



# Development and thermal behavior of a new type of polymer materials with reduced combustibility based on epoxy–amine composites modified with copper(II) hexafluorosilicate

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## Abstract

The polyamine chelate complex of copper(II) hexafluorosilicate—[Cu(*eda*)(*deta*)]SiF<sub>6</sub>—(a flame retardant-hardener of epoxy resins) and CuSiF<sub>6</sub>-containing epoxy–amine composites—*DGEBA/pepa*-CuSiF<sub>6</sub>—with reduced combustibility and with the varied content of CuSiF<sub>6</sub> were obtained in the *DGEBA-pepa*-CuSiF<sub>6</sub> system (*pepa*—H<sub>2</sub>N[–C<sub>2</sub>H<sub>4</sub>NH–]<sub>*n*</sub>H, *n* = 1 (*eda*—NH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>) and *n* = 2 (*deta*—NH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>); *DGEBA*—bisphenol A diglycidyl ether). These samples were characterized by IR spectra, thermal analysis and flammability studies. The results of Thermogravimetric analysis (TGA) showed that thermal decomposition of [Cu(*eda*)(*deta*)]SiF<sub>6</sub> is completed at 368 °C and the maximal temperature of the gaseous combustion products was 488 °C. TGA data for *DGEBA/pepa*-CuSiF<sub>6</sub>(22) confirm that the incorporation of [Cu(*eda*)(*deta*)]SiF<sub>6</sub> into *DGEBA* significantly increases thermal stability and anti-flammability of CuSiF<sub>6</sub>-containing epoxy–amine composites. Ignition and self-ignition temperatures have been measured for all CuSiF<sub>6</sub>-containing epoxy–amine composites in accordance with ASTM D1929-16. Depending on the quantity of added CuSiF<sub>6</sub>, the *t*<sub>ignition</sub> for this type of composite increases by 15–34 °C, and the *t*<sub>self-ignition</sub> increases by 25–58 °C compared to *DGEBA/pepa*. The flammability of the samples was evaluated by means of UL94 BH methods. The burning rate of the *DGEBA/pepa*-CuSiF<sub>6</sub>(66) and *DGEBA/pepa*-CuSiF<sub>6</sub>(88) epoxy–amine composites is severely slowed down (these samples do not propagate flame), while *r*<sub>burn</sub> value for the unmodified epoxy–amine sample (*DGEBA/pepa*) is 25.13 mm min<sup>–1</sup>.

**Keywords** Flame retardant-hardener · Copper(II)-coordinated epoxy–amine composites · Reduced combustibility · Thermal analysis · Thermal degradation of polymer materials

## Introduction

The most common and efficient way to reduce the combustibility of polymer materials, including polymer materials on an epoxide basis, is the use of flame retardants. However, among many known flame retardants, reactive flame retardants are becoming more popular, while the use of additive flame retardants is gradually declining. Obviously, the use

of reactive flame retardants gives many advantages. Unlike additive flame retardants, which are mechanically connected to polymers, reactive flame retardants chemically react with the molecular chains of the polymer at the stage of its preparation. Another advantage is that reactive flame retardant additives are able to maintain the physical, mechanical and physical and chemical properties of polymer materials at the proper level.

Among the different classes of chemicals that are successfully used to reduce the combustibility of polymer materials based on epoxy resins, the amino complexes of transition metals deserve special attention. There in particular is a report in [1] about the additives of ammonia, monoethanolamine and diethanolamine complexes of copper(II) cyanurate and diallylisocyanurate, improving the fire resistance of epoxy resins. It was shown that when the metal content in the complex increases, the limit oxygen index (LOI) first increases to its maximum value, after

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which it decreases evenly. Moreover, epoxy composites containing of copper(II) diallylisocyanurate amino complexes have a lower LOI value, and to achieve the maximum LOI value, the metal content should be higher than in the case of copper(II) cyanurate amino complexes.

There is a report in [2] 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 resulting composite has high fire resistance even with a small zinc content (3 mass%), the LOI value is 27.5 mass%, and the carbon residue is 20.5 mass%. It is also important to note that the presence of flame retardant in the epoxy–amine composite contributes to a decrease in the density of smoke, the initial temperature of degradation of the composite and an increase in the amount of zinc and phosphorus in the residue.

A rather complicated dependence of LOI on the metal content [3] is observed in epoxy polymers modified with triethylenetetramine (*teta*) complexes of various metal salts. In all these cases, the nature of metal and anion determines the nature of this dependence. However, a significant increase in LOI is observed only when the  $[\text{Mn}(teta)]\text{Cl}_2$  is added in an amount that corresponds to 0.08–0.24 mass% Mn. It is interesting that the addition of this complex does not impair the physical and mechanical properties of the composite, and the Vikat softening temperature (VST) decreases with an increase in LOI.

It was proposed to use 3(5)-methylpyrazole complexes of transition metal salts as flame 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 the binder have not only high fire resistance, but also high VST, Brinell hardness and bending stress. The data also show that the composites containing cobalt and manganese complexes have the largest fire-protection effect, and nickel complexes—the least [4].

Tris(halogenalkyl)phosphate complexes of metal chlorides and *teta* were used as initiators of curing of epoxy composite prepared from bisphenol A diglycidyl ether (*DGEBA*), phosphate modifier and amine hardener [5]. These additives strengthen polymers and give them flame retardant properties. For example, epoxy composites, modified with tris(halogenalkyl)phosphate complexes of  $\text{SnCl}_2$  (or  $\text{TiCl}_2$ ), 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 to such donor heteroatoms of organic substances, as N, S, O, etc., can be very effective flame retardants. So, in [6–9] the synthesis of a new generation of flame retardant-hardeners for epoxy resins in the form of crystalline chelate complexes of inorganic copper(II) salts with polyamines was described in detail.

The studies presented in [10–14] confirm the ability of such copper(II) chelate complexes to effectively suppress the combustibility of epoxy–amine composites. In particular, it was shown that epoxy polymers modified with the copper(II) chelate complexes have higher ignition and self-ignition temperatures, lower flame propagation rates and smoke formation, as well as lower temperatures for combustion gases compared to composites that do not contain the copper(II) chelate complexes. It should be noted that the use of such flame retardant-hardeners does not impair the basic physical and mechanical properties of epoxy–amine composites [15–17].

That is why finding new flame retardant-hardeners that can effectively reduce the combustibility of polymer materials based on epoxy resins is a priority objective for fire safety. In this regard, the addition of an inorganic salt such as copper (II) hexafluorosilicate to the epoxy–amine polymer seems highly preferred since this salt has all the necessary flame retardant properties. In view of the above, we have undertaken an attempt to develop a new type of copper(II)-coordinated epoxy–amine composites with reduced combustibility, containing non-combustible inorganic salt— $\text{CuSiF}_6$  as a flame retardant.

