

RESEARCH ARTICLE

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

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SUMMARY

The study reports the development of a new type of wood-sawdust (WS) composite based on CuSiF₆-modified epoxy-amine polymers (EAPs) with reduced combustibility. The thermo-oxidative behavior of the obtained WS/EAP-CuSiF₆ and WS/EAP specimens was studied using the complex thermal analysis. Thermal analysis data show that incorporating CuSiF₆ (flame retardant) into WS/EAP increases the thermal oxidation resistance of WS/EAP-CuSiF₆. It is shown that for WS/EAP-CuSiF₆ and WS/EAP, thermo-oxidative destruction ends at 571°C and 625°C, and the maximum temperature of this exothermic process is 435°C and 499°C, respectively. The combustibility of WS/EAP-CuSiF₆ and WS/EAP was studied by the “ceramic tube” (CT) method. The CT results obtained demonstrate impressive differences in the combustibility of these two composites; the maximum temperature of gaseous combustion products for WS/EAP-CuSiF₆ is 265°C, and for WS/EAP, it is 910°C. Flammability tests for WS/EAP-CuSiF₆ and WS/EAP were carried out in accordance with ASTM D635-18 and ASTM D3801-19a. According to the results of vertical burning tests, the WS/EAP-CuSiF₆ composite material was classified as V-0.

KEYWORDS

Flame-retardant hardener, flammability tests, modified wood-sawdust epoxy-amine composites, reduced combustibility, thermo-oxidative degradation

1 | INTRODUCTION

Epoxy resins have high physical, mechanical, dielectric, and chemical properties, due to which materials based on epoxy resins are widely used in various fields of industry. Epoxy resins are most often used to make adhesives, pouring compounds, compacted materials, paint-and-lacquer coatings, binders for fiberglass plastics, putties, pre-mixes, sealants, pouring floors, and so on. With the development of technology, polymer materials based on epoxy resins are increasingly used in new industries, where these successfully compete with other materials.¹

One of the promising areas of application of epoxy resins is the development of composite materials based on wood-sawdust (WS),^{2,3} in particular chipboard, oriented strand boards, fiberboards, etc., which are nonetheless highly fire hazardous materials.⁴ Unlike binders such as urea-formaldehyde and phenol-formaldehyde resins, the use of epoxy resins to bond WS composite materials is not accompanied by the release of toxic substances (phenol, formaldehyde, solvents) both in the synthesis process and the manufacture and operation of finished products.^{5,6} Moreover, epoxy resins cure with little shrinkage at both normal and elevated temperatures without the release of by-products. As a result, products with high physical, mechanical, and

dielectric characteristics are formed. The advantages of using epoxy resins as an adhesive for consolidating wood particles are high adhesion and strength, good technological characteristics, and the ability to use for a long time in a wide temperature range. The high resistance to diffusion permeability and destructive effects of aggressive external media deserve special attention. The use of epoxy resins gives a significant technical and economic effect.⁷ However, there is a problem of heightened fire hazard at the production of WS composite materials. This problem can be solved mainly by reducing the combustibility of epoxy resins used to bond sawdust.

The most effective flame retardants for various polymers,^{8,9} including epoxy ones, are metal-containing flame retardants. Most often, in practice, to reduce the fire hazard of materials based on epoxy resins, it is proposed to use inorganic compounds, in particular, oxides, hydroxides, or salts of *s*- and *p*-metals.¹⁰⁻¹³ For the most part, such compounds act as inert fillers; these do not affect the composition and amount of polymer pyrolysis products in the gas phase and the amount of pyrolytic residue under combustion.

Recently, to reduce the combustibility of polymer composite materials, inorganic salts of transition metals¹⁴ have been used as reactive flame retardants, which are devoid of the inherent disadvantages in nonreactive flame retardants.¹⁵⁻¹⁷ Structural studies of coordination compounds of transition metals (mostly inorganic copper(II) salts) with organic nitrogen-containing hardeners of epoxy resins¹⁸⁻²² indicate an exceptionally high tendency of *d*-metals to coordinate with such curing agents.²³⁻²⁷ Undoubtedly, the ability to form strong Cu(II)-N coordination bonds makes inorganic salts of copper(II) extremely effective fire retardants.

