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Metal-Coordinated Epoxy-Amine Composition with Reduced Fire Risk: Elaboration, Thermal and Ignition Resistance

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Abstract

A new flame retardant-hardener for epoxy resins has been prepared. The flame retardant-hardener is a coordination compound of a chelate type, aqua-bis(ethylenediamine)-chloro-copper(II) chloride, $[Cu(eda)_2(H_2O)(Cl)]Cl$ (*eda* – $NH_2C_2H_4NH_2$). The incorporation of the flame retardant curing agent, $[Cu(eda)_2(H_2O)(Cl)]Cl$, into the epoxy polymer matrix results in the production of new generation polymeric materials with reduced fire risk based. Bonding in the [hardener – flame retardant] system involve the interaction of a combustible nitrogen-containing curing agent (ethylenediamine) with a non-combustible inorganic *d*-metal salt (copper(II) chloride) into an aminocopper(II) chelate compound through strong Cu–N coordination bonds. The strength of bonding between the copper(II) salt and the amine hardener, as well as the participation of the resulting aminocopper(II) chelate compound in the formation of the polymer matrix framework, determine the resistance of modified epoxy-amine compositions to thermal oxidative degradation and ignition. The inclusion of the flame retardant-hardener in the epoxy resin reduces the segmental mobility of the interconnecting molecular links and leads to the creation of a denser polymer matrix. As a result, metal-coordinated epoxy-amine compositions are formed, which display good thermal resistance and self-extinguishing properties under combustion conditions.

Keywords

reduced fire risk, flame retardant-hardeners, metal-containing epoxy-amine composites, thermal resistance, ignition resistance

1 Introduction

The protection of the population, business facilities, and national wealth from fires and their consequences is a crucial aspect of any country's national security policy. However, according to the International Association of Fire and Rescue Services report, many countries have experienced an increase in the number of fires in recent years [1].

The rapid growth in industrial production and the use of polymeric materials in various spheres of life are among the reasons for this dynamic. Fires caused by the ignition and combustion of polymer products are complex due to intense temperature rise, melt spreading and dripping, high smoke density, and high toxicity of decomposition and combustion products [2]. In recent years, fires involving the burning of polymers have been most common in residential buildings and structures (29.3–45.9%), followed by vehicles (2.6–5.5%), industrial buildings (0.5–1.3%), trade and catering facilities (0.8–1.1%), and socio-cultural, public, and administrative buildings (0.5–1.0%).

Epoxy-based materials are prominent among the wide range of polymeric materials available on the global market due to their valuable properties, including high adhesion, strength, rigidity, and chemical resistance. Compared to many other classes of synthetic polymers, epoxy resins are superior. Epoxy polymers are versatile materials that can be used as adhesives, sealants, protective coatings, paints, varnishes, casting compounds, and binders for reinforced glass and organic plastics in various industries, including construction, radio engineering, vehicle manufacturing, aircraft, rocketry, and shipbuilding [3]. However, the use of epoxy polymers in these critical areas of life is only possible if their inherent drawbacks, particularly their fire hazard, are eliminated.

Reducing the fire hazard of polymeric materials requires active intervention in each stage of combustion using physical or chemical means. It is important to consider the multi-stage nature of diffusion combustion. Therefore,

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modern methods for reducing the fire hazard of polymeric materials involve controlling the chemical structure, composition, and ratio of initial components. This results in changes in the mode of action and kinetics of chemical reactions in the condensed and gas phases, inhibiting combustion reactions of polymer pyrolysis products in the gas phase, reducing heat and mass transfer between the combustion zone and the condensed phase, and cooling the reaction mixture due to heat loss to the environment. In practice, the fire hazard of polymeric materials is typically reduced by combining various methods based on the intended use, required technological, physical, and mechanical properties, and cost.

One common method of reducing the fire hazard of epoxy materials is to incorporate inert or reactive flame retardants during the manufacturing process. Inert flame retardants are typically physically combined with the polymer, providing a cost-effective and time-efficient way to increase the flame retardancy of commercial polymers. However, this type of flame retardant has several significant disadvantages, including a high tendency to migrate, poor compatibility with the polymer, and a negative impact on the physical and chemical properties of the polymer. These limitations significantly restrict their use.

