

## THE EFFECT OF PREPARATION TECHNOLOGY AND THE COMPLEXING ON THE SERVICE PROPERTIES OF SELF-EXTINGUISHING COPPER(II) COORDINATED EPOXY-AMINE COMPOSITES FOR POURING POLYMER FLOORS

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### ABSTRACT

Making technology of copper(II)-coordinated epoxy-amine composites with reduced combustibility has been developed that allowed to form the basis of a new type of polymer with enhanced physicochemical and mechanical properties to improve the process of pouring polymer floors. A proposed simple method allows preparing and incorporating into the epoxy resin matrix the fire retardant-hardeners. These are considered to be the interaction products of the polyethylenepolyamine (PEPA) with inorganic copper(II) salts (specifically,  $\text{CuSO}_4$ ,  $(\text{CuOH})_2\text{CO}_3$  and  $\text{CuSiF}_6$ ). The combustibility of the *DGEBA/PEPA*, *DGEBA/PEPA-CuSO<sub>4</sub>*, *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>* and *DGEBA/PEPA-CuSiF<sub>6</sub>* composites obtained (*DGEBA* is bisphenol A diglycidyl ether) were investigated using ceramic tube (CT) method. The flammability of the polymer samples has been evaluated using the UL94 test method according to ASTM 635–14 and ASTM D1929–16. The physical-mechanical properties were determined by considering surface hardness, tensile strength, water absorption, and chemical resistance. The effects of inorganic salts of copper(II) on the fire-hazardous indices and the performance properties of the modified epoxy-amine composites were described. The results of the CT study reveal that the maximum temperature of gases produced through combustion is appreciably decreased, along with weight loss, for modified epoxy-amine composites compared to unmodified composites. The modified polymer composites are attributed to the medium flammability substance class and can be successfully used to pour polymer floors.

**Keywords:** Fire-hazardous indices; Performance properties; Pouring polymer floors; Self-extinguishing epoxy-amine composites

### 1. INTRODUCTION

Polymer coatings for floors have become increasingly popular when repairing or decorating because their pouring requires less time and effort when compared to known coatings (Subagia et al., 2017), such as concrete, linoleum, glaze, etc. Moreover, the polymer coatings are of increased resistance to corrosive agents, enhanced impact strength, a higher wearing capacity, and greater chemical resistance to corrosive agents (acids, alkalis, solvents, etc.).

Currently, epoxy-amine composites are considered to be the best polymer coatings for floors. These coatings can be used in most industries (Lavrenyuk, 2012). Coatings based on epoxy resins are unique because they improve flooring properties, viz., have greater solidity, higher abrasion

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resistance, and absolute water impermeability. Aside from these structural improvements, the polymer coatings improve aesthetics. However, epoxy-polymers are of one significant disadvantage, this is their natural combustibility. All organic polymers are flammable substances (Turekova et al., 2013). Therefore, a major priority is the creation of a new generation of epoxy-amine composites that would possess the reduced combustibility and satisfactory performance properties for pouring polymer floors. Using reactive fire retardant agents would solve this problem, since these substances are able to physically and chemically interact with both epoxy resin and curing agents. Substances of this kind include some transition metal salts, which bond readily with curing agents containing amines to form chelate complexes. These d-metal chelate complexes can act as fire retardant-hardeners that would efficiently reduce the combustibility of epoxy-amine composites. To solve this problem, the authors of works (Ghaemy et al., 2003; Tian et al., 2004; Giroux et al., 2005; Nie et al., 2008; Mohamed & Al-Halim, 2008; Zhang et al., 2009; Hou et al., 2017) have focused on the use of the organic salts of d-metals (mostly Mn, Co, Ni, Cu, Zn, etc.) Unlike organic salts, inorganic salts are non-combustible. That is why our work developing epoxy-amine composites (Lavrenyuk et al., 2015; Lavrenyuk & Mykhalichko, 2015; Lavrenyuk et al., 2016a; Lavrenyuk et al., 2018a; Lavrenyuk et al., 2018b) has used chelate complexes composed of exclusively inorganic salts from copper(II) and polyethylenepolyamine (PEPA).

