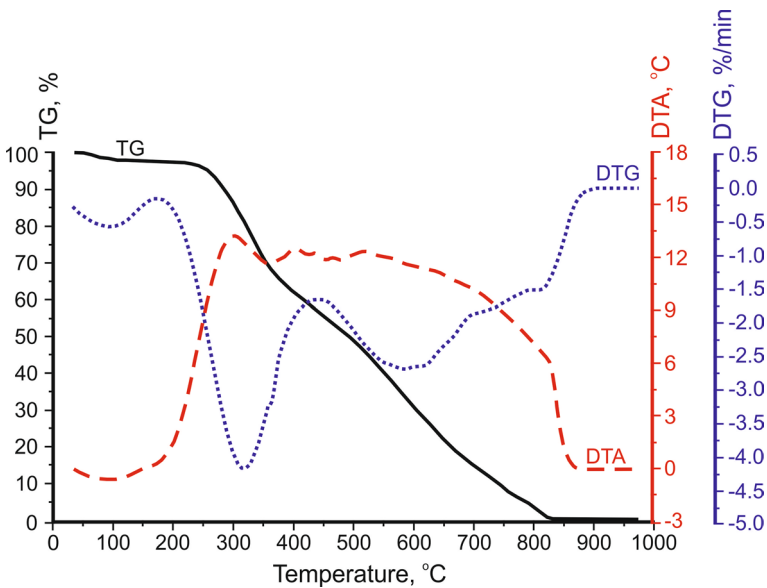


Fig. 7 TG, DTG, and DTA curves of EAP

are generated that is able to readily recombine forming hydrogen peroxides [46, 47]. The process of burning volatile products formed during the decomposition of EAP is considered in the third stage. The temperature range of this process is 360–460 °C, and the mass loss is 12.1 wt%. On the DTA curve, the exothermic maximum of this stage was recorded at 400 °C. The fourth stage includes a temperature range from 460 to 900 °C. Here, the pyrolytic residue burns completely. At this stage of thermal decomposition, the mass loss of the EAP sample is the greatest (52.0 wt%).

The process of EA–CuSiF₆(22) degradation is more complex, although it is represented by only three stages (Fig. 8). In the first stage of thermolysis of EA–CuSiF₆(22) (20–127 °C), as in the case of EAP (stage I), volatile particles are formed, which results in a weight loss of 6.4 wt%. This process is endothermic and has extremum at 82 °C (see DTA curve). However, unlike EAP, the

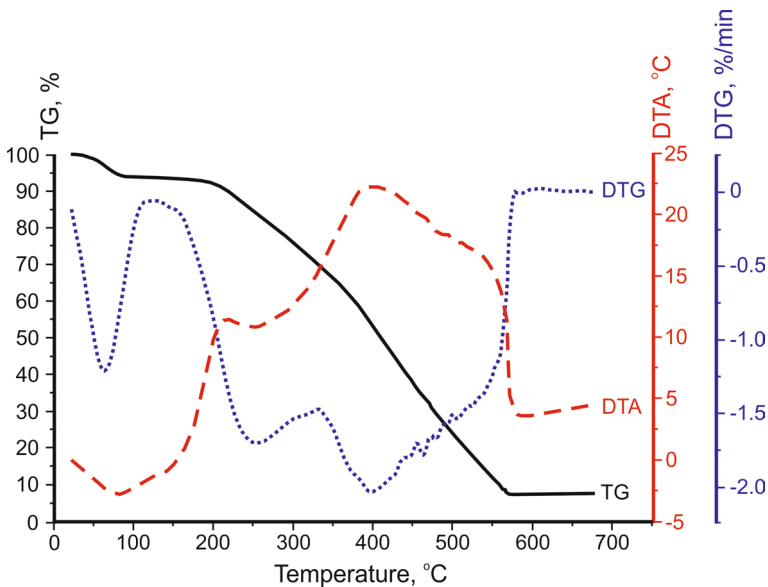


Fig. 8 TG, DTG, and DTA curves of EA-CuSiF₆(22)

thermolysis of EA-CuSiF₆(22) in the second stage (127–320 °C) is accompanied by both partial decomposition of the inorganic component of the composite, resulting in the release of SiF₄ particles, and thermal-oxidative degradation of the organic component of EA-CuSiF₆(22) ($\Delta m = 21.2$ wt%). At the DTA curve, this exothermic process has maximum at 210 °C.