This study reports on the identification of the  $[\text{Cu}(eda)(deta)]\text{SiF}_6$  chelate complex [18] obtained in the *DGEBA*—*pepa*— $\text{CuSiF}_6$  system (*pepa*—polyethylenepolyamine containing ethylenediamine (*eda*) and diethylenetriamine (*deta*)), on methods of the  $[\text{Cu}(eda)(deta)]\text{SiF}_6$  incorporation in the epoxy resin framework, as well as on the thermal study and flammability of a series of samples of epoxy–amine composites—*DGEBA/pepa*— $\text{CuSiF}_6$  containing various amounts of copper(II) salt (see Table 1).

## Experimental

To develop copper(II)-coordinated epoxy–amine composites with reduced combustibility, the following chemicals are required: the fire retardant agent—copper(II) hexafluorosilicate hexahydrate ( $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$ ) (light blue crystals,  $\Delta t_{\text{dehydration}} = 100\text{ }^\circ\text{C}$ ,  $\Delta t_{\text{decomposition}} = 174\text{--}446\text{ }^\circ\text{C}$ ); the curing agent of epoxy resins—polyethylenepolyamine (*pepa*— $\text{H}_2\text{N}[-\text{C}_2\text{H}_4\text{NH}-]_n\text{H}$ , where  $n = 1$  (*eda*) and 2 (*deta*) (yellow transparent viscous liquid,  $\overline{M}_r = 120$ ,  $d^{20} = 1.011\text{ g cm}^{-3}$ ,  $n_D = 1.5120$ ,  $t_{\text{boiling}} = 250\text{ }^\circ\text{C}$ ,  $t_{\text{flash}} = 110\text{ }^\circ\text{C}$ ,  $t_{\text{ignition}} = 136\text{ }^\circ\text{C}$ ,  $t_{\text{self-ignition}} = 393\text{ }^\circ\text{C}$ ); the binder—bisphenol A diglycidyl ether (*DGEBA*) (colorless resin, ED-20 grade with almost 22% epoxy groups content, viscosity value from 12 to 18 Pa s (at 25 °C),  $\overline{M}_r = 390\text{--}430$  ( $\overline{M}_r = 410$ )). All reagents have been purchased through commercial sources and used as-received without further purification.

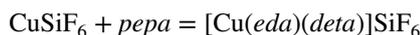
The  $[\text{Cu}(eda)(deta)]\text{SiF}_6$  chelate complex (flame retardant-hardener for epoxy resins) in a solid state has been

**Table 1** Stoichiometry of epoxy–amine composites

Composite	Ingredients/molar ratio			Ingredients/mass p		
	<i>DGEBA</i>	<i>pepa</i>	CuSiF <sub>6</sub>	<i>DGEBA</i>	<i>pepa</i>	CuSiF <sub>6</sub>
<i>DGEBA/pepa</i>	2.5	1	0	100	12	0
<i>DGEBA/pepa</i> -CuSiF <sub>6</sub> (11)	2.5	1	0.5	100	12	11
<i>DGEBA/pepa</i> -CuSiF <sub>6</sub> (22)	2.5	1	1	100	12	22
<i>DGEBA/pepa</i> -CuSiF <sub>6</sub> (44)	2.5	1	2	100	12	44
<i>DGEBA/pepa</i> -CuSiF <sub>6</sub> (66)	2.5	1	3	100	12	66
<i>DGEBA/pepa</i> -CuSiF <sub>6</sub> (88)	2.5	1	4	100	12	88

synthesized by direct interaction of anhydrous copper(II) hexafluorosilicate with polyethylenepolyamine [18, 19]. First, copper(II) hexafluorosilicate hexahydrate was synthesized. Black CuO powder (80 g, 1 mol) was dissolved in a 40% aqueous solution of hexafluorosilicate acid (320 g) to product a homogeneous dark blue solution. After evaporation of water, dark blue hexagonal crystals CuSiF<sub>6</sub>·6H<sub>2</sub>O appeared. Anhydrous salt (CuSiF<sub>6</sub>) was obtained by drying-out CuSiF<sub>6</sub>·6H<sub>2</sub>O at a temperature of 110 °C in an oven to form a white powder with a barely perceptible bluish color.

The resulting CuSiF<sub>6</sub> (2.05 g, 0.01 mol) was placed in a porcelain mortar; *pepa* (1.75 cm<sup>3</sup>, 0.02 mol) was added and then triturated until a homogeneous dark blue suspension appeared. That suspension was left for a few days at room temperature to form crystals of the [Cu(*eda*)(*deta*)]SiF<sub>6</sub> complex (the product yield was 3.6 g (98%)):



The necessary ingredients for preparation of CuSiF<sub>6</sub>-containing epoxy–amine composites with reduced combustibility in molar ratio and mass parts (mass p.) are given in Table 1. Those can be prepared in two ways. The first way supposes the direct involvement in the epoxy-polymerization of the said flame retardant-hardener; the [Cu(*eda*)(*deta*)]SiF<sub>6</sub> chelate complex (36.8 g) is added to the *DGEBA* binder (100 g). The resulting mixture is thoroughly mixed until a homogeneous aesthetically attractive dark blue thick liquid is formed. The composite material obtained by this way is denoted in Table 1 as *DGEBA/pepa*-CuSiF<sub>6</sub>(22).

According to the second way, a certain ratio of *DGEBA* to *pepa* (see Table 1) was placed in a container and stirred for

5–10 min; appropriate amounts of anhydrous copper(II) hexafluorosilicate were added to this *DGEBA*–*pepa* mixture and stirred again to a homogeneous consistency formed. Thus prepared samples of epoxy–amine composites with the different content of the CuSiF<sub>6</sub> (in Table 1, these composites are designated as *DGEBA/pepa*-CuSiF<sub>6</sub>(11), *DGEBA/pepa*-CuSiF<sub>6</sub>(22), *DGEBA/pepa*-CuSiF<sub>6</sub>(44), *DGEBA/pepa*-CuSiF<sub>6</sub>(66), and *DGEBA/pepa*-CuSiF<sub>6</sub>(88)) acquire dark blue color due to complexing.

