

## RESEARCH ARTICLE

# Metal-coordinated epoxy polymers with suppressed combustibility. Preparation technology, thermal degradation, and combustibility test of new epoxy-amine polymers containing the curing agent with chelated copper(II) carbonate

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**Summary**

The diethylenetriamine chelate complex of copper(II) carbonate—*DETA*-CuCO<sub>3</sub> (a fire retardant hardener of epoxy resins)—and the CuCO<sub>3</sub>-containing epoxy-amine polymers—*DGEBA/DETA*-CuCO<sub>3</sub>(6), *DGEBA/DETA*-CuCO<sub>3</sub>(12), *DGEBA/DETA*-CuCO<sub>3</sub>(40), and *DGEBA/DETA*-CuCO<sub>3</sub>(80) with suppressed combustibility—have been obtained in the *DETA*-*DGEBA*-CuCO<sub>3</sub> system (*DETA* and *DGEBA* are diethylenetriamine and bisphenol A diglycidyl ether, respectively). The *DETA*-CuCO<sub>3</sub> chelate complex was characterized by X-ray powder diffraction, infrared spectra, and thermal analysis. The thermal gravimetric analysis results have revealed that thermal destruction of *DETA*-CuCO<sub>3</sub> was finished at 400°C, and the maximal temperature of the combustion gases amounted to 520°C. The thermal behavior and combustibility of the CuCO<sub>3</sub>-containing epoxy-amine polymers were studied using thermal analysis and "Ceramic tube" (CT) method. Thermal gravimetric analysis confirms that incorporation of the *DETA*-CuCO<sub>3</sub> into *DGEBA* appreciably heightens the thermal stability and antifiammability of the CuCO<sub>3</sub>-containing epoxy-amine polymers. Results of CT measurement reveal that maximal temperature of the combustion gases under burning of the *DGEBA/DETA*-CuCO<sub>3</sub>(12) sample in comparison with unmodified epoxy-amine polymer (*DGEBA/DETA*) is lowered on 219°C and the loss of weight is decreased on 20.5 wt%. According to ASTM 635-14, ASTM D2863-13, and ASTM D1929-16, the flame propagation rate, limiting oxygen index, and temperatures of ignition and self-ignition have been measured for the elaborated polymer samples.

**KEYWORDS**

cupric-coordinated epoxy-amine polymers, fire retardant-hardener, self-extinguishing character of burning, suppressed combustibility

## 1 | INTRODUCTION

The polymers generally<sup>1</sup> and the epoxy polymers in particular<sup>2</sup> have long ago substituted many conventional materials in our everyday life. The epoxy polymers also proceed to confidently hold positions in industry, mainly, owing to their proper physical-mechanical properties.<sup>3</sup> But, apart from the numerous advantages, the most polymers have a one serious drawback; they have low resistance to fire. Such characteristic features of epoxy resins as a low thermal stability, a little fire resistance, and high fire hazard strongly restrict utilization of the epoxy polymers in the pure state in industry. That is why the searching

of the ways of combustibility lowering of the polymer materials based on epoxy resins is one of the overall objectives of the fire safety.<sup>4</sup>

On the other hand, epoxy resins themselves possess high compatibility with many types of polar organic substances. Consequently, a substantial cohesion can spring up between the various types of fillers and the binder. All this opens up wide possibilities for modification of epoxy resins. There are many technological elaborations concerning the increase of fire resistance of the epoxy polymer materials. This is, first of all, the use of inherent flame retardant polymers,<sup>5</sup> the modifying the polymer backbone,<sup>6,7</sup> incorporation of flame retardants into polymer matrix, and so forth.

Currently, the varied types of the fire retardants, more exactly, of the reactive fire retardants are widely used for the effective combustibility lowering of epoxy resins.<sup>8</sup> There are several different kinds of fire retardant polymers obtained by incorporation of Si, N, B, and P atoms into the monomer units directly at the polymer synthesis.<sup>9–13</sup> In the latter time, the fire retardants containing the complexes of *d*-metal salts (mainly, the salts of Mn, Co, Ni, Cu, Zn, etc and organic acids)<sup>14,15</sup> find a wide application. The distinguishing feature of the epoxy polymers modified by transition metal salts is the formation of chelate complexes, which are directly incorporated into the framework of such polymers.<sup>16–18</sup> Here, the chelate complexes play a part of both modifiers and curing agents of epoxy resins concurrently.<sup>19</sup>

Earlier, the crystalline chelate complex of the diethylenetriamine with copper(II) sulfate (*DETA*-CuSO<sub>4</sub>)<sup>20</sup> and samples of the epoxy-amine polymers (*DGEBA/DETA*-CuSO<sub>4</sub>)<sup>21</sup> have been obtained in the *DETA-DGEBA*-CuSO<sub>4</sub> system (*DETA* and *DGEBA* are diethylenetriamine and bisphenol A diglycidyl ether, respectively). When studying the combustibility of the *DGEBA/DETA*-CuSO<sub>4</sub> polymer materials with variant content of incombustible inorganic salt,<sup>22</sup> it has been ascertained that composition, structure, and type of cupric salt participating in the complex formation can significantly influence the polymer's combustibility. Proceeding further in influence study of the cupric salts onto combustibility of the epoxy-amine polymers, we have replaced the copper(II) sulfate by the copper(II) carbonate in above system. As a result, the chelate complex denoted as *DETA*-CuCO<sub>3</sub><sup>23</sup> that further was used as a fire retardant hardener of epoxy resins have been educed out of the *DETA-DGEBA*-CuCO<sub>3</sub> system.

To obtain new epoxy-amine polymers with lowered combustibility, it was necessary to elaborate an uncomplicated technique of incorporation of the fire retardant hardener (*DETA*-CuCO<sub>3</sub>) into the binder matrix. Owing to the elaborated technique, the fit samples of the epoxy-amine polymers with different content of CuCO<sub>3</sub> (see Table 1) have been prepared and characterized. Thus, the obtained CuCO<sub>3</sub>-containing epoxy-amine polymers are next representatives of a new generation of the polymers in which the inorganic cupric salt coordinated by curing agent plays a pivotal role in the suppressing the combustibility of the epoxy-amine polymers.

The identification of the *DETA*-CuCO<sub>3</sub> chelate complex (the fire retardant hardener) gained in the *DGEBA-DETA*-CuCO<sub>3</sub> system, the detection of the *DETA*-CuCO<sub>3</sub> chelate core in the elaborated CuCO<sub>3</sub>-containing epoxy-amine polymers, and the study of their thermal and combustible properties are reported in the present article.

**TABLE 1** Stoichiometry of the CuCO<sub>3</sub>-containing epoxy-amine polymers

Samples	<i>DGEBA:DETA:CuCO<sub>3</sub></i>	
	Molar ratio	Weight ratio
<i>DGEBA/DETA</i>	5:2:0	100:10:0
<i>DGEBA/DETA-CuCO<sub>3</sub>(6)</i>	5:2:1	100:10:6
<i>DGEBA/DETA-CuCO<sub>3</sub>(12)</i>	5:2:2	100:10:12
<i>DGEBA/DETA-CuCO<sub>3</sub>(40)</i>	5:2:6.667	100:10:40
<i>DGEBA/DETA-CuCO<sub>3</sub>(80)</i>	5:2:13.333	100:10:80

## 2 | EXPERIMENTAL

### 2.1 | Materials

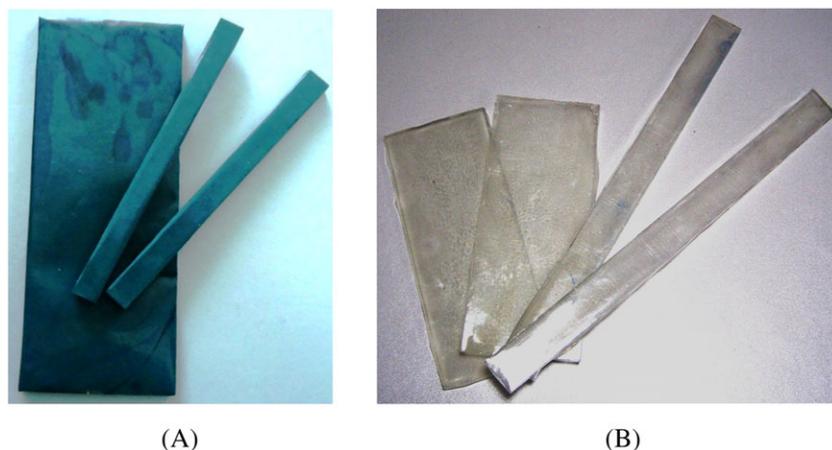
For synthesis of the fire retardant hardener (*DETA*-CuCO<sub>3</sub>) and elaborating the CuCO<sub>3</sub>-containing epoxy-amine polymers, the following chemicals were used: the fire retardant—copper(II) carbonate, CuCO<sub>3</sub>,<sup>24</sup> (gray green powder,  $M = 123.5 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 3.7 \text{ g}\cdot\text{cm}^{-1}$ ,  $\Delta T_{\text{decomposition}} = 250\text{--}350^\circ\text{C}^{25}$ ); the curing agent of epoxy resins—diethylenetriamine (*DETA*), NH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>, (colorless liquid,  $M = 103.17 \text{ g}\cdot\text{mol}^{-1}$ ,  $d^{20} = 0.955 \text{ g}\cdot\text{cm}^{-1}$ ,  $T_{\text{boiling}} = 204.1^\circ\text{C}$ ,  $T_{\text{ignition}} = 97^\circ\text{C}$ ,  $T_{\text{self-ignition}} = 350^\circ\text{C}^{26}$ ); and the binder—bisphenol A diglycidyl ether (*DGEBA*) (colorless resin, ED-20 grade with almost 22% epoxy groups content,  $M = 390\text{--}430 \text{ g}\cdot\text{mol}^{-1}$  [ $\bar{M} = 410 \text{ g}\cdot\text{mol}^{-1}$ ]). All reagents have been purchased through commercial sources and used as received without further purification.