In this study, we report the development of novel copper(II)-coordinated epoxy-amine composites with reduced combustibility containing different inorganic salts of copper(II) (specifically,  $\text{CuSO}_4$ ,  $(\text{CuOH})_2\text{CO}_3$ , and  $\text{CuSiF}_6$ ). The composites elaborated are considered to be the basis for pouring polymer floors. Combustibility was investigated using the ceramic tube (CT) method, and flammability was evaluated using UL94 tests. Physical-mechanical properties of the samples were studied by considering the measurements of surface hardness, tensile strength, water absorption, and chemical resistance. The influence of complex formation processes on the fire-hazardous indices and performance characteristics of the obtained epoxy-amine composites is also considered in this work.

## 2. EXPERIMENTAL SETUP

### 2.1. Materials

To synthesize copper(II)-coordinated epoxy-amine composites suited for pouring polymer floors, the following chemicals are needed: fire retardants – copper(II) sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (light blue crystals,  $M_r = 249.5$ ,  $\Delta t_{\text{dehydration}} = 90\text{--}280^\circ\text{C}$ ,  $\Delta t_{\text{decomposition}} = 640\text{--}828^\circ\text{C}$ ), copper(II) carbonate hydroxide,  $(\text{CuOH})_2\text{CO}_3$  (bright green powder,  $M_r = 211.11$ ,  $d^{20} = 4.0 \text{ g}\cdot\text{cm}^{-1}$ ,  $\text{p}K_s = 33.78$ ,  $\Delta t_{\text{decomposition}} = 200^\circ\text{C}$ ), copper(II) hexafluorosilicate tetrahydrate,  $\text{CuSiF}_6 \cdot 4\text{H}_2\text{O}$  (light blue crystals,  $M_r = 277.6$ ,  $d^{20} = 2.6 \text{ g}\cdot\text{cm}^{-1}$ ,  $\Delta t_{\text{dehydration}} = 100^\circ\text{C}$ ,  $\Delta t_{\text{decomposition}} = 174\text{--}446^\circ\text{C}$ ); epoxy resin to serve as the curing agent – polyethylenepolyamine (PEPA –  $\text{H}_2\text{N}[-\text{C}_2\text{H}_4\text{NH}-]_n\text{H}$ , where  $n = 1\text{--}5$ ) (yellow transparent viscous liquid,  $M_r = 120$ ,  $d^{20} = 1.011 \text{ g}\cdot\text{cm}^{-1}$ ,  $n_D = 1.5120$ ,  $t_{\text{boiling}} = 250^\circ\text{C}$ ,  $t_{\text{flash}} = 110^\circ\text{C}$ ,  $t_{\text{ignition}} = 136^\circ\text{C}$ ,  $t_{\text{self-ignition}} = 393^\circ\text{C}$ ), IR (KBr cuvette,  $\text{cm}^{-1}$ ): 3372, 3254, and 3210 ( $\nu\text{NH}$ ); 2934, 2908, and 2790 ( $\nu\text{CH}$ ); 1600 ( $\delta\text{NH}$ ); 1460 ( $\delta\text{CH}$ )); and a binding agent – bisphenol A diglycidyl ether (DGEBA) (colorless resin, ED-20 grade with almost 22% epoxy groups content, viscosity value from 12 to 18 Pa·s (at  $25^\circ\text{C}$ ),  $M_r = 390\text{--}430$ ). All reagents have been purchased through commercial sources and used as received without further purification.

### 2.2. Preparation Technology

To explore ways of obtaining copper(II)-coordinated epoxy-amine composites, we tested the sequence used to combine ingredients to ensure that the optimal technological regime is used to

produce the composite materials necessary for pouring polymer floors. As a result, structurally homogeneous and aesthetically attractive glossy composite materials were obtained.