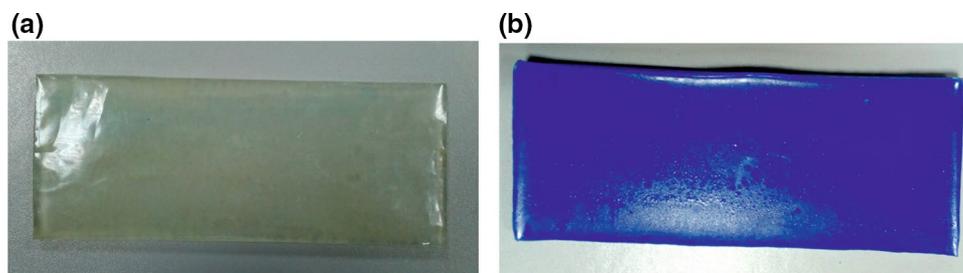
The polymer composite that does not contain CuSiF<sub>6</sub> at all also has been prepared of the binding agent (*DGEBA*) and curing agent (*pepa*), according to the standard technology; the *DGEBA/pepa* is light-yellow and clear.

All prepared composites were poured into molds and left at room temperature to cure for 24 h. Images of molded samples of simple epoxy resin (*DGEBA/pepa*) and copper(II) coordinated epoxy–amine composite (*DGEBA/pepa*-CuSiF<sub>6</sub>(22)) are shown in Fig. 1.

Infrared (IR) absorption spectra were recorded in the spectral range from 4000 to 500 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> on the PerkinElmer Spectrum Two spectrometer. IR spectra were studied on solid samples *DGEBA/pepa*, [Cu(*eda*)(*deta*)]SiF<sub>6</sub> and *DGEBA/pepa*-CuSiF<sub>6</sub>(22), pressed into tablets with spectroscopically pure KBr, or on a liquid *pepa* sample using KBr cuvette.

Thermogravimetric analysis (TGA), differential thermogravimetric (DTG) analysis and differential thermal analysis (DTA) for samples of CuSiF<sub>6</sub>·6H<sub>2</sub>O, *pepa*, [Cu(*eda*)(*deta*)]SiF<sub>6</sub>, *DGEBA/pepa*, and *DGEBA/pepa*-CuSiF<sub>6</sub>(22) 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 per minute. All

**Fig. 1** The molded samples of the *DGEBA/pepa* (a) and the *DGEBA/pepa*-CuSiF<sub>6</sub>(22) (b)



measurements were carried out dynamically in the air environment. Each sample mass was 100 mg. Aluminum oxide was used as a standard.

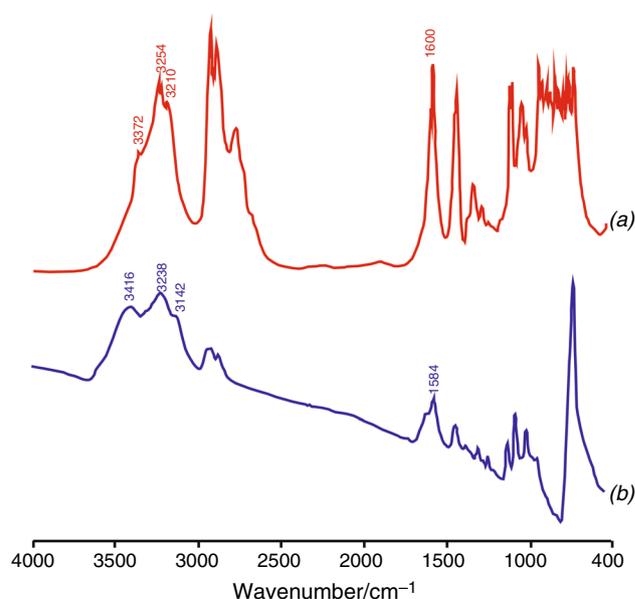
The ignition point ( $t_{\text{ignition}}$ ) and self-ignition point ( $t_{\text{self-ignition}}$ ) for polymer samples of *DGEBA/pepa*, *DGEBA/pepa-CuSiF<sub>6</sub>*(11), *DGEBA/pepa-CuSiF<sub>6</sub>*(22), *DGEBA/pepa-CuSiF<sub>6</sub>*(44), *DGEBA/pepa-CuSiF<sub>6</sub>*(66), and *DGEBA/pepa-CuSiF<sub>6</sub>*(88), as well as *pepa* and [Cu(*eda*)(*deta*)]SiF<sub>6</sub>, were measured on the TF device in accordance with ASTM D1929-16 [20].

Flammability tests were carried out in accordance with the ASTM D635-18 standard [21] using UL 94 BH methods. For testing, samples of epoxy-amine composites (*DGEBA/pepa-CuSiF<sub>6</sub>*(11), *DGEBA/pepa-CuSiF<sub>6</sub>*(22), *DGEBA/pepa-CuSiF<sub>6</sub>*(44), *DGEBA/pepa-CuSiF<sub>6</sub>*(66), *DGEBA/pepa-CuSiF<sub>6</sub>*(88), and *DGEBA/pepa*) with dimensions of 125 × 10 × 5 mm<sup>3</sup> were made. Three specimens from each composite were tested. Prior to testing specimens were conditioned for 48 h at 25 °C and 50% relative humidity. UL 94 BH results for the said composites are presented in Table 2.

## Experimental results and discussion

The interaction of *pepa* (curing agent) with CuSiF<sub>6</sub> (flame retardant) in many respects predetermines the properties of the obtained [Cu(*eda*)(*deta*)SiF<sub>6</sub>] chelate complex to be the flame retardant-hardener of epoxy resins. Said complex was isolated from the *DGEBA-pepa-CuSiF<sub>6</sub>* system and characterized with IR spectra (Fig. 2) [18]. The bonding of copper(II) salt with polyamine into the chelate complex can be detected by shifts of the N–H absorption bands. Therefore, the absorption bands caused by stretching and bending vibrations of the –NH<sub>2</sub> and –NH– groups in coordinated and free polyamine molecules are of particular interest to us.

So, for free *pepa* (Fig. 2a), absorption bands of the high-frequency region at 3372 and 3254 cm<sup>−1</sup> are related to stretching of –NH<sub>2</sub> groups, while the band observed at



**Fig. 2** IR spectra recorded for *pepa* (a) and for [Cu(*eda*)(*deta*)]SiF<sub>6</sub> (b)

3210 cm<sup>−1</sup> is ascribed to stretching of –NH– group; the observed oscillation frequency at 1600 cm<sup>−1</sup> is attributed to bending of N–H bond [22].

After bonding of the *pepa* (*eda* + *deta*) with CuSiF<sub>6</sub> (Fig. 2b), one of the N–H absorption bands is shifted to the high-frequency region observed at 3416 cm<sup>−1</sup>, whereas two other bands are shifted to the low frequency region (3238 and 3142 cm<sup>−1</sup>). The observed wavenumber at 1584 cm<sup>−1</sup> attributed to bending of N–H bond is also shifted to low frequency region.

To prove the involvement of the flame retardant-hardener agent in the formation of the epoxy polymer framework, the IR spectra for the epoxy composites cured with both *pepa* (*DGEBA/pepa*) and [Cu(*eda*)(*deta*)]SiF<sub>6</sub> (*DGEBA/pepa-CuSiF<sub>6</sub>*(22)) were recorded (Fig. 3).

