

# The Effect of a Copper(II) Chelate Coordination Compound on the Combustibility and Fire Behavior of Epoxy-Amine Composite Materials

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## Abstract

This study investigates the impact of a novel copper(II)-based flame retardant on the combustibility and fire risk of epoxy composites. The flame retardant is a chelate-type coordination compound of copper(II) chloride and diethylenetriamine (*deta*) –  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  – and was synthesized through the direct reaction of  $\text{CuCl}_2$  and polyethylenepolyamine (*pepa*). When incorporated into epoxy resin, the synthesized coordination compound exhibits bifunctional properties, acting as both a flame retardant and a curing agent. Epoxy composites containing  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  are significantly less combustible, as demonstrated by a decrease in the maximum temperature of the gaseous combustion products and the mass loss of composite samples due to combustion. The flammability of the synthesized composition was evaluated using the vertical burning method in accordance with the UL 94 standard, and the composition met the criteria for the V-1 class. Incorporating the synthesized flame retardant-hardener into the epoxy resin reduces smoke emission intensity during burning and smoldering. The increased fire resistance of the modified compositions is due to the formation of Cu–N coordination bonds in the polymer matrix and the catalytic effect of copper-containing centers on carbonization and oxidation processes. This is in addition to the formation of a dense, carbonized protective layer during thermal decomposition. These results confirm the potential of using copper(II) chelate coordination compounds as multifunctional components in epoxy systems that combine the roles of curing agent and flame retardant. This opens up opportunities for creating a new generation of polymer materials with enhanced fire safety for various applications.

## Keywords

fire risk, metal-containing flame retardants, epoxy-amine compositions, combustibility, flame spread, smoke generation

## 1 Introduction

The development of industrial technologies has sparked growing interest in epoxy resins and materials, expanding the scope of their practical applications. However, significant drawbacks of epoxy composite materials limit their use in new fields. These drawbacks include relatively low heat and thermal resistance, as well as an increased fire hazard. Depending on the intended use, the required technological and physical-mechanical properties of the materials, and their cost, the fire hazard of polymer materials based on epoxy resins can be reduced by applying various methods [1, 2]. Currently, the most common approach to addressing this issue is to alter the elemental composition and chemical structure of epoxy polymers using reactive flame retardants. Consequently, the range of flame retardant types is constantly expanding [3–5].

Metal-containing flame retardants deserve special attention. Among the wide range of compounds in this class, the most common are salts, oxides, and hydroxides of *s*- or *p*-elements [6–8]. These flame retardants primarily act through physical mechanisms, such as heat absorption during thermal decomposition, releasing non-flammable gases, or forming a protective oxide layer on the surface of the material. However, their effectiveness often depends on the degree of dispersion and uniformity of distribution within the polymer. However, a significant drawback of these systems is that flame retardant particles tend to migrate to the surface of the material during use, which can lead to a gradual loss of fire resistance. Additionally, a high content of mineral additives often negatively affects the physical and mechanical properties of composites, particularly reducing

strength, elasticity, and adhesive properties. These limitations restrict their use in high-load structural materials and drive the search for more effective reactive flame retardants.

In this context, using metal coordination compounds significantly expands the possibilities for producing epoxy polymer materials with reduced fire hazards and varying other properties. Organometallic compounds are most often proposed for this purpose. In this case, the complexing agents are transition metal atoms, such as copper, cobalt, nickel, and zinc, while the ligands are phosphorus-, nitrogen-, or silicon-containing compounds.

To improve the fire resistance of epoxy resins, the flame retardant DOPO-Salen-Ni has been proposed. It is based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and the Salen-Ni ligand. Studies have shown that with a flame retardant content of 5 wt.%, the oxygen index increases to 32.2%, and the material achieves a UL-94 V-0 rating [9]. Additionally, significant reductions in heat release and smoke generation are observed. This synergistic effect in the gas and condensed phases achieves the fire-retardant effect, making the proposed approach promising for developing effective next-generation flame-retardant systems.

Using Zn- and Fe-based organometallic coordination compounds that are modified with phosphonitrile groups significantly improves the fire resistance, smoke generation capacity, and thermal stability of epoxy resins [10]. Zn-containing coordination compounds have been shown to be more effective than Fe-containing ones, increasing the oxygen index by up to 29.8%. The primary fire-retardant mechanism occurs in the condensed phase due to the synergistic action of catalytic carbonization driven by metal ions and the flame-retardant effect of phosphonitrile fragments, which promote the formation of a stable, protective, graphitized layer. Additionally, gas-phase processes associated with the release of phosphorus- and nitrogen-containing radicals during thermal decomposition were found to play an important role in flame suppression, particularly in systems containing zinc(II) coordination compounds.

A phosphorus-containing organozinc compound (Zn-PDH), obtained using zinc and iron as the metal center and 4-aminopyridine as the organic ligand, which contains P-N fragments of phosphazene (PDH), has fire-retardant properties and a mechanism of action. The same is true of Zn-PDH/tris-(3-DOPO-1-propyl)-triazine tri-one (TAD) in epoxy resin [11]. The composition demonstrated the best flame retardancy, smoke suppression, and heat release reduction when TAD and Zn-PDH were added to the epoxy resin in a 3:1 ratio. Furthermore, the gas phase and Zn-PDH contributed primarily to charring,

providing a barrier and protective effect in the condensed phase. TAD, on the other hand, released phosphorus-containing and phenoxy radicals during decomposition, primarily exerting a quenching effect in the gas phase. In the condensed phase, Zn-PDH promoted the decomposition of the polymer matrix, forming a greater number of aromatic structures and rapidly creating a dense, carbonized layer rich in cross-linked P-O-C structures at high temperatures. Meanwhile, more nitrogen (N) entered the gas phase as an inert gas, diluting the concentration of combustible gas and helping to inhibit the combustion reaction.

Additionally, significant attention has been devoted to studies aimed at using metal coordination compounds as curing agents for epoxy resins. One such coordination compound is the epoxy-imidazole adduct of phenylglycidyl ether with 2-ethyl-4-methylimidazole (PGE-EMI) and its acetate and chloride salts with transition metals (Mn, Co, Ni, Cu, Zn, and Ag). These coordination compounds have been proposed as epoxy resin curing agents [12, 13]. The thermal stability of the coordination compounds depends on the transition metal and the anion. Notably, coordination compounds with acetate anions were found to be less thermally stable than their chloride counterparts.

Metal-coordinated epoxy polymers were obtained using bisphenol-A diglycidyl ether as a hardener for copper(II) salts of organic acids (acetic acid, salicylic acid, and anthranilic acid), as well as copper(II) salicylaldehydes with aliphatic amines (e.g., ethylenediamine, diethylenetriamine, triethylenetetramine, and cyanoethylated diethylenetriamine) [14, 15]. The effects of different ligands and anions on polymer properties were investigated. Copper-containing polymers were found to exhibit significant thermal-oxidative stability up to 280 °C.