### 2.2 | Preparation of the CuCO<sub>3</sub>-containing epoxy-amine polymers

The indispensable ingredients for a synthesis of the CuCO<sub>3</sub>-containing epoxy-amine polymers are given in the Table 1.

The samples of the epoxy-amine polymers containing the different quantities of CuCO<sub>3</sub> have been prepared in 2 stages. At first, the necessary quantities of copper(II) carbonate (6, 12, 40, and 80 g) have been placed into the individual containers whereupon the *DETA* (10 g, 0.1 mol) has been added to each container. In all 4 cases, the added curing agent (*DETA*) has vigorously interacted with the copper(II) carbonate, forming the chelate complex (*DETA*-CuCO<sub>3</sub>). The complexing is accompanied by the heating up of the reaction mixture and by its intensively dark blue coloration with following crystallization. It should be noted that the dark blue polycrystalline powder of the *DETA*-CuCO<sub>3</sub> isolated out of the reaction mixture was afterwards studied by X-ray powder diffraction (XRPD). Next, the *DGEBA* (100 g, 0.25 mol) has been batched to each of 4 containers with the *DETA* + CuCO<sub>3</sub> mixtures. Ultimately, each of the 4 prepared ternary mixtures (*DGEBA* + *DETA* + CuCO<sub>3</sub>) was diligently stirred for 5 to 10 minutes till formation of homogeneous consistence resembling a thick honey and having an esthetically attractive blue-green color. Further, the obtained viscous liquids have been poured into the molds and left at room temperature to cure for 24 hours. After curing, all 4 samples of the CuCO<sub>3</sub>-containing epoxy-amine polymers (*DGEBA/DETA*-CuCO<sub>3</sub>(6), *DGEBA/DETA*-CuCO<sub>3</sub>(12), *DGEBA/DETA*-CuCO<sub>3</sub>(40), and *DGEBA/DETA*-CuCO<sub>3</sub>(80)) have acquired the characteristic blue-green color (Figure 1A).

The samples of the CuCO<sub>3</sub>-containing epoxy-amine polymer, where the molar ratio *DGEBA:DETA:CuCO<sub>3</sub>* is 5:2:2, can also be obtained on the basis of the  $[\{\text{Cu}(\text{DETA})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}] \cdot 6\text{H}_2\text{O}$  chelate complex whose synthesis was described in detail in Lavrenyuk et al.<sup>23</sup> According to the alternative method of obtaining the *DGEBA/DETA*-CuCO<sub>3</sub>(12), the *DETA*-CuCO<sub>3</sub> polycrystalline powder (22 g, 0.1 mol) prepared by dehydration of the  $[\{\text{Cu}(\text{DETA})(\text{H}_2\text{O})(\mu\text{-CO}_3)\}] \cdot 6\text{H}_2\text{O}$  was added to *DGEBA* (100 g). All further manipulations with the reaction mixture were performed in accordance with above-said procedures of preparing the CuCO<sub>3</sub>-containing epoxy-amine



**FIGURE 1** The photographs of the epoxy-amine polymer samples. A, DGEBA/DETA-CuCO<sub>3</sub>(80). B, DGEBA/DETA [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

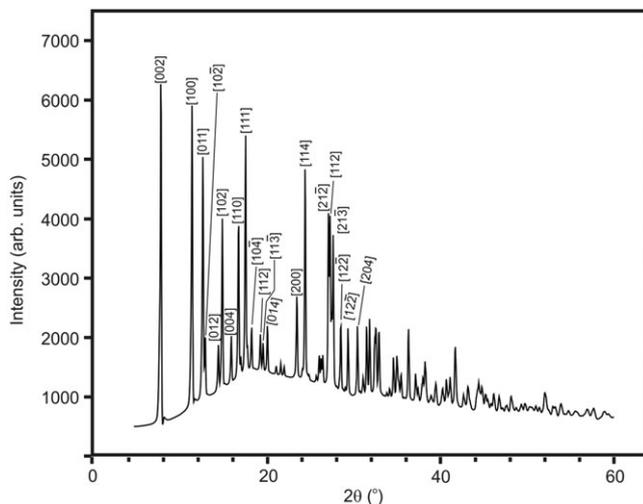
polymers. The combustibility study of the polymer samples of the DGEBA/DETA-CuCO<sub>3</sub>(12) prepared by different methods has shown their thorough identity.

The usual colorless unmodified epoxy-amine polymer DGEBA/DETA (see Figure 1B) also has been prepared by combination of DGEBA (100 g) and DETA (10 g).

## 2.3 | Characterization and measurement

### 2.3.1 | X-ray powder diffraction

The XRPD pattern (Figure 2) made from the polycrystalline sample of the DETA-CuCO<sub>3</sub> gained in synthesis process of the CuCO<sub>3</sub>-containing epoxy-amine polymers has been used for the phase identification. The XRPD experiment was performed at room temperature on the HZG-4A diffractometer (Cu K $\alpha$  radiation, Bragg-Brentano geometry, angular range  $5 \leq 2\theta \leq 60^\circ$  with a step size of  $0.02^\circ$  and exposition time per point 20 s). The profile and structural parameters were refined by the Rietveld method using the package of program FullProf Suite.<sup>27</sup> The indexing of the XRPD pattern was fulfilled automatically by means of the method described in Louër and Louër,<sup>28</sup> using DICVOL91 software package.<sup>29</sup> The structure model was taken from single crystal data of the  $[\text{Cu}(\text{DETA})(\text{H}_2\text{O})(\mu\text{-CO}_3)] \cdot 6\text{H}_2\text{O}$  chelate complex.<sup>23</sup>



**FIGURE 2** The X-ray powder diffraction pattern of the DETA-CuCO<sub>3</sub> chelate complex

### 2.3.2 | Infrared spectroscopy

Infrared (IR) absorption spectra (Figure 3) were recorded in the spectral range of 4000 to 500 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> on a PerkinElmer Spectrum Two FTIR spectrometer. The IR spectroscopic measurements were performed on the solid samples of the DGEBA/DETA, DETA-CuCO<sub>3</sub>, and DGEBA/DETA-CuCO<sub>3</sub>(80) pressed into pellets with the spectroscopically pure KBr, or on the liquid sample of DETA with using a KBr cuvette.

