

RESEARCH ARTICLE

New copper(II)-coordinated epoxy-amine polymers with flame-self-extinguishment properties: Elaboration, combustibility testing, and flame propagation rate measuring

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Summary

In the *DGEBA* - *pepa* - CuSiF_6 system (*DGEBA* is diglycidyl ether of bisphenol A; *pepa* is polyethylenepolyamine containing ethylenediamine (*eda*) and diethylenetriamine (*deta*)), a new flame retardant-hardener for epoxy resins in the form of a chelate complex $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$ was synthesized and incorporated into the *DGEBA* to obtain a number of CuSiF_6 -containing epoxy-amine polymers with reduced combustibility and flame-self-extinguishment properties. The resulting samples of the *DGEBA/pepa-CuSiF}_6(I-V) were characterized using FTIR spectra, combustibility, and flammability tests and the smoke formation factor measurements. The combustibility of the polymer samples were investigated using "Ceramic tube" (CT) method. Results of CT measurement reveal that maximal temperature of gaseous products of combustion for modified epoxy-amine polymers in comparison with the unmodified epoxy appreciably goes down and weight loss lessen. The flammability of the samples was evaluated by means of UL94 BH and UL94 BV methods. The burning rate of the *DGEBA/pepa-CuSiF}_6(III) and *DGEBA/pepa-CuSiF}_6(IV) polymers containing 44 and 66 weight fractions of CuSiF_6 , respectively, is dramatically reduced compared to that for unmodified epoxy (these samples do not support flame propagation). The r_{burn} . Values for the unmodified epoxy-amine sample (*DGEBA/pepa*) is $25.13 \text{ mm}\cdot\text{min}^{-1}$.***

KEYWORDS

copper(II)-coordinated epoxy-amine polymers, flame retardant-hardener, flame-self-extinguishment properties, reduced combustibility

1 | INTRODUCTION

The modern rates of industrial production and construction are in need of new polymer materials, including those based on epoxy resins, the development of which is growing steadily. Epoxy resins are widely used both in industry and in everyday life for the manufacture and repair of various products, components of adhesives and putties, paints and coatings, fillers, sealants, impregnating compounds, and so forth. With the development of industry, epoxies are increasingly finding new uses. This is facilitated by the unique combination of physico-chemical and mechanical properties of epoxy resins, in particular, such

as easiness of curing, low viscosity, high adhesion, high mechanical and electrical insulation properties, as well as chemical resistance.¹

Nevertheless, the main disadvantage of epoxy-polymer materials is their high fire hazard. But significant reactivity, along with the presence of a large number of functional groups of various types, opens up great opportunities for controlling structural changes and, therefore, improving the properties of epoxy-polymer materials. One of the most promising ways to reduce the fire hazard of epoxy-polymer materials is their chemical modification, based on varying the structure of the epoxy matrix and choosing a suitable hardener. To do this, hardeners with flame retardant properties are increasingly used.²

Among the many curing agents for epoxies with flame retardant properties are considered the following group of substances. These are halogen-containing amine hardeners³ such as 2,4,6-tribromomethaphenylenediamine and 2,4-diamino-2',4',6'-tribromodiphenyl ether, mixtures of tribromomethaphenyl diamine with *m*-phenyl diamine or 3,3-dichloro-4,4-diaminodiphenylbenzylidene, addition compounds of aliphatic amines with dibromocresylglycidyl ether, pentachlorophenol and pentabromophenol, brominated bisphenoxy compounds and chlorendic anhydride, 3,3-dichloro-4,4-diaminophenylmethan, dichlor-*p*-aminobenzimidazole chlorine-containing anhydrides obtained by condensation of hexachlorocyclopentadiene and 5,5-dialkoxytetrachlorocyclopentadiene with anhydrides of 4-cyclohexane-1,2-dicarboxylic acid, and so forth.

Fairly often, phosphorus-containing hardeners are used to reduce the combustibility of epoxy polymers. These are, primarily, phosphorus-containing glycidyl compounds, aminophosphates, phosphinic acid, di- and trioxyphenyl ethers of methylphosphonic and phosphoric acids, mono-, di- and trialkylphosphine, aminocyclophosphazenes, polymetalophosphates, and 1-dopyl-1,2-(4-hydroxyphenyl)ethene. Phosphorus-containing hardeners, as a rule, reduce the polymer decomposition temperature and increase the yield of carbon residue during combustion.⁴⁻⁷

Recently, some chelate complexes of *d*-metals are used to reduce the fire hazard of epoxy polymers. Said complexes are a new generation of compounds that simultaneously play the role of both flame retardants and epoxy hardeners. These are prepared by the interaction of inorganic salts of transition metals (mainly copper (II)) with traditional amine hardeners of epoxy resins.⁸⁻¹¹ Said studies were started relatively recently and those are currently developing rapidly. Already the first tests carried out in this area revealed a high fire-retardant ability of substances of this type.¹²⁻¹⁶ In particular, it was found that epoxy resins cured by amine complexes of *d*-metals have higher ignition and self-ignition temperatures, spread flame more slowly and are characterized by lower values of the maximum temperature of gaseous products of combustion and smoke formation in comparison with the known epoxides cured by traditional amine hardeners. And what is more, the use of the flame retardant-hardeners not only reduces the combustibility of polymeric materials, but it also keeps the physical-mechanical properties and operational characteristics of modified epoxides.¹⁷⁻¹⁹ That is why this area of research is very promising.