Images of the epoxy-amine composites made are presented in Figure 1. In particular, Figure 1a shows the polymer composite that does not contain any copper(II) salt. This sample – *DGEBA/PEPA* – has been prepared of the binding agent (*DGEBA*) and curing agent (*PEPA*) according to the standard technology; it is light-yellow and clear.

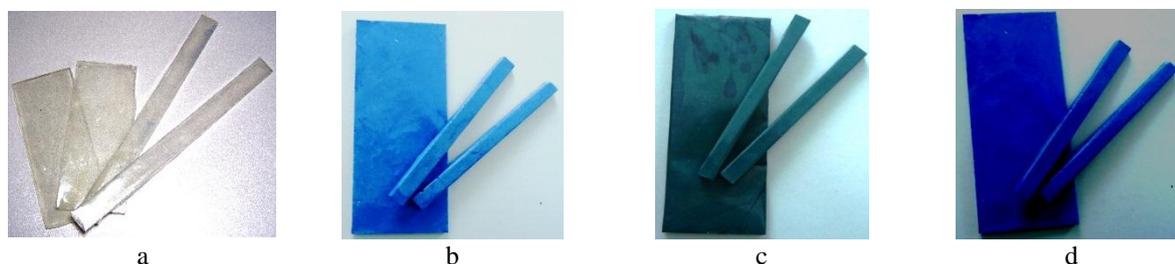


Figure 1 The samples of the epoxy-amine composites: *a* – *DGEBA/PEPA*; *b* – *DGEBA/PEPA-CuSO<sub>4</sub>*; *c* – *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>*; *d* – *DGEBA/PEPA-CuSiF<sub>6</sub>*

The sample of the *DGEBA/PEPA-CuSO<sub>4</sub>* composite (Figure 1b) contains copper(II) sulfate, and the preparation feature of the *DGEBA/PEPA-CuSO<sub>4</sub>* consists in preliminary dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , because  $\text{H}_2\text{O}$  negatively affects the curing process. The copper vitriol was dried in an oven at 150–250°C until the crystallization water loss.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  dehydration was accompanied by the blue crystals changing into fine-dispersed white powder. The binding agent (*DGEBA*) and curing agent (*PEPA*) in the required proportion (Table 1) were placed into a container. This mix was stirred for 5–10 min; then the anhydrous  $\text{CuSO}_4$  was added and stirred until the homogeneous suspension formation, which eventually turned into an aesthetically attractive blue composite.

Table 1 Stoichiometry of the epoxy-amine composites

Composite	Ingredients (mass p.)				
	<i>DGEBA</i>	<i>PEPA</i>	$\text{CuSO}_4$	$(\text{CuOH})_2\text{CO}_3$	$\text{CuSiF}_6$
<i>DGEBA/PEPA</i>	100	12	–	–	–
<i>DGEBA/PEPA-CuSO<sub>4</sub></i>	100	12	16	–	–
<i>(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub></i>	100	12	–	12	–
<i>DGEBA/PEPA-CuSiF<sub>6</sub></i>	100	12	–	–	21

The sample of the *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>* composite (Figure 1c) was prepared in the following way. Malachite ( $(\text{CuOH})_2\text{CO}_3$ ) was added to the (*DGEBA+PEPA*) mix. This ternary mix was stirred until the homogeneous suspension formation. After the copper(II) carbonate hydroxide addition, the *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>* sample acquired a dark blue-green color.

The sample of the *DGEBA/PEPA-CuSiF<sub>6</sub>* composite (Figure 1d) was modified by  $\text{CuSiF}_6$ . Copper(II) hexafluorosilicate tetrahydrate was also preliminary dehydrated. The  $\text{CuSiF}_6 \cdot 4\text{H}_2\text{O}$  was dried in an oven at 120–150°C until the blue crystals turned into a fine-dispersed white powder. After adding the anhydrous  $\text{CuSiF}_6$  to the (*DGEBA+PEPA*) mix, the *DGEBA/PEPA-CuSiF<sub>6</sub>* blue-violet composite was formed and packed into molds.