Due to the behavior of the coordination compounds *d*-metal, there has been growing interest in recent years in using them as multifunctional additives that can serve as flame retardants, hardeners, plasticizers, foaming agents, structure-forming agents, and surfactants. This work particularly proposes using Cu(II) and Co(II) coordination compounds modified with ammonium polyphosphates as multifunctional additives in epoxy systems [16]. The synthesized coordination compounds have been shown to act as co-curing agents, improve compatibility between components of the composition, and enhance the material's mechanical properties and thermal insulation characteristics. At the same time, the complexes ensure a significant reduction in heat release and smoke generation during combustion, indicating an effective improvement in the fire safety of epoxy coatings.

It has been proposed to use a phosphorus-containing copper(II) coordination compound obtained from the reaction of  $\text{CuCl}_2$  and a phosphorus-containing imidazole as a multifunctional latent curing agent for one-component epoxy systems [17]. The introduction of this coordination compound has been shown to ensure high storage stability, rapid curing upon heating, and increased thermal stability of the resulting materials. The compositions are particularly characterized by a long shelf life (up to 43 days), a short gelation time, and a high glass transition temperature. At the same time, significant increases in fire resistance (Limiting Oxygen Index (LOI) up to 37.8% and UL-94 V-0 rating) and substantial reductions in smoke generation were achieved.

To create epoxy thermosetting materials with enhanced fire safety without compromising performance, phosphorus-containing transition metal coordination compounds were used as multifunctional curing agents [18]. Introducing 15 wt.% of a Zn-based coordination compound has been shown to achieve a high level of fire resistance (UL-94 V-0, LOI 36.5%), as well as a significant reduction in heat release rate and smoke generation. Similar results were obtained for systems containing cobalt. Furthermore, these compositions have latent curing ability, low viscosity, and improved dielectric properties due to the uniform distribution of the coordination compounds in the polymer matrix.

Direct interaction between organic amines and inorganic copper(II) salts, such as  $(\text{CuOH})_2\text{CO}_3$  [19],  $\text{CuSiF}_6$  [20–22], and  $\text{CuSO}_4$  [23, 24], resulted in a chelate-type coordination compound formation. Incorporating these coordination compounds into an epoxy matrix creates metal-coordinated compositions in which the Cu(II)-containing compounds act as flame retardants and curing agents. These compositions promote the formation of a dense polymer network and reduce combustibility. They also increased resistance to thermal-oxidative degradation and raised the ignition and self-ignition temperatures. Furthermore, they reduced burning intensity and smoke generation, forming self-extinguishing materials.

A review of the pertinent literature and the results of previous studies indicates that d-metal coordination compounds are promising multifunctional components of epoxy systems, capable of acting as curing agents and flame retardants simultaneously. Previously, a copper-containing flame retardant-hardener of the composition  $[\text{Cu}(\text{eda})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}$  (*eda*—ethylenediamine) [25] was used to obtain metal-coordinated epoxy-amine composites with reduced fire risk. At the same time, the effect of new Cu(II) chelate coordination compounds, formed with

the participation of polyethylenepolyamine (*pepa*), on the structuring processes and fire risk of epoxy-amine composites remains insufficiently studied. Therefore, the aim of this work is to determine the effect of the chelate-type coordination compound  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (*deta*—diethylenetriamine) on the combustibility, flame spread, and smoke-forming ability of epoxy-amine composites. Particular attention is paid to elucidating the role of Cu(II)–N coordination interactions in the formation of a three-dimensional polymer network and the mechanisms underlying the increased fire resistance of metal-coordinated epoxy materials.

## 2 Experiments

### 2.1 Materials

ED-20 epoxy resin is a colorless, viscous liquid with a mass fraction of epoxy groups of 21.6%. Its dynamic viscosity at 25 °C is 18 Pa·s, its average molecular mass  $M$  is  $410 \text{ g}\cdot\text{mol}^{-1}$ , and it is manufactured by TM Technobudresurs in Ukraine. The flame retardant hardener is a coordination compound of copper(II) chloride,  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (non-combustible green-blue crystals,  $M = 171.5 \text{ g}\cdot\text{mol}^{-1}$ , the specific gravity at 20 °C is  $2.51 \text{ g}\cdot\text{cm}^{-3}$ , the dehydration temperature is 110 °C, manufacturer: TM Klebrig Ukraine) and polyethylenepolyamine, *pepa* –  $\text{H}_2\text{N}[-\text{C}_2\text{H}_4\text{NH}-]_n\text{H}$ , where  $n = 2$  is *deta* –  $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$  (colorless liquid,  $M = 103.17 \text{ g}\cdot\text{mol}^{-1}$ , the specific gravity at 20 °C is  $0.955 \text{ g}\cdot\text{cm}^{-3}$ , the boiling point is 204.1 °C, the ignition temperature is 97 °C, the self-ignition temperature is 350 °C, manufacturer: TM Tekhnobudresurs, Ukraine).

### 2.2 Flame retardant-hardener synthesis

The flame-retardant hardener, in the form of crystals of the chelate-type coordination compounds  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$ , was prepared by directly reacting copper(II) chloride with *pepa*. The first step in the procedure was to dry the  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  crystals in an oven set at 110 °C. This was done to remove all of the water of crystallization. The dehydration process was accompanied by the transformation of the greenish-blue  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  crystals into a finely dispersed yellow-brown powder of anhydrous  $\text{CuCl}_2$ . A specimen of  $\text{CuCl}_2$  was meticulously placed in a porcelain mortar, followed by the judicious addition of an excess of *pepa*. The reaction mixture was ground until a homogeneous, dark blue liquid suspension formed. The mixture was left at room temperature for several days until the crystalline phase appeared. The product yield was 98%. The structure of the resulting coordination compound is studied in detail in reference [26].

### 2.3 Epoxy-amine composites preparation

Metal-coordinated epoxy-amine compositions were obtained by incorporating a flame retardant-hardener into the binder. The crystals of the  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  coordination compound, as described in Section 2.2, were mixed with the ED-20 epoxy oligomer at a specific ratio and stirred thoroughly until a homogeneous composition formed. Meanwhile, an unmodified epoxy-amine composition was prepared without the addition of a flame retardant-hardener, by mixing the ED-20 epoxy oligomer with the amine hardener *pepa*. The compositions were then poured into aluminium foil moulds and left to cure at room temperature. Complete curing of the compositions occurred within 24 h. Notably, the chelate-type coordination compound  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  exhibited bifunctional properties in the epoxy compositions, acting as both a flame retardant and a curing agent. Consequently, a series of epoxy-amine composite samples were obtained with the following molar ratios of reagents: ED/*pepa* (ED-20 : *pepa* :  $\text{CuCl}_2 = 2.5:1:0$ ); ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (I) (ED-20 : *pepa* :  $\text{CuCl}_2 = 2.5:1:1$ ); ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (II) (ED-20 : *pepa* :  $\text{CuCl}_2 = 2.5:1:3$ ).

