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FIRE-RESISTING COMPOSITES BASED ON POLYMER MATRIX

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Abstract. In the present work we have studied the thermal stability, flammability, and fume evolution of epoxy matrix composites with different types and amounts of hardeners, fillers, plasticizers, and fire retardants. It is shown that chemical composition of fillers has little effect on the flammability of epoxy composites when the content of mineral fillers is less than 45 % by mass. Smoke formation decreases linearly with increase of the filling degree. It is shown that to obtain low-combustible materials the oxygen index should exceed 31 %. It was found that the optimal concentration of industrial brominated fire retardants is 8–10 % by mass. To reduce the flammability of epoxy composites, additive brominated fire retardants in the form of a solution in *N*,*N*-dimethyl-2,4,6-tribromoaniline have been proposed. The high efficiency of acetyl- and α-hydroxyethyl ferrocene as a smoke suppressor of epoxy composites is shown.

Keywords: brominated fire retardants, flammability, combustibility, fume evolution index, epoxy matrix composites, fillers, plasticizers, ferrocene derivatives.

1. Introduction

Nowadays, epoxy oligomers are widely used as binders in construction industry. Constructional composites with epoxy matrices – epoxy matrix composites (EMC) – are often characterized by unique combinations of operational properties. Broad range of available epoxy resins and hardeners allows precise control of elastic modulus (in case of continuous reinforcement fibers, the well-known application is composite reinforcement), compressive and tensile strength, water, frost and chemical resistance of EMC [1-5]. Epoxy resins are used as binders for production of composite reinforcement (with carbon, basalt and glass fibers), chemically resistant paint coatings, polymer mortars and concretes, foams, adhesives and monolithic floor coverings [6-10]. EMC often outperform even advanced building materials with inorganic matrices [11], especially when the dispersed phases were subject to special processing [12].

It is known that properties related to fire safety can be controlled by different means, including special mineral fillers and fire retardants [13-20, 47]. The common approaches to improvement of PMC performance against fire hazards involve the usage of:

- flame retardants that reduce polymer combustibility, smoke and toxic fume production [21, 22];
- intumescent surface coatings [21, 23].

At present, comprehensive nomenclature of flame retardants include halogen-based [24, 25] and phosphorus-based [26-30] substances. Recent achievements in flame retardant development are represented by organometallic [31], *e.g.* ferrocene [18, 32-34], and organosilicon (*e.g.* silsesquioxane) [1, 35] compounds. In particular addition of ferrocene leads to decrease of smoke density caused by sooting during combustion of both unsaturated [33] and saturated hydrocarbons. Ferrocene structures embedded in polymer chains lead to increase of thermal stability and/or fire resistance [32], though at least for several ferrocene derivatives there is a negative correlation between smoke suppression and flame retardancy [34].

Still, quantitative dependencies between amount, chemical type of admixtures and properties related to fire safety of EMC till now have not been revealed in detail. The purpose of this work is to study the dependencies between flammability, combustibility, fume evolution of EMC, and the amount and chemical type of fillers and admixtures.

2. Experimental

Epoxy polymers were prepared on the base of ED-20 epoxy resin. Several types of hardeners are used: polyethylene polyamine (PEPA), diethylenetriamine, triethylenetetramine, imidazolines of “UP-0640”, “UP-0641” and “UP-0642”, and mono-ethanediethylethylene triamine “UP-0633M”. The elastic characteristics of the composites were regulated by the use of low-molecular mass butadiene-nitrile carboxylate rubbers “SKN-18-1A” and “SKN-26-1A”, phosphate plasticizers (properties of these

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plasticizers are summarized in [35]), as well as "Parachlor-380" chlorpaffin with 54–57 % of chlorine. Oxides and hydroxides of various metals, goethite, marshalite, andesite, quartz sand, and hydrate-containing minerals have dimensions from 3 to 25 microns. The thermophysical properties of the metal oxides are summarized in [36]. Thermal properties of hydrate-containing minerals and decomposing mineral fillers are summarized in [37, 38].

Industrial grades of brominated-organic fire retardants and synthesized "Redant" bromine-containing compounds were used to reduce the flammability of EMC. Physicochemical and thermal properties of "Redant" compounds are given in [39]. Ferrocene derivatives were used as smoke suppressors (properties of ferrocene derivatives are summarized in [40]). Depending on the degree of bromination of the initial chloroalkyl aromatic compound, the "Redant" fire retardants contain 15.5–26.5 % chlorine and 44–46 % bromine. For comparison, microencapsulated chladone "114B2", CCl_4, ammonium polyphosphate and decabromodiphenyloxide (DBDFO), halogen-containing epoxy oligomers "Oksilin-6" and "UP-631", as well as bromination products of ED-22 epoxy oligomer and aniline-modified diglycidyl ether of tetrabromodian were used.