Our further research will be aimed at searching for new amine complexes of copper(II), which can quite effectively reduce the combustibility of polymer materials based on epoxy resins. This will not only expand the range of competitive flame retardants, but also solve such a practical problem as obtaining epoxy-polymer materials with increased fire safety.

This work is devoted to the development of a new type of polymer materials with the flame-self-extinguishment properties based on epoxy-amine polymers modified by copper(II) hexafluorosilicate of the DGEBA - *pepa* - CuSiF₆ system (DGEBA is diglycidyl ether of bisphenol A; *pepa* is polyethylenepolyamine).

2 | EXPERIMENTS

2.1 | Materials

Samples of CuSiF₆-containing epoxy-amine polymers were synthesized from DGEBA (colorless resin, ED-20 grade with almost 22% epoxy groups content, viscosity value from 12 to 18 Pa·s (at 25°C), $M_r = 390-430$ ($M_w = 410$)), *pepa* ($H_2N[-C_2H_4NH-]_nH$, where $n = 1$ (*eda* - $H_2NC_2H_4NH_2$) and 2 (*deta* - $H_2NC_2H_4NHC_2H_4NH_2$)) (yellow transparent viscous liquid, $M_r = 120$, $d^{20} = 1.011$ g·cm⁻³, $n_D = 1.5120$, $t_{boiling} = 250^\circ C$, $t_{flash} = 110^\circ C$, $t_{ignition} = 136^\circ C$, $t_{self-ignition} = 393^\circ C$, IR [KBr cuvette, cm⁻¹]: 3372, 3254, and 3210 (ν_{NH}); 2934, 2908, and 2790 (ν_{CH}); 1600 (δ_{NH}); 1460 (δ_{CH})), and copper(II) hexafluorosilicate hexahydrate (CuSiF₆·6H₂O) (light blue crystals, $\Delta t_{dehydration} = 100^\circ C$, $\Delta t_{decomposition} = 174-446^\circ C$). All reagents have been purchased through commercial sources and used as-received without further purification.

2.2 | Technology for the preparation of CuSiF₆-containing epoxy-amine polymers

In this section, a unique development that made it possible to create a new type of polymer materials with reduced combustibility based on copper(II)-coordinated epoxy-amine polymers is presented. As a result, structurally homogeneous, glossy, and aesthetically attractive samples were obtained. Resulting polymers are also distinguished by peculiar properties of self-extinguishing flame.

2.2.1 | Flame retardant-hardener synthesis

The [Cu(*eda*)(*deta*)]SiF₆ chelate complex (IR (KBr tablet, cm⁻¹): 3416, 3238, and 3142 (ν_{NH}); 1584 (δ_{NH})²⁰) with the properties of a flame retardant-hardener labeled as *pepa*-CuSiF₆ was obtained according to the procedure described in.^{20,21} First, anhydrous salt (CuSiF₆) was obtained by dehydration of CuSiF₆·6H₂O at 110°C in a drying oven until a white powder with a slightly noticeable bluish tint formed. Then, the flame retardant hardener in the form of the crystalline [Cu(*eda*)(*deta*)]SiF₆ chelate complex was obtained by direct interaction of copper(II) hexafluorosilicate and *pepa* (*eda* + *deta*). Polycrystalline CuSiF₆ (20.5 g, 0.1 mol) was placed in a porcelain vessel and *pepa* (1.75 cm³, 0.15 mol) was added. The reaction mixture was triturated until a homogeneous dark blue liquid suspension appeared. This suspension was left for several days at room temperature until a dark blue crystalline phase of the said *pepa*-CuSiF₆ appeared.

2.2.2 | Preparation of DGEBA/*pepa*-CuSiF₆ polymers

The necessary components for the synthesis of CuSiF₆-containing epoxy-amine polymers labeled as DGEBA/*pepa*-CuSiF₆ are given in Table 1.

There are two ways to obtain samples of CuSiF₆-containing epoxy-amine polymers. The peculiarity of the first way is that the

polymer sample is obtained starting from the flame retardant-hardener (see section 2.2.1). For this, *pepa*-CuSiF₆ (34 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 polymer sample prepared in the first way is indicated in Table 1 as DGEBA/*pepa*-CuSiF₆(II).

To obtain polymer samples of DGEBA/*pepa*-CuSiF₆ containing various levels of CuSiF₆ (second way), 11, 22, 44, 66, or 88 g of copper(II) hexafluorosilicate is placed in a container and added 12 g *pepa*. In each of such a case, the added *pepa* actively interacts with copper(II) hexafluorosilicate, forming *pepa*-CuSiF₆. Complexation is accompanied by heating of the reaction mixture and its transformation into a dark blue suspension. Next, DGEBA (100 g, 0.25 mol) is added to each of these containers and thoroughly stirred for 5 to 10 minutes until an aesthetically attractive dark blue homogeneous mass resembling thick honey formed. The resulting viscous liquids are poured into molds and left to cure for 24 hours at room temperature. After curing, all five samples of CuSiF₆-containing epoxy-amine polymers - DGEBA/*pepa*-CuSiF₆(I), DGEBA/*pepa*-CuSiF₆(II), DGEBA/*pepa*-CuSiF₆(III), DGEBA/*pepa*-CuSiF₆(IV), and DGEBA/*pepa*-CuSiF₆(V) - have acquired a characteristic dark blue color (Figure 1A). This can have a broad prospect of application, for example, as coatings for pouring polymer floors in industrial premises, in warehouses, in workshops, shops, etc., as well as to produce decorative polymer coatings.