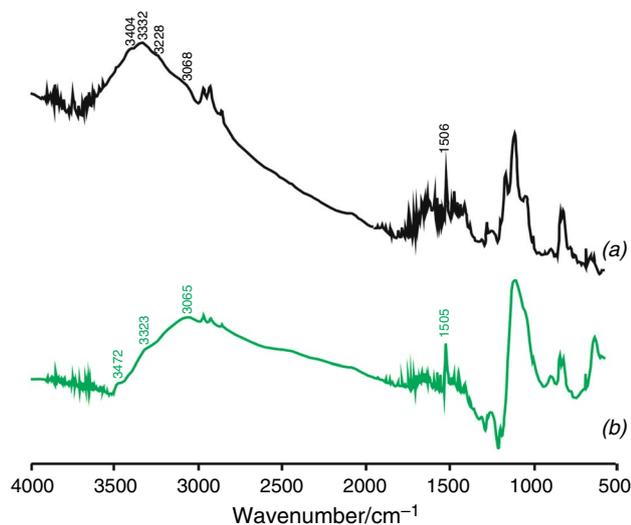
**Table 2** UL 94 horizontal flame test results

CuSiF <sub>6</sub> content/mass p	Burning time/s per length/cm						$r_{\text{av.}}$ /mm min <sup>−1</sup>	$\tau_{\text{free burning}}$ /s
	1	2	3	4	5	6		
0	22	51	80	101	125	146	25.13	*
11					**			41
22					**			42
44					**			41
66					***			0
88					***			0

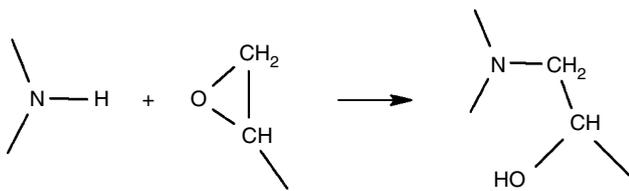
\*The sample burns until it is extinguished by force

\*\*Samples do not spread flame; the flame goes out even before the zero line

\*\*\*The sample stops burning immediately after the flame has been removed



**Fig. 3** IR spectra recorded for *DGEBA/pepa* (a) and *DGEBA/pepa-CuSiF<sub>6</sub>(22)* (b)



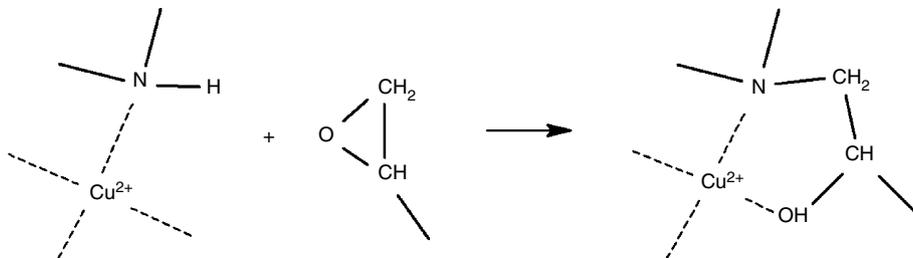
**Scheme 1** Curing of epoxy with *pepa*

The curing of epoxy composites using either *pepa* or  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  is accompanied by the disappearance of N–H bonds, the formation of N–C bonds and the appearance of new O–H bonds. In Fig. 3a (IR spectrum for *DGEBA/pepa*), besides the absorption bands characteristic of *DGEBA* [23], the absorption band at  $3332\text{ cm}^{-1}$ , that is in the widened range of  $3404$  to  $3068\text{ cm}^{-1}$ , is recognized as stretching of O–H bond [24, 25].

Thus, the structurization of epoxy polymers in the *pepa* involvement results from the cross-linking of the amino groups of the hardener and the epoxy groups of the binder followed Scheme 1.

However, in IR spectrum of *DGEBA/pepa-CuSiF<sub>6</sub>(22)* (see Fig. 3b), the same absorption band ( $3323\text{ cm}^{-1}$ )

**Scheme 2** Curing of epoxy with  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$



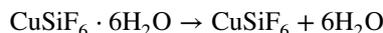
belonging to the O–H stretching is more widened and appreciably weakened due to  $\text{Cu}(\text{II})\text{--OH}$  bonding. It can be explained by involving the additional oxygen atom into the coordination sphere of the chelated  $\text{Cu}^{2+}$  ion through the  $\text{Cu}(\text{II})\text{--OH}$  coordination [25] shown in Scheme 2.

Thus, the analysis of the IR spectra showed that structuring in the *DGEBA-pepa-CuSiF<sub>6</sub>* system during the curing of copper(II)-containing epoxy-amine composites is accompanied by the bonding of  $\text{CuSiF}_6$  with *pepa* (*eda* + *deta*) and the formation of a flame retardant-hardener in the form of the  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  chelate complex [18] shown in Fig. 4.

In order to predict the effectiveness of the proposed flame retardant-hardener, a comparative assessment of the combustibility of the traditional hardener of epoxy resins (*pepa*) and the developed flame retardant-hardener ( $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$ ) was carried out. Since the combustion of any sample always starts from the stage of destruction, the thermal-oxidative degradation of *pepa*,  $\text{CuSiF}_6$ , and  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  was studied.

The thermogravimetric analysis results, presented in Fig. 5, indicate that *pepa* completely evaporates in the temperature range from  $20$  to  $170\text{ }^\circ\text{C}$ , and this process is endothermic (see DTA curve).

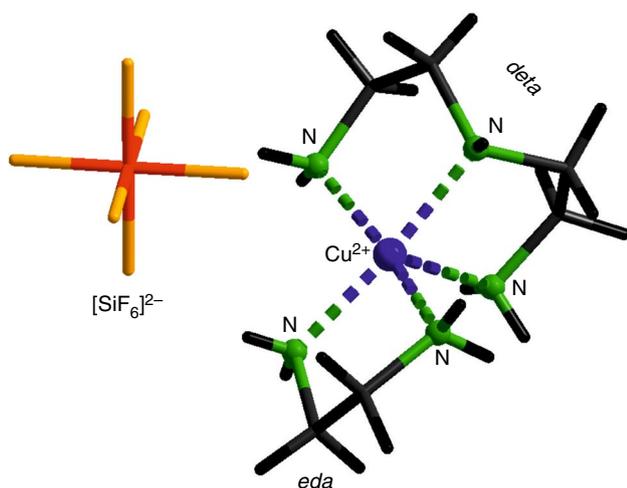
Crystalline copper(II) hexafluorosilicate hexahydrate decomposes in two stages. The first stage of thermolysis occurs in the temperature range from  $20$  to  $174\text{ }^\circ\text{C}$ . According to DTG and TG curves (Fig. 6), the mass loss at this stage is  $34.0\text{ mass}\%$ , which corresponds to the loss of six molecules of crystallization water:



The endothermic effect is observed on the DTA curve of this temperature range. In the temperature range from  $174$  to  $446\text{ }^\circ\text{C}$ , the second stage of decomposition for the already dehydrated copper (II) hexafluorosilicate occurs, resulting in the release of gaseous silicon fluoride:



This process is accompanied by mass loss ( $32.8\text{ mass}\%$ ), and an endothermic effect appears on the DTA curve. These



**Fig. 4** Structure of flame retardant-hardener

experimental data are in good agreement with the calculation results (Table 3).