The molded samples of all epoxy-amine composites were left at room temperature and relative air humidity (80–90%) to cure for 24 hours.

The basic fire-hazardous indices, as well as some performance characteristics, were determined for all prepared epoxy-amine composites.

### 2.3. Determination Techniques of the Fire-hazardous Indices

The combustibility parameters for the *DGEBA/PEPA*, *DGEBA/PEPA-CuSO<sub>4</sub>*, *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>* and *DGEBA/PEPA-CuSiF<sub>6</sub>* composites were determined according to all-Union State Standard 12.1.044-89 using the ceramic tube (CT) method, which is described in detail in (Lavrenyuk et al., 2018b). Its gist consists of temperature conditions that promote polymer material combustion.

Table 2 Data of the CT measurements of the epoxy-amine composites

Sample	TC	$t_{\max}$	$\Delta t_{\max}$	$\Delta \tau$	WL	CG/IC
<i>DGEBA/PEPA</i>	200	867(5)	667(5)	150(1)	89.0(1)	CA/F
<i>DGEBA/PEPA-CuSO<sub>4</sub></i>	200	638(5)	438(5)	215(1)	78.0(1)	CA/MF
<i>(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub></i>	200	648(5)	448(5)	210(1)	68.5(1)	CA/MF
<i>DGEBA/PEPA-CuSiF<sub>6</sub></i>	200	610(5)	410(5)	240(1)	74.4(1)	CA/MF

Notes; TC (°C), the temperature of ceramic chamber before samples bringing;  $t_{\max}$  (°C), the maximum temperature of the gaseous products of the combustion;  $\Delta t_{\max}$  (°C), the maximal increment temperature;  $\Delta \tau$  (s), the period of time required to reach the maximum temperature of the combustion gases; WL (wt%), the weight loss of samples; CG, the combustibility group; IC, inflammability class (CA – combustible agent, F – flammable, MF – moderately flammable).

Before testing, all samples were brought to the optimal conditions and weighed, whereupon individually taken samples were placed into a ceramic tube, which was heated in advance to 200°C by a gas burner flame. The maximum combustion temperature of gaseous products ( $t_{\max}$ ) and period of its reaching ( $\Delta \tau$ , s) were experimentally measured. The maximal increment temperature ( $\Delta t_{\max}$ , °C) and loss of mass ( $\Delta m$ , %) were calculated.

Table 3 Data of fire tests of the epoxy-amine composites

Sample	$t_{\text{ign}}$ , °C	$t_{\text{self-ign}}$ , °C	$r_{\text{burn}}$ , mm·min <sup>-1</sup>	$\Delta \tau_{\text{burn}}$ , s	FC
<i>DGEBA/PEPA</i>	320(1)	545(1)	25.2(5)	**	PH
<i>DGEBA/PEPA-CuSO<sub>4</sub></i>	350(1)	567(1)	*	76(1)	PV
<i>(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub></i>	355(1)	558(1)	*	93(1)	PV
<i>DGEBA/PEPA-CuSiF<sub>6</sub></i>	325(1)	553(1)	*	5(1)	PV

Notes; FC, Flammability Category (PH – to Propagate Horizontally, PV – to Propagate Vertically); \* – Flame does not propagate; sample has been self-extinguished till zero-gauge mark reaching; \*\* – Samples are in fire as far as moment of forced extinguishing.

The combustibility group was characterized by  $\Delta t_{\max}$  and  $\Delta m$  values, while the inflammable class was estimated by  $\Delta \tau$  value. If values of  $\Delta t_{\max}$  and  $\Delta m$  did not exceed 60°C and 60%, respectively, then the samples were subsumed as hardly-combustible substances; otherwise, they were combustible substances. The combustible substances were subdivided into three inflammable classes. When  $\Delta \tau > 240$  s,  $\Delta \tau = 30 \div 240$  s, and  $\Delta \tau < 30$  s, the samples were nonflammable, moderately flammable, and flammable, respectively. The CT test results are presented in Table 2.