The results of experimental studies have shown that the addition of even a small amount of an inorganic copper(II) salt to epoxy-amine polymers (EAPs) provides a significant reduction in the combustibility of epoxy-based polymer materials.^{28,29} In particular, the controlled addition of copper(II) hexafluorosilicate (flame retardant) to ordinary epoxy-amine composites increases their ignition and self-ignition temperatures by an average of 15°C-34°C and 25°C-58°C, respectively. The combustion of the organic component of epoxy-amine composites modified with CuSiF₆ is completed at a temperature of 320°C lower than that of the unmodified polymer. At the same time, depending on the amount of added flame retardant, the maximum temperature of gaseous combustion products and the weight loss during combustion of modified composites, as compared to unmodified ones, decrease by 204°C-647°C and 7.8%-84.1%, respectively. Epoxy-amine composites containing copper(II) hexafluorosilicate as a fire retardant are unable to spread the flame horizontally at all. It is also important to note that the above flame-retardant additives (inorganic copper(II) salts) for epoxy polymers, in addition to reducing combustibility, improve some physical and mechanical properties.³⁰⁻³²

Thus, the EAPs containing inorganic copper(II) salts as a fire retardant were the basis to form a new type of WS composite materials with reduced combustibility. This research reports developing new functional WS composite materials based on epoxy resins modified with copper(II) hexafluorosilicate (WS/EAP-CuSiF₆) as well as

studying the effect of the flame-retardant additive (CuSiF₆) on the thermo-oxidative degradation progress and combustibility. To date, there are no works dealing with the influence study of the nature of inorganic copper(II) salts on the thermo-oxidative resistance and combustibility of WS composites based on EAPs.

2 | EXPERIMENTAL PART

2.1 | Materials

To produce the WS epoxy-amine composites modified with copper(II) hexafluorosilicate, WS/EAP-CuSiF₆, the following substances and materials were used: the wood filler—dried pine sawdust; the flame retardant—copper(II) hexafluorosilicate hexahydrate, CuSiF₆·6H₂O (light blue crystals, Δ*t*_{dehydration} = 100°C, Δ*t*_{decomposition} = 174-446°C); the binder—bisphenol A diglycidyl ether, DGEBA (colorless resin, ED-20 grade with almost 22% epoxy groups content, viscosity at 25°C is 12-18 Pa·s), and the curing agent of epoxy resins—polyethylenepolyamine, *pepa* (H₂N[—C₂H₄NH—]_{*n*}H, where *n* = 1-3, yellow transparent viscous liquid, containing about 90% diethylenetriamine (*deta*), curing ability as to ED-20 is not less than 60 minutes, *d*²⁰ = 1.05 g·cm⁻¹, IR [KBr cuvette, cm⁻¹]: 3372, 3254, and 3210 (ν_{NH}); 2934, 2908, and 2790 (ν_{CH}); 1600 (δ_{NH}); and 1460 (δ_{CH})).

2.2 | Elaboration of WS epoxy-amine composites

To obtain the WS/EAP-CuSiF₆ composite, the combination possibilities of components in one system and the ability of these components to cure in the presence of copper(II) hexafluorosilicate were studied. For it, the pine sawdust was predried. The sawdust was dried according to all-Union Standard 16588-91³³ at (103 ± 2)°C. The drying process was controlled by weighing. The first weighing was carried out not earlier than 6 hours after the start of drying. Subsequent weighings were carried out every 2 hours of drying. The maximum drying time of the specimens did not exceed 20 hours. Specimens were considered dried if the change in weight of control specimens between two successive weighings did not exceed 1%. In this case, the result of the last weighing is taken as the mass of the dried specimen. Further, various options for the sequence of combining the ingredients were studied, and the optimal technological mode (temperature and time) to cure the composites was chosen.

TABLE 1 Stoichiometry of wood-sawdust (WS) epoxy-amine polymer (EAP) composites

Specimens	Ingredients, mass part			
	DGEBA	pepa	CuSiF ₆	WS
WS/EAP	100	12	0	20
WS/EAP-CuSiF ₆	100	12	66	20

The binder (*DGEBA*) and the hardener (*pepa*), taken in the corresponding mass parts (Table 1), were stirred for 5–10 minutes, after which the required amount of the flame retardant (anhydrous CuSiF_6) and WS were added. The prepared mixture was continued to stir to form a homogeneous consistency. Note that after adding inorganic copper(II) salt, the color of the mixture began to change from light yellow to dark blue, which indicates the interaction of nitrogen-containing *pepa* molecules with copper(II) hexafluorosilicate during the curing.