The use of chemically active flame retardants is the most effective method for polymers combustion prevention. This involves developing new fire resistant polymers or modifying existing ones by incorporating a flame retardant into the main or side chains [4, 5]. Inorganic transition metal compounds are particularly noteworthy in this regard. A crucial requirement for this selection is the remarkable propensity of transition metal ions to react chemically with nitrogen-containing organic molecules, resulting in the creation of coordination compounds of a chelate type [6].

In recent years, developments in this field has been actively progressing. The effectiveness of using coordination compounds composed of inorganic copper(II) salts and amine hardeners of epoxy resins to decrease the fire risk of epoxy compositions has been demonstrated [7–10]. Therefore, expanding the range of metal-containing flame retardants for epoxy compositions, conducting systematic studies on the effect of flame retardants of this type on fire safety and performance properties of compositions, as well as determining the areas of practical application of the developed epoxy-amine compositions is extremely relevant [11–14].

2 Experiments

2.1 Materials

To obtain metal-coordinated epoxy-amine compositions with reduced fire hazard, commercially available reagents were used. The *ED*-20 brand epoxy resin (a colorless epoxy diane oligomer (*ED*) with an epoxy group content of about 22%) was chosen as a binder. Polyethylenepolyamine (*pepa*), which includes ethylenediamine (*eda*), diethylene triamine (*deta*), triethylenetetramine (*teta*), etc, was used as a curing agent. The inorganic salt of copper(II), $CuCl_2$, served as a flame retardant.

2.2 Flame retardant-hardener synthesis

A flame retardant-hardener was produced in the form of a coordination compound of a chelate type, $[Cu(eda)_2(H_2O)(Cl)]Cl$. The synthesis of this compound involves the direct interaction of copper(II) chloride dihydrate with polyethylenepolyamine. The crystal structure of the chelate compound $[Cu(eda)_2(H_2O)(Cl)]Cl$ has previously been described [15]. Crystalline $CuCl_2{\cdot}2H_2O$ (1.7 g, 0.01 mol) was placed in a porcelain mortar and an excess of *pepa* was added. The reaction mixture was ground until a homogeneous dark blue liquid suspension formed. It was then kept at room temperature for several days until a crystalline phase appeared.

$$\begin{aligned} &CuCl_2 \cdot 2H_2O + pepa \\ &= \left[Cu\left(eda\right)_2\left(H_2O\right)\left(Cl\right)\right]Cl + H_2O \end{aligned} \tag{1}$$

2.3 Epoxy-amine composites preparation

Two methods were used to prepare the metal-coordinated epoxy-amine composition *ED*/*pepa*-$CuCl_2$. In the first method, a pre-synthesized flame retardant-hardener $[Cu(eda)_2(H_2O)(Cl)]Cl$ was added to a corresponding weight of the epoxy oligomer *ED*-20 and stirred until a homogeneous suspension was obtained.

The second method involved drying green-blue crystals of $CuCl_2 \cdot 2H_2O$ in an oven at 110 °C [16] to obtain yellow-brown $CuCl_2$ powder. The epoxy resin was mixed with an appropriate amount of *pepa* (curing agent) and $CuCl_2$ (flame retardant) in alternating additions until the composition was homogenized. Additionally, an initial unmodified epoxy-amine composition *ED*/*pepa* was prepared without the addition of a flame retardant. The compositions were poured into molds made of aluminum foil and left at room temperature. The curing process was complete within 24 hours.

Table 1 presents the qualitative and quantitative formulation of the compositions obtained, while Fig. 1 displays their photographs.

2.4 Characterization and measurement

2.4.1 Infrared spectroscopy

The infrared (IR) spectra of *ED*/*pepa* and *ED*/*pepa*-$CuCl_2$ were recorded using PerkinElmer Spectrum Two FTIR and Philips PU 9800 FT infrared spectrometers, respectively. The frequency range was 4000–500 cm^{-1} with a resolution of 2 cm^{-1} for both spectra. The solid-phase samples of polymer compositions were compressed into pellets with spectroscopically pure KBr.