TABLE 1 Stoichiometry of epoxy-amine polymers

Samples	DGEBA: <i>pepa</i> : CuSiF ₆	
	molar ratio	mass ratio
DGEBA/ <i>pepa</i>	2.5:1: 0	100:12: 0
DGEBA/ <i>pepa</i> -CuSiF ₆ (I)	2.5:1: 0.5	100:12: 11
DGEBA/ <i>pepa</i> -CuSiF ₆ (II)	2.5:1: 1	100:12: 22
DGEBA/ <i>pepa</i> -CuSiF ₆ (III)	2.5:1: 2	100:12: 44
DGEBA/ <i>pepa</i> -CuSiF ₆ (IV)	2.5:1: 3	100:12: 66
DGEBA/ <i>pepa</i> -CuSiF ₆ (V)	2.5:1: 4	100:12: 88

The epoxy-amine polymer that does not contain the flame retardant—CuSiF₆—was prepared of DGEBA (100 g) and *pepa* (12 g); the resulting sample of DGEBA/*pepa* (see Figure 1B) was light-yellow and clear.

2.3 | Methods

2.3.1 | FTIR characterization

FTIR spectra were recorded in the spectral range from 4000 to 500 cm⁻¹ with a resolution of 2 cm⁻¹ on the PerkinElmer Spectrum Two spectrometer. FTIR spectra were studied on solid samples DGEBA/*pepa* and DGEBA/*pepa*-CuSiF₆(II) (Table 2), pressed into tablets with spectroscopically pure KBr.

2.3.2 | Combustibility tests

Combustibility parameters were determined for samples of DGEBA/*pepa*-CuSiF₆(I), DGEBA/*pepa*-CuSiF₆(II), DGEBA/*pepa*-CuSiF₆(III), and DGEBA/*pepa*-CuSiF₆(IV), as well as DGEBA/*pepa* (for comparison) according to all-Union State Standard 12.1.044-89 (Supporting Information), which is described in detail in,¹⁵ using the “Ceramic tube” (CT) apparatus. The results of the CT measurements are presented in Table 3.

2.3.3 | Flammability tests

Flammability tests were carried out in accordance with the ASTM D635-14 standard²² and ASTM 3801-19a standard²³ using UL 94 BH and UL 94 BV methods, respectively. For testing, samples of epoxy-amine polymers (DGEBA/*pepa*-CuSiF₆(I), DGEBA/*pepa*-CuSiF₆(II), DGEBA/*pepa*-CuSiF₆(III), DGEBA/*pepa*-CuSiF₆(IV), DGEBA/*pepa*-CuSiF₆(V), and DGEBA/*pepa*) with dimensions of 125 × 10 × 5 mm³ were made. Three samples for each type of polymer were tested.

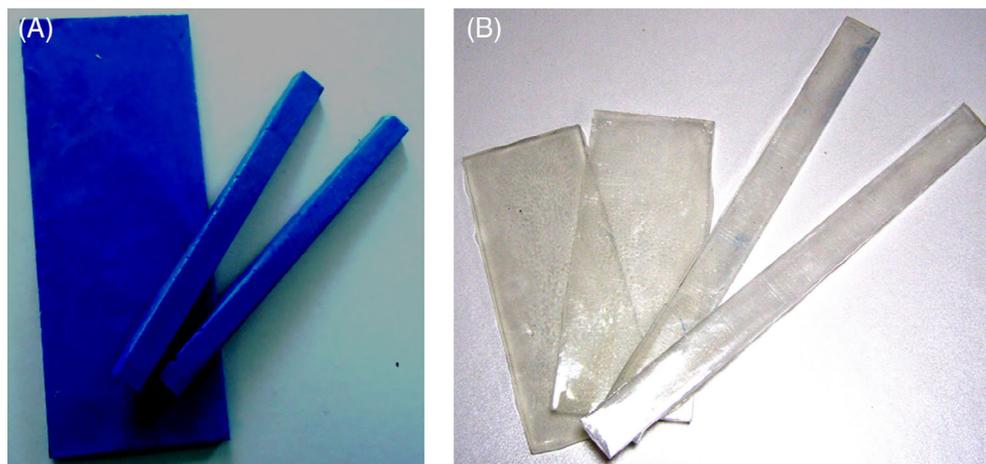


FIGURE 1 Photographs of samples of epoxy-amine polymers. A, DGEBA/*pepa*-CuSiF₆. B, DGEBA/*pepa* [Colour figure can be viewed at wileyonlinelibrary.com]

Prior to testing the samples were conditioned for 48 hours at 25°C and 50% relative humidity. UL 94 BH and UL 94 BV results for the said polymer samples are presented in Tables 4 and 5, respectively.