The selection of this composition of components was based on the stoichiometric ratios between the epoxy groups of the resin and the amine groups of the flame retardant-curing agent. Furthermore, the investigation was driven by the necessity to examine the effect of increasing the flame retardant-curing agent content on the fire risk properties of epoxy composites. This investigation was undertaken while maintaining the system's processability and the capacity for complete curing. The ratio ED-20 : *pepa* :  $\text{CuCl}_2 = 2.5:1:1$  corresponds to the minimum additive content at which changes in the material's properties are observed, whereas ED-20 : *pepa* :  $\text{CuCl}_2 = 2.5:1:3$  is the maximum concentration that does not cause a noticeable deterioration in the composition's processing characteristics.

### 2.4 Feature and measuring

#### 2.4.1 Combustibility testing

The combustibility of the epoxy-amine composites was determined in accordance with DSTU 8829:2019 [27] (clause 7.3), using the method detailed in reference [28]. Three samples measuring  $150 \text{ mm} \times 60 \text{ mm} \times 5 \text{ mm}$  were prepared for each composite. Prior to testing, the samples were kept in a ventilated drying oven at a temperature of  $(60 \pm 5)^\circ\text{C}$  for 20 h. Without removing them from the oven, the samples were then cooled to room temperature, weighed and placed in glass fibre bags.

A gas burner was inserted into the ceramic chamber and the gas flow rate was adjusted to achieve a temperature of  $(200 \pm 5)^\circ\text{C}$  for the gaseous combustion products. The test sample, secured in a holder in a vertical position, was placed in the chamber. The sample was then exposed to the flame for 300 s or until the maximum temperature of the combustion products was reached. The time taken for the maximum temperature of the combustion products to be reached was recorded. The burner was then turned off and the sample was left in the chamber until it had cooled completely. Once cooled, the sample was removed from the chamber and weighed.

Based on the test results, the maximum temperature rise ( $\Delta t_{\text{max}}$ ), the mass loss of the sample ( $\Delta m$ ) and the combustibility group of the materials were determined: combustible materials –  $\Delta t_{\text{max}} > 60^\circ\text{C}$  and/or  $\Delta m > 60\%$ ; difficult-to-combustible materials –  $\Delta t_{\text{max}} < 60^\circ\text{C}$  and  $\Delta m < 60\%$ . Combustible materials were classified by the time ( $\tau$ ) taken to reach the maximum temperature as follows: difficult-to-flammable –  $\tau > 240 \text{ s}$ ; moderately flammable –  $30 \text{ s} \leq \tau \leq 240 \text{ s}$ ; highly flammable –  $\tau < 30 \text{ s}$ .

It is important to acknowledge that the method for determining combustibility, as outlined in DSTU 8829:2019, does not have a direct equivalent in the present system of international or European standards for evaluating the fire hazard of materials. Concurrently, the standard EN ISO 1182 [29], entitled "Reaction to fire tests for products – Non-combustibility test," is the closest in terms of the general testing principle, though it is not fully equivalent.

#### 2.4.2 Flammability testing

The burning resistance of the tested samples under a gas burner flame was determined according to DSTU EN 60695-11-10:2014 [30], which is similar to UL 94 [31]. Samples measuring  $125 \text{ mm} \times 13 \text{ mm} \times 5 \text{ mm}$  were prepared for the tests. Prior to testing, the samples were conditioned for 48 h at a temperature of  $25^\circ\text{C}$  and a relative humidity of 50%. All samples were tested using the horizontal burning (HB) method. When the flame spread rate could not be determined using the HB method (i.e., when the sample extinguished after the burner flame was removed), additional testing was performed using the vertical burning (VB) method. This enabled a higher level of fire resistance to be established and the maximum fire resistance category to which the material could be assigned to be determined. Each test was conducted on five samples of the corresponding composition.

### 2.4.3 Smoke-forming capability determination

The smoke-forming capability was evaluated based on the smoke generation coefficient, in accordance with DSTU 8829:2019 (clause 7.19) [27]. Ten samples of each composition measuring 20 mm × 20 mm × 10 mm were prepared for the experiments. Prior to testing, the samples were conditioned at a temperature of 20 °C for 48 h and weighed. The samples were tested in two modes: smouldering and burning. In burning mode, the tests were conducted at a heat flux density of 35 kW·m<sup>-2</sup>, and in smouldering mode, at 25 kW·m<sup>-2</sup>. The power supply to the setup was turned on to ensure the required heat flux density, and the light source and receiver were activated. The initial light transmittance value was set to 100%. The sample was placed in a stainless steel container and introduced into the burning chamber. The test was conducted until the minimum light transmittance value was reached. Once the test was complete, the container containing the residue was removed from the burning chamber. The apparatus was then ventilated until the initial light transmittance value was reached in the measurement chamber. Five samples were tested in each mode. The smoke generation coefficient ( $D_m$ ) was calculated and used to classify materials by smoke-forming capability: D1 group, with low smoke-forming capability –  $D_m \leq 50 \text{ m}^2\cdot\text{kg}^{-1}$ ; D2 group, with moderate smoke-forming capability –  $50 \text{ m}^2\cdot\text{kg}^{-1} < D_m < 500 \text{ m}^2\cdot\text{kg}^{-1}$ ; D3 group, with high smoke-forming capability –  $D_m > 500 \text{ m}^2\cdot\text{kg}^{-1}$ .

## 3 Results and discussion

### 3.1 The role of the flame retardant-hardener in reducing the combustibility of epoxy composites

The results evaluating the effect of the flame retardant-hardener  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  on the combustibility of epoxy composite materials, as determined by the maximum temperature rise  $\Delta t_{\text{max}}$ , mass loss  $\Delta m$  during combustion, and time to reach the maximum temperature  $\tau$ , are presented in Table 1. The experimental data showed that the maximum temperature rise for all the samples tested exceeds 60 °C, the mass loss exceeds 60%, and the time taken to reach the maximum temperature ranges from 30

to 240 s. Therefore, in accordance with DSTU 8829:2019, all the composite samples are classified as moderately flammable combustible materials.

However, the highest maximum temperature rise value ( $\Delta t_{\text{max}} = 667 \text{ °C}$ ) was recorded for unmodified ED/*pepa* epoxy compositions. Introducing a flame retardant-hardener into the epoxy compositions decreased this value by 9 °C for the ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (I) composition and by 37 °C for the ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (II) composition, compared to the unmodified composition. Using a flame-retardant hardener in epoxy compositions reduces the mass loss of the samples during combustion: for the ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (I) composition, by 7.3%, and for the ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (II) composition, by 11%. Additionally, the flame retardant-hardener increases the time required to reach the maximum temperature of the gaseous combustion products of the epoxy compositions. Specifically, this parameter increases by 17 s for the ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (I) composition and by 22 s for the ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (II) composition, compared to the ED/*pepa* composition.