For comparison, the flame retardant-free WS composite material based on the epoxy-amine polymer (WS/EAP) was additionally prepared by mixing *DGEBA*, *pepa*, and SW in the corresponding ratio.

Specimens of the WS/EAP- CuSiF_6 and WS/EAP composites were molded by hot pressing; their images are shown in Figure 1.

2.3 | Characterization

2.3.1 | Complex thermal analysis

Thermogravimetric (TG), differential thermogravimetric (DTG) analyses, and differential thermal analysis (DTA) for WS/EAP and WS/EAP- CuSiF_6 (100 ± 5 mg for each specimen) have been carried out on the thermal analyzer Q-1500D (F. Paulik, J. Paulik, L. Erdey system) in the temperature range from 25°C to 1000°C with a ramp temperature of $5^\circ\text{C}\cdot\text{min}^{-1}$. Each individual specimen was tested three times. The results of three replicate measurements were coincided. All measurements were carried out under the dynamic mode in an oxidizing atmosphere of air. The T_{peak} value was determined from the DTA curve as the maximum temperature of exothermic effect at which the most mass loss is observed.

2.3.2 | Combustibility test

The combustibility of the WS/EAP and WS/EAP- CuSiF_6 specimens was determined using the “ceramic tube” (CT) method according to

all-Union State Standard 12.1.044-89,³⁴ described in “Data S1.” Specimens were prepared with a length of (160 ± 1) mm, a width of (65 ± 1) mm, and a thickness of (5 ± 1) mm, which were then wrapped in fiberglass cloth. Specimens prior to testing-to-fire were preconditioned and weighed. These were kept in a ventilated drying cabinet at $(60 \pm 5)^\circ\text{C}$ for at least 20 hours, then cooled to ambient temperature without removing from the cabinet. After conditioning, the specimens were weighed to an accuracy of ± 0.01 g. The specimens were placed in a ceramic chamber preheated to 200°C and then exposed to a burner flame ($50 \text{ kW}\cdot\text{m}^{-2}$). The maximum temperature of gaseous combustion products (T_{max} , $^\circ\text{C}$) and time to reach the T_{max} value (τ , s) were measured. The maximal temperature increment (ΔT_{max} , $^\circ\text{C}$) and the relative mass loss during combustion (Δm , %) were determined as.

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

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

where, m_b and m_a are mass (g) of the specimen before and after testing, respectively.

The combustibility group indices were defined by the ΔT_{max} and Δm values, while the combustibility of specimens was evaluated by the τ value. The results of the CT measurements are presented in Table 2.

2.3.3 | Flammability test

Flammability tests of WS/EAP and WS/EAP- CuSiF_6 were carried out in accordance with the ASTM D635-18³⁵ and ASTM D3801-19a.³⁶ Standard bar specimens ($125 \times 10 \times 5 \text{ mm}^3$) were made. Three specimens for each composite were tested. All specimens were preconditioned at $(23 \pm 2)^\circ\text{C}$ and $(50 \pm 10)\%$ relative humidity for a minimum of 48 hours. The testing results are presented in Tables 3 and 4.

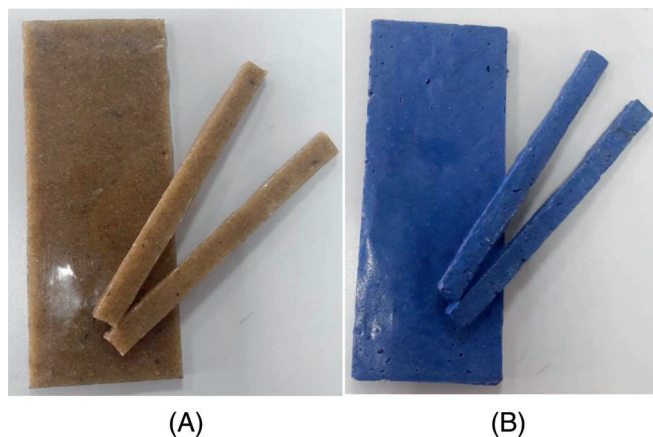


FIGURE 1 The molded specimens of wood-sawdust (WS) epoxy-amine polymer (EAP) composites. A, WS/EAP, and B, WS/EAP- CuSiF_6

3 | RESULTS AND DISCUSSION

3.1 | Thermo-oxidative behavior

The TG, DTG, and DTA curves recorded for WS/EAP and WS/EAP- CuSiF_6 are shown in Figures 2 and 3, respectively.