Thermal oxidative degradation of the flame retardant hardener— $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$ —proceeds more complexly and has four stages (Fig. 7) [18]. The first stage of thermolysis is observed in the temperature range from 20 to 160 °C, while the mass loss of the sample is 13.4 mass%. The DTA curve shows an endothermic effect with a maximum at 112 °C.

The second stage includes a temperature range from 160 to 253 °C. This corresponds to a mass loss of 14.3 mass% and the appearance of another minimum on the DTA curve. In this temperature range, an endothermic effect is observed at a temperature of 212 °C. It is assumed that gaseous silicon fluoride is released at these stages.

The third stage of thermolysis occurs in the temperature range from 253 to 368 °C. Here,  $\Delta m = 39.9$  mass%. All indicates that the third stage is responsible for the partial destruction of the amine component of the chelate complex. That destruction is accompanied by a sequence of complex thermo-oxidative processes, which is reflected in the DTA curve by the presence of exothermic and endothermic effects.

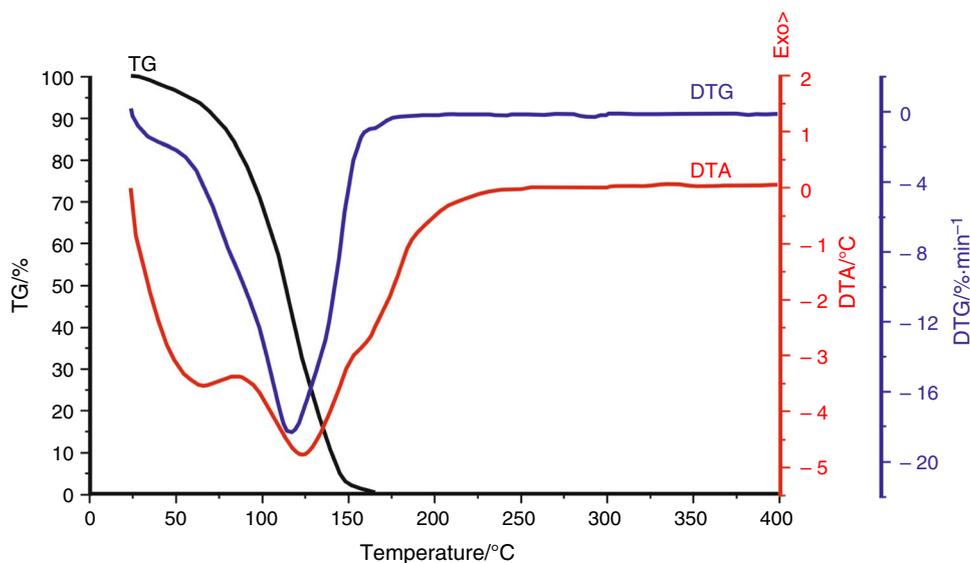
The fourth stage (from 368 to 544 °C) corresponds to the complete combustion of the destruction products of the organic components of the complex. This is accompanied by the appearance of a pronounced exothermic effect on the DTA curve with a maximum at 488 °C. Mass loss at this final stage is 15.3 mass% (Table 4).

*Pepa* molecules are known to be 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 easy ignites. In contrast, in the  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  chelate complex, which is a flame retardant-hardener of epoxy resins, *pepa* (*eda* + *deta*) molecules are strongly bonded to copper(II) hexafluorosilicate by Cu–N bonds, which make difficulties for evaporation and then ignition of *pepa*. All of the above is in good agreement with the experimental data.

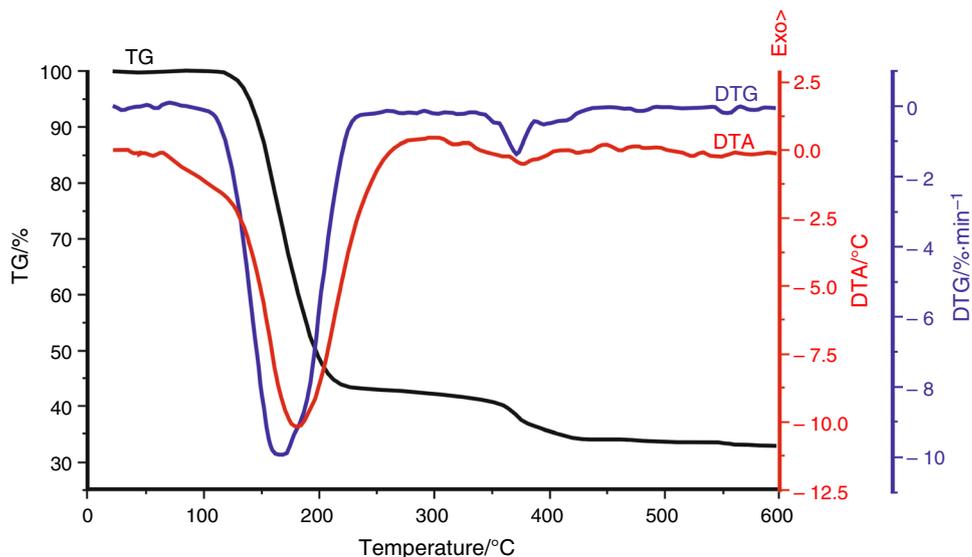
Here, we will consider the thermal behavior of polymer composites based on epoxy resins cured by both *pepa* and the  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  chelate complex (Table 5).

The *DGEBA/pepa* epoxy–amine composite thermal degrades in four stages (Fig. 8). The first stage involves 20–180 °C, corresponds to the mass loss of 3.1 mass% and has a minor endothermic minimum on the DTA curve. These data are in a good agreement with the incipient destruction process of the polymer framework resulting in the formation of the volatile species.