2.4.2 Thermogravimetric analysis

Thermogravimetric analysis of the epoxy-amine compositions was carried out using Q-1500D thermal analyzer (F. Paulik, J. Paulik, L. Erdey system). The measurements were conducted in a dynamic mode in an air atmosphere, with the samples heated at a rate of 5 °C min^{-1}. The sample weight was 100 mg, and the reference substance used was aluminum oxide.

2.4.3 Flammability test

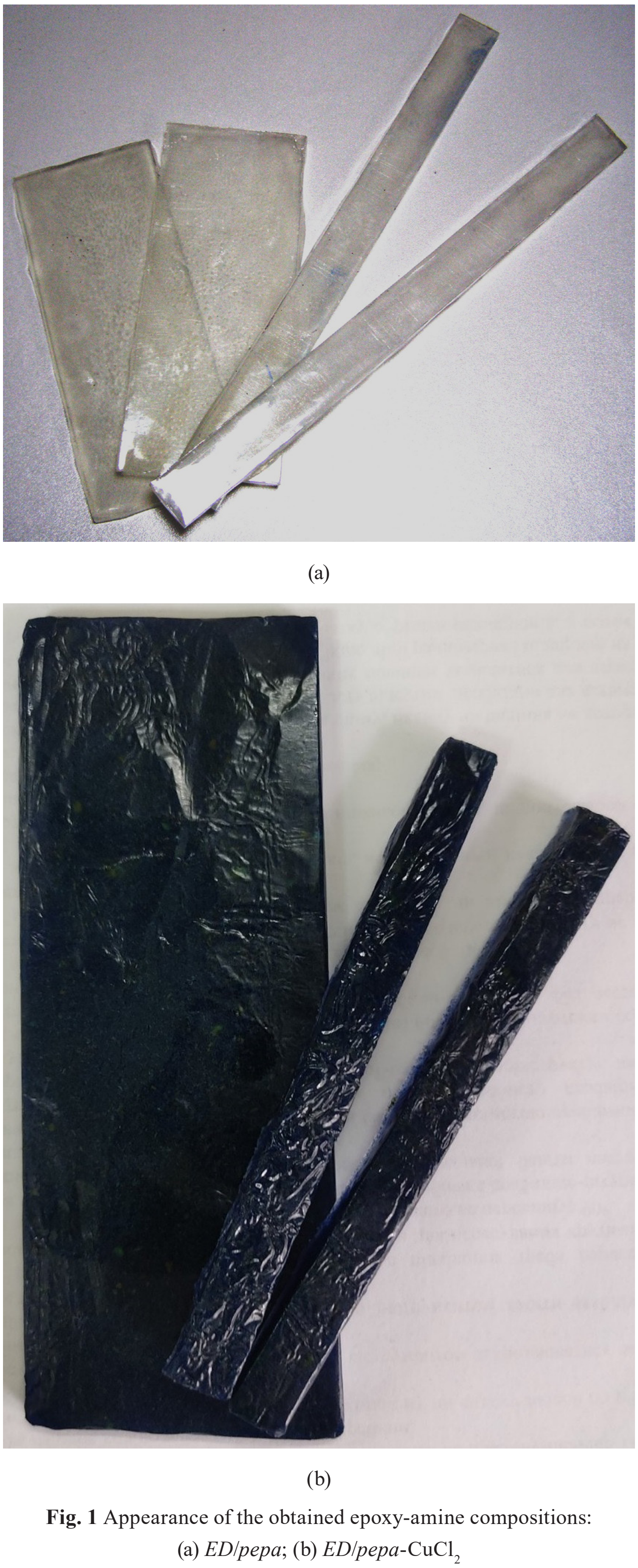
The ignition (t_{ign}) and self-ignition ($t_{self\text{-}ign}$) temperatures of *ED*/*pepa*, *ED*/*pepa*-$CuCl_2$(14), and *ED*/*pepa*-$CuCl_2$(40) samples were determined using a TF device in accordance with ASTM D1929-20 [17]. For this purpose, ten cylindrical samples were prepared for each type of sample tested, each weighing 3 g. Prior to the test, the samples were conditioned.