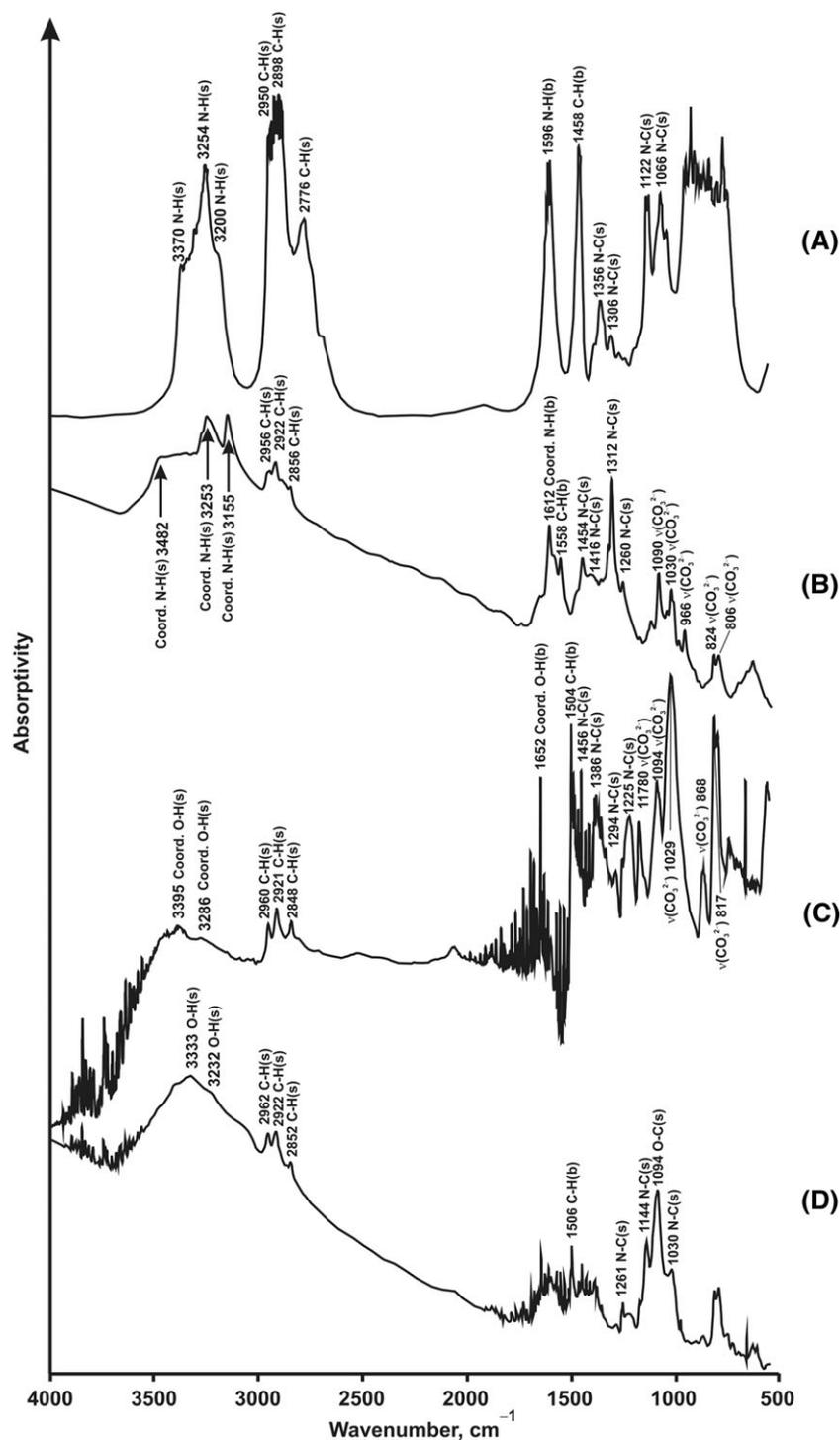
### 2.3.3 | Thermal analysis

Thermal gravimetric analysis (TGA), differential thermogravimetric (DTG) analysis, and differential thermal analysis (DTA) for samples of CuCO<sub>3</sub>, DETA, DETA-CuCO<sub>3</sub>, DGEBA/DETA, and DGEBA/DETA-CuCO<sub>3</sub>(80) were fulfilled on a Q-1500D thermal analyzer (F. Paulik, J. Paulik, L. Erdey system) in the temperature range from 25°C to 1000°C with a heating rate of 5°C/min. All measurements were performed at dynamical regime in medium of air. The weight of each sample amounted to 100 mg. Aluminum oxide has been used as standard.

### 2.3.4 | Ceramic tube test

The combustibility parameters of the DGEBA/DETA-CuCO<sub>3</sub>(6), DGEBA/DETA-CuCO<sub>3</sub>(12), DGEBA/DETA-CuCO<sub>3</sub>(40), DGEBA/DETA-CuCO<sub>3</sub>(80), and DGEBA/DETA (for comparison) have been determined according to all-Union State Standard<sup>30</sup> 12.1.044-89 using the “Ceramic tube” apparatus displayed in Figure 4. The gist of CT method consists in making the temperature conditions that are able to promote burning the materials.

The apparatus is made of ceramic tube having the squared shape whose inner surface is sheeted by 2 layers of an aluminum foil. The tube is plumbed on the supporting block whereon is mounted a gas burner. A sample is set in the center of the tube by means of holder. All samples having dimension of  $150 \times 60 \times 5 \text{ mm}^3$  were wrapped in fiberglass cloth. The measurements have been performed for samples taken in triplicates. The values obtained a minimum from 3 measurements are averaged. All samples before testing were air conditioned and weighed. Next, separate samples were placed into ceramic tube that in advance was heated to temperature of 200°C by means of gas burner flame. The maximal temperature of the combustion gases ( $T_{\text{max}}$ ) and time of  $T_{\text{max}}$  reaching ( $\Delta t$ , s) were experimentally measured. The maximal increment of temperature ( $\Delta T_{\text{max}}$ , °C) and relative loss of the mass ( $\Delta m$ , %) have been determined as



**FIGURE 3** Infrared spectra of A, DETA; B, DETA-CuCO<sub>3</sub>; C, DGEBA/DETA-CuCO<sub>3</sub>(80); and D, DGEBA/DETA

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

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

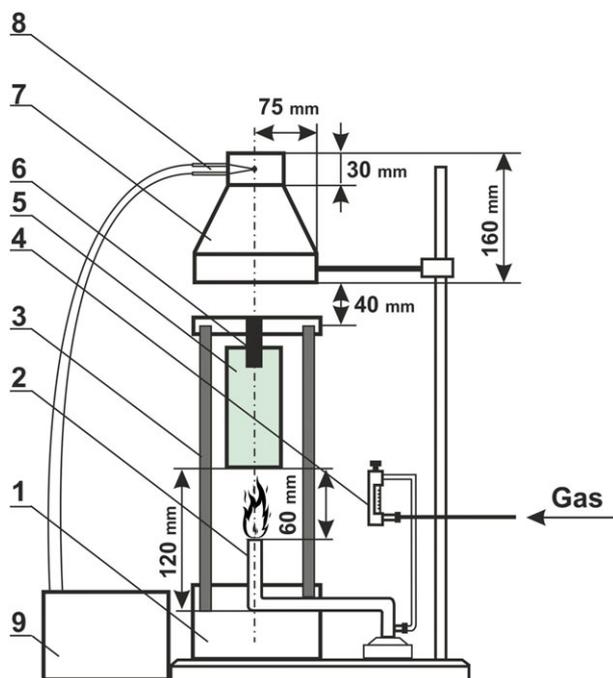
where  $m_0$  and  $m_b$  are mass (g) of sample up to and after testing, respectively.

The combustibility group of the substances was specified by means of the  $\Delta T_{\max}$  and  $\Delta m$  values while the flammability of the substances was assessed by value of  $\Delta \tau$ . If values of  $\Delta T_{\max}$  and  $\Delta m$  do not exceed 60°C and 60%, respectively, then substances are difficultly combustible ones; otherwise, they are combustible substances. In turn, the combustible substances are subdivided onto 3 flammability classes

depending on values  $\Delta \tau$ . When values of  $\Delta \tau$  exceed 240 seconds, the combustible substances are referred to the low-flammability class. The medium-flammability class is specified by values of  $\Delta \tau = 30 \div 240$  seconds. And, at last, for high-flammability class, the values of  $\Delta \tau$  amount to less 30 seconds. The results of the CT measurements are presented in Table 2.

### 2.3.5 | Bench-scale combustibility testing

The flammability rating of DGEBA/DETA-CuCO<sub>3</sub>(6), DGEBA/DETA-CuCO<sub>3</sub>(12), DGEBA/DETA-CuCO<sub>3</sub>(40), DGEBA/DETA-CuCO<sub>3</sub>(80), and DGEBA/DETA was determined by means of the UL94 BH method.



**FIGURE 4** “Ceramic tube” apparatus<sup>30</sup>: 1 = supporting block; 2 = gas burner; 3 = ceramic tube; 4 = gas flowmeter; 5 = test sample; 6 = sample holder; 7 = funnel cover; 8 = thermocouple; 9 = potentiometer [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

The flame-spread rate was assessed according to ASTM D635-14.<sup>31</sup> Each testing sample was mounted horizontally to its long axis and at an angle of 45° to its short axis. The made samples by 125 mm length, 10 mm width, and 5 mm thickness were exposed to a 20-mm-high blue Bunsen burner flame at an angle of 45°. Before testing, the polymer samples were air conditioned for 48 hours, at 25°C, and of 50% relative humidity. The movement time of the flame front between 2 gauge marks ( $\Delta\tau_{\text{burning}}$ , s) was measured, and the flame-spread rate ( $r_{\text{burning}}$ , mm·min<sup>-1</sup>) was calculated.

The limiting oxygen index (LOI) for the samples of the epoxy-amine polymers (*DGEBA/DETA*, *DGEBA/DETA-CuCO<sub>3</sub>(6)*, *DGEBA/DETA-CuCO<sub>3</sub>(12)*, *DGEBA/DETA-CuCO<sub>3</sub>(40)*, and *DGEBA/DETA-CuCO<sub>3</sub>(80)*) was determined according to ASTM D2863-13.<sup>32</sup>

The ignition point ( $T_{\text{ignition}}$ ) and self-ignition point ( $T_{\text{self-ignition}}$ ) for *DGEBA/DETA*, *DGEBA/DETA-CuCO<sub>3</sub>(6)*, *DGEBA/DETA-CuCO<sub>3</sub>(12)*, *DGEBA/DETA-CuCO<sub>3</sub>(40)*, *DGEBA/DETA-CuCO<sub>3</sub>(80)*, and *DETA* and

*DETA-CuCO<sub>3</sub>* were measured on a TF device according to ASTM D1929-16.<sup>33</sup>

The polymer samples were taken in triplicates and used for each run; the gained values of 3 measurements were averaged. The final results of the bench-scale combustibility testing are presented in Table 3.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Processes of cross bonding in the *DGEBA-DETA-CuCO<sub>3</sub>* system

Before beginning a consideration of the processes that occur in the *DGEBA-DETA-CuCO<sub>3</sub>* system at the forming the epoxy-amine polymers with lowered combustibility, it is necessary to understand how a modifier nature can influence onto fire safety of the polymers, what a role pertains to the *DETA-CuCO<sub>3</sub>* chelate complex in the combustibility suppressing process of the epoxy-amine polymers. Therefore, the influence studying of the copper(II) carbonate onto the combustibility parameters of the epoxy-amine polymers must be in the center of our attention. For it, foremost, one must identify the dark blue polycrystalline phase gained by the mixing the equimolar quantities of the *CuCO<sub>3</sub>* and *DETA* and characterize obtained substance. The identification of the crystal *DETA-CuCO<sub>3</sub>* was performed by XRPD. All reflections from crystal lattice (see Figure 2) have been indexed; unit cell parameters have been refined ( $a = 7.6504(4)$ ,  $b = 7.1991(3)$ ,  $c = 22.088(1)$  Å,  $\beta = 98.493(5)^\circ$ , space group  $P2_1/c$ ). Hence, the *DETA-CuCO<sub>3</sub>* is a dehydrated analog of the  $[\text{Cu}(\text{DETA})(\text{H}_2\text{O})(\text{M}-\text{CO}_3)_2] \cdot 6\text{H}_2\text{O}$  chelate complex whose crystal structure has been studied earlier.<sup>23</sup>