The epoxy-amine composites' flammability was evaluated using the UL94 test and the flame propagation rate was determined according to ASTM D635-14. The polymer samples were tested after conditioning for 48 h at 25°C and of 50% relative humidity. The time ( $\Delta \tau_{\text{burn}}$ , s) of the flame front transit between two gauge marks was measured and the burning rate ( $r_{\text{burn}}$ , mm·min<sup>-1</sup>) of the polymer samples was calculated. The ignition point ( $t_{\text{ign}}$ ) and self-ignition point ( $t_{\text{self-ign}}$ ) were

measured on a TF device according to ASTM D1929-16. The fire test results are presented in Table 3.

#### 2.4. Performance Properties Determination

Physical-mechanical properties of the elaborated composite materials were studied by measuring surface hardness, tensile strength, water absorption, and chemical resistance. The samples' surface hardness was measured on the Höppler's consistometer by indentation of a steel cone at an angle of  $53^{\circ}08'$  and loading in 50 N for 60 s.

Uniaxial tensile tests were determined on the samples according to all-Union State Standard 11262-80 at room temperature using a P-0.5 type tensile testing machine. Rectangular samples with dimensions of  $250 \times 10 \times 3$  mm<sup>3</sup> were used. A displacement rate of  $100 \text{ mm} \cdot \text{min}^{-1}$  was adopted. The tensile properties were averaged from the results obtained from a minimum of three samples.

Table 4 Physical-mechanical and physicochemical properties of the epoxy-amine composites

Sample	SH	TS	WAD (%)	EWA (%)	ES <sub>a</sub> (%)	ES <sub>b</sub> (%)
DGEBA/PEPA	130(5)	10(2)	0.026	0.8	1.2	1.4
DGEBA/PEPA-CuSO <sub>4</sub>	143(5)	10(2)	0.015	0.4	0.9	1.0
(DGEBA/PEPA) <sub>2</sub> -(CuOH) <sub>2</sub> CO <sub>3</sub>	155(5)	18(2)	0.018	0.6	0.8	0.7
DGEBA/PEPA-CuSiF <sub>6</sub>	159(5)	5(2)	0.016	0.5	0.9	0.8

Notes; SH (MN·m<sup>-2</sup>), surface hardness; TS (MN·m<sup>-2</sup>), tensile strength; WAD, water absorption for day; EWA, equilibrium water absorption; ES<sub>a</sub>, Equilibrium swelling in 10% H<sub>2</sub>SO<sub>4</sub>; ES<sub>b</sub>, Equilibrium swelling in 10% NaOH.

The water absorption or chemical resistance was studied by gravimetric method. A weight change of the polymer films was measured after their immersion into distilled water or corrosive medium for a certain time. The measurement results of the surface hardness, tensile strength, water absorption, and chemical resistance carried out for the elaborated polymer samples are presented in Table 4.

### 3. RESULTS AND DISCUSSION

#### 3.1. The Fire-hazardous Indices

The experimental measurement results of the fire-hazardous indices confirm that combustibility of the epoxy-amine composites after the addition of the copper(II) salts are appreciably reduced. Figure 2 shows one of the fire-hazardous indices of the polymer composites estimated by the ignition point and self-ignition point. In the case of the epoxy-amine composites modified by copper(II) salts, the  $t_{\text{ign}}$  and  $t_{\text{self-ign}}$  increase compared to the unmodified composite. Apparently, the copper(II) salts addition delays the decomposition rate of the epoxy-amine composites in the low-temperature range. At the same time, the formation rate of combustible gases decreases, their diffusion into the environment and the oxidation are delayed, and so the ignition takes place at higher temperatures.