2.4.4 UL94 tests

Flame propagation tests were performed in accordance with ASTM D635-22 [18] and ASTM D3801-19a [19] using UL 94 BH and UL 94 BV methods, respectively. Samples of *ED*/*pepa*, *ED*/*pepa*-$CuCl_2$(14), and *ED*/*pepa*-$CuCl_2$(40) with dimensions of 125 × 10 × 5 mm^3 were made. Three samples from each composition were tested. Before testing, the samples were kept for 48 hours at 25 °C and 50% relative humidity.

Table 1 Stoichiometry of epoxy-amine compositions

Composite	Mole ratio			Mass ratio		
	ED	*pepa*	$CuCl_2$	*ED*	*pepa*	$CuCl_2$
ED/*pepa*	2.5	1	0	100	12	0
ED/*pepa*-$CuCl_2$(14)	2.5	1	1	100	12	14
ED/*pepa*-$CuCl_2$(40)	2.5	1	3	100	12	40



(a)

(b)

Fig. 1 Appearance of the obtained epoxy-amine compositions: (a) *ED*/*pepa*; (b) *ED*/*pepa*-$CuCl_2$

3 Results and discussion

3.1 Structuring epoxy-amine compositions

To evaluate the effect of the obtained flame retardant-hardener on the structure of epoxy-amine compositions, a comparative analysis of the IR spectra of modified (*ED*/*pepa*-$CuCl_2$) and unmodified (*ED*/*pepa*) epoxy-amine compositions has been conducted (Fig. 2). In both cases, the curing process of the epoxy compositions is accompanied by a significant decrease in the intensity of the absorption band at 915 cm^{-1}, which describes the vibrations of epoxy groups inherent in the epoxy diane oligomer.

IR spectra of *ED*/*pepa* (Fig. 2 (1.)) revealed that the curing process of epoxy resin with the participation of pepa results in the appearance of new absorption bands that correspond to the vibrations of the newly formed N–C and O–H bonds. However, the absorption bands that describe the vibrations of the N–H bond are almost absent. Broad absorption bands at 3333 and 3232 cm^{-1} were also identified, which are apparently responsible for the valence vibrations of OH groups. It confirms that the curing process of epoxy resin with *pepa* occurs due to the interaction between the epoxy group of the *ED*-20 epoxy oligomer and the amino group of the hardener, following the known epoxy polymerization mechanism (Scheme 1) [20–22].

IR spectra of the *ED*/*pepa*-$CuCl_2$ (Fig. 2 (2.)) showed that the interaction of the flame retardant-hardener $[Cu(eda)_2(H_2O)(Cl)]Cl$ with the binder *ED*-20 leads to the disappearance of N–H bonds in the amino groups. Instead, N–C bonds are formed and new O–H bonds appear. It should be noted that in the chelate compound $[Cu(eda)_2(H_2O)(Cl)]Cl$, which acts as a flame retardant-hardener [23] of epoxy resins, the coordination site occupied by the H_2O molecule can be replaced by the OH group after structuring the composition (Scheme 2).

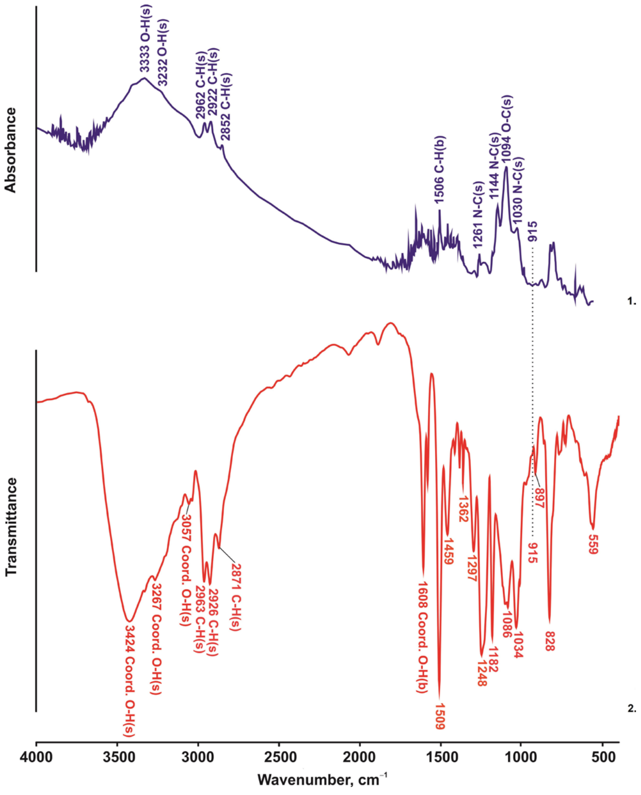
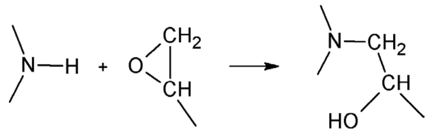