Thermal analysis of fillers, flame retardants, ferrocene derivatives and EMC in air and nitrogen flow was carried out using "DuPont-9900" automated modular thermoanalytical system (heating rate was 10 K/min). Limiting oxygen index (LOI), ignition (T_i) and autoignition (T_{si}) temperature, fume evolution index (D_m) in pyrolysis and flame combustion mode, heat of combustion, critical density of heat flux of ignition (q_{cr}), limiting concentration of oxygen (c_l) and velocity of flame propagation (V_{pn}) on the horizontal surface of epoxy polymers and EMC based on such polymers at different oxygen concentrations in the oxidizer stream were determined according to the state standards and methods given in [35-37].

3. Results and Discussion

The presence of epoxy (1–24 %) and hydroxyl (0.2–10 %) functional groups in diane epoxy resins allows them to be cured by various classes of organic, inorganic and organoelement compounds [3-5]. It has been established that the chemical structure of amine curing agents has little effect on the flammability and smoke-forming ability of epoxy composites [41]. Therefore, the choice of amine curing agents should be carried out only taking into account the required technological and operational parameters of epoxy composites.

An effective method of increasing the modulus and strength of EMC is the modification by various compounds [24]. Low-molecular organic compounds increase the combustibility and D_m of EMC. Industrial grades of phosphate plasticizers increase the LOI and T_{si} of epoxy binders from 22.1 % and 743 K up to 23.1–24.5 % and 773–783 K, respectively, and reduce the q_{cr} value from 11.7 to 9.2–10.7 kW/m^2 [20]. The low efficiency of phosphate plasticizers is due to their relatively high combustibility: LOI of plasticizers is 23.1–29.9 %, while LOI of ED-20 polymer is 21.6–22.3 % [14]. At the same time, chemical type of plasticizers has a significant effect on the smoke-forming ability of EMC. For example, D_m in pyrolysis and flame combustion mode of epoxy polymer plasticized by 8.3–15.4 % by diphenyl(2-ethylhexyl)phosphate is reduced from 980 and 990 m^2/kg down to 910–640 and 840–970 m^2/kg, respectively. Trichloroethyl(propyl)phosphates increase D_m in the pyrolysis mode.

Table 1

Properties related to fire safety of EMC

Fillers	Properties					
	T_{si}, K	LOI, %	c_l, %	q_l, kW/m^2	D_m, m^2/kg, for	
					pyrolysis	combustion
–	743	19.3	20.1	10.9	1350	890
CaO	753	21.2	27.0	11.7	520	350
$CaCO_3$	768	20.5	25.1	11.4	790	390
$Ca(OH)_2$	753	20.1	23.8	11.2	410	290
MgO	763	20.6	25.6	11.7	720	400
Al_2O_3	763	20.1	23.3	10.8	800	460
CuO	753	19.8	21.8	10.6	590	480
Fe_2O_3	773	21.9	29.7	–	760	500
Sb_2O_3	783	20.6	25.4	11.2	630	470
Goethite	773	21.5	28.2	11.4	760	500
Grinded quartz sand	753	21.6	28.8	12.7	840	540
$Mg(OH)_2$	773	22.1	30.9	14.8	680	330
$Al(OH)_3$	788	22.3	31.6	16.2	780	360

If mass rate of mineral filler is less than 45 %, the chemical nature of filler has little effect on the fire hazard properties of epoxy composites: LOI is 19.8–22.3 %, T_i is 553–583 K, T_{si} is 753–788 K, q_{cr} is 10.6–16.2 kW/m^2, D_m in the pyrolysis and combustion mode is 520–840 and 350–540 m^2/kg, respectively (Table 1; amount of fillers is 43.5 % by mass, amount of plasticizer is 8.7 % by mass). Significant reduction of the fire hazard of EMC is observed when mass rate of mineral filler exceeds 50 %: for 61 % LOI grows up to 30.8 %, T_i – up to 563–593 K, T_{si} – up to 763–793 K, q_{cr} is linearly increased from 10.3 to 12.2–18.5 kW/m^2. If mass rate of mineral filler is more than 20 %, than fume evolution index in the pyrolysis and flame combustion mode linearly decreases from 1470 and 800 m^2/kg up to 460–550 and 190–250 m^2/kg, respectively. This index only slightly depends on the chemical nature of the fillers [20].