As shown in Figure 2A, the TG curve of the WS/EAP thermolysis process is represented by five stages. The first stage occurs in the temperature range from 20°C to 104°C , corresponds to the weight loss of 1.7 wt%, and has a minor endothermic minimum (DTA curve, Figure 2B), which is caused by the evaporation of chemically unbound water. The second stage includes 104°C to 176°C and is accompanied by a slight weight loss (0.3 wt%) and a little endothermic effect. At this stage, processes of the EAP framework destruction with the

Combustible characteristics	Specimens	
	WS/EAP	WS/EAP-CuSiF ₆
The initial test temperature, T_0 , °C	200	200
The maximum temperature of gaseous combustion products, T_{max} , °C	910 ± 5	265 ± 5
The maximal temperature increment, ΔT_{max} , °C	710 ± 5	65 ± 5
Time to reach the T_{max} , τ , s	100 ± 1	300 ± 1
The mass loss, Δm , %	84.0 ± 0.1	9.4 ± 0.1
The combustibility group	combustible/moderately flammable	hardly combustible

TABLE 2 Ceramic tube (CT) measurement data

TABLE 3 Flammability test results of horizontally fastened specimens (ASTM D635-18)

Composites	Time of burning (s) per length of:					r_{av} , mm·min ⁻¹	$\tau_{free\ burning}$, s
	1 cm	2 cm	3 cm	4 cm	5 cm		
WS/EAP	27 ± 1	51 ± 1	80 ± 1	104 ± 1	127 ± 1	23.87 ± 1	^a
WS/EAP-CuSiF ₆	^b						19 ± 1

^aThe specimen burns until forced extinguishing occurs.

^bSpecimens do not support burning; the flame goes out even before the zero mark.

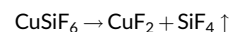
TABLE 4 Flammability test results of vertically fastened specimens (ASTM D3801-19a)

Evaluation criteria	WS/EAP-CuSiF ₆
Afterflame time for an individual specimen after the first or the second flame application, s	8
Total afterflame time for the five specimens after the first and the second flame applications, s	45
Afterflame plus afterglow time for an individual specimen after the second flame application, s	13
Afterflame or afterglow of a specimen up to the holding clamp	No
Cotton indicator ignited by flaming particles or drops	No

formation of volatile species occur. The third stage occurs in the temperature range from 176°C to 308°C. In this case, the weight loss (18.5 wt%) is accompanied by a pronounced exothermic effect on the DTA curve with a maximum at 264°C that is caused by wood pyrolysis³⁷ and thermo-oxidative destruction of the EAP component of the composite. The combustion of the volatile products of wood pyrolysis takes place at the fourth stage in a temperature range from 308°C to 400°C ($\Delta m = 16.0\%$). This temperature interval of the DTA curve contains the exothermic maximum at 382°C (Figure 2B). The final combustion of the pyrolytic residue occurs at the fifth stage of the WS/EAP thermolysis process in the temperature range from 400°C to 625°C as an exothermic process with a maximum at 499°C. At this stage, the maximum weight loss is observed (60.6 wt%).

The WS/EAP-CuSiF₆ thermolysis process occurs in a slightly more complicated manner, although the TG curve also consists of five stages (Figure 3A). The first stage of thermolysis involves 20°C to 109°C and is accompanied by a small endothermic minimum (Figure 3B). The evaporation of chemically unbound water takes place (weight loss is 16.0 wt%). The second stage occurs at temperatures from 109°C to 182°C. As in the case of WS/EAP, this part of the thermogram is associated with the incipient processes of the EAP framework destruction and volatile species are producing. This process corresponds to a weight loss of 3.7 wt% and is endothermic.

The third stage of thermolysis covers temperature range from 182°C to 272°C; the weight loss (17.6 wt%) is accompanied by an exothermic effect on the DTA curve with a maximum at 224°C. It is resulted from wood pyrolysis and thermo-oxidative destruction of the EAP component of WS/EAP-CuSiF₆. This process is somewhat complicated by the partial decomposition of flame retardant, which is accompanied by the release of SiF₄:



It should be noted that the composite containing the flame retardant has, although insignificant, but still higher, thermo-oxidative resistance compared to the composite with no flame retardant (Table 5). The start of destructive process in WS/EAP-CuSiF₆ is some shifted towards higher temperatures (182°C) as compared to WS/EAP (176°C). The observed temperature shift can be explained by the ability of CuSiF₆ to retard the destruction processes at the initial stages of thermolysis. So, the thermo-oxidative destruction occurring at the