The processes of the third stage are also exothermic and occur in the temperature range from 320 to 580 °C. This stage, where occurs the largest weight loss (65.1 wt%), covers a wide range of thermochemical reactions, including thermal decomposition of the coordination core of PEPA-CuSiF₆ embedded into the framework of the polymer matrix, thermal-oxidative degradation of the organic component of EA-CuSiF₆(22), and complete combustion of the pyrolytic residue of the polymer sample.

It should be noted that samples of EA-CuSiF₆ composites have higher thermal resistance than samples of ordinary EAP. This is evidenced by a less intense mass loss in the EA-CuSiF₆(22) sample ($\Delta m = 21.2\%$) than in the EAP sample ($\Delta m = 32.0\%$) during thermo-oxidative degradation in the second stage of thermolysis (Table 4). At this stage, the maximum weight loss of the epoxy composite cured by PEPA is 4.30%/min, and the epoxy composite cured by PEPA-CuSiF₆ is 1.75%/min (Table 5). In addition, the thermo-oxidative degradation of the EAP sample has the greatest exothermic effect with a maximum at 300 °C (see DTA curve in Fig. 7), while in the case of EA-CuSiF₆(22), the largest exothermic effect is observed at 394 °C; this corresponds to the combustion of the pyrolytic residue of the sample. Apparently, the slowdown in the thermal decomposition of epoxy-amine composites, which occurs when CuSiF₆ is added to the epoxy

Table 5 Comparative characteristics of thermal-oxidative degradation of EAP and EA–CuSiF₆(22)

Characteristic	Sample	
	EAP	EA–CuSiF ₆ (22)
Temperature of maximum exothermic effect, °C	300	394
Maximum rate of weight loss during thermo-oxidative degradation, %/min	4.23	1.75
Maximum rate of weight loss during combustion, %/min	2.72	2.02
Temperature of complete combustion, °C	900	580
Maximum weight loss, wt% at 400 °C	37.9	46.7
Maximum weight loss, wt% at 600 °C	69.3	92.7

polymer, is associated with the formation of Cu(II)–N coordination bonds, which require additional thermal energy for their break.

The pyrolytic residue of the organic component of the EA–CuSiF₆(22) sample burns in a narrower temperature range compared to the EAP sample. The combustion temperature of the carbonized residue is 580 and 900 °C for EA–CuSiF₆(22) and EAP, respectively. This indicates the self-extinguishing nature of the combustion of copper(II)-coordinated epoxy–amine composites.

Thus, the thermal-oxidative stability of EA–CuSiF₆ composites was significantly higher than that of EAP. Here, the stabilizing role belongs to copper(II) hexafluorosilicate, which exhibits an exceptional ability to complexation. The incorporation of this non-combustible inorganic salt in the structure of *DGEBA* facilitates to densify the polymer matrix and reduce the molecular mobility of internodes in the epoxy–amine network. This results in a decrease in the reactivity of polymer chains during thermal-oxidative degradation. The flame self-extinguishing effect observed for EA–CuSiF₆ composites results from such structural stabilization.

In turn, copper (II) hexafluorosilicate incorporated into the epoxy–amine matrix decomposes in the temperature range from 176 to 446 °C (Fig. 5) to form copper(II) fluoride and silicon(IV) fluoride. Since a large amount of non-combustible substances is formed, the thermal decomposition characteristics of the modified epoxy–amine polymers change. In particular, gaseous silicon(IV) fluoride can act as a combustion phlegmatizer and thus reduce the concentration of components of the combustible mixture. This, of course, affects the burning time of composite materials based on epoxy resins. The results of thermal analysis show that the combustion rate of the epoxy polymer in the presence of gaseous SiF₄ is reduced by 0.7% (Table 5).