2.3.4 | Determination of smoke formation factor

The smoke formation factor for the DGEBA/pepa-CuSiF₆(I), DGEBA/pepa-CuSiF₆(II), DGEBA/pepa-CuSiF₆(III), DGEBA/pepa-CuSiF₆(IV), DGEBA/pepa-CuSiF₆(V), and DGEBA/pepa polymers was measured in the combustion chamber according to ASTM D2843-19.²⁴ The optical density of the smoke generated by a certain amount of solid material was determined. For it, samples 40 × 40 × 5 mm³ in size were made. Before testing, all samples were kept at 20°C for 48 hours and weighed. The tests were carried out in two modes. In the smoldering

mode, the sample was exposed only to a heat flux with a density of 35 ± 3.5 kW·m⁻², and in the burning mode, the heat flux emanating from an open flame affected the samples. The smoke formation factor (D_m , m²·kg⁻¹) was calculated by the ratio:

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

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

3 | RESULTS AND DISCUSSION

3.1 | Structuring processes in the DGEBA - pepa - CuSiF₆ system

Structuring processes taking place in the DGEBA-pepa-CuSiF₆ system is that pepa, as the curing agent, is able to coordinate with CuSiF₆, which, in turn is the flame retardant. As a result of it, the flame retardant-hardener in the form of the pepa-CuSiF₆ chelate complex is formed (Figure 2A). Such complex was characterized using FTIR

TABLE 2 IR absorption bands characteristic of DGEBA/pepa and DGEBA/pepa-CuSiF₆(II)

Samples	Wavenumber, cm ⁻¹			
	ν_{NH}	ν_{OH}	ν_{NC}	δ_{NH}
DGEBA/pepa	-	3404; 3332; 3068	1506	-
DGEBA/pepa-CuSiF ₆ (II)	-	3472; 3323; 3065	1505	-

TABLE 3 Results of CT measurements (all-Union State Standard 12.1.044-89)

Combustibility parameters	CuSiF ₆ content, weight fractions				
	0	11	22	44	66
The initial test temperature, T_0 , °C	200	200	200	200	200
The maximum temperature of the gaseous products of combustion, T_{\max} , °C	867 ± 5	663 ± 5	657 ± 5	630 ± 5	220 ± 5
The maximum temperature increment, ΔT_{\max} , °C	667 ± 5	463 ± 5	457 ± 5	430 ± 5	20 ± 5
The time of achievement of T_{\max} , τ (s)	150 ± 1	130 ± 1	184 ± 1	240 ± 1	300 ± 1
The weight loss, Δm (%)	89.0 ± 0.1	81.2 ± 0.1	78.6 ± 0.1	79.6 ± 0.1	4.9 ± 0.1
The combustibility group	Combustible/Moderate flammable				Hard combustible

TABLE 4 UL 94 horizontal flame test results (ASTM D635-14 standard)

CuSiF ₆ content, weight fractions	Burning time per length, s						r_{av} , mm·min ⁻¹	$\tau_{\text{free burning}}$, s
	1 cm	2 cm	3 cm	4 cm	5 cm	6 cm		
0	22 ± 1	51 ± 1	80 ± 1	101 ± 1	125 ± 1	146 ± 1	25.13 ± 1	*
11	**							41 ± 1
22	**							42 ± 1
44	**							41 ± 1
66	***							0
88	***							0

*The sample burns until it is extinguished by force.

**Samples do not support flame propagation; the flame goes out even before the zero line.

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

TABLE 5 UL 94 vertical flame test results (ASTM D380 standard)

Assessment criteria	CuSiF ₆ content, weight fractions				
	11	22	44	66	88
Total time of one sample burning, s	404 ± 1	28 ± 1	8 ± 1	9 ± 1	11 ± 1
Total time of burning for a series of five samples, s	2022 ± 1	138 ± 1	41 ± 1	47 ± 1	56 ± 1
Duration of burning and smoldering of the sample after second flame exposure, s	218 ± 1	21 ± 1	14 ± 1	11 ± 1	15 ± 1
Number of fully burnt samples	5	0	0	0	0
The formation of burning droplets, from which cotton sublayer ignites.	+	–	–	–	–

spectra.²⁰ The Cu(II)-(pepa) chelating is clear detected by the shift of the vibration frequencies of N–H bonds. For free *pepa*, the absorption bands of the N–H stretching of –NH₂ and –NH– groups were found in the high-frequency region at 3372, 3254, and 3210 cm⁻¹. The bending frequency of N–H bonds is found in the low-frequency region at 1600 cm⁻¹.²⁵ After the Cu(II)-N coordinating, the shift of the corresponding absorption bands is observed at 3416, 3238 and 3142 cm⁻¹ for the N–H stretching, and at 1548 cm⁻¹ for the N–H bending. To prove the involvement of *pepa*-CuSiF₆ chelate complex in the formation of the epoxy polymer framework, FTIR spectra were recorded for both *DGEBA/pepa* and *DGEBA/pepa*-CuSiF₆(II) (see Table 2).

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. It shows in Scheme 1.

FTIR spectra recorded for *DGEBA/pepa* show that in addition to the frequencies characteristic for *DGEBA*,²⁶ there is an absorption band (3332 cm⁻¹) responsible for stretching of O–H bond.^{27,28} Thus, the curing of epoxy polymers with *pepa* is the result of crosslinking of the amino groups of the hardener and the epoxy groups of the binder. However, FTIR spectrum of *DGEBA/pepa*-CuSiF₆(II) shows that the absorption band (3323 cm⁻¹) related to the O–H stretching is noticeably weakened due to Cu(II)-O coordinating. This can be explained by the involvement of an additional oxygen atom in the coordination sphere of the chelated Cu²⁺ ion²⁹ (see Scheme 2).