A visual assessment of the samples' behavior under flame indices that those based on unmodified ED/*pepa* composites ignite rapidly, with active combustion accompanied by intense smoke emission and soot formation. In contrast, samples based on modified ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  compositions are characterized by delayed ignition; they burn less intensely and virtually no smoke is emitted during combustion.

The observed combustion characteristics of epoxy composite materials can be explained by the following considerations. The primary condition for the initiation of combustion in epoxy composites is the continuous and intense formation of combustible products resulting from thermal-oxidative decomposition. This process occurs when the concentration of these products in the gas-air mixture exceeds the lower limit required for flame propagation. As the results of the studies have shown, modified epoxy composites are characterised by a significant reduction in the rate at which combustible products of thermal decomposition are released. At the same time, their diffusion into the surrounding environment slows down and the intensity of oxidation processes decreases, indicating an increase in fire resistance. This is primarily due to the formation of strong Cu–N bonds during the curing of the modified epoxy composite. These bonds arise from donor-acceptor interactions between the  $\text{Cu}^{2+}$  ion in the non-flammable copper(II) chloride and the nitrogen atom of the flammable *pepa* molecule. This contributes to the formation of a more stable spatial structure

**Table 1** Results of experimental determination of the combustibility group indices

| Compositions                                     | $\Delta t_{\text{max}}$ (°C) | $\Delta m$ (%) | $\tau$ (s) |
|--------------------------------------------------|------------------------------|----------------|------------|
| ED/ <i>pepa</i>                                  | 667                          | 89.0           | 150        |
| ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$ (I)  | 658                          | 81.7           | 167        |
| ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$ (II) | 630                          | 78.0           | 172        |

of the material. The formation of these bonds contributes to the formation of a more stable spatial structure, while the molecules of the flammable organic amine *pepa* are firmly held within the ion-molecular complex. Breaking these chemical bonds requires an additional supply of thermal energy, which slows down the thermal decomposition process of the epoxy composition [32, 33].

When analyzing the effect of flame retardant-hardener on the flammability of epoxy composites, it is important to note that not all of the copper(II) chloride participates in the formation of complexes. Some of it may remain in the matrix in an unbound state. This component can influence the course of chemical transformations in the system by promoting oxidative dehydrogenation reactions, which form conjugated double bonds, and intermolecular cross-linking. These reactions are characteristic of the curing process in the presence of inorganic additives. Additionally, it can act as a catalyst in esterification, dehydration, and other reactions.

Furthermore, copper(II) chloride can intensify the carbonization process of the epoxy composition by blocking the active sites of the polymer surface responsible for thermal degradation processes. However, this mechanism only occurs when thermally stable structural fragments with higher bond energies form in place of highly reactive functional groups under the influence of temperature. In some cases, copper(II) chloride may also catalyze thermal degradation, promoting the formation of a protective carbonized layer on the surface of the material. The reduction in the combustibility of epoxy composites in the presence of copper(II) chloride can be explained by reactions that incorporate copper atoms into the carbonized residue's structure [18, 34].

### 3.2 Fire behavior

One of the key criteria for evaluating the fire risk of polymeric materials is how they behave when exposed to an open flame. Table 2 presents the results of experimental studies of polymeric samples based on epoxy-amine composites using the Horizontal Burning Test.

**Table 2** Results of experimental studies of polymer samples based on epoxy-amine composites using the Horizontal Burning Test

| Compositions                                             | Result                                                                                                                                                                                                           |
|----------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| ED/ <i>pepa</i>                                          | Flame front passed the 25 mm and 100 mm marks;<br>time elapsed between the 25 mm and 100 mm marks $\tau = 179$ s;<br>calculated linear burning rate<br>$r_{\text{burn}} = 25.1 \text{ mm} \cdot \text{min}^{-1}$ |
| ED/[Cu( <i>deta</i> ) <sub>2</sub> ]Cl <sub>2</sub> (I)  | Flame front passed the 25 mm mark;<br>flame front did not pass the 100 mm mark;<br>damaged length $L = 9$ mm;<br>elapsed time $\tau = 75$ s                                                                      |
| ED/[Cu( <i>deta</i> ) <sub>2</sub> ]Cl <sub>2</sub> (II) | Flame front did not pass the 25 mm mark                                                                                                                                                                          |

As the results show, the sample based on an unmodified ED/*pepa* composition ignited easily when placed horizontally under the action of the flame. The flame front rapidly spread across the sample, passing the 25 mm and 100 mm marks. The burning time between the 25 mm and 100 mm marks was 179 s, and the calculated linear burning rate was  $25.1 \text{ mm} \cdot \text{min}^{-1}$ . It should be emphasized that a significant amount of smoke and soot was emitted during the burning of this composition, and burning particles fell from the sample. This led to the ignition of the cotton wool beneath the sample. Under real fire conditions, these processes can contribute to faster flame spread and cause new ignition sources, increasing danger to people. Thus, the studies indicate that the material sample based on the ED/*pepa* composition is classified as HB according to UL 94 since its burning rate over a 75 mm length does not exceed  $40 \text{ mm} \cdot \text{min}^{-1}$ . The sequence of frames obtained during the video recording of the experiment is presented in Fig. 1.

Modifying epoxy composites with the [Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> coordination compound increases their resistance to flame spread. Horizontally positioned samples based on the ED/[Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> (I) composition, in particular, ignited under the action of a burner flame. The flame front crossed the 25 mm mark, but did not cross the 100 mm mark. The flame spread over a 9 mm section and then extinguished itself. The burning time was 75 s.

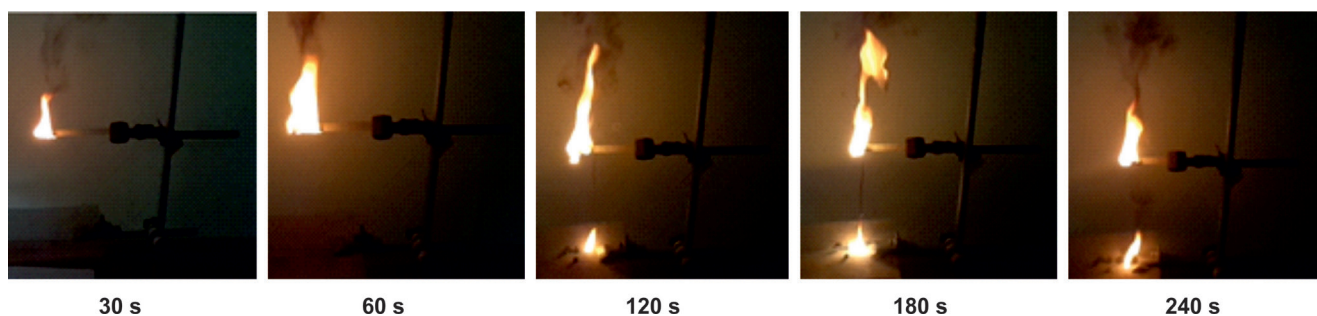


**Fig. 1** A sequence of images illustrating flame spread across samples of the unmodified ED/*pepa* composition placed horizontally

Samples based on the ED/[Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> (II) composition also ignited when placed horizontally under a burner flame. However, the flame front did not cross the 25 mm mark (Fig. 2). Importantly, significantly less smoke was visually emitted during the combustion of samples based on modified epoxy compositions than during the combustion of samples based on unmodified compositions. The underlying cotton wool did not ignite.