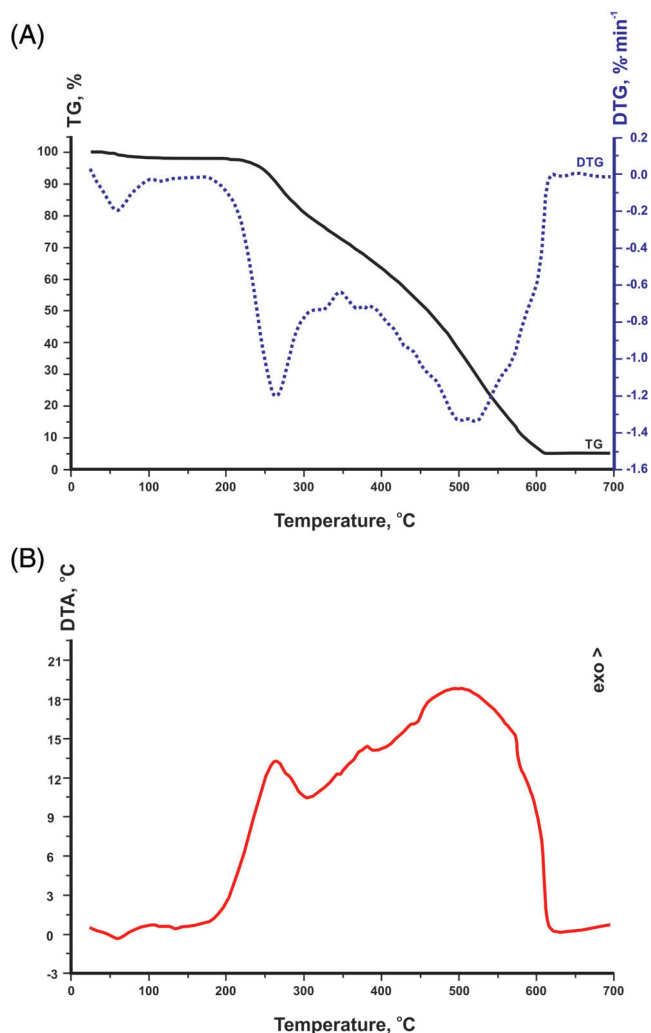


FIGURE 2 A, Thermogravimetric (TG) and DTG curves, and B, DTA curve for the wood-sawdust (WS)/epoxy-amine polymer (EAP) composite

third stage of thermolysis is less intense for WS/EAP-CuSiF₆ than for WS/EAP, mainly due to the partial decomposition of flame retardant.

The fourth stage of thermolysis occurs in the temperature range from 272°C to 392°C and is accompanied by the appearance of exothermic maximum at 373°C at the DTA curve (Figure 3B). The weight loss at IV stage is 27.8 wt% from the combustion of volatile wood decomposition products and the organic component of the flame-retardant hardener and binder. The fifth stage of thermolysis from 392°C to 571°C corresponds to complete combustion of the pyrolytic residue of WS/EAP-CuSiF₆ ($\Delta m = 36.0$ wt%). This process is exothermic with a maximum of 435°C.

It should be noted that the maximum of exothermic effect of the III stage that is responsible for thermo-oxidative destruction of the organic component of WS/EAP-CuSiF₆ (224°C) in comparison with the WS/EAP (264°C) is shifted into a lower temperature region. It indicates the somewhat higher thermo-oxidative resistance of the CuSiF₆-containing composite materials. Furthermore, thermolysis of WS/EAP-CuSiF₆ occurs in more restricted temperature intervals than