Fig. 2 IR spectra of *ED*/*pepa* (1.) and *ED*/*pepa*-$CuCl_2$ (2.)

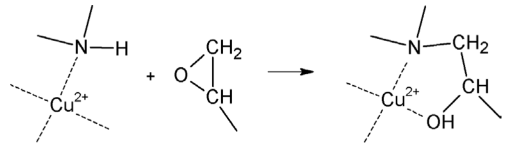
3.2 Thermal characteristics

The thermogram (Fig. 3) shows that the thermo-oxidative degradation of *ED*/*pepa* occurs in four stages [24]. The first stage of thermolysis occurs in the temperature range from 20 and 180 °C, and is accompanied by the release of volatile gaseous decomposition products that are not bound into the polymer's spatial network. An endothermic effect is observed on the DTA curve in this temperature range. The sample suffers a mass loss of 3.1% (Table 2).

During the second stage of thermolysis, the sample experienced a 32% loss in mass within the temperature range of 180–360 °C. Additionally, the DTA curve recorded an exothermic effect with a maximum at 300 °C. This effect is attributed to the thermo-oxidative destruction of the sample through a free radical mechanism involving alkyl and peroxide radicals, resulting in the formation of hydroperoxides [25–27].



Scheme 1 Curing epoxy resin with *pepa*



Scheme 2 Curing epoxy resin with $[Cu(eda)_2(H_2O)(Cl)]Cl$

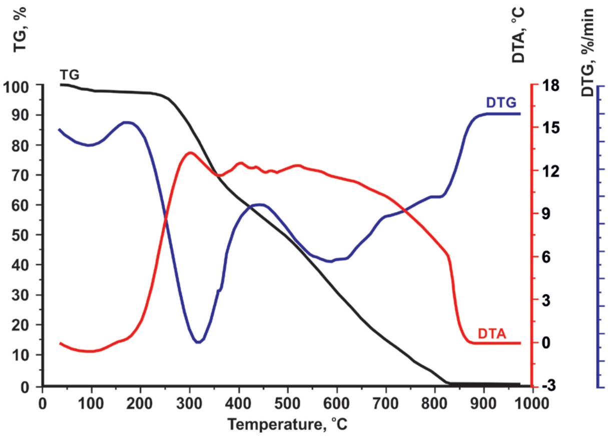


Fig. 3 Thermogram of *ED*/*pepa*

Table 2 Thermolysis results of *ED*/*pepa* and *ED*/*pepa*-$CuCl_2$

Sample	Stage	Temperature rang (°C)	Weight loss (%)
ED/*pepa*	1	20–180	3.1
	2	180–360	32.0
	3	360–460	12.1
	4	460–900	52.0
ED/*pepa*-$CuCl_2$	1	20–138	2.27
	2	138–216	1.59
	3	216–326	18.48
	4	326–480	33.33
	5	480–640	30.83

The third stage of thermo-oxidative degradation takes place between 360–460 °C. During this stage, the organic components of the original sample undergo thermolysis and burn, resulting in a 12.1% loss of mass. This is evidenced by the exothermic effect on the DTA curve, which peaks at 400 °C.

During the fourth stage of thermolysis, which occurs in the temperature range of 460–900 °C, the pyrolytic residue of the sample undergoes combustion, resulting in a 52% mass loss. Additionally, an exothermic effect is observed on the DTA curve at this stage.