**Fig. 5** TG, DTG, and DTA curves recorded for *pepa*



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



**Table 3** Thermal decomposition results of  $\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$

Sample	Stage	Temperature range/°C	$\Delta m_{\text{exp.}}/\text{mass}\%$	$\Delta m_{\text{calc.}}/\text{mass}\%$
$\text{CuSiF}_6 \cdot 6\text{H}_2\text{O}$	I	20–174	34.0	34.4
	II	174–446	32.8	33.1

The second stage occurs in the temperature range from 18 to 360 °C ( $\Delta m = 32 \text{ mass}\%$ ). This exothermic effect with maximum at 300 °C stems from the thermal-oxidative destruction of the *DGEBA/pepa* polymer. The mechanism of this process is free-radical where the alkyl particles ( $\cdot\text{R}$ )

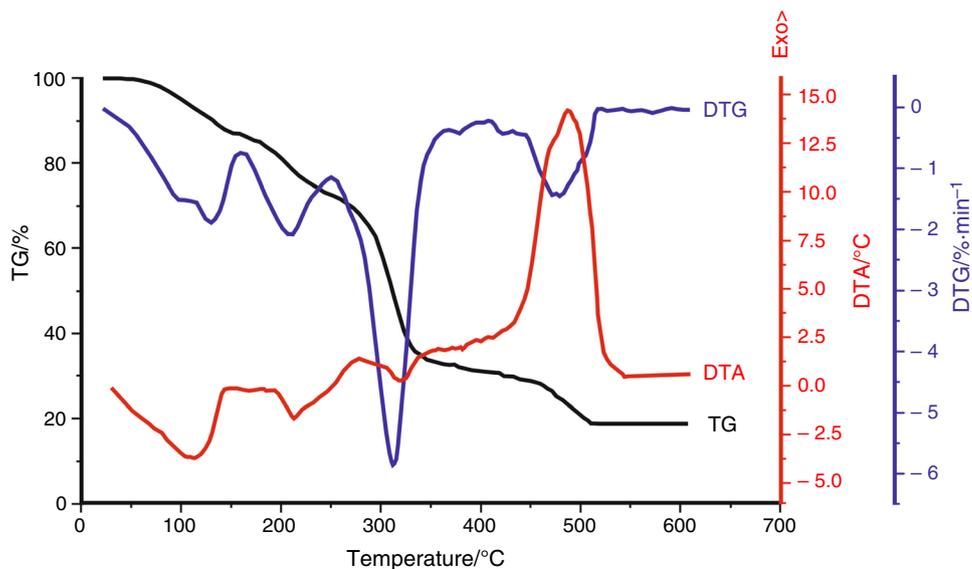
and peroxide particles ( $\cdot\text{O}-\text{OR}$ ) take part in formation of hydroperoxides ( $\text{HO}-\text{OR}$ ) [10].

The combustion of the products of the *DGEBA/pepa* destruction takes place at the third stage in temperature range from 360 to 460 °C ( $\Delta m = 12.1 \text{ mass}\%$ ). This temperature interval of the DTA curve contains the exothermic maximum at 400 °C.

The final combustion of the pyrolytic residue occurs at the fourth stage of the *DGEBA/pepa* thermolysis in temperature range from 460 to 900 °C ( $\Delta m = 52 \text{ mass}\%$ ); this process is exothermic.

The thermal degradation process of the *DGEBA/pepa*- $\text{CuSiF}_6(22)$  epoxy-amine composite is more complicated, although it is only represented by three stages (Fig. 9). The first stage occurs from 20 to 127 °C and is accompanied by

**Fig. 7** TG, DTG, and DTA curves recorded for  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$



**Table 4** Thermal decomposition results of [Cu(*eda*)(*deta*)]SiF<sub>6</sub>

Sample	Stage	Temperature range/°C	$\Delta m/\text{mass}\%$
[Cu( <i>eda</i> )( <i>deta</i> )]SiF <sub>6</sub>	I	20–160	13.4
	II	160–253	14.3
	III	253–368	39.9
	IV	368–544	15.3

**Table 5** Thermogravimetric analysis results of epoxy–amine composites

Sample	Stage	Temperature range/°C	$\Delta m/\text{mass}\%$
<i>DGEBA/pepa</i>	I	20–180	3.1
	II	180–360	32.0
	III	360–460	12.1
	IV	460–900	52.0
<i>DGEBA/pepa</i> -CuSiF <sub>6</sub> (22)	I	20–127	6.4
	II	127–320	21.2
	III	320–580	65.1

an appearance of the endothermic effect on the DTA curve with extremum at 82 °C. Here, as in case of *DGEBA/pepa* (stage I), the formation of volatile species takes place ( $\Delta m = 6.4 \text{ mass}\%$ ).

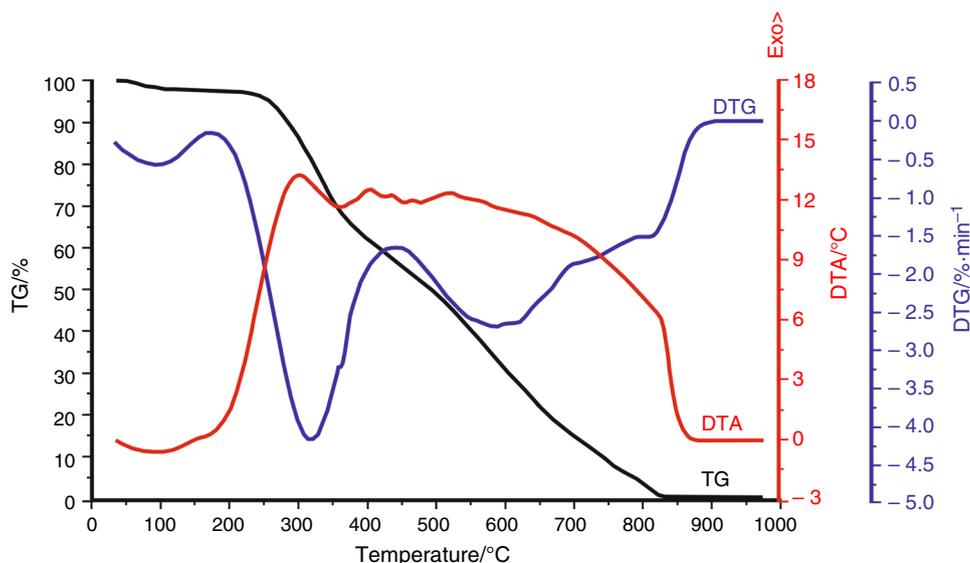
The second stage occurs at temperature range from 127 to 320 °C. This stage is related to partial decomposition of the inorganic part of the composite with SiF<sub>4</sub> emission as well as thermal-oxidative destruction of the organic constituent of the sample. This process is exothermic with maximum at 210 °C (the DTA curve) and  $\Delta m = 21.2 \text{ mass}\%$ .