The interaction of *DETA* (a hardener of epoxy resins) with non-combustible inorganic salt (copper(II) carbonate) in many respects predetermines the properties of *DETA-CuCO<sub>3</sub>* as fire retardant hardener. That fact that  $\text{Cu}^{2+}$  ion is coordinated with *DETA* into a chelate complex can be seen on the IR spectra<sup>34,35</sup> recorded for *DETA* and *DETA-CuCO<sub>3</sub>* (see Figure 3A,B). So, for *DETA* (Figure 3A), absorption bands of the high-frequency region at 3370 and 3254 cm<sup>-1</sup> are related to stretching of N–H bonds of primary amine, whereas the band observed at 3200 cm<sup>-1</sup> is ascribed to stretching of N–H bond of secondary amine; the observed oscillation frequency at 1596 cm<sup>-1</sup> is attributed to bending of N–H bond. Absorption bands at 2950, 2898, 2776, and 1458 cm<sup>-1</sup> are related to stretching and bending of

**TABLE 2** Data of the “Ceramic tube” measurements of the epoxy-amine polymers

Sample	TC	$T_{\text{max}}$	$\Delta T_{\text{max}}$	$\Delta\tau$	$\Delta m$	CG/FC
<i>DGEBA/DETA</i>	200	867 ± 5	667 ± 5	30 ± 1	89.0 ± 1	CS/HF
<i>DGEBA/DETA-CuCO<sub>3</sub>(6)</i>	200	702 ± 5	502 ± 5	160 ± 1	76.8 ± 1	CS/MF
<i>DGEBA/DETA-CuCO<sub>3</sub>(12)<sup>a</sup></i>	200	648 ± 5	448 ± 5	210 ± 1	68.5 ± 1	CS/MF
<i>DGEBA/DETA-CuCO<sub>3</sub>(40)</i>	200	650 ± 5	450 ± 5	210 ± 1	68.5 ± 1	CS/MF
<i>DGEBA/DETA-CuCO<sub>3</sub>(80)</i>	200	662 ± 5	462 ± 5	200 ± 1	70.3 ± 1	CS/MF

TC (°C), the temperature of ceramic tube prior to bringing in the samples;  $T_{\text{max}}$  (°C), the maximal temperature of the combustion gases;  $\Delta T_{\text{max}}$  (°C), the maximal increment of temperature;  $\Delta\tau$  (s), the time of attaining to maximal temperature;  $\Delta m$  (%), relative loss of the mass; CG, the combustibility group; FC, flammability class (CS, combustible substance; HF, high-flammability; MF, medium-flammability).

<sup>a</sup>The gained values apply to polymer samples of the *DGEBA/DETA-CuCO<sub>3</sub>(12)* prepared by both methods (see Section 2.2).

**TABLE 3** Data of the bench-scale fire tests

Sample	$T_{\text{ignition}}, ^\circ\text{C}$	$T_{\text{self-ignition}}, ^\circ\text{C}$	$r_{\text{burning}}, \text{mm}\cdot\text{min}^{-1}$	$\Delta t_{\text{burning}}, \text{s}$	FR	LOI, %
DETA	97 ± 1	350 ± 1	–	–	–	–
DETA-CuCO <sub>3</sub>	b	b	–	–	–	–
DGEBA/DETA	320 ± 1	545 ± 1	25.2 ± 5	d	PH	19.8 ± 5
DGEBA/DETA-CuCO <sub>3</sub> (6)	333 ± 1	550 ± 1	24.6 ± 5	d	PH	27.0 ± 5
DGEBA/DETA-CuCO <sub>3</sub> (12) <sup>a</sup>	355 ± 1	558 ± 1	c	93 ± 1	NPH	29.5 ± 5
DGEBA/DETA-CuCO <sub>3</sub> (40)	368 ± 1	560 ± 1	c	87 ± 1	NPH	33.0 ± 5
DGEBA/DETA-CuCO <sub>3</sub> (80)	371 ± 1	563 ± 1	c	86 ± 1	NPH	38.2 ± 5

Abbreviations: FR, flammability rating (PH, propagation horizontally; NPH, nonpropagation horizontally); LOI, limiting oxygen index.

<sup>a</sup>The same remark that is given in Table 2.

<sup>b</sup>Ignition (or self-ignition) was not observed up to temperature of 450°C (or 600°C).

<sup>c</sup>Flame is itself extinguished before a zero gauge mark.

<sup>d</sup>Samples are on fire as far as moment of forced extinguishing.

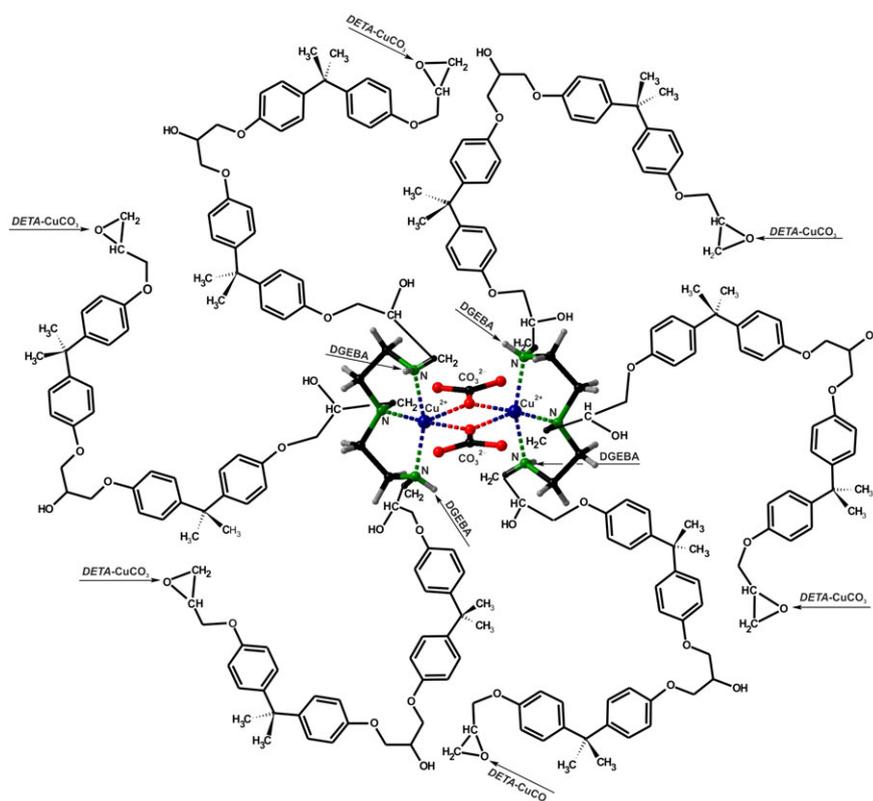
C–H bonds. Frequencies observed at region 1356 to 1066 cm<sup>-1</sup> are absorption bands for C–N bonds.

After bonding of the DETA with copper(II) carbonate (Figure 3B), one of the N–H absorption bands is shifted to high-frequency region (3482 cm<sup>-1</sup>), whereas 2 other bands are shifted to low-frequency region (3253 and 3155 cm<sup>-1</sup>). The observed wavenumber (1612 cm<sup>-1</sup>) attributed to bending of N–H bond is also shifted to high-frequency region. Absorption bands at 2956, 2922, 2856, and 1458 cm<sup>-1</sup> ascribed to stretching and bending of C–H bonds are also shifted. Moreover, the absorption frequencies at 1090, 1030, 966, 824, and 806 cm<sup>-1</sup> induced by the CO<sub>3</sub><sup>2-</sup> anion oscillations are observed on the IR spectra of DETA-CuCO<sub>3</sub> complex.

Interlinking the incombustible inorganic salt with combustible nitrogen-containing curing agent into chelate complex is decisive step at the forming the epoxy-amine polymers with suppressed

combustibility. At curing, the DETA-CuCO<sub>3</sub> complex can be incorporated into the epoxy-amine polymer matrix. So IR spectra of the DGEBA/DETA polymer (Figure 3D) reveal that in case of epoxy resin cured by DETA, the absorption bands belonged to N–H bonds disappear at all. Instead of these, the absorption bands of N–C bonds spring up at 1261, 1144, and 1030 cm<sup>-1</sup>, as well as new absorption bands induced by the O–H bonds oscillations arise at 3333 and 3232 cm<sup>-1</sup>. However, on the IR spectra recorded for the DGEBA/DETA-CuCO<sub>3</sub>(80) (Figure 3C), one can see that absorption bands ascribed to stretching and bending of O–H bonds are shifted to high-frequency region (3395, 3286, and 1652 cm<sup>-1</sup>) and significantly weakened due to Cu–N bonding.

Thus, cross bonding process taking place at curing the CuCO<sub>3</sub>-containing epoxy-amine polymers is accompanied by an interaction of the epoxide groups of the epoxy oligomer and the amine groups



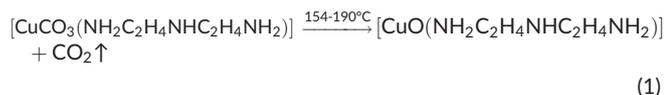
**FIGURE 5** The framework of the CuCO<sub>3</sub>-containing epoxy-amine polymer (expected structure) [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

coordinated with  $\text{Cu}^{2+}$  ions of the  $\text{DETA-CuCO}_3$  chelate complex. Because  $\text{DGEBA}$  molecule contains at least 2 epoxide groups, the epoxy-amine polymerization and formation of the polymer framework will be occurring concurrently. Undoubtedly, the  $\text{DETA-CuCO}_3$  chelate complex plays a role of the fire retardant hardener in this process. The cross-interlinking of the  $\text{CuCO}_3$ -coordinated  $\text{DETA}$  with  $\text{DGEBA}$  is represented in Figure 5. All it certainly influences onto change of the respective combustibility parameters as well as of the performance characteristics of the polymer materials produced out of the  $\text{CuCO}_3$ -containing epoxy-amine polymers.