The sample *ED*/*pepa*-$CuCl_2$ undergoes thermo-oxidative degradation in five stages (refer to Table 2), as shown in Fig. 4. During the initial stage, which takes place between 20–138 °C, there is a slight decrease in sample mass (Δm = 2.27%). This corresponds to the release of volatile degradation products that do not contribute to the formation of the spatial network of the epoxy-amine composition. An endothermic effect is observed on the DTA curve in this temperature range.

During the second thermolysis step, which occurs between 138–216 °C, the coordinated amine epoxy hardener undergoes partial thermo-oxidative degradation. The DTA curve shows an exothermic effect resulting from this process, with a maximum at 199 °C, and a slight mass loss of the sample (Δm = 1.59%).

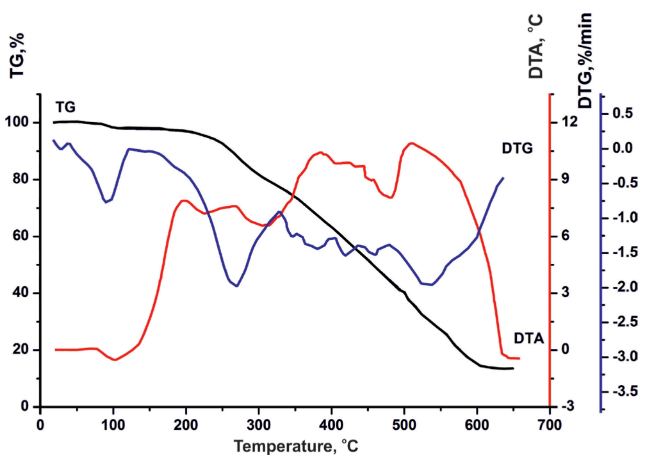


Fig. 4 Thermogram of *ED*/*pepa*-$CuCl_2$

The third stage of thermolysis occurs within the temperature range of 216–326 °C. During this stage, the flame retardant curing agent undergoes complete thermal decomposition. However, this process is complicated by thermal oxidation processes in the epoxy resin. As a result, the sample experiences a mass loss of 18.48%. Additionally, an exothermic effect is observed on the DTA curve at 266 °C. It should be noted that the destructive processes in the *ED*/*pepa*-$CuCl_2$ sample begin at lower temperatures compared to the *ED*/*pepa* sample. This is likely due to the course of destruction in the coordination compound. The thermo-oxidative destruction processes of the epoxy component of the composition containing a flame retardant are less intense compared to the composition without a flame retardant. This is evidenced by the appearance of a less intense exo-effect on the DTA curve.

During the fourth stage of thermolysis, which takes place between 326–480 °C, the epoxy resin undergoes deep thermal oxidation processes. This results in the combustion of the organic components of the sample. The TG curve shows a significant mass loss (33.33%) during this stage of degradation, while the DTA curve displays an exothermic effect with a maximum at 385 °C.

The fifth and final stage of thermolysis occurs within the temperature range of 480–640 °C. At this point, the pyrolytic residue of the sample is completely burned, resulting in a significant mass loss of 30.83%. This process is accompanied by an exothermic effect on the DTA curve, with the maximum temperature of this effect being 511 °C.

The combustion of a polymer always occurs after the thermo-oxidative degradation stage. Combustion becomes impossible once the material has completed decomposition and no more combustible gases are released into the environment. The thermogravimetric analysis results indicate that the thermo-oxidative degradation and combustion of the carbonized residue of the *ED*/*pepa*-$CuCl_2$ conclude at 640 °C, whereas for the *ED*/*pepa*, these processes continue until 900 °C. This suggests that the combustion of the modified composition terminates earlier than that of the unmodified composition. This also indicates, although not directly, the self-extinguishing nature of the combustion of the composition containing the flame retardant.

3.3 Flammability

To investigate the effect of copper(II) chloride as a flame retardant on the flammability of the epoxy-amine composites, we compared the ignition and self-ignition temperatures of the unmodified starting composite and composites with varying amounts of copper(II) chloride (refer to Table 3). The results showed that the *ED*/*pepa* composition had an ignition temperature of 320 °C and a self-ignition temperature of 545 °C.