To determine the maximum fire resistance rating, samples based on modified compositions were tested in a vertical position. It was found that, for samples based on ED/[Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> (I) and ED/[Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> (II), the afterflame time for each specimen did not exceed 30 s. The total afterflame time for all specimens in each condition was less than 250 s, and the afterflame and afterglow time for each specimen after the second flame application was less than 60 s.

None of the specimens burned or smoldered past the holding clamp during the afterflame or afterglow. During combustion, no falling burning polymer particles were observed; thus, the cotton placed under the specimen did not ignite (Fig. 3). Based on these results, samples of epoxy-amine composites modified with [Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> are classified as V-1 according to UL 94.

### 3.3 Smoke-forming capacity during burning and smoldering

The smoke-forming capacity during epoxy composite burning and smoldering, as well as the impact of the novel flame retardant on these factors, were assessed using the smoke generation coefficient (Fig. 4). Analysis of the results shows that the effect of the chelate coordination compound

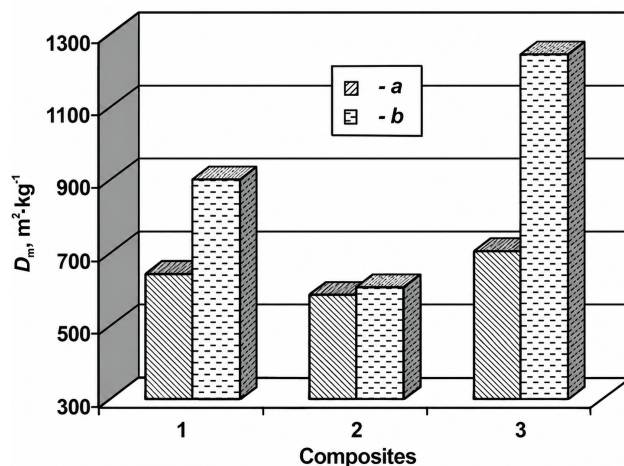


Fig. 4 Results of experimental determination of the smoke generation coefficient during burning (a) and smoldering (b) of materials based on epoxy composites: 1 – ED/*pepa*; 2 – ED/[Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> (I); 3 – ED/[Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> (II)

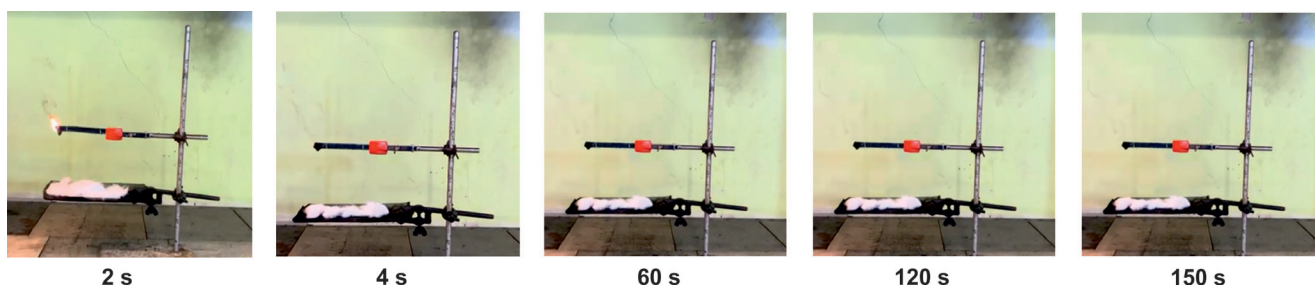


Fig. 2 A sequence of images illustrating flame spread across samples of the modified composition ED/[Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> (II) placed horizontally

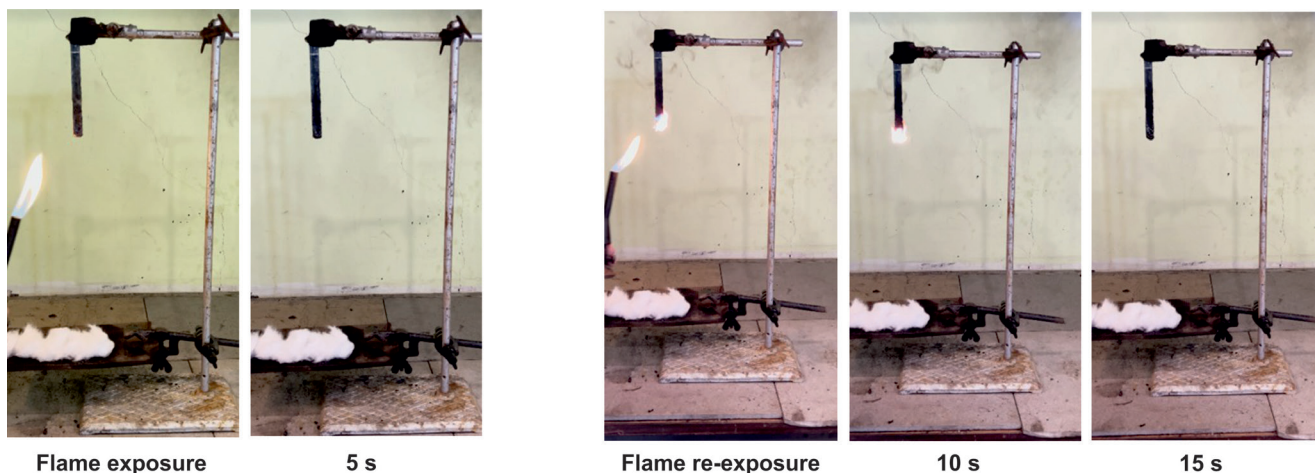


Fig. 3 A sequence of images illustrating flame spread across samples of the modified composition ED/[Cu(*deta*)<sub>2</sub>]Cl<sub>2</sub> (II) placed vertically

$[\text{Cu}(\text{deta})_2]\text{Cl}_2$  on the smoke generation of epoxy-amine composites is nonlinear and significantly dependent on its content in the system. For the ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (I) composition with a low flame retardant content, a noticeable decrease in the smoke generation coefficient was observed: 9.2% in burning mode and 32.9% in smoldering mode. This decrease can be explained by the fact that, at low concentrations, the copper-containing coordination compound primarily acts as a catalyst.  $\text{Cu}^{2+}$  ions accelerate the carbonization of the polymer matrix and the formation of a denser, more stable carbonized layer. This layer acts as a barrier that limits mass and heat transfer and reduces the yield of volatile organic products that lead to smoke formation. At the same time, there is partial inhibition of aromatic fragment formation in the gas phase, which reduces smoke generation further [35, 36].