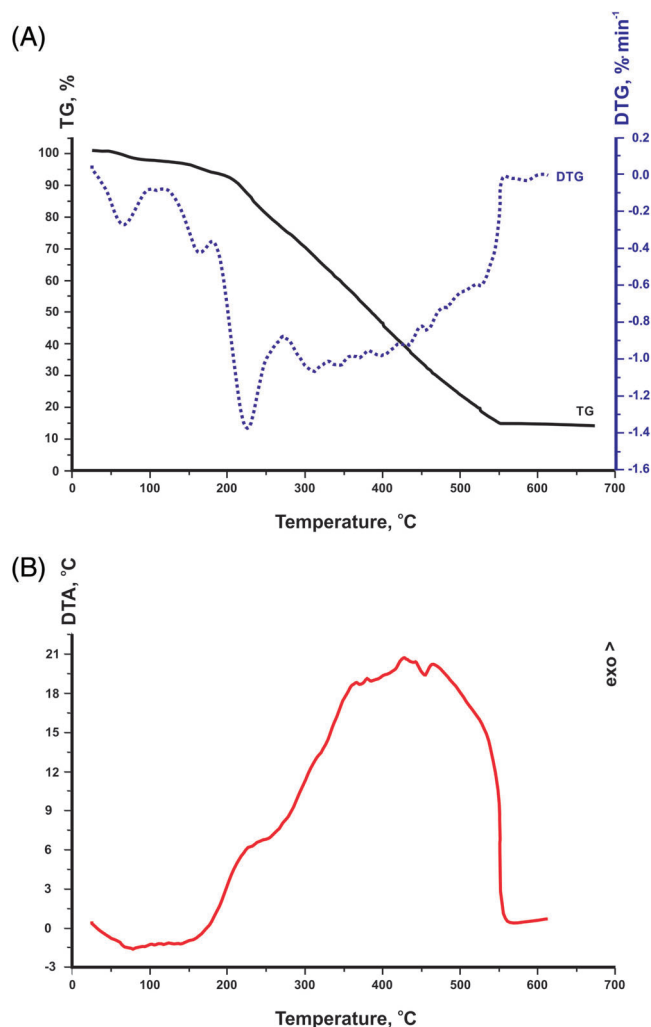


FIGURE 3 A, Thermogravimetric (TG) and DTG curves, and B, DTA curve for the wood-sawdust (WS)/epoxy-amine polymer (EAP)-CuSiF₆ composite

WS/EAP. In particular, the complete combustion of pyrolytic residue ends at 625°C for WS/EAP and 571°C for WS/EAP-CuSiF₆. The T_{peak} value for WS/EAP-CuSiF₆ is 64°C which is lower than for WS/EAP. It is presumed that the gaseous SiF₄ produced during thermal destruction of CuSiF₆ hinders the inflow of atmospheric oxygen required to combustion of WS/EAP-CuSiF₆. All this indicates the self-extinguishing nature of the combustion of the WS/EAP-CuSiF₆ specimens.

3.2 | Combustibility

The fire hazard of the developed WS composites based on epoxy resins (WS/EAP and WS/EAP-CuSiF₆) was evaluated by their belonging to the specified combustibility group, that is, by the ability of these materials to burn and spread the flame.

Specimens of WS/EAP (with no flame retardant) are easily ignited, burnt with the release of extremely large amounts of smoke

Specimens	Stage	Temperature ranges, °C	Weight loss, wt%	T_{peak} , °C
WS/EAP	I	20-104	1.7	499
	II	104-176	0.3	
	III	176-308	18.5	
	IV	308-400	16.0	
	V	400-625	60.6	
WS/EAP-CuSiF ₆	I	20-109	2.9	435
	II	109-182	3.7	
	III	182-272	17.6	
	IV	272-392	27.8	
	V	392-571	33.4	

TABLE 5 The WS/EAP-CuSiF₆ and WS/EAP thermo-oxidative degradation results

Abbreviations: EAP, epoxy-amine polymers; WS, wood-sawdust.

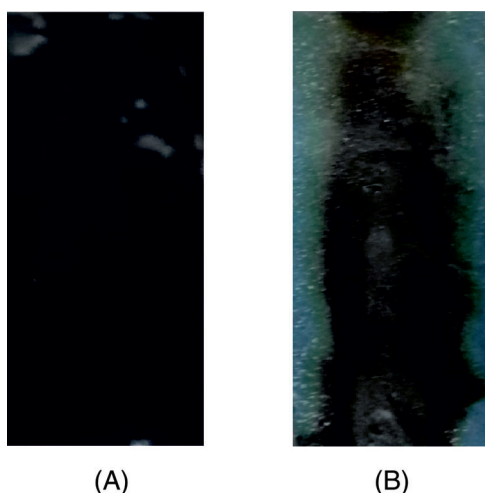


FIGURE 4 The specimens of wood-sawdust (WS) epoxy-amine polymer (EAP) composites after combustibility testing. A, WS/EAP, and B, WS/EAP-CuSiF₆

and soot (Figure 4A), and are difficult to extinguish. Data of the experimental determination of combustibility indices for the WS/EAP composite showed (see Table 2) that the maximum temperature increment during the combustion of these specimens is 710°C (ie, >60°C), and the mass loss is 84.0% (ie, >60%). All these suggest that this composite is a combustible material. However, since the time to reach the maximum temperature of gaseous combustion products is within $0.5 \leq \tau \leq 4$ minutes, the WS/EAP composite is considered a moderately flammable material.