Among the basic fire-hazardous indices, the combustibility parameter characterizes a predisposition of the substances and materials to free burning. Under conditions of fire, the copper(II)-coordinated epoxy-amine composites' exposure to heat results in the release of the incombustible volatile substances into the flame's gas phase and accelerates the carbonization process. The polymers structuring (cross-linking, cyclization, as well as Cu(II)-N bonding) that takes place during the copper(II)-coordinated epoxy-amine composites' curing process also favors combustibility reduction. In the chelate complexes incorporated into the polymer products' framework, the PEPA molecules owing to Cu(II)-N bonds firmly hold the polymer matrix; therefore the vaporization and inflammation of these composites are strong difficult. Really, to

break down the coordination bonds, a significant amount of the heat energy going out of flame should be used up (Lavrenyuk et al., 2018c; Lavrenyuk & Mykhalichko, 2018). This apparently is a main cause combustibility reducing of the copper(II)-coordinated epoxy-amine composites.

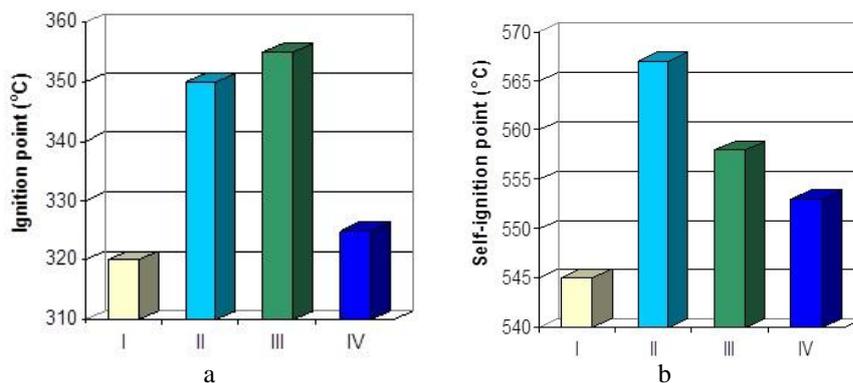


Figure 2 The ignition point; (a) and self-ignition point; (b) of the epoxy-amine composites (I – *DGEBA/PEPA*; II – *DGEBA/PEPA-CuSO<sub>4</sub>*; III – *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>*; IV – *DGEBA/PEPA-CuSiF<sub>6</sub>*) (SD of temperature measurement is  $\pm 1^{\circ}\text{C}$ )

The combustibility results for the epoxy-amine composites are presented in Table 2. As seen, the weight loss in all the composites exceeds 60%, and the maximum temperature of the gaseous products of the combustion is  $>60^{\circ}\text{C}$ . The amount of time required to reach the maximum temperature of the combustion gases ranged from 3.5 min to 4 min. Thus, the copper(II)-coordinated epoxy-amine composites are combustible materials, but they have moderate inflammability. However, the maximum temperature of the combustion gases was lower ( $219\text{--}257^{\circ}\text{C}$ ) for the metal-coordinated epoxy-amine composites in comparison to the unmodified composite. At that temperature range, the weight loss decreases 19.0% for *DGEBA/PEPA-CuSO<sub>4</sub>*, 20.5% for *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>*, and 14.6% for *DGEBA/PEPA-CuSiF<sub>6</sub>*. Thus, incorporating copper(II) salts into the polymer framework increases the amount of time needed to reach the maximum temperature of the gaseous products of combustion.

Other fire-hazardous indices, such as flame propagation, can appreciably influence the combustibility of polymers due to heat-transfer. The predisposition of polymers to propagate the flame along the surfaces of the samples determines the rate at which the combustible substances enter the burning zone. It causes the temperature in the environment to increase, and it affects the heat flow value that is directed to the part of the polymer material that is not yet taken into the fire. The data analysis seen in Table 3 reveals that incorporating copper(II) salts into the polymer matrix can substantially retard the flame spread along the surface of the sample oriented horizontally. The epoxy-amine composite samples that do not contain the inorganic salt of copper(II) continue to burn until the moment of their forced extinguishing. The average burning rate is  $25.2\text{ mm}\cdot\text{min}^{-1}$ . When burning this sample, we observed that droplets from the burning polymer fell onto the laid cotton sheet. In a fire, polymer floors based on epoxy-amine polymers can quickly propagate a flame, endangering the lives of people. In case of copper(II)-coordinated epoxy-amine polymers, a flame is extinguished till zero-gauge mark reaching; the free burning duration did not exceed 1.5 min and ignition of the cotton sheet was not observed.