The third stage covers the temperature range from 320 to 580 °C and is accompanied by the appearance of the pronounced exothermic effect at the DTA curve. The mass loss at this stage is 65.1 mass% owing to the thermal destruction of the [Cu(*eda*)(*deta*)]SiF<sub>6</sub> coordination cores inbuilt into polymer matrix, thermal-oxidative destruction of organic constituent part of the *DGEBA/pepa*-CuSiF<sub>6</sub>(22), and complete combustion of the pyrolytic residue of the polymer sample.

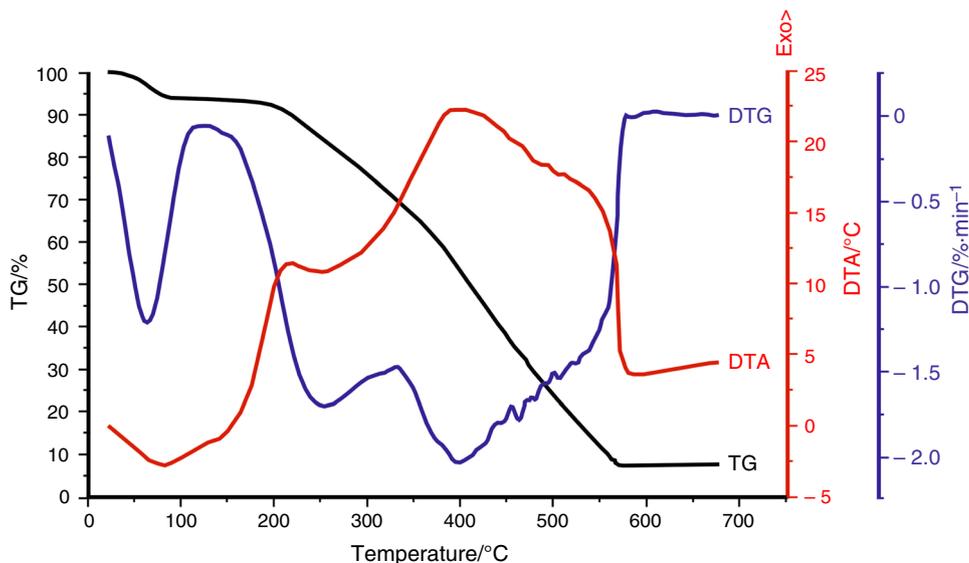
It should be noted that samples of CuSiF<sub>6</sub>-containing epoxy–amine composites have a higher thermal resistance than the conventional epoxy–amine composite. This is evidenced by a less intense mass loss in the *DGEBA/pepa*-CuSiF<sub>6</sub>(22) sample ( $\Delta m = 21.2 \text{ mass}\%$ ) than in the *DGEBA/pepa* sample (32.0 mass%) during thermal-oxidative destruction at the second stage of thermolysis (see Table 5). At this stage, the maximum mass loss rate of a sample of an epoxy composite cured with *pepa* is  $4.23\% \cdot \text{min}^{-1}$ , and an epoxy composite cured with [Cu(*eda*)(*deta*)]SiF<sub>6</sub> is  $1.75\% \cdot \text{min}^{-1}$  (Table 6). Moreover, the thermal-oxidative destruction of the *DGEBA/pepa* sample is accompanied by the largest exo-effect on the DTA curve, with a maximum at 300 °C, while the largest exo-effect for the *DGEBA/pepa*-CuSiF<sub>6</sub>(22) sample is observed at a temperature of 394 °C and that corresponds to the combustion of a pyrolytic residue of the sample.

Apparently, the slowdown in the decomposition of epoxy–amine composites, observed upon the addition of the CuSiF<sub>6</sub>, is associated with the formation of coordination bonds Cu(II)–N, which require additional thermal energy to break them.

The pyrolytic residue of the organic constituent of the *DGEBA/pepa*-CuSiF<sub>6</sub>(22) sample compared to the *DGEBA/pepa* sample combusts in a narrower temperature

**Fig. 8** TG, DTG, and DTA curves recorded for *DGEBA/pepa*

**Fig. 9** TG, DTG, and DTA curves recorded for *DGEBA/pepa-CuSiF<sub>6</sub>(22)*



**Table 6** Comparative characteristics of thermal-oxidative destruction of *DGEBA/pepa-CuSiF<sub>6</sub>(22)* and *DGEBA/pepa* polymer samples

Characteristic	Samples	
	<i>DGEBA/pepa</i>	<i>DGEBA/pepa-CuSiF<sub>6</sub>(22)</i>
The temperature of the maximal exothermic effect/°C	300	394
The maximal mass loss rate in the process of thermal oxidative degradation/%·min <sup>-1</sup>	4.23	1.75
The maximal mass loss rate during combustion/%·min <sup>-1</sup>	2.72	2.02
The completion temperature of the combustion process/°C	900	580
The maximal mass loss/mass% at:		
400 °C	37.9	46.7
600 °C	69.3	92.7

range. The combustion temperature of the carbonized residual is 580 °C and 900 °C for the *DGEBA/pepa-CuSiF<sub>6</sub>(22)* and the *DGEBA/pepa*, respectively. That indicates the self-extinguishing nature of the combustion of the copper(II)-coordinated epoxy-amine composites.

Thus, the thermal oxidative stability of the *CuSiF<sub>6</sub>*-containing epoxy-amine composites has appeared to be significantly higher than that of the *DGEBA/pepa*. Here, the stabilizing role belongs to copper(II) hexafluorosilicate, which demonstrates an exceptional ability to complexation. The incorporation of that non-combustible inorganic salt in the framework of the epoxy-amine polymer contributes to the compaction of the polymer matrix and the reduction of the molecular mobility of the inter-node sections of the epoxy-amine network. This results in a decrease in the reactivity of polymer chains in the process of thermal-oxidative destruction. The flame self-extinguishing effect observed for the *CuSiF<sub>6</sub>*-containing epoxy-amine composites results from such structural stabilization.

In turn, copper(II) hexafluorosilicate, which was included in the epoxy-amine composite, in the temperature range from 176 to 446 °C (see Fig. 6) decomposes into copper(II) fluoride and silicon(IV) fluoride. Due to the formation of a large number of the non-combustible products, the characteristics of thermal degradation of the epoxy-amine polymers change. In particular, gaseous silicon(IV) fluoride can act as a burning phlegmatizator and in such a way reduce the concentration of the combustible mixture components, which surely affects the duration of the combustion of composite materials based on epoxy resins. According to thermal analysis, the mass loss rate during combustion of the epoxy polymer in the presence of gaseous *SiF<sub>4</sub>* is reduced by 0.7%·min<sup>-1</sup> (see Table 6).