However, as the flame retardant content in the epoxy composition ED/ $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  (II) increases, the smoke generation coefficient increases in both burning and smoldering modes. This change in the flame retardant's effect is associated with the system's transition from a predominantly catalytic regime to one characterized by intensified thermo-oxidative degradation processes and an increased yield of volatile smoke-generating products. At elevated concentrations of the coordination compound, the proportion of free or weakly bound copper(II) chloride increases. This allows the copper(II) chloride to more actively influence the polymer's thermal degradation processes. The reactions of dehydrochlorination and oxidative decomposition of the epoxy matrix accelerate in this case, leading to the formation of a significant amount of unsaturated and aromatic intermediate products. These compounds subsequently participate in soot and smoke formation processes, resulting in an increased smoke generation coefficient. Additionally, an excess of chlorine-containing fragments may contribute to the incomplete oxidation of volatile products, further intensifying smoke emission [37].

For all studied compositions, the smoke generation coefficient exceeds  $500 \text{ m}^2 \cdot \text{kg}^{-1}$  in both burning and smoldering modes, which, according to DSTU 8829:2019, corresponds to D3 group – materials with high smoke-forming capability.

### 3.4 Influence of chelation in ED-*pepa*- $\text{CuCl}_2$ system on crosslinking, and fire behavior of epoxy-amine composite materials

A critical element in the development of epoxy-amine composite materials with diminished fire hazard is the

incorporation of a metal-coordinated curing agent into the crosslinking process of the epoxy-amine composition. In the preceding research [38], the rheological properties of the ED-*pepa*-copper(II) salt system were examined. The results indicated that the samples of epoxy composites, which were prepared and subsequently cured with *pepa* and a copper(II) chelate coordination compound, exhibited comparable rates of viscosity increase. This finding suggests, albeit not explicitly, that the polymerization mechanisms of modified and unmodified epoxy-amine composites are analogous. To better understand this mechanism, it is necessary to incorporate the results of a quantum-chemical analysis of the complexation processes occurring in ED-*pepa*-copper(II) salt systems during the formation of metal-coordinated epoxy-amine composites with reduced combustibility. The calculations demonstrated that the electron density of the N atoms in the *pepa* molecules within the coordination sphere is effectively shifted toward the central  $\text{Cu}^{2+}$  ion due to the chelation effect.

Consequently, the electron density on the N atoms of the copper(II)-coordinated amino groups experiences a substantial decrease, while it undergoes a significant increase on the central  $\text{Cu}^{2+}$  ion. This redistribution of electron density in the coordination center of the flame retardant-hardener results in an increase in the positive charge on the H atoms of the coordinated amino groups (compared to the uncoordinated ones). Consequently, the  $\text{Cu}(\text{II})$ -*pepa* chelation effect induces a polarization of the N-H bonds, thereby enhancing the electrophilic character of the H atoms within the coordinated amino groups. This process facilitates the electrophilic addition of an H atom to an O atom of the oxirane ring and, concurrently, enables the nucleophilic attack of an N atom on one of the two C atoms of the epoxy group that contains fewer alkyl substituents (Fig. 5).

The curing mechanism for epoxy-amine composites modified with inorganic copper(II) salts is consistent with the mechanism of oxirane ring opening under conditions of electrophilic attack on the oxygen atom, which leads to the polymerization of the epoxy resin [39–41]. Therefore,

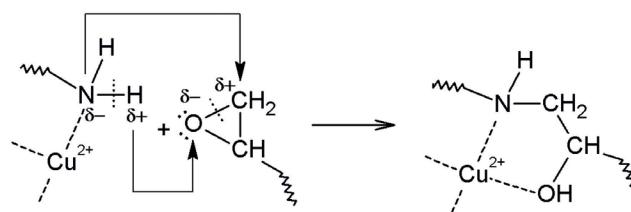


Fig. 5 Cross-linking mechanism of metal-coordinated epoxy-amine composites in the ED-*pepa*- $\text{CuCl}_2$  system

an analysis of the charge distribution on atoms in chelate coordination compounds clearly demonstrates that *pepa*, when coordinated to a Cu(II) atom, functions as a more effective curing agent for epoxy resins than in its free state.

#### 4 Conclusion

This study investigated the effect of the chelate-type coordination compound  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  as a flame retardant-hardener on the combustibility, smoke-generating capacity, and fire behavior of ED-20-based epoxy compositions. The study found that modifying the epoxy composition with a copper(II)-amine coordination compound reduces its combustibility, as evidenced by a lower maximum temperature rise and mass loss and a longer time to reach the maximum temperature during combustion. UL-94 testing revealed that the modified composites exhibit higher fire resistance than the unmodified samples. The unmodified epoxy composites were classified as HB, whereas the flame retardant-hardener modified composites corresponded to the higher fire resistance rating of V-1. This is due to the formation of Cu–N coordination bonds between the  $\text{Cu}^{2+}$  ions of the inorganic salt, copper(II) chloride, and the amine fragments of the organic amine, *pepa*. This leads to an increase in the degree of cross-linking and the thermodynamic stability of the epoxy network. This increases the energy barrier for thermal-oxidative degradation and reduces the rate of formation of combustible

volatile products. Additionally, copper-containing centers have been shown to exhibit catalytic activity in the carbonization processes of the polymer matrix, promoting the formation of a dense, structurally ordered carbonized layer. This layer effectively limits mass and heat transfer, as well as oxygen access to the combustion reaction zone.

The effect of the flame retardant on smoke formation has been shown to be nonlinear and dependent on its concentration. At low concentrations of  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$ , a predominantly catalytic mechanism is realized. This mechanism contributes to the stabilization of the condensed phase, a reduction in the yield of volatile products, and a decrease in the smoke generation coefficient. Conversely, higher concentrations of the coordination compound are associated with increased smoke formation due to intensified thermo-oxidative degradation and an increased proportion of low-molecular-weight, unsaturated, and aromatic decomposition products that contribute to the formation of the dispersed phase of smoke and soot.

These results confirm that the chelate coordination compound  $[\text{Cu}(\text{deta})_2]\text{Cl}_2$  plays a multifunctional role in epoxy systems by combining the functions of a flame retardant and a curing agent. It also provides controlled influence over the processes of thermal degradation, carbonization, combustion, and smoke formation. These findings suggest the potential for developing a new generation of epoxy materials with adjustable fire-hazard characteristics.