### 3.2. The mechanical properties

In addition to aesthetic attractiveness and cost, performance properties play an important role in the choice of the polymers used to pour floors (Nurjaya et al., 2015).

It is experimentally ascertained (see Table 4) that copper(II)-coordinated epoxy-amine composites (Figure 3a (II–IV)) are characterized by higher surface hardness values than the initial epoxy resins (Figure 3a (I)). Apparently, owing to the interaction of the inorganic salts of copper(II) with a nitrogen-containing curing agent in the formation of the three-dimensional structure of epoxy-amine composites, the polymer framework becomes more compact. This decreases the kinetic mobility of the particles within the lattice, which, in turn, results in higher surface hardness values.

The tensile strength (TS) measurements (Figure 3b) clearly demonstrate that the TS value for the modified epoxy-amine composites is characterized by the maximum value only in case of the  $(DGEBA/PEPA)_2-(CuOH)_2CO_3$  epoxy-polymer (Figure 3b (III)). The insolubility of the malachite in water used to make this composite might be one explanation for this outcome.

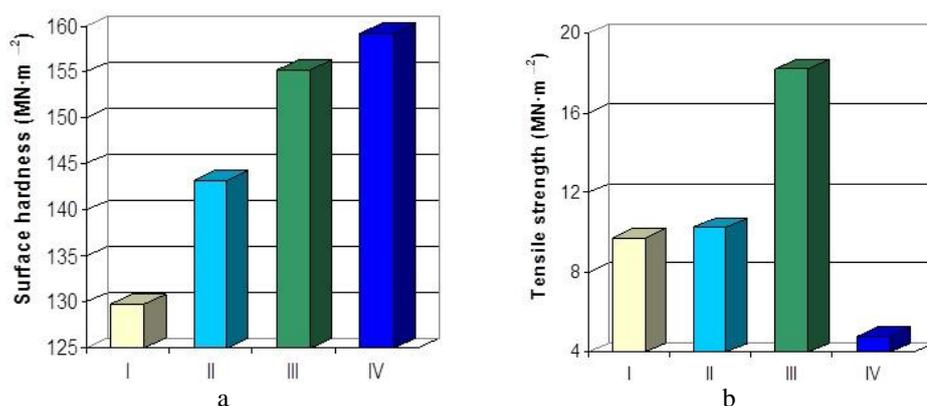


Figure 3 The surface hardness: (a) and tensile strength; (b) of the epoxy-amine composites (I –  $DGEBA/PEPA$ ; II –  $DGEBA/PEPA-CuSO_4$ ; III –  $(DGEBA/PEPA)_2-(CuOH)_2CO_3$ ; IV –  $DGEBA/PEPA-CuSiF_6$ ) (SD of surface hardness and tensile strength measurements are  $\pm 5$  and  $\pm 2$   $MN \cdot m^{-2}$ , respectively)

### 3.3. The Physicochemical Properties

The insulation ability is another important feature of the protective action of the polymer coatings used to pour floors. Since the majority of corrosive mediums are aqueous solutions of electrolytes, the study of water diffusion through anticorrosion polymer films is needed to identify the mechanism of the protective action of the copper(II)-coordinated epoxy-amine composites.