Thus, the polymerization proceeding in the *DGEBA-pepa*-CuSiF₆ system results in the formation of copper(II)-coordinated epoxy-amine polymers. It is accompanied by the interlinking of CuSiF₆ and *pepa* into *pepa*-CuSiF₆ chelate complex, which has the properties of both flame retardant and hardener of epoxy resins. The framework of epoxy-amine polymers modified with CuSiF₆ is presented in Figure 2C.

Unlike *DGEBA/pepa*-CuSiF₆(II) (see Figure 2C), the CuSiF₆ content in *DGEBA/pepa*-CuSiF₆(III), *DGEBA/pepa*-CuSiF₆(IV) and *DGEBA/pepa*-CuSiF₆(V) exceeds the level required for complete curing of the resin. This excessive amount of CuSiF₆ acts as a chemically active additive compound, which is retained in the polymer framework through strong coordination bonds Cu(II)-OHR.

3.2 | Combustibility properties

The fire hazard of the obtained epoxy-polymer materials was evaluated by combustibility, that is, by the ability of the materials to burn and spread the flame. However, it should be noted here that it is practically impossible to achieve the effect of absolute incombustibility of organic polymeric materials. But, given that most fires result from low-power ignition sources, it is very important to reduce the ability of the polymer to ignite. It is necessary to make the polymer material burned poorly, spread the flame slowly, and needed harder conditions for its ignition.

The combustibility group defined for epoxy-amine polymers modified with copper(II) hexafluorosilicate indicates the positive effect of CuSiF₆ on such a fire hazard parameter as combustibility (Table 3).

In particular, it was found that epoxy polymers that do not contain flame retardant have the highest value of the maximum temperature increment ($\Delta T_{\max} = 667^{\circ}\text{C}$) and weight loss ($\Delta m = 89.0$ wt.%) during combustion. For *DGEBA/pepa*, the duration of reaching the maximum temperature of the gaseous products of combustion is 150 seconds.

The addition of the flame retardant in the amount of 11, 22, and 44 weight fractions reduces indices of the combustibility group, in particular, the maximum temperature increment decreases by 204°C to 327°C, and weight loss - by 7.8 to 10.4 wt%. The duration of reaching the maximum temperature of the gaseous products of combustion ranges from 130 seconds to 240 seconds.

As for the above samples, because the maximum temperature increment exceeds 60°C and the weight loss - 60%, these are attributed to combustible materials (see Supporting Information). But, depending on the time to reach the maximum temperature, which is in the range $0.5 \leq \tau \leq 4$ minutes, the samples are classified as moderate flammable materials.

Regarding the peculiarities of the combustion process itself, it should be noted that the sample of the polymer 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. Polymer samples containing flame retardant are more resistant to combustion. The addition of 66 weight fractions of CuSiF₆ especially markedly improves the combustibility group of polymer

(A)

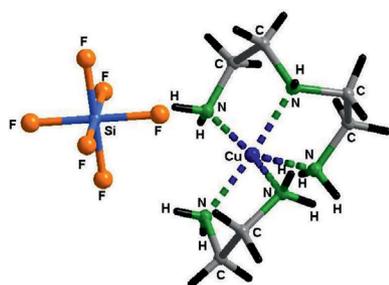
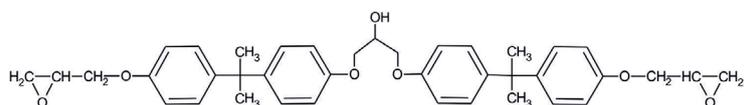
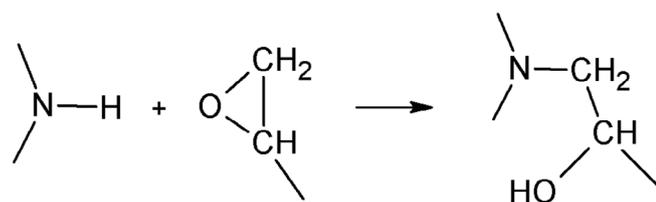
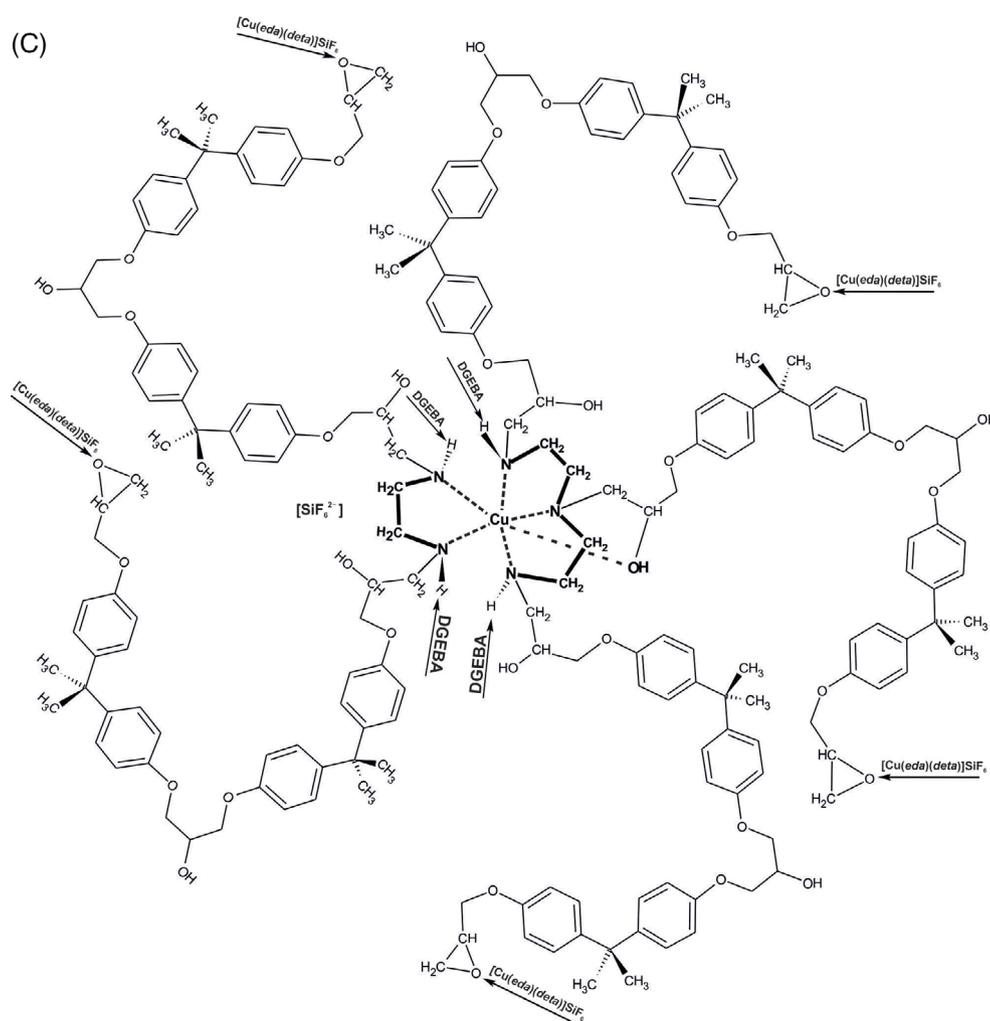