The DTA data obtained are in good agreement with the results of determining the ignition and self-ignition temperatures. The values of  $t_{\text{ignition}}$  and  $t_{\text{self-ignition}}$  measured for crystals of the chelate complex  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  show that *eda* and *deta* in the bonded state turn into practically non-combustible substances. So, *pepa* (comprising *eda* and

*deta*) after bonding to copper(II) hexafluorosilicate does not ignite or self-ignite even at temperatures of 450 °C and 600 °C, respectively. For comparison, the values of  $t_{\text{ignition}}$  and  $t_{\text{self-ignition}}$  for free *pepa* are 136 °C and 393 °C, respectively (Table 7).

Undoubtedly, this is due to coordination bonds that arise between the amino groups of the combustible *pepa* (*eda* + *deta*) and copper(II) atoms of the non-combustible  $\text{CuSiF}_6$ . To break these  $\text{Cu(II)-N}$  bonds, it is necessary to use up a large amount of thermal energy of the flame.

Let's say more in order to ignite the released *eda* and *deta*, it is necessary to form a vapor-air mixture in which the concentration of saturated vapors of *eda* and *deta* would have exceeded the lower concentration limit of flame propagation. However, even at temperatures > 450 °C, the ignition of *eda* and *deta* vapors over molten  $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$  was not observed, which indicates an insufficient concentration of *eda* and *deta* in the reaction mixture.

The flame retardant addition ( $\text{CuSiF}_6$ ) to the samples of the epoxy-amine polymers significantly affects their ignition and self-ignition temperatures. As can be seen from data of Table 7, the epoxy-amine composite that does not contain  $\text{CuSiF}_6$  is characterized a minimum value of the ignition and self-ignition temperatures. Depending on the quantity of added  $\text{CuSiF}_6$ , the ignition temperature for copper(II)-coordinated epoxy-amine composites on average increases by 15–34 °C, and the self-ignition temperature does by 25–58 °C compared to the *DGEBA/pepa*. The maximum values of the ignition temperature (359 °C) and the self-ignition temperature (588 °C) have epoxy-amine composites containing 88 mass parts of  $\text{CuSiF}_6$ . All these data are in good agreement with the thermogravimetric analysis results.

At low temperatures,  $\text{CuSiF}_6$ -containing epoxy-amine composites are characterized by half the degradation rate compared to *DGEBA/pepa*. This is due to the giving rise of strong coordination bonds of the  $\text{Cu(II)-N}$  type, which are formed in the *DGEBA-pepa-CuSiF}\_6* system at the stage of composite preparation.

It should be noted that the maximum mass loss at 400 °C and 600 °C, in contrast, is higher for copper(II)-coordinated epoxy-amine composites (see Table 6). This, at first glance, contradictory dependence can be explained by a change in the ratio between degradation products in the direction of increasing the amount of non-combustible gases. Indeed, the degradation of  $\text{CuSiF}_6$ -containing epoxy-amine composites releases non-combustible gaseous  $\text{SiF}_4$ . This, apparently, is one of the main causes of the increase in temperatures of ignition and self-ignition for this type of composites.

An important quantitative characteristic of the combustibility of polymer materials is the flame propagation rate, which determines both the rate of involvement of combustible substances in the combustion process and the intensification of combustion. The studying results of the mechanism of flame propagation on the surface of samples of epoxy-polymer materials modified with copper(II) hexafluorosilicate in a horizontal position are shown in Table 2. These experimental data show that the incorporation of  $\text{CuSiF}_6$  in the epoxy-amine framework significantly affects the flame propagation rate.

In fact, samples of the original *DEBA/pepa* (unmodified epoxy-amine composite) did not stop burning until these were extinguished by force. The average burning rate was  $25.13 \text{ mm min}^{-1}$ . Since the burning rate of the sections between the marks did not exceed  $40 \text{ mm min}^{-1}$ , such material is classified as HP "Horizontal Propagation." During the combustion of such a composite, burning droplets fall, as a result of which the sublayer of the cotton sheet ignites. This can produce the appearance of new seats of fire and, thus, increase the area covered by the flame.

The addition of even a small amount of copper(II) hexafluorosilicate to the epoxy-amine composite is able to affect significantly the rate of flame propagation on the surface of a sample located horizontally. Although composite samples containing 11, 22, and 44 mass p. of  $\text{CuSiF}_6$  per 100 mass p. of a binder burn under the influence of the burner flame, nevertheless free burning after was removed the flame was short; the flame went out even before it reached zero-mark. The free burning duration for these composites did not exceed 45 s. The ignition of the cotton sublayer did not happen either.

When samples of composites containing 66 and 88 mass p. of  $\text{CuSiF}_6$  per 100 mass p. of *DGEBA* were exposed to the burner flame, thermal-oxidative decomposition of these samples was observed, but after removal of the flame, the combustion of these samples stopped.

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

Sample	$t_{\text{ignition}}/^\circ\text{C}$	$t_{\text{self-ignition}}/^\circ\text{C}$
<i>pepa</i>	136	393
$[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$	Without ignition (at 450 °C)	Without self-ignition (at 600 °C)
<i>DGEBA/pepa</i>	325	530
<i>DGEBA/pepa-CuSiF}_6(11)</i>	340	555
<i>DGEBA/pepa-CuSiF}_6(22)</i>	349	565
<i>DGEBA/pepa-CuSiF}_6(44)</i>	351	582
<i>DGEBA/pepa-CuSiF}_6(66)</i>	353	583
<i>DGEBA/pepa-CuSiF}_6(88)</i>	359	588

## Conclusions

Another representative of a new type of the copper(II)-coordinated epoxy–amine composites (*DGEBA/pepa*-CuSiF<sub>6</sub>) with reduced combustibility has been obtained in the in the *DGEBA*—*pepa*—CuSiF<sub>6</sub> system and characterized by thermal analysis. The preparation technology developed for that type of polymer composites involves first synthesizing the [Cu(*eda*)(*deta*)]SiF<sub>6</sub> chelate complex and then incorporating it into *DGEBA*. The structurization of the epoxide polymers cured by the [Cu(*eda*)(*deta*)]SiF<sub>6</sub> was studied by IR spectroscopy. It has been found out that CuSiF<sub>6</sub>—(*pepa*) interlinking which is accompanied by forming the Cu(II)–N coordination bonds within the polymer framework predetermines the thermal stability and reduced combustibility of CuSiF<sub>6</sub>-containing epoxy–amine composites. Thermal analysis showed that the thermal stability of the *DGEBA/pepa*-CuSiF<sub>6</sub>(22) relative to the *DGEBA/pepa* increases considerably. A study of the regularity of flame propagation on the surface of samples of epoxy-polymer materials showed that composites containing 44 and 66 mass p. of copper(II) hexafluorosilicate do not spread flame and belong to the highest category of combustion resistance.

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