#### References

- [1] Liu, Q., Wang, D., Li, Z., Li, Z., Peng, X., Liu, C., Zhang, Y., Zheng, P. "Recent developments in the flame-retardant system of epoxy resin", *Materials*, 13(9), 2145, 2020.  
<https://doi.org/10.3390/ma13092145>
- [2] Gérard, C., Fontaine, G., Bourbigot, S. "New trends in reaction and resistance to fire of fire-retardant epoxies", *Materials*, 3(8), pp. 4476–4499, 2010.  
<https://doi.org/10.3390/ma3084476>
- [3] Zhi, M., Yang, X., Fan, R., Yue, S., Zheng, L., Liu, Q., He, Y. "A comprehensive review of reactive flame-retardant epoxy resin: fundamentals, recent developments, and perspectives", *Polymer Degradation and Stability*, 201, 109976, 2022.  
<https://doi.org/10.1016/j.polymdegradstab.2022.109976>
- [4] Dagdag, O., Kim, H. "Advances in Flame Retardant Technologies for Epoxy Resins: Chemical Grafting onto Carbon Fiber Techniques, Reactive Agents, and Applications in Composite Materials", *Molecules*, 29(24), 5996, 2024.  
<https://doi.org/10.3390/molecules29245996>
- [5] Yuan, Y., Lin, W., Xiao, Y., Yu, B., Wang, W. "Flame-retardant epoxy thermosets derived from renewable resources: research development and future perspectives", *Journal of Materials Science and Technology*, 195, pp. 29–40, 2024.  
<https://doi.org/10.1016/j.jmst.2024.02.006>
- [6] Zhang, T., Liu, W., Wang, M., Liu, P., Pan, Y., Liu, D. "Synergistic effect of an aromatic boronic acid derivative and magnesium hydroxide on the flame retardancy of epoxy resin", *Polymer Degradation and Stability*, 130, pp. 257–263, 2016.  
<https://doi.org/10.1016/j.polymdegradstab.2016.06.011>
- [7] Chen, M.-J., Lin, Y.-C., Wang, X.-N., Zhong, L., Li, Q.-L., Liu, Z.-G. "Influence of Cuprous Oxide on Enhancing the Flame Retardancy and Smoke Suppression of Epoxy Resins Containing Microencapsulated Ammonium Polyphosphate", *Industrial and Engineering Chemistry Research*, 54(51), pp. 12705–12713, 2015.  
<https://doi.org/10.1021/acs.iecr.5b03877>
- [8] Chai, G., Zhu, G., Gao, S., Zhou, J., Gao, Y., Wang, Y. "On improving flame retardant and smoke suppression efficiency of epoxy resin doped with aluminum tri-hydroxide", *Advanced Composites Letters*, 28, pp. 1–12, 2019.  
<https://doi.org/10.1177/2633366X19894597>
- [9] Liu, H., Lv, Y., Tang, A., Xu, W., Wang, T., ..., Dai, L. "Novel organic-metal hybrid coordination complex constituted by DOPO and Salen-Ni for enhancing flame retardancy of epoxy resins", *European Polymer Journal*, 238, 114225, 2025.  
<https://doi.org/10.1016/j.eurpolymj.2025.114225>

- [10] Xu, B., Wei, S., Liu, Y., Wu, M. "Effects of different metal ions in phosphonitrile-modified organometallic complexes on flame retardancy of epoxy resin", *Polymer Degradation and Stability*, 214, 110407, 2023.  
<https://doi.org/10.1016/j.polymdegradstab.2023.110407>
- [11] Xu, B., Wu, M., Liu, Y., Wei, S. Study on Flame Retardancy Behavior of Epoxy Resin with Phosphaphenanthrene Triazine Compound and Organic Zinc Complexes Based on Phosphonitrile, *Molecules*, 28(7), 3069, 2023.  
<https://doi.org/10.3390/molecules28073069>
- [12] Barton, J. M., Buist, G. J., Hamerton, I., Howlin, B. J., Jones, J. R., Liu, S. "Preparation and characterization of imidazole-metal complexes and evaluation of cured epoxy networks", *Journal of Materials Chemistry*, 4(3), pp. 379–384, 1994.  
<https://doi.org/10.1039/JM9940400379>
- [13] Brown, J., Hamerton, I., Howlin, B. J. "Preparation, characterization, and thermal properties of controllable metal-imidazole complex curing agents for epoxy resins", *Journal of Applied Polymer Science*, 75(2), pp. 201–217, 2000.  
<https://doi.org/10.1002/jap.10021>
- [14] Kurnoskin, A. V. "Epoxy chelate copper-containing polymers: their chemistry and production", *Polymer-Plastics Technology and Engineering*, 31(5–6), pp. 505–525, 1992.  
<https://doi.org/10.1080/03602559208017764>
- [15] Kurnoskin, A. V. "Diane oligomers: heat resistance increase by metal ions", *Polymer-Plastics Technology and Engineering*, 30(7), pp. 737–750, 1991.  
<https://doi.org/10.1080/03602559108020147>
- [16] Lian, R., Ou, M., Guan, H., Cui, J., Zhao, Z., Liu, L., Chen, X., Jiao, C. "Cu(II) and Co(II) complexes decorated ammonium polyphosphate as co-curing agents on improving fire safety and mechanical properties of epoxy-based building coatings", *Construction and Building Materials*, 389, 131786, 2023.  
<https://doi.org/10.1016/j.conbuildmat.2023.131786>
- [17] Wang, Ji., Wang, Ju., Yang, Sh., Wu, Ch., Chen, Xi, Chen, K., Song, P., Wang, H., Huo, S. "Development of single-component epoxy resin with superb thermal stability, flame retardancy, smoke suppression, and latency via Cu-based phosphorus/imidazole-containing complex", *Polymer Degradation and Stability*, 228, 110906, 2024.  
<https://doi.org/10.1016/j.polymdegradstab.2024.110906>
- [18] Lu, J.-H., Xu, Y.-J., Chen, L., Chen, J.-H., He, J.-H., Li, Z., Li, S.-L., Wang, Y.-Z. "Facile fabrication of intrinsically fire-safety epoxy resin cured with phosphorus-containing transition metal complexes for flame retardation, smoke suppression, and latent curing behavior", *Chemical Engineering Journal*, 442, 136097, 2022.  
<https://doi.org/10.1016/j.cej.2022.136097>
- [19] Lavrenyuk, H., Mykhalichko, B. "Principles of controlled effects on performance properties of self-extinguishing epoxy-amine composites modified by copper(II) carbonate", *Voprosy Khimii i Khimicheskoi Tekhnologii*, 5(126), pp. 58–64, 2019.  
<https://doi.org/10.32434/0321-4095-2019-126-5-58-64>
- [20] Lavrenyuk H., Mykhalichko B., Parhomenko V.-P. "Quantum-chemical simulation of the behavior of  $[\text{Cu}(\text{H}_2\text{NC}_2\text{H}_4\text{NH}_2)(\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)]\text{SiF}_6$  chelate complex, a fire retardant-hardener of epoxy resins, under the conditions of burning", *Voprosy khimii i khimicheskoi tekhnologii*, 3(118), pp. 31–36, 2018.
- [21] Lavrenyuk, H., Mykhalichko, B., Garanyuk, P., Mykhalichko, O. "New copper(II)-coordinated epoxy-amine polymers with flame-self-extinguishment properties: Elaboration, combustibility testing, and flame propagation rate measuring", *Fire and Materials*, 44(6), pp. 825–834, 2020.  
<https://doi.org/10.1002/fam.2879>
- [22] Kochubei, V., Mykhalichko, B., Lavrenyuk, H. "Elaboration, thermogravimetric analysis, and fire testing of a new type of wood-sawdust composite materials based on epoxy-amine polymers modified with copper(II) hexafluorosilicate", *Fire and Materials*, 46(3), pp. 587–594, 2022.  
<https://doi.org/10.1002/fam.3001>
- [23] Lavrenyuk, H., Mykhalichko, B. "DFT study on thermochemistry of the combustion of self-extinguishing epoxy-amine composites modified by copper(II) sulfate", *Voprosy khimii i khimicheskoi tekhnologii*, 6(121), pp. 42–48, 2018.  
<https://doi.org/10.32434/0321-4095-2018-121-6-42-48>
- [24] Lavrenyuk, O. I., Mykhalichko, B. M. "X-ray powder diffraction and infra-red spectroscopic analysis of the structuring process of modified epoxy-amine composites with the participation of flame retardant  $[\text{Cu}(\text{Diethylenetriamine})\text{H}_2\text{O}]\text{SO}_4 \cdot \text{H}_2\text{O}$ ", *Voprosy Khimii i Khimicheskoi Tekhnologii*, 5–6(109), pp. 73–77, 2016.
- [25] Kochubei, V., Kozyar, N., Lavrenyuk, H., Mykhalichko, B. "Metal-Coordinated Epoxy-Amine Composition with Reduced Fire Risk: Elaboration, Thermal and Ignition Resistance", *Periodica Polytechnica Chemical Engineering*, 68(3), pp. 446–453, 2024.  
<https://doi.org/10.3311/PPCh.36543>
- [26] Mykhalichko, B., Lavrenyuk, H., Olijnyk, V., Slyvka, Y., Mykhalichko, O., Starodub, Y. "Synthesis, Crystal and Electronic Structure, and Thermal Behavior of a New Flame Retardant-Hardener  $[\text{Cu}(\text{diethylenetriamine})_2]\text{C}_{12}\text{H}_2\text{O}$  for Epoxy Resins", *Acta Chimica Slovenica*, 72(1), pp. 86–95, 2025.  
<https://doi.org/10.17344/acta.2024.9051>
- [27] State Standard of Ukraine " DSTU 8829:2019 Fire and explosion hazard of substances and materials. Nomenclature of indicators and methods for their determination. Classification", Ukrainian Scientific-Research and Training Center of Standardization, Certification and Quality Problems (UkrNDNC), Kyiv, Ukraine, 2019. [online] Available at: <https://budstandart.co> [Accessed: 10 May 2026]
- [28] Mykhalichko, B., Lavrenyuk, H. "Flame Protection Technologies for Wood: Developing and Testing for Fire of Timbers with a Flame-retardant Coating Based on the Epoxy-amine Composite Modified by Copper(II) Hexafluorosilicate", *Periodica Polytechnica Chemical Engineering*, 66(2), pp. 304–312, 2022.  
<https://doi.org/10.3311/PPCh.19050>
- [29] European Committee for Standardization "ISO 1182:2020, Reaction to fire tests for products - Non-combustibility test", CEN, Brussels, Belgium, 2020.