FIGURE 2 A, the structure of $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$. B, DGEBA molecule. C, DGEBA/pepa- $\text{CuSiF}_6(\text{II})$ framework (expected structure) [Colour figure can be viewed at wileyonlinelibrary.com]

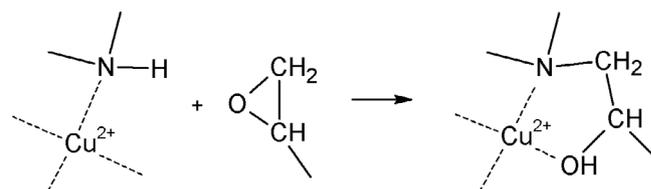
(B)



(C)



SCHEME 1 The curing of epoxy polymers with *pepa*



SCHEME 2 The curing of epoxy polymers with $[\text{Cu}(\text{eda})(\text{deta})]\text{SiF}_6$

materials. Since the maximum temperature increment for sample of the *DGEBA/pepa*-CuSiF₆(IV) does not exceed 60°C ($\Delta T_{\max} = 20^\circ\text{C}$) and the weight loss during combustion is less than 60 wt% ($\Delta m = 4.9 \text{ wt.}\%$), this polymer sample can be assigned to the group of hard combustible materials. The maximum temperature of gaseous products of combustion is reached in 300 seconds. The sample of the *DGEBA/pepa*-CuSiF₆(IV) is able to burn only when directly exposed to an open flame and stops burning immediately after the flame is removed (Figure 3).

3.3 | Flame-self-extinguishment properties

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



FIGURE 3 The sample of the *DGEBA/pepa*-CuSiF₆(IV) after combustibility testing [Colour figure can be viewed at wileyonlinelibrary.com]

the mechanism of flame propagation on the surface of samples of epoxy-polymeric materials modified with copper(II) hexafluorosilicate in a horizontal position are shown in Table 4. These experimental data show that the incorporation of CuSiF₆ in the epoxy-amine framework significantly affects the flame propagation rate.

In fact, samples of the original *DEBA/pepa* (unmodified epoxy-amine polymer) did not stop burning until these were extinguished by force. The average burning rate was 25.13 mm·min⁻¹. Since the burning rate of the sections between the marks did not exceed 40 mm / min, such material is classified as HP "Horizontal Propagation". When such a polymer sample burns, a fall of burning droplets is observed, as a result of which the sublayer of the cotton sheet ignites (Figure 4A). 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 polymer is able to affect significantly the rate of flame propagation on the surface of a sample located horizontally. Although polymer samples containing 11, 22, and 44 weight fractions of CuSiF₆ per 100 weight fractions 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 polymer samples did not exceed 45 seconds. The ignition of the cotton sublayer did not happen either.

When the burner flame affected polymer samples containing 66 and 88 weight fractions of CuSiF₆ per 100 weight fractions of *DGEBA*, deformation of these samples was observed, but after removal of the flame the samples did not burn (Figure 4B).