Combustibility of EA–CuSiF₆

Given the fact that most fires occur from low-power ignition sources, it is very important to reduce the flammability of polymers. It is necessary to provide conditions under which polymeric materials would burn poorly, spread the flame more slowly, and ignite in more severe conditions. The fire hazard of the elaborated epoxy

Table 6 “Ceramic tube” measurement data

Sample	TC	T_{\max}	ΔT_{\max}	$\Delta\tau$	Δm	CG/FC
EAP	200	867 ± 5	667 ± 5	30 ± 1	89.0 ± 1	CS/HF
EA–CuSiF ₆ (66)	200	220 ± 5	20 ± 5	300 ± 1	4.9 ± 1	DC/–

TC (°C)—the temperature of the ceramic tube before the flame exposure to the samples, T_{\max} (°C)—the maximal temperature of combustion gases, ΔT_{\max} (°C)—the maximal increment of temperature, $\Delta\tau$ (s)—the time of maximal temperature reaching, Δm (%)—relative loss of the mass, CG— the combustibility group, FC—the flammability class (CS—combustible substance, DC—difficult-to-combustible, HF—highly flammable)

**Fig. 9** The samples of EAP (a) and EA–CuSiF₆(66) (b) after combustibility testing

polymer materials was assessed by their belonging to the combustibility group, that is, by the ability of the materials to burn and spread the flame. The combustibility group determined for EA–CuSiF₆(66) samples indicates the positive effect of added CuSiF₆ on the epoxy polymer’s ability to burn (Table 6).

The EAP sample (without flame retardant) is very easily and quickly ignited, burns with the release of extremely large amounts of smoke and soot, and is difficult to extinguish (Fig. 9a). Samples of composites containing flame retardant are more resistant to combustion. The addition of 66 weight fractions of CuSiF₆ especially

markedly improves the combustibility group of polymer materials. Since the maximum temperature increment for sample of the EA–CuSiF₆(66) composite does not exceed 60 °C (Table 6) and during combustion the relative loss of the mass is less than 60 wt.%, this composite can be assigned to the group of difficult-to-combustible materials. The maximum temperature of combustion gases is reached in 300 s. The EA–CuSiF₆(66) sample is able to burn only when directly exposed to an open flame and stops burning immediately after the flame is removed (Fig. 9b).

Flammability of EA–CuSiF₆

The obtained TGA data are in good agreement with the results of determining the ignition and self-ignition temperatures. The values of t_{ignition} and $t_{\text{self-ignition}}$, measured for crystalline PEPA–CuSiF₆, show that PEPA in the bonded state is turned into a practically non-combustible substance. So, PEPA after bonding to copper(II) hexafluorosilicate does not ignite or self-ignite even when the temperature reaches 450(1) and 600(1) °C, respectively. For comparison, the values of t_{ignition} and $t_{\text{self-ignition}}$ for free PEPA are 136(1) and 393(1) °C, respectively (Table 7).

Undoubtedly, this is due to coordination bonds arising between the amino groups of the combustible PEPA and the Cu(II) atoms of the non-combustible CuSiF₆. To break these Cu(II)–N bonds, it is necessary to absorb a large amount of thermal energy of the flame. But, to ignite the released PEPA, it is necessary to form a vapor–air mixture in which the concentration of saturated vapor of PEPA would exceed the lower concentration limit of flame propagation. However, even at temperatures > 450 °C, the ignition of PEPA vapors over molten PEPA–CuSiF₆ was not observed, which indicates an insufficient concentration of PEPA in the reaction mixture.