- [30] State Standard of Ukraine "DSTU EN 60695-11-10:2014 Fire hazard testing - Part 11-10: Test flames - 50 W horizontal and vertical flame test methods", Ukrainian Scientific-Research and Training Center of Standardization, Certification and Quality Problems (UkrNDNC), Kyiv, Ukraine, 2014. [online] Available at: <https://budstandart.com> [Accessed: 10 May 2026]
- [31] Underwriters Laboratories "UL 94, Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances", UL, Northbrook, IL, USA, 2023.
- [32] Chen, J., Lehner, S., Teng, S. Y., Gaan, S., Passerone, D., Heuberger, M., Gooneie, A. "Thermal decomposition mechanisms of phosphorus flame retardants: A combined theoretical and experimental approach", *Polymer Degradation and Stability*, 241, 111543, 2025. <https://doi.org/10.1016/j.polymdegradstab.2025.111543>
- [33] Bao, G., Abe, R. Y., Akutsu, Y. "Bond dissociation energy and thermal stability of energetic materials", *Journal of Thermal Analysis and Calorimetry*, 143, pp. 3439–3445, 2020. <https://doi.org/10.1007/s10973-020-10273-1>
- [34] Ikoma, S., Nakasako, S., Yokoi, H. "Thermal Decomposition of Copper(II) Polyamine Complexes", *Bulletin of the Chemical Society of Japan*, 63(12), pp. 3692–3694, 1990. <https://doi.org/10.1246/bcsj.63.3692>
- [35] He, L., Chen, T., Wang, T., Zhao, H.-B., Deng, J.-N., Li, T.-T., Fu, Z.-C., Dong, Q., Chen, M.-J. "Extra strong Cu<sup>2+</sup>-doped intumescent char to protect epoxy resin against fire", *Composites Part B: Engineering*, 253, 110539, 2023. <https://doi.org/10.1016/j.compositesb.2023.110539>
- [36] Ilyas, R. A., Sapuan, S. M., Asyraf, M. R. M., Dayana, D. A. Z. N., Amelia, J. J. N., ..., Razman, M. R. "Polymer composites filled with metal derivatives: a review of flame retardants", *Polymers*, 13(11), 1701, 2021. <https://doi.org/10.3390/polym13111701>
- [37] Pasternak, M., Zinn, B. T., Browner, R. F. "Studies of the chemical mechanism of smoke particulates formation during the combustion of chlorinated polymers", *Combustion Science and Technology*, 28(5–6), pp. 263–270, 1982. <https://doi.org/10.1080/00102208208952560>
- [38] Lavrenyuk, H., Hamerton, I., Mykhalichko, B. "Tuning the properties for the self-extinguishing epoxy-amine composites containing copper-coordinated curing agent: Flame tests and physical-mechanical measurements", *Reactive and Functional Polymers*, 129, pp. 92–105, 2018. <https://doi.org/10.1016/j.reactfunctpolym.2017.10.013>
- [39] Hamerton, I., Howlin, B., Jepson, P. "Metals and coordination compounds as modifiers for epoxy resins", *Coordination Chemistry Reviews*, 224(1–2), pp. 67–85, 2002. [http://doi.org/10.1016/S0010-8545\(01\)00393-9](http://doi.org/10.1016/S0010-8545(01)00393-9)
- [40] Penn, L. S., Ciao, T. T. "Epoxy resins", In: Lubin, G. (ed.) *Handbook of Composites*, Boston: Springer, 1982, pp. 57–88. ISBN 978-1-4615-7139-1 [https://doi.org/10.1007/978-1-4615-7139-1\\_5](https://doi.org/10.1007/978-1-4615-7139-1_5)
- [41] Hamerton, I. "Recent Developments in Epoxy Resins", *Rapra Review Reports*, 8(7), p. 186, 1996.