Samples of CuSiF₆-containing epoxy-amine polymers that do not propagate flame horizontally were studied using UL 94 BV tests. It was found (Table 5) that samples of epoxy-amine polymers with a

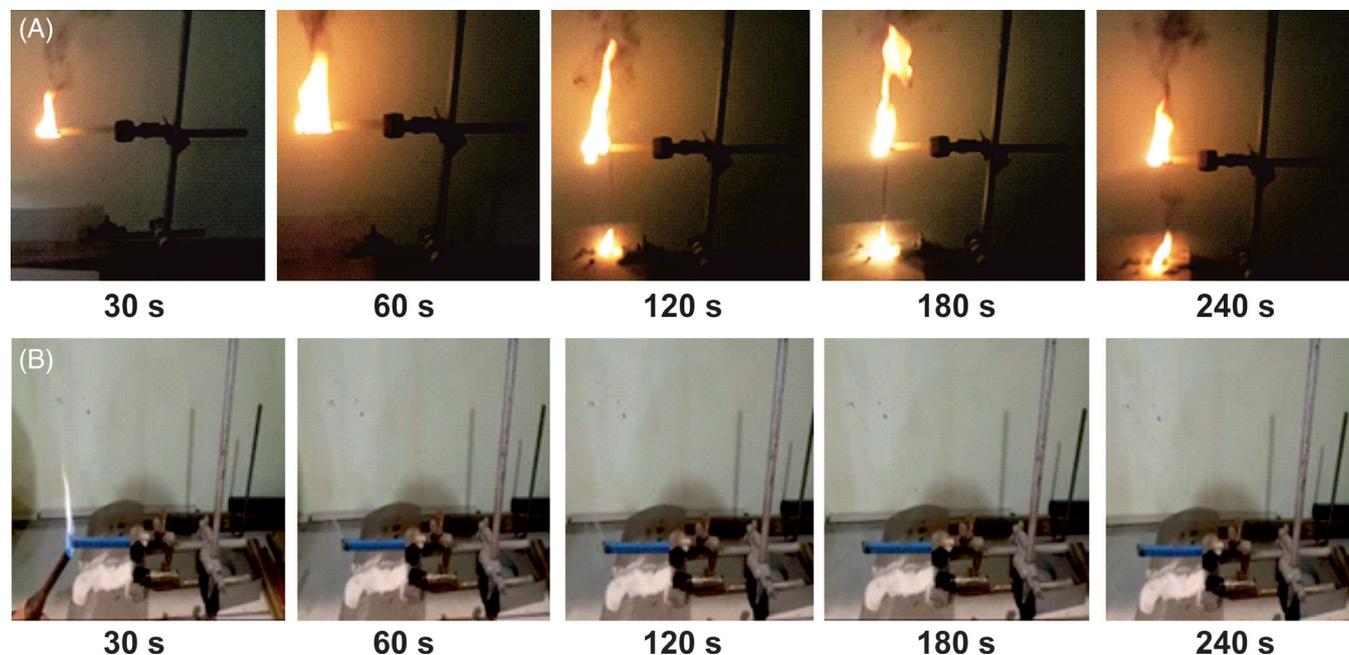


FIGURE 4 Demonstration of UL 94 BH tests. A, *DGEBA/pepa*. B, *DGEBA/pepa*-CuSiF₆ [Colour figure can be viewed at wileyonlinelibrary.com]

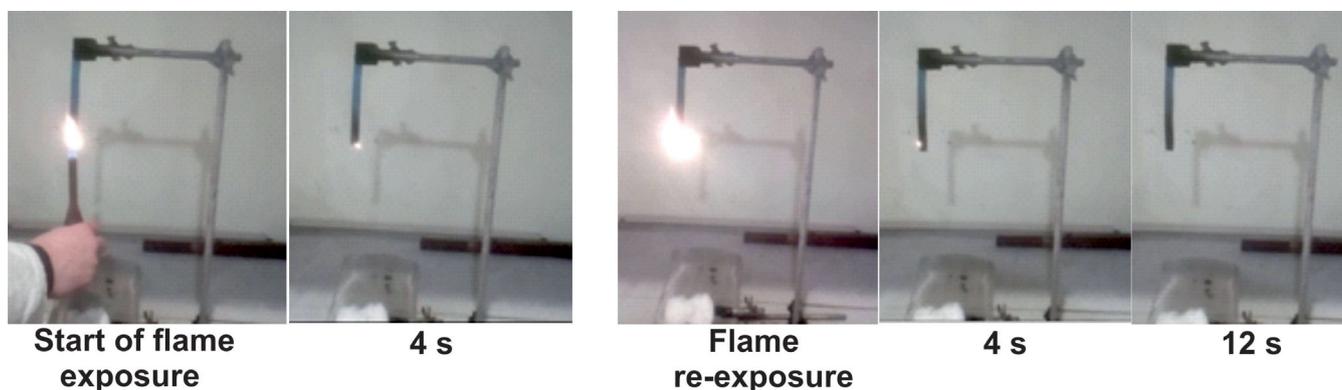


FIGURE 5 Demonstration of UL 94 BV tests for the *DGEBA/pepa-CuSiF₆(IV)* sample [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 6 Burning resistance category for epoxy-amine polymers containing various levels of *CuSiF₆*

Characteristic	<i>CuSiF₆</i> content, weight fractions					
	0	11	22	44	66	88
Burning resistance category	VP	-	VP-1	VP-0	VP-0	VP-1

content of 44 and 66 weight fractions of the flame retardant per 100 weight fractions of the binder (*DGEBA/pepa-CuSiF₆(III)*) and *DGEBA/pepa-CuSiF₆(IV)*) have the best performance. The burning of these samples in the vertical position lasted less than 10 seconds after flame re-exposure. The total time of burning for the five-sample series did not exceed 50 seconds. None of the samples have burned or smoldered to the end (ie, to the clamp). The cotton sublayer did not ignite too, as there was no fall of burning droplets. These samples did not burn or smelt within 30 seconds after the second flame removal (Figure 5).