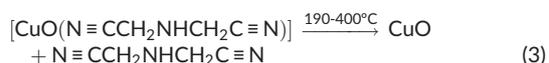
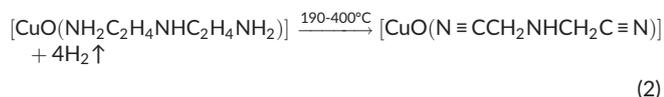
### 3.2 | Thermal analysis of the fire retardant hardener

The thermal behavior of  $\text{DETA-CuCO}_3$  chelate complex as would-be fire retardant hardener as well as  $\text{DETA}$  and  $\text{CuCO}_3$  have been studied by means of TGA, DTG analysis, and DTA; the corresponding curves are displayed in Figure 6. The results of the stage-by-stage thermal degradation for the  $\text{DETA-CuCO}_3$ ,  $\text{DETA}$ ,  $\text{CuCO}_3$  as well as  $\text{DGEBA/DETA}$ , and  $\text{DGEBA/DETA-CuCO}_3(80)$  are given in Table 4.

As shown in Figure 6A, the TGA curve of the thermal decomposition of the originally hydrated  $\text{DETA-CuCO}_3$  complex<sup>23</sup> is represented by 4 sections. The first section involves the temperature range from 20°C to 154°C. It corresponds to a loss of weight of 18.6 wt% and the appearance of a minimum on the DTA curve (see Figure 6C). At this temperature interval (DTA curve), an endothermic process is observed at temperature of 110°C. This part of the curve is related to the dehydration process and formation of anhydrous chelate complex. The second section is in the temperature range from 154°C to 190°C ( $\Delta m = 21.6$  wt%). The thermal decomposition of the inorganic part of the complex takes place in this range of temperature:

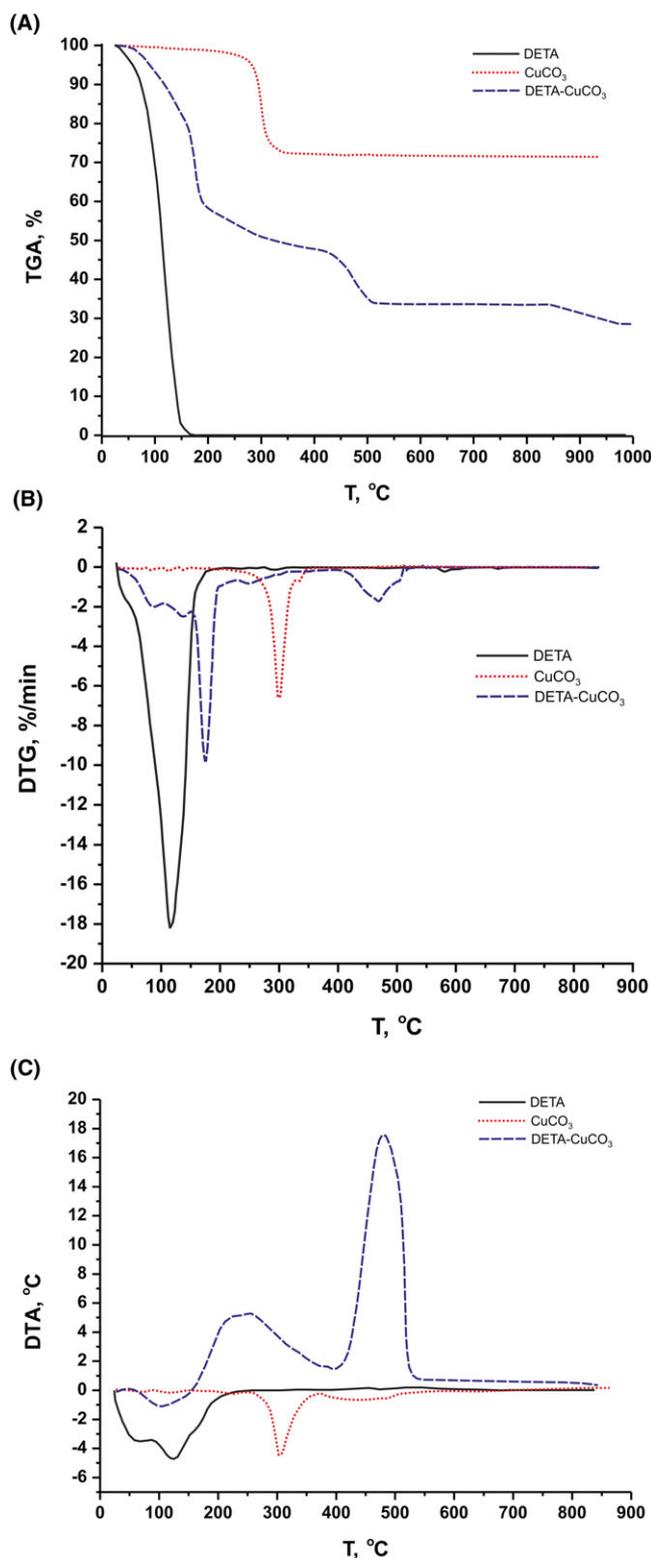


The third section occurs in the temperature range from 190°C to 400°C. At this temperature interval of the DTA curve, one can see 2 successive exothermic maximums (at 220°C and 250°C, respectively). The loss of weight amounts to 11.6 wt% from the partial thermal-oxidative destruction of the  $[\text{CuO}(\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)]$  complex produced in reaction 1 with a concurrent dehydrogenization of the coordinated  $\text{DETA}$ ,<sup>21,36,37</sup> as seen in the following reaction equations:



Hydrogen *in statu nascendi* (see reaction 2) together with a part of aminonitrile produced in reaction 3 combusts immediately; it is cause of heat evolution.

The fourth section (from 400°C to 520°C) corresponds to a complete combustion of the destruction products of organic aminonitrile



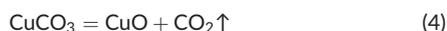
**FIGURE 6** A, Thermal gravimetric analysis (TGA); B, differential thermogravimetric (DTG); and C, differential thermal analysis (DTA) curves for  $\text{DETA}$ ,  $\text{CuCO}_3$ , and  $\text{DETA-CuCO}_3$  [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

and the pyrolytic residuals of organic constituents of the complex. It is accompanied by the appearance of a pronounced exothermic effect at the DTA curve with a maximum at 480°C. The weight loss at this final stage is 14 wt%.

**TABLE 4** The thermal degradation results of the samples under study

Sample	Stage	Temperature Range, °C	Weight Loss, wt%
DETA	I	20-170	100
CuCO <sub>3</sub>	I	250-350	28.0
DETA-CuCO <sub>3</sub>	I	20-154	18.6
	II	154-190	21.6
	III	190-400	11.6
	IV	400-520	14.0
DGEBA/DETA	I	20-180	3.1
	II	180-360	32.0
	III	360-460	12.1
	IV	460-900	52.0
DGEBA/DETA-CuCO <sub>3</sub> (80)	I	20-150	2.1
	II	150-275	2.7
	III	275-357	30.4
	IV	357-690	36.0

Unlike DETA-CuCO<sub>3</sub>, full loss of weight for DETA occurs in the temperature range from 20°C to 170°C with pronounced endothermic minimum (the DTA curve, Figure 6C). It corresponds to total volatilization of liquid DETA.<sup>26</sup> Contrariwise, the thermal decomposition of the CuCO<sub>3</sub> occurs in temperature range from 250°C to 350°C; the loss of weight amounts to 28.0 wt% at the expense of the gas evolution (CO<sub>2</sub>↑)<sup>25</sup>:



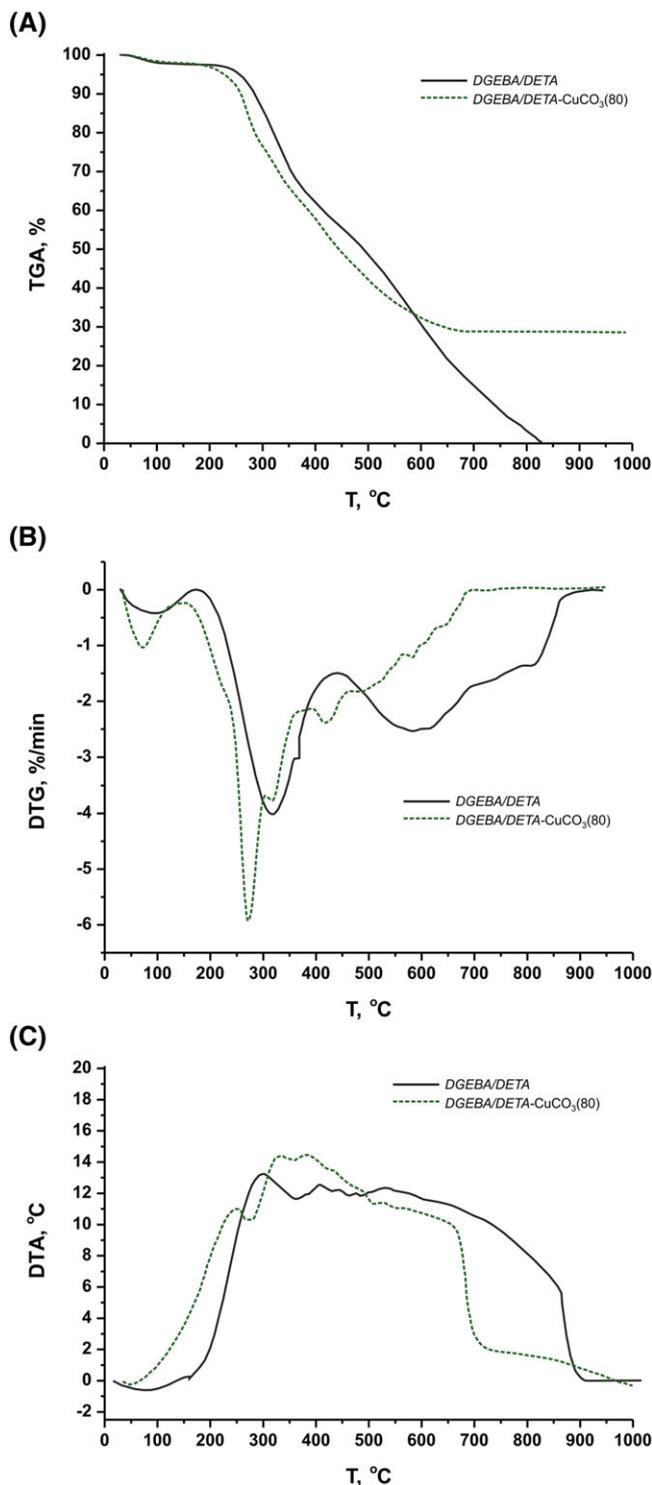
The extremum of endothermic effect on the DTA curve (Figure 6C) is observed at temperature of 306°C.