Adding 14 mass parts $CuCl_2$ per 100 mass parts *ED*-20 to the epoxy-amine composition results in a slight decrease of 6 °C in ignition temperature and 15 °C in self-ignition temperature. Increasing the flame retardant content to 40 mass parts $CuCl_2$ per 100 mass parts *ED*-20 significantly decreases the ignition temperature, while the self-ignition temperature remains practically unchanged.

3.4 Flame self-extinguishing effect

The horizontally placed sample based on the unmodified epoxy-amine composition *ED*/*pepa* was ignited by the burner flame. The sample continued to burn until it was forcibly extinguished. The sample burned for 179 seconds over a length of 75 mm, resulting in a calculated linear burning rate of 25.14 mm min^{-1}. The material sample based on the *ED*/*pepa* composition is classified as HB according to UL 94 (the burner flame is the source of ignition of a horizontally fixed sample) because its burning rate between the 25 mm and 100 mm marks does not exceed 40 mm min^{-1}.

It should be noted that burning a sample of this composition (*ED*/*pepa*) resulted in intense smoke formation and the release of burning drops of decomposition products. This caused the cotton wool placed under the sample to ignite. During a fire, this process can not only increase the fire area but also create new ignition points, posing an additional threat to human life.

The addition of copper(II) chloride to epoxy-amine compositions as a flame retardant has a significant impact on the rate of flame propagation. Samples containing the *ED*/*pepa*-$CuCl_2$(14) composition ignited and combusted under the influence of the burner flame, but the flame extinguished before reaching a distance of 75 mm. The burner flame caused ignition and combustion of the *ED*/*pepa*-$CuCl_2$(40) samples, which lasted for 3 seconds after the burner was removed. The flame then spontaneously went out before reaching the 25 mm mark. No ignition centers were detected during the combustion of samples based on modified compositions on a cotton wool substrate.

Table 3 Results of flammability tests

Indicator	Content of $CuCl_2$ (mass parts)		
	0	14	40
Ignition temperature (t_{ign}, °C)	320	314	279
Self-ignition temperature ($t_{self\text{-}ign}$, °C)	545	520	518

Samples based on compositions containing copper(II) chloride did not meet the requirements of the HB category. Therefore, the resistance to burning of samples placed in a vertical position was studied. The samples with a flame retardant content of 40 mass parts $CuCl_2$ per 100 mass parts *ED*-20 met the best criteria. The afterflame time for each sample did not exceed 30 seconds. The total afterflame time for the 5 samples was less than 250 seconds. Additionally, the afterflame plus afterglow time for each sample after the second flame application was less than 60 seconds. None of the samples burned or smoldered up to the holding clamp, and the lined cotton wool did not ignite, as there were no falling burning drops. According to UL 94, samples composed of *ED*/*pepa*-$CuCl_2$(40) can be classified as V-1. However, during the combustion of samples composed of *ED*/*pepa*-$CuCl_2$(14), burning particles fell and ignited the lined cotton wool in some cases. As a result, these samples only meet the requirements of V-2.

Thus, $CuCl_2$-modified epoxy-amine compositions exhibit excellent thermal and flame resistance, as well as self-extinguishing properties during combustion.

4 Conclusion

A method has been developed for forming metal-coordinated epoxy-amine compositions with reduced fire hazard. The method involves synthesizing an aminecopper(II) chelate compound, which acts as a flame retardant-hardener for epoxy resins, and introducing it into the epoxy polymer matrix. The IR spectroscopy results suggest that the formation of metal-coordinated epoxy-amine compositions involves the binding of a non-combustible inorganic salt to a combustible nitrogen-containing epoxy hardener via strong Cu(II)–N coordination bonds. DTA and UL94 studies have confirmed that epoxy-amine compositions modified with copper(II) chloride exhibit increased resistance to thermal oxidative degradation and flame. The self-extinguishing effect of the modified epoxy-amine compositions during combustion depends on the strength of the bond between the copper(II) salt and the amine hardener, as well as the participation of the aminecopper(II) chelate compound in forming the polymer matrix framework.

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