Thus, samples of *DGEBA/pepa-CuSiF₆(III)* and *DGEBA/pepa-CuSiF₆(IV)* belong to the highest burning resistance category of polymeric materials - VP-0 (VP is vertical propagation) (Table 6).

3.4 | Smoke formation

Along with the considered fire hazard parameters, smoke is the most dangerous for people during indoor fires. Therefore, it is extremely important to study epoxy-amine polymers as for the effect of flame retardant on the processes of smoke formation under conditions of burning and smoldering. To assess the smoke formability, the smoke formation factor in burning and smoldering modes was determined (Figure 6).

The lowest value of the smoke formation factor in smoldering mode is characteristic of the *DGEBA/pepa-CuSiF₆(III)*, containing 44 weight fractions of flame retardant. This polymer sample is referred to materials with the moderate smoke formation. Since the smoke formation factor for other polymer samples in smoldering mode exceeds $500 \text{ m}^2 \cdot \text{kg}^{-1}$, these relate to materials with a high degree of smoke formation.

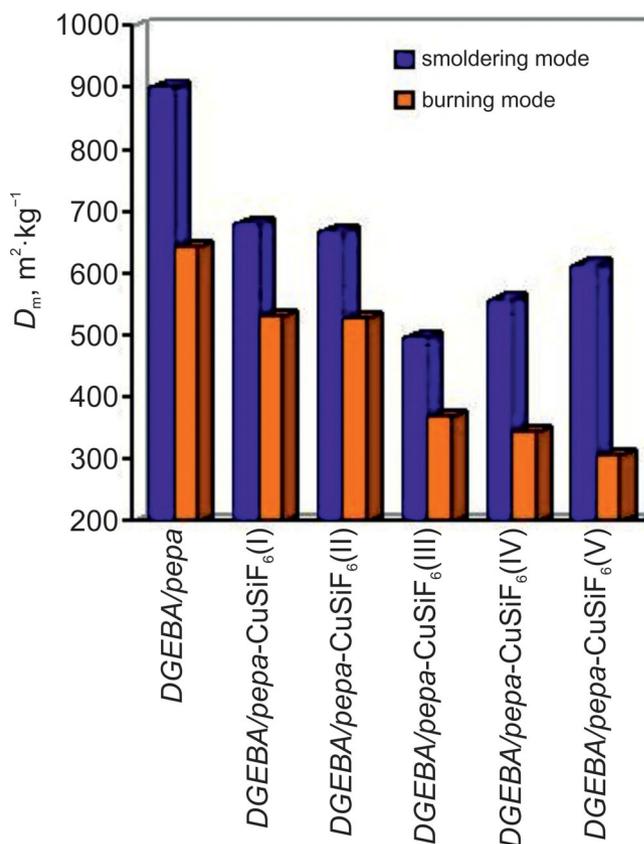


FIGURE 6 The dependence of the smoke formation factor value on the flame retardant content in epoxy-amine polymers. The measurements were carried out in smoldering and burning modes [Colour figure can be viewed at wileyonlinelibrary.com]

There is a different pattern with respect to the smoke formation factor measured in burning mode of materials. The addition of a flame

retardant in an amount of 44 weight fractions and more carries these epoxy-amine polymers from the group of materials with high smoke-forming ability into the moderate group. The smoke formation factor value for the DGEBA/pepa-CuSiF₆(V), containing 88 weight fractions of flame retardant is almost two times greater than for DGEBA/pepa.

4 | CONCLUSIONS

A unique technology for the preparation of CuSiF₆-containing epoxy-amine polymers was developed. The essence of the development is to use the product of the interaction of the non-combustible inorganic salt of copper(II) and the amine hardener of epoxy resins as a flame retardant-hardener with its further incorporation into the DGEBA polymer framework. That made it possible to generate a new type of polymer materials with flame-self-extinguishment properties. Thus, the controlled introduction of copper(II) hexafluorosilicate into the epoxy-amine matrix allowed to obtain a number of epoxy-amine polymers with a different contain of inorganic salt—DGEBA/pepa-CuSiF₆(I), DGEBA/pepa-CuSiF₆(II), DGEBA/pepa-CuSiF₆(III), DGEBA/pepa-CuSiF₆(IV), and DGEBA/pepa-CuSiF₆(V)—which have reduced combustibility.

The results of CT measurements show 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 this polymer sample from the group of combustible materials with medium flammability to the group of hard-combustible materials.

A study of the regularity of flame propagation on the surface of samples of epoxy-amine polymers showed that samples containing 44 and 66 weight fractions of copper(II) hexafluorosilicate do not support flame propagation and belong to the highest category of combustion resistance, that is, to the VP-0 category.

Introduction of a flame retardant into epoxy-amine polymer also facilitates to decrease the smoke formation during both in smoldering and burning modes. It allowed assigning the said epoxy-amine polymers into the group of materials with moderate smoke-forming ability; for comparison, DGEBA/pepa polymer belongs to the group of materials with highest smoke-forming ability.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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