It is interesting to compare the ability of free and coordinated DETA to the ignition (self-ignition). So, if noncoordinated DETA ignites or self-ignites at 97°C or 350°C, respectively,<sup>26</sup> then the ignition (or self-ignition) of the DETA-CuCO<sub>3</sub> chelate complex is not observed up to temperature of 450°C (or 600°C). Thus, one can assert that the combustible DETA after DETA-CuCO<sub>3</sub> chelation becomes a practically incombustible substance. The cause of it lies in the chemical bonds that form between the Cu<sup>2+</sup> ions of the CuCO<sub>3</sub> and the amino groups of the DETA at the complexing. To break down the Cu(II)-(NH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>NHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>) coordinated bonds, a large amount of heat should be used up. Undoubtedly, these coordination bonds, along with some other factors, are responsible for the combustibility suppressing of the CuCO<sub>3</sub>-containing epoxy-amine polymers.

### 3.3 | Thermal behavior of the CuCO<sub>3</sub>-containing epoxy-amine polymers

Incorporation of the DETA-CuCO<sub>3</sub> to DGEBA results in forming the CuCO<sub>3</sub>-containing epoxy-amine polymers with suppressed combustibility. The TGA, DTG, and DTA curves recorded for DGEBA/DETA and DGEBA/DETA-CuCO<sub>3</sub>(80) are represented in Figure 7.

As shown in Figure 7A, the TGA curve of the thermal degradation of the DGEBA/DETA is represented by 4 sections. The first section involves 20°C to 180°C, corresponds to the loss of weight of 3.1 wt%, and has a minor endothermic minimum (the DTA curve, Figure 7C). These data are in a good agreement with incipient process of the destruction of the polymer framework resulting in the formation of the volatile species. The second section occurs in the temperature



**FIGURE 7** A, Thermal gravimetric analysis (TGA); B, differential thermogravimetric (DTG); and C, differential thermal analysis (DTA) curves for DGEBA/DETA and DGEBA/DETA-CuCO<sub>3</sub>(80) [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

range from 180°C to 360°C ( $\Delta m = 32$  wt%). Here, the exothermic effect with maximum at 300°C stems from the thermal-oxidative destruction of the DGEBA/DETA polymer. The mechanism of this process is free radical where the alkyl particles ( $\cdot R$ ) and peroxide particles ( $\cdot O-OR$ ) take part in formation of hydroperoxides ( $HO-OR$ ).<sup>38,39</sup> The combustion of these products takes place at the third stage in temperature range from 360°C to 460°C ( $\Delta m = 12.1$  wt%). This temperature

interval of the DTA curve contains the exothermic maximum at 400°C. The final combustion of the pyrolytic residue occurs at the fourth stage of the *DGEBA/DETA* thermolysis in temperature range from 460°C to 900°C ( $\Delta m = 52$  wt%) as the exothermic process.

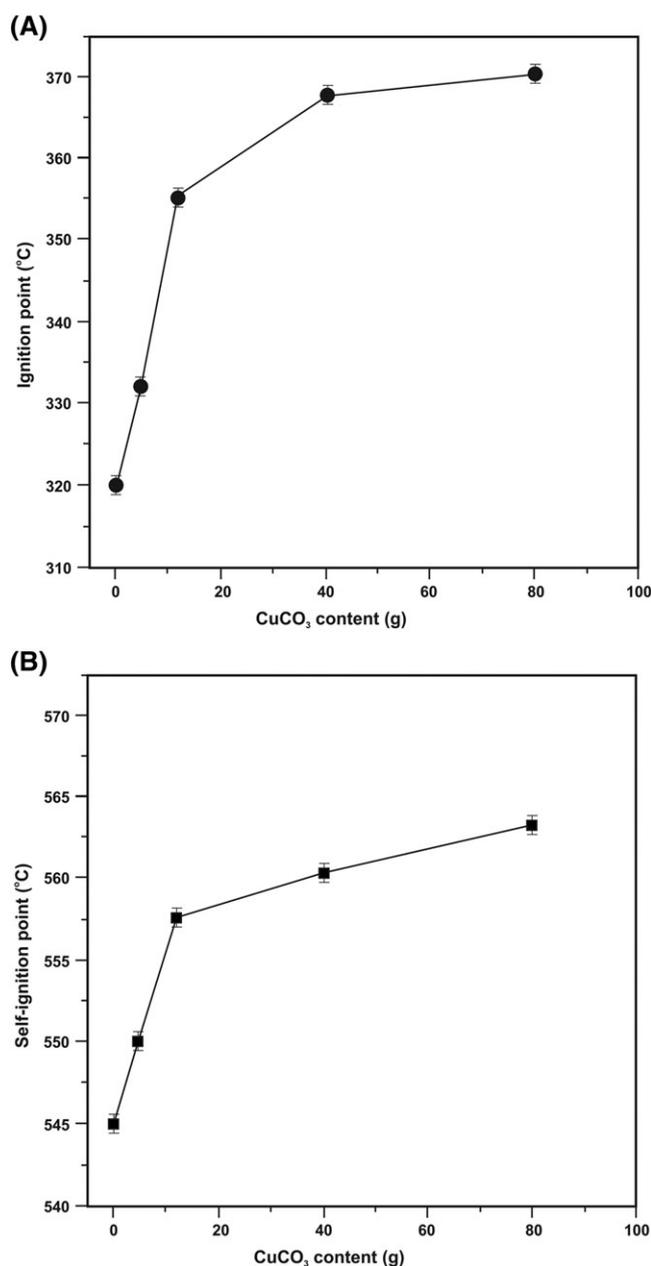
The thermal degradation process of the  $\text{CuCO}_3$ -containing epoxy-amine polymer, *DGEBA/DETA-CuCO}\_3(80)*, is more complicated, although the TGA curve is also represented by 4 sections (see Figure 7). The first section occurs from 20°C to 150°C and is accompanied by an appearance of the endothermic effect without well-marked extremum on the DTA curve (Figure 7C). Here, as in case of *DGEBA/DETA* (stage I), the emission of volatile species takes place ( $\Delta m = 2.1$  wt%). The second section occurs at temperature range from 150°C to 275°C. This part of the curve is related to partial decomposition of the inorganic part of the complex with  $\text{CO}_2$  emission and thermal-oxidative destruction of the coordinated *DETA* (dehydrogenization) with simultaneous  $\text{H}_2$  combustion. This is exothermic process with maximum at 250°C (the DTA curve) and the 2.7 wt% loss of weight. The third section covers the temperature range from 275°C to 357°C and is accompanied by the appearance of exothermic maximum at 333°C at the DTA curve (Figure 7C). The loss of weight at this stage amounts to 30.4 wt% from the thermal destruction of the *DETA-CuCO}\_3* coordination cores inbuilt into polymer matrix and, further, thermal-oxidative destruction of organic constituent part of the *DGEBA/DETA-CuCO}\_3(80)*. The fourth stage of thermal destruction from 357°C to 690°C corresponds to complete combustion of the pyrolytic residue of the polymer sample ( $\Delta m = 36.0$  wt%).

As shown in Figure 7C, the maximum of exothermic effect that is responsible for thermal-oxidative destruction of organic constituent of the *DGEBA/DETA-CuCO}\_3(80)* (333°C) in comparison with the *DGEBA/DETA* (300°C) is shifted into higher temperature region. It testifies the somewhat higher thermal stability of the  $\text{CuCO}_3$ -containing epoxy-amine polymers. Furthermore, the combustion of pyrolytic residue of organic constituent of the *DGEBA/DETA-CuCO}\_3(80)* occurs in more restricted temperature interval than the *DGEBA/DETA*. So, if in case of the *DGEBA/DETA* the combustion of pyrolytic residue is ended at 900°C, then the same process for the *DGEBA/DETA-CuCO}\_3(80)* is finished at 690°C. The maximal weight loss rate observed at 316°C (Figure 7B) for the *DGEBA/DETA-CuCO}\_3(80)* is lower on the 0.37% than it is for the *DGEBA/DETA*. Apparently, one of the reasons of it consists in ability of an incombustible inorganic salt to coordinate the organic part of the  $\text{CuCO}_3$ -containing epoxy-amine polymer. In this connection, the  $\text{CuCO}_3$  can be considered a vastly effective fire retardant that is able to significantly suppress the combustibility of the epoxy-amine polymers owing to the forming the  $\text{Cu(II)-N}$  and  $\text{Cu(II)-O}$  bonds. By the way, the performed quantum chemical calculations for the structural fragment displayed in Figure 5 have revealed that the sum of energy of all  $\text{Cu(II)-N}$  and  $\text{Cu(II)-O}$  bonds in the  $[\{\text{Cu}(\text{NR}_2\text{C}_2\text{H}_4\text{NRC}_2\text{H}_4\text{NR}_2)(\text{CO}_3)\}_2]$  coordination core amounts to 674.64.32  $\text{kJ}\cdot\text{mol}^{-1}$ .