Adding flame retardant (CuSiF₆) to EAP samples significantly affects the ignition and self-ignition temperatures of the resulting composites. As can be seen from the data in Table 7, the EAP that does not contain CuSiF₆ is characterized by a minimum value of ignition and self-ignition temperatures. Depending on the amount of added CuSiF₆, the ignition temperature for EA–CuSiF₆ composites increases on average by 15–34 °C, and the self-ignition temperature increases by 25–58 °C compared to

Table 7 The results of the ignition temperature and self-ignition temperature measurements

Sample	Ignition temperature, °C	Self-ignition temperature, °C
PEPA	136 ± 1	393 ± 1
PEPA–CuSiF ₆	> 450 (without ignition)	> 600 (without self-ignition)
EAP	325 ± 1	530 ± 1
EA–CuSiF ₆ (11)	340 ± 1	555 ± 1
EA–CuSiF ₆ (22)	349 ± 1	565 ± 1
EA–CuSiF ₆ (44)	351 ± 1	582 ± 1
EA–CuSiF ₆ (66)	353 ± 1	583 ± 1
EA–CuSiF ₆ (88)	359 ± 1	588 ± 1

EAP. Epoxy–amine composites containing 88 parts by weight of CuSiF_6 have maximum ignition temperatures ($359(1)^\circ\text{C}$) and self-ignition temperatures ($588(1)^\circ\text{C}$). All these data are in good agreement with the results of DTA.

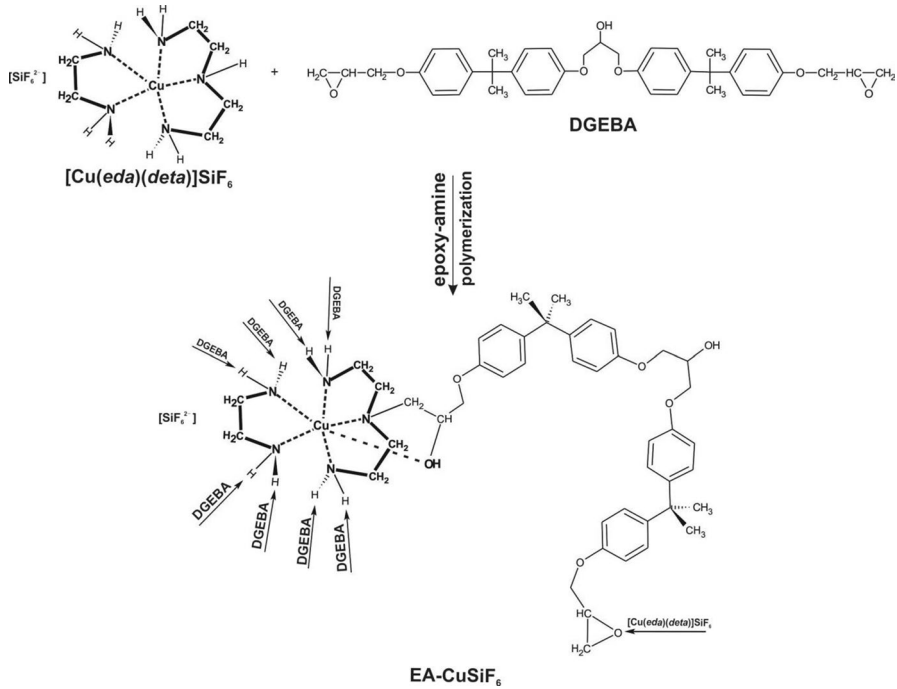
At low temperatures, the decomposition rate of EA– CuSiF_6 composites is half that of EAP. This is due to coordination bonding of the Cu(II)–N type, which takes place in the *DGEBA–PEPA–CuSiF₆* system at the stage of composite preparation. In contrast, maximum weight loss at 400 and 600 °C is higher for EA– CuSiF_6 composites than for EAP (Table 5). This seemingly contradictory dependence can be explained by an increase in the amount of non-combustible gases in the degradation products. In fact, the degradation of EA– CuSiF_6 composites results in the release of non-combustible gaseous SiF_4 that, apparently, is one of the main reasons for the increase in the ignition and self-ignition temperature for this type of composites.