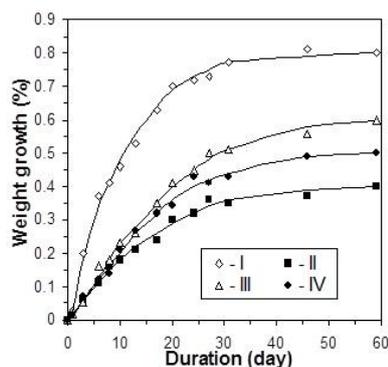


Figure 4 Water absorption of the epoxy-amine composites: I –  $DGEBA/PEPA$ ; II –  $DGEBA/PEPA-CuSO_4$ ; III –  $(DGEBA/PEPA)_2-(CuOH)_2CO_3$ ; IV –  $DGEBA/PEPA-CuSiF_6$

Figure 4 demonstrates the water absorption kinetics for four epoxy-amine composites—*DGEBA/PEPA*, *DGEBA/PEPA-CuSO<sub>4</sub>*, *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>*, and *DGEBA/PEPA-CuSiF<sub>6</sub>*. On the data curve, one can see how the polymer samples swell after their immersion into water. Thus, over the first three days of water exposure, the weight increase did not exceed 0.2% per day. During the next 10–20 days, the water sorption rate by the epoxy-amine composite films decreased up to 0.04–0.07% per day. After 25–30 days of exposure, the system is equilibrated; thus, the amount of absorbed and desorbed water is equal. Therefore, water absorption by the modified epoxy-amine composite films is a one-stage process that demonstrates the homogeneity of the polymer system.

Absolute values of the mass increase of films in water primarily depend on the chemical composition of the polymer material. In the structures of the materials investigated in the present study, there are residual amine or epoxy groups because diffusive or stoichiometric difficulties do not entirely interact. Moreover, secondary hydroxyl groups are formed by the interaction between the epoxy and the amine fragments. All these functional groups are polar, and they can attract H<sub>2</sub>O molecules to the framework because the interaction occurs at the participation of water-soluble salts, such as copper(II) sulfate and copper(II) hexafluorosilicate. When CuSO<sub>4</sub> and CuSiF<sub>6</sub> bond to the polymer framework, these inorganic salts can be eluted by means of water, which negatively influences the protective properties of the coatings.

Incorporating (CuOH)<sub>2</sub>CO<sub>3</sub> into the polymer framework decreases the ability of epoxy-amine composites to absorb alkalis or acids from their aqueous solutions (see Table 4). Apparently, this reduction in diffusion permeability can explain the decrease in the defectiveness in the samples due to the decrease in the internal stress (Rogers, 1964; Shimbo et al., 1985). The Cu–N coordination bonds play a decisive role in the structure of epoxy-amine composites (Lavrenyuk et al., 2016b), and, as best as possible, this impedes the particles' ability to percolate into polymer films from a corrosive medium. The study's polymer film sorption results demonstrate that the most compact framework of the epoxy-amine composites is formed under the influence of (CuOH)<sub>2</sub>CO<sub>3</sub>.

Thus, the value of mass change for the films after immersion into water can be one of the important characteristics that can be used to determine the protective properties of polymer coatings. The comparative analysis of the water absorption of the polymer samples gives us reason to consider that the water resistance of the copper(II)-coordinated epoxy-amine polymers is acceptable.

#### 4. CONCLUSION

Copper(II)-coordinated epoxy-amine composites with suppressed combustibility – *DGEBA/DETA-CuSO<sub>4</sub>*, *(DGEBA/PEPA)<sub>2</sub>-(CuOH)<sub>2</sub>CO<sub>3</sub>*, and *DGEBA/DETA-CuSiF<sub>6</sub>* – were developed. The combustibility of these polymer samples was characterized using the ceramic tube method. The flame propagation rates and ignition point and self-ignition point were evaluated using UL94 tests. The physical-mechanical properties were determined by considering surface hardness, tensile strength, water absorption, and chemical resistance. The influence of the inorganic salts of copper(II) on the fire-hazardous indices and performance properties of the modified epoxy-amine composites was considered. It has been ascertained that the Cu(II)–(*PEPA*) interaction that triggers the formation of the Cu(II)–N coordination bonds within the polymer framework predetermines the suppressing combustibility of the copper(II)-coordinated epoxy-amine polymers. The study's results for the combustibility of the copper(II)-coordinated epoxy-amine polymers enable us to attribute these samples to the medium flammability substance class, and these can be successfully used for pouring polymer floors.

## 5. REFERENCES

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