### 3.4 | Combustibility of the $\text{CuCO}_3$ -containing epoxy-amine polymers

The fire hazard of polymer materials based on epoxy resins is in many respects specified by their susceptibility to flame and by behavior

under burning. From performed experiments, one can draw an unambiguous conclusion that the first cause of combustibility lowering of the  $\text{CuCO}_3$ -containing epoxy-amine polymers is the effective  $\text{Cu(II)-(NH}_2\text{C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)$  interlinking that, eventually, results in forming the *DETA-CuCO}\_3* chelate complex functioning as a fire retardant hardener in epoxy-amine polymerization process. So the values of  $T_{\text{ignition}}$  and  $T_{\text{self-ignition}}$  for the epoxy resin cured by amine (*DGEBA/DETA*) amount to 320°C and 545°C, respectively. However, after the adding of the fire retardant ( $\text{CuCO}_3$ ), the same values for the  $\text{CuCO}_3$ -containing epoxy-amine polymers have been heightened. Interestingly, the  $T_{\text{ignition}}$  and  $T_{\text{self-ignition}}$  acquire the maximal values when the  $\text{CuCO}_3$  content in the epoxy-amine polymer amounts to 80 g per 100 g of *DGEBA*. Influence of the  $\text{CuCO}_3$  content onto the values of  $T_{\text{ignition}}$  and  $T_{\text{self-ignition}}$  of the  $\text{CuCO}_3$ -containing epoxy-amine polymers is revealed in Figure 8. The same trend is observed in case of



**FIGURE 8** A, Ignition point and B, self-ignition point dependence on the  $\text{CuCO}_3$  content in the  $\text{CuCO}_3$ -containing epoxy-amine polymers

the values of the minimum oxygen concentration required for supporting the candle-like combustion of the  $\text{CuCO}_3$ -containing epoxy-amine polymers (Table 3). So the maximum value of the LOI (38.2%) is characteristic for the *DGEBA/DETA-CuCO<sub>3</sub>(80)*, while the LOI value for *DGEBA/DETA* is 19.8%.

The combustibility group for the  $\text{CuCO}_3$ -containing epoxy-amine polymers has been determined by means of "CT" method. Test data (Table 2) reveal that adding of even a little amount of fire retardant (6 g of  $\text{CuCO}_3$  per 100 g of *DGEBA*) can appreciably decrease combustibility of the  $\text{CuCO}_3$ -containing epoxy-amine polymers as compared with unmodified polymers. However, significant changes in combustibility become particularly weighable when amount of the  $\text{CuCO}_3$  in epoxy-amine polymers runs up to 80 g per 100 g of *DGEBA*. In turn, the time of attaining to maximal temperature ( $\Delta\tau$ ) under burning of the  $\text{CuCO}_3$ -containing epoxy-amine polymers ranges from 160 to 210 seconds. It allows attributing all of these epoxy-amine polymers except *DETA/DGEBA* to the class of the medium-flammability substances. Besides, the maximal temperature under burning of the *DGEBA/DETA-CuCO<sub>3</sub>(6)*, *DGEBA/DETA-CuCO<sub>3</sub>(12)*, *DGEBA/DETA-CuCO<sub>3</sub>(40)*, and *DGEBA/DETA-CuCO<sub>3</sub>(80)* in comparison with the *DGEBA/DETA* lowers by 165°C, 219°C, 217°C, and 205°C, respectively. For the same sequence of the polymer samples, the loss of weight relatively the *DGEBA/DETA* decreases by 12.2%, 20.5%, 20.5%, and 18.7%, respectively.

The flame propagation is known to be one of the very important fire hazard index characterizing the combustibility of the polymer materials. This combustibility parameter is specified by the velocity of the combustible mixture formation on the surface of a sample whose value directly depends on chemical composition of the polymer material. The experimental data (Table 3) reveal that adding of 6 g of the  $\text{CuCO}_3$  to epoxy resin does not much influence onto the flame propagation over the sample placed horizontally. In particular, a horizontally fastened sample of the *DGEBA/DETA-CuCO<sub>3</sub>(6)* likewise to the *DGEBA/DETA* does not cease to burn till moment of forced extinguishing the fire. However, the *DGEBA/DETA-CuCO<sub>3</sub>(12)*, *DGEBA/DETA-CuCO<sub>3</sub>(40)*, and, especially, the *DGEBA/DETA-CuCO<sub>3</sub>(80)* samples situated in horizontality do not propagate flame at all (the flame is itself extinguished just before a zero gauge mark). Moreover, in case of a sample of the *DGEBA/DETA-CuCO<sub>3</sub>(80)*, the time of a free burning does not exceed 90 seconds. Nevertheless, for the samples of the *DGEBA/DETA-CuCO<sub>3</sub>(6)* and the *DGEBA/DETA*, the flame propagation over the horizontal surface amounts to about 25 mm·min<sup>-1</sup>, and their burning is followed by the dripping of fire. That is why these 2 samples were subsumed a PH (propagation horizontally) under the flammability rating. The rest polymer samples—the *DGEBA/DETA-CuCO<sub>3</sub>(12)*, *DGEBA/DETA-CuCO<sub>3</sub>(40)*, and *DGEBA/DETA-CuCO<sub>3</sub>(80)*—do not propagate flame horizontally (NPH); therefore, these can be attributed to a class of PV (propagation vertically).

Thus, an analysis of the combustibility study results has clearly revealed that the fire hazard parameters of the  $\text{CuCO}_3$ -containing epoxy-amine polymers mostly depend on their chemical composition, or more exactly, on the fire retardant quantity in a polymer material. Considering dependences of some fire hazard parameters of the epoxy-amine composites from the fire retardant content, it can be

seen that the increasing the  $\text{CuCO}_3$  quantity in a polymer composite results in improving the fire safety indexes. In particular, the  $T_{\text{ignition}}$ ,  $T_{\text{self-ignition}}$ , and LOI are regularly increased for such sequence of polymer samples: *DGEBA/DETA*, *DGEBA/DETA-CuCO<sub>3</sub>(6)*, *DGEBA/DETA-CuCO<sub>3</sub>(12)*, *DGEBA/DETA-CuCO<sub>3</sub>(40)*, and *DGEBA/DETA-CuCO<sub>3</sub>(80)*. However, the influence of the fire retardant quantity in the  $\text{CuCO}_3$ -containing epoxy-amine polymers onto such combustibility parameters as  $T_{\text{max}}$ ,  $\Delta T_{\text{max}}$ ,  $\Delta\tau$ , and  $\Delta m$  (see Section 2.3.4 and Table 2) is not so appropriate. Given this, a sequence of the epoxy-amine polymers mentioned above can be conditionally divided into 3 principal groups. The first group involves the 2 first representatives of the samples listed in Table 2. Here, the appropriate combustibility parameters evenly improve at the transition from the *DGEBA/DETA* to the *DGEBA/DETA-CuCO<sub>3</sub>(6)*. The polymer samples of the *DGEBA/DETA-CuCO<sub>3</sub>(12)* and *DGEBA/DETA-CuCO<sub>3</sub>(40)* of the second group are characterized by the optimal combustibility parameters. But these parameters for *DGEBA/DETA-CuCO<sub>3</sub>(80)* (third group) are somewhat worsened in comparison with second group. Thus, the optimal quantity of the fire retardant in the epoxy-amine polymer must be 12 to 40 g of  $\text{CuCO}_3$  per 100 g of *DGEBA* to show the best results at the combustibility testing.

## 4 | CONCLUSIONS

The representatives of a new type of the metal-coordinated epoxy-amine polymers—the *DGEBA/DETA-CuCO<sub>3</sub>(6)*, *DGEBA/DETA-CuCO<sub>3</sub>(12)*, *DGEBA/DETA-CuCO<sub>3</sub>(40)*, and *DGEBA/DETA-CuCO<sub>3</sub>(80)*—with suppressed combustibility have been gained in the *DGEBA/DETA-CuCO<sub>3</sub>* system and characterized by means of the thermal analysis, the method of "Ceramic tube", and the measurements of the flame propagation rate (UL94 BH), the LOI, and temperatures of ignition and self-ignition. The preparation technology elaborated for given polymers provides for the first time the obtaining of the *DETA-CuCO<sub>3</sub>* chelate complex (the fire retardant hardener) with its subsequent incorporation to the *DGEBA*. The cross bonding processes of the epoxy polymers cured by the *DETA-CuCO<sub>3</sub>* were studied by means of XRPD analysis and IR spectra. It has been ascertained that the  $\text{CuCO}_3$ —(*DETA*) interlinking that is accompanied by the forming the Cu(II)—N coordination bonds within the polymer framework predetermines the combustible properties of the  $\text{CuCO}_3$ -containing epoxy-amine polymers. The thermal analysis has shown that thermal stability of the polymer sample of the *DGEBA/DETA-CuCO<sub>3</sub>(80)* relatively to the *DGEBA/DETA* is increased on 33°C, while the temperature of the combustion gases is decreased on the 210°C. The bench-scale combustibility testing has revealed that the combustibility of the  $\text{CuCO}_3$ -containing epoxy-amine polymers in comparison with the *DGEBA/DETA* is appreciably suppressed, the ignition point and self-ignition point are gone up, the time of attaining the maximal temperature of the combustion gases is increased, and the relative loss of weight under burning of given polymers is decreased. All of these data, along with the results of CT measurements, have let us attribute the polymer samples of the *DGEBA/DETA-CuCO<sub>3</sub>(6)*, *DGEBA/DETA-CuCO<sub>3</sub>(12)*, *DGEBA/DETA-CuCO<sub>3</sub>(40)*, and *DGEBA/DETA-CuCO<sub>3</sub>(80)* to the medium-

flammability substance class. Nevertheless, the best results at the combustibility testing demonstrate the polymer samples in which the content of the fire retardant amounts to 12 to 40 g of  $\text{CuCO}_3$  per 100 g of DGEBA.