Combustibility reduction mechanism

In this section, we would like to consider in detail the mechanism of the chemical effect of copper(II) hexafluorosilicate on the combustibility of CuSiF_6 -containing epoxy–amine composites. The interaction of *PEPA–CuSiF₆* results in the formation of the $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$ chelate complex (*PEPA–CuSiF₆*), which directly affects the flammability of the coordinated *PEPA*. So, if the ignition point for free *PEPA* is 136°C , then *PEPA* bonded to the chelate complex does not ignite at all. In other words, *PEPA* (epoxy hardener), which is a combustible substance, after bonding with copper(II) hexafluorosilicate (fire retardant), essentially turns into a non-combustible substance.

A similar tendency occurs with the ignitability of epoxy resins. In particular, the ignition point of the epoxy–amine polymer after the addition of CuSiF_6 increases from 325 to 359 °C. This is due to additional chemical bonds formed during the polymerization of epoxy–amines in the presence of a copper (II) salt. The results of quantum chemical calculations of the bonds energy in the square-pyramidal core of Cu(II), performed for the $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$ chelate complex [37], showed that the total energy of the five Cu–N bonds is $338.94\text{ kJ mol}^{-1}$. Thus, after the addition of the flame retardant (*PEPA–CuSiF₆*) to the epoxy oligomer (bisphenol A diglycidyl ether (*DGEBA*)), the coordinated *PEPA* (*eda + deta*) proceeds to function as a curing agent, polymerizing according to Scheme 4.

As a result, the framework of the polymer matrix contains a chemically bound non-combustible inorganic salt— CuSiF_6 . The coordination bonds that arise between the Cu(II) of this salt and the N atoms of the curing agent are responsible for reducing the combustibility of the epoxy–amine composite. To break these coordination bonds, it is necessary to expend a significant amount of heat energy. It is important to note that the final combustion of the pyrolytic residue of epoxy resin cured with *PEPA* alone is complete at 900 °C. However, combustion of the pyrolytic residue of epoxy resin cured with *PEPA–CuSiF₆* stops already at 580 °C. This may indicate the self-extinguishing nature of the combustion of epoxy–amine composites filled with copper(II) salts. Thus, this gives us reason to consider *PEPA–CuSiF₆* as



Scheme 4 Formation of EA-CuSiF₆ framework (expected structure)

an extremely effective flame-retardant hardener for reducing the combustibility of epoxy–amine composites.

Conclusions

The synthesis of the new fire-retardant hardener for epoxy resins in the form of the *PEPA*–CuSiF₆ chelate complex and the method of its incorporation into the framework of *DGEBA* served as the basis for the development of a new type of polymer materials with reduced combustibility based on CuSiF₆-containing epoxy–amine composites. The resulting EA–CuSiF₆ samples were characterized using FTIR, TGA, and ignition and self-ignition temperatures. FTIR revealed that in the *DGEBA*–*PEPA*–CuSiF₆ system, the formation of EA–CuSiF₆ composites is accompanied by chelation of the non-combustible inorganic salt (CuSiF₆) with *PEPA* in the polymer matrix, which ultimately leads to the suppression of their combustibility. TGA showed that the thermal-oxidative stability of EA–CuSiF₆ relative to EAP is significantly increased. The results of CT measurements showed that the addition of a flame retardant in the form of a non-combustible inorganic salt in the amount of 66 weight fractions of CuSiF₆ per 100 weight fractions of *DGEBA* results in the rapid decrease in the combustibility group index moving the composite from the group of combustible substances to the difficult-to-combustible group.

The measured ignition and self-ignition temperatures demonstrate that epoxy polymers cured with *PEPA*- CuSiF_6 have higher t_{ignition} and $t_{\text{self-ignition}}$ in comparison with EAP, which was cured with *PEPA*. The widespread use of the developed composites EA- CuSiF_6 instead of traditional epoxy polymers will significantly reduce the fire load in the premises of various buildings and constructions, which, in general, will ensure a proper increase in the level of fire safety of such facilities.

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