The effect of a flame retardant on reducing the combustibility of composite materials is to increase the time (τ) to reach the maximum temperature of the gaseous combustion products (T_{max}). Thus, the τ value for WS/EAP-CuSiF₆ is 300 seconds, and for WS/EAP, $\tau = 100$ s (see Table 2). For WS/EAP-CuSiF₆, compared to WS/EAP, the T_{max} is reduced by 645°C. However, the main advantage of the WS/EAP-CuSiF₆ composite is a significant reduction in mass loss during combustion ($\Delta m = 9.4\%$). Based on the data obtained, it can be concluded that the WS/EAP-CuSiF₆ composite is resistant to combustion. This

specimen cannot burn without an ignition source, that is, it burns only when directly exposed to an open flame and stops to burn immediately after the flame removed (Figure 4B). Thus, the WS/EAP-CuSiF₆ composite is considered a hardly combustible material.

3.3 | Flammability

The addition of copper(II) hexafluorosilicate to the WS epoxy-amine composite also affects the combustion rate of WS/EAP-CuSiF₆ specimens (see Table 3). Unlike WS/EAP-CuSiF₆, WS/EAP specimens (with no flame retardant) are highly flammable and burn until forced extinguishing occurs. The rate of flame propagation over the surface of WS/EAP specimens located in a horizontal position does not exceed $40 \text{ mm} \cdot \text{min}^{-1}$. Therefore, these should be classified as HB, “horizontal burning.” It should be noted that the combustion of WS/EAP specimens is accompanied by the ignition of the cotton sublayer by flaming particles or droplets. In the event of a fire, the flaming droplets can produce new sources of ignition, which will increase the total area covered by the flames.

When exposed to a burner flame on the WS/EAP-CuSiF₆ specimen, its ignition and combustion were observed. However, the free burning of this specimen after moving away from the flame was short-lived, and the flame extinguished even before the zero mark. The total duration of free burning and smoldering of the WS/EAP-CuSiF₆ specimen in a horizontal position did not exceed 19 seconds. Since the burning rate of these specimens is not measurable, the material cannot be classified as HB. In this case, the duration of burning and smoldering should be determined for vertically located samples (Table 4).

It was found that the afterflame time for the WS/EAP-CuSiF₆ specimen after the first or second flame applications did not exceed 10 seconds, and the total afterflame time for the five specimens after first and second flame applications did not exceed 50 seconds. The afterflame time + the afterglow time for the WS/EAP-CuSiF₆ specimen after the second flame application did not exceed 30 seconds. None of these specimens burned down up to the holding clamp. The cotton sublayer did not ignite by flaming particles or drops. Thus, the

developed WS/EAP–CuSiF₆ composite material is attributed to the highest category of burning resistance—V-0.

4 | CONCLUSIONS

One of the most promising areas of application of EAP modified with copper(II) hexafluorosilicate is to produce a new type of WS composite materials with a reduced fire hazardous. The resulting specimens of WS composite materials based on epoxy resins—WS/EAP–CuSiF₆ and WS/EAP—have been exposed to various external effects, such as the thermo-oxidative and flame effects. The combustibility of the WS/EAP–CuSiF₆ and WS/EAP composites was studied using the CT method, and the flammability tests were carried out in accordance with ASTM D635-18 and ASTM D3801-19a. Unlike WS/EAP, the WS/EAP–CuSiF₆ composite during the combustion demonstrates of somewhat more highly thermo-oxidative resistance, a longer time to reach the maximum temperature of gaseous combustion products, and a lower mass loss. The results obtained are in good agreement with the nature of the flame-retardant additive, that is, with the ability of CuSiF₆ to chelate the curing agent of epoxy resins. The data obtained allowed to classify the WS/EAP–CuSiF₆ composite as a hardly combustible material. Based on the results of the flammability tests, the WS/EAP–CuSiF₆ composite material was classified as the highest category of burning resistance (V-0).

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SUPPORTING INFORMATION

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

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