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## REFERENCES

- McCrum NG, Buckley CP, Bucknall CB. *Principles of Polymer Engineering*. New York: Oxford University Press; 1997.
- Lee H, Neville K. *Handbook of Epoxy Resins*. New York: McGraw-Hill; 1967.
- Hosin VG. *The Strengthening of Epoxy Polymer*. Kazan: PIK Dom Pechati; 2004.
- Mouritz AP, Gibson AG. *Fire Properties of Polymer Composite Materials*. Dordrecht: Springer; 2006.
- Bourbigot S, Flambard X. Heat resistance and flammability of high performance biber: a review. *Fire Mater*. 2002;26(4-5):155-168. <https://doi.org/10.1002/fam.799>
- Chen DQ, Wang YZ, Hu XP, Wang DY, Qu MH, Yang B. Flame-retardant and anti-dripping effects of a novel char-forming flame retardant for the treatment of poly(ethylenetereftalate) fabrics. *Polym Degrad Stab*. 2005;88(2):349-356. <https://doi.org/10.1016/j.polymdegradstab.2004.11.010>
- Choi J, Yee AF, Laine RM. Organic/inorganic hybrid composites from cubic silsesquioxanes epoxy resins of octa(dimethylsiloxylepoxy) silsesquioxane. *Macromolecules*. 2003;36(15):5666-5682. <https://doi.org/10.1021/ma030172r>
- Lu S-Y, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. *Prog Polym Sci*. 2002;27(8):1661-1712. [https://doi.org/10.1016/S0079-6700\(02\)00018-7](https://doi.org/10.1016/S0079-6700(02)00018-7)
- Levchik SV, Weil ED. A review of recent progress in phosphorus-based flame retardants. *J Fire Sci*. 2006;24(5):345-364. <https://doi.org/10.1177/0734904106068426>
- Hsiue GH, Wang WJ, Chang FC. Synthesis, characterization, thermal and flame-retardant properties of silicon-based epoxy resins. *J Appl Polym Sci*. 1999;73(7):1231-1238. [https://doi.org/10.1002/\(SICI\)1097-4628\(19990815\)73:7%3C1231::AID-APP17%3E3.0.CO;2-U](https://doi.org/10.1002/(SICI)1097-4628(19990815)73:7%3C1231::AID-APP17%3E3.0.CO;2-U)
- Yang H, Wang X, Yu B, Song L, Hu Y, Yuen RK. Effect of borates on thermal degradation and flame retardancy of epoxy resins using polyhedral oligomeric silsesquioxane as a curing agent. *Thermochimica Acta*. 2012;535:71-78. <https://doi.org/10.1016/j.tca.2012.02.021>
- Liu W, Varley RJ, Simon GP. A phosphorus-containing diamine for flame-retardant, high-functionality epoxy resins. I. Synthesis, reactivity, and thermal degradation properties. *J Appl Polym Sci*. 2004;92(4):2093-2100. <https://doi.org/10.1002/app.20145>
- Liu W, Varley RJ, Simon GP. Phosphorus-containing diamine for flame retardancy of high functionality epoxy resins. Part II the thermal and mechanical properties of mixed amine systems. *Polymer*. 2006;47(6):2091-2098. <https://doi.org/10.1016/j.polymer.2005.12.083>
- Barton JM, Buist GJ, Hamerton I, Howlin BJ, Jones JR, Liu S. Preparation and characterization of imidazole-metal complexes and evaluation of cured epoxy networks. *J Mater Chem*. 1994;4(3):379-384. <https://doi.org/10.1039/JM9940400379>
- Brown J, Hamerton I, Howlin BJ. Preparation, characterization, and thermal properties of controllable metal-imidazole complex curing agents for epoxy resins. *J Appl Polym Sci*. 2000;75(2):201-217. [http://onlinelibrary.wiley.com/doi/10.1002/\(SICI\)1097-4628\(200011\)75:2%3C201::AID-APP2%3E3.0.CO;2-%23/pdf](http://onlinelibrary.wiley.com/doi/10.1002/(SICI)1097-4628(200011)75:2%3C201::AID-APP2%3E3.0.CO;2-%23/pdf)
- Kurnoskin AV. Diane oligomers: heat resistance increase by metal ions. *Polym-Plast Technol Eng*. 1991;30(7):737-750. <https://doi.org/10.1080/03602559108020147>
- Kurnoskin AV. Epoxy chelate copper-containing polymers: their chemistry and production. *Polym-Plast Technol Eng*. 1992;31(5-6):505-525. <https://doi.org/10.1080/03602559208017764>
- Hamerton I, Howlin B, Jepson P. Metals and coordination compounds as modifiers for epoxy resins. *Coord Chem Rev*. 2002;224(1-2):67-85. [https://doi.org/10.1016/S0010-8545\(01\)00393-9](https://doi.org/10.1016/S0010-8545(01)00393-9)
- Kurnoskin AV. Metal-containing epoxy polymers: a review. In: Cheremisinoff N, Cheremisinoff P, eds. *Handbook of Applied Polymer Processing Technology*. Marcel Dekker, Inc.: New York; 1996: 703-765.
- Lavrenyuk H, Mykhalichko O, Zarychta B, Olijnyk V, Mykhalichko B. A new copper(II) chelate complex with tridentate ligand: synthesis, crystal and molecular electronic structure of aqua-(diethylenetriamine-N, N', N'')-copper(II) sulfate monohydrate and its fire retardant properties. *J Mol Struct*. 2015;1095:34-41. <https://doi.org/10.1016/j.molstruc.2015.03.039>
- Lavrenyuk H, Mykhalichko B. Epoxy composite with lowered combustibility, patent no 109187 UA, 2015 (in Ukraine).
- Lavrenyuk H, Kochubei V, Mykhalichko O, Mykhalichko B. A new flame retardant on the basis of Diethylenetriamine copper(II) sulfate complex for combustibility suppressing of epoxy-amine composites. *Fire Saf J*. 2016;80:30-37. <https://doi.org/10.1016/j.firesaf.2016.01.001>
- Lavrenyuk H, Mykhalichko O, Zarychta B, Olijnyk V, Mykhalichko B. Synthesis, structural, and thermal characterization of a new binuclear copper(II) chelate complex bearing an amine-hardener for epoxy resins. *J Coord Chem*. 2016;69(18):2666-2676. <https://doi.org/10.1080/00958972.2016.1212340>
- Seidel H, Viswanathan K, Johannes W, Ehrhardt H. Darstellung, Struktur und Eigenschaften von Kupfer(II)-Carbonat. *Z Anorg Allg Chem*. 1974;410(2):138-148. <https://doi.org/10.1002/zaac.19744100207>
- Galwey AK, Brown ME. *Thermal Decomposition of Ionic Solids*. Amsterdam: Elsevier Science B.V; 1999.
- Baratov AN, Korolchenko A. Ya. *Fire and Explosion Hazard of Substances and Materials and Fire Extinguishing Agents. Reference Book. Part 1*. Moscow: Khimia; 1990.
- Rodríguez-Carvajal J. Recent developments of the program FullProf, commission on powder diffraction. *IUCr Newsletter*. 2001;26:12-19.
- Louër D, Louër M. Méthode d'Essais et Erreurs Pour l'Indexation Automatique des Diagrammes de Poudre. *J Appl Cryst*. 1972;5(4):271-275. <https://doi.org/10.1107/S0021889872009483>
- Boultif A, Louër D. Indexing of powder diffraction patterns for low-symmetry lattices by the successive dichotomy method. *J Appl Cryst*. 1991;24(6):987-993. <https://doi.org/10.1107/S0021889891006441>
- All-Union State Standard 12.1.044-89. Occupational safety standards system. Fire and explosion hazard of substances and materials. Nomenclature of indices and methods of their determination.
- ASTM D635-14. Standard test method for rate of burning and/or extent and time of burning of plastics in a horizontal position.
- ASTM D2863-13. Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (oxygen index).
- ASTM D1929-16. Test method for determining ignition temperature of plastics.
- Gordon AJ, Ford RA. *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*. New York: Wiley-Interscience Publication; 1972.
- Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. New York: Wiley; 1997.

36. Roberts JD, Caserio MC. *Basic Principles of Organic Chemistry*. New York: W. A. Benjamin, Inc.; 1977.
37. Dyumaeva IV, Rekuta Sh F, Egorov NA. Synthesis and calculations of aminonitriles and their complexes with salts of metals of transitive valence. *Bashkir Chem J*. 2009;16:178-180.
38. Korshak VV. *Thermostable Polymers*. Moscow: Nauka; 1969.
39. Blagonravova AA, Nepomniashchii AI. *Lacquered Epoxy Resins*. Moscow: Khimia; 1970.

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