For all the studied composites, a linear dependence between 100/LOI and relative content of mineral fillers (*k*) is observed. The tangent of the slope of the lines to the abscissa axis (tgα) is proportional to the specific heat absorption of the filler (Fig. 1). The value of tgα can be used to evaluate the efficiency of fillers as fire retardants [16]. The values of tgα for the plasticized ED-20 polymer are given below:

Filler	tgα
Al_2O_3	0.04
$CaCO_3$	0.13
CaO	0.24
Serpentine	1.07
$Al(OH)_3$	1.2
$Mg(OH)_2$	1.25
Limonite	1.32

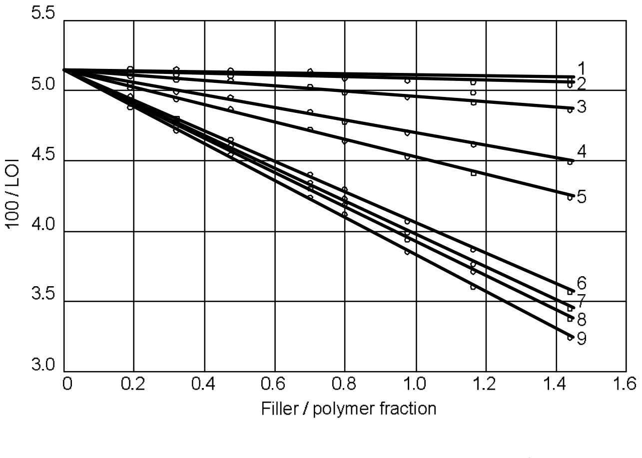

Fig. 1. Dependencies between 100/LOI end mineral filler/epoxy polymer fraction for PCM filled with: Al_2O_3 (1); $CaCO_3$ (2); CaO (3); SiO_2 (4); goethite (5); serpentine (6); $Al(OH)_3$ (7); $Mg(OH)_2$ (8) and limonite (9)

An effective method of reducing the flammability of epoxy composites is the use of additive brominated fire retardants. As a rule, LOI of such retardants exceeds 90 % (for *N*(2,4,6-tribromophenyl) maleimide LOI is 65 %). Their heat of combustion is 9.4–10.8 kJ/kg. The influence of the chemical structure of brominated fire retardants (amount is 5.7 % by mass) on the fire hazard of epoxy composites modified with SKN-26-1A synthetic rubber and filled with grinded quartz sand (amount is 41 % by mass) is presented in Table 2.

As it follows from Table 2, aromatic brominated fire retardants reduce the combustibility and flammability of EMC:LOI; c_l of composites increases from 21.6 and 34.0 % up to 27.2–28.8 and 36.1–39.6 %, respectively; V_{FS} decreases from 0.41 to 0.23–0.31 mm/s; T_i decreases by ~20 K0, and T_{si} is 733–753 K. D_m of epoxy composites in the pyrolysis mode slightly increases from 410 to 440–490 m^2/kg, and in the combustion mode it increases from 570 to 890–990 m^2/kg. At the same time, the chemical structure of industrial grades of additive aromatic brominated fire retardants has a negligible effect on the combustibility of epoxy composites. It should be noted that purified hexachlorobenzene, while being less efficient than hexabromobenchole, practically does not increase the smoke forming ability of EMC. The mechanism of their action is caused both by inhibition of radical chains of processes in the flame and by the phlegmatization of the flame by products of decomposition of brominated fire retardants.

It should be noted that LOI of glass-reinforced bromine-containing epoxy resins is well correlated with the flammability index when tested by the ceramic pipe method (Fig. 2). As it can be seen from Fig. 2, the flame-retardant (low-combustible) composites can be obtained when LOI is more than 31 %, and incombustible (moderately combustible) – when LOI is more than 27 %.

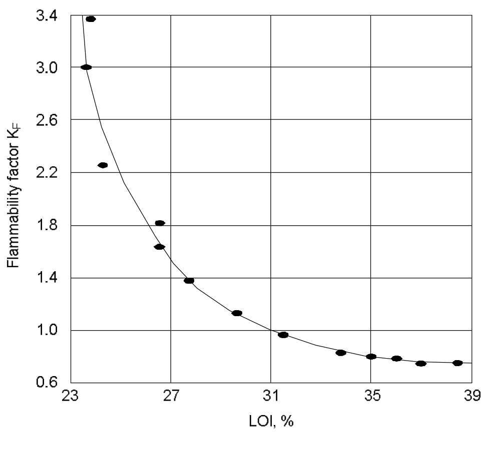

Fig. 2. Dependence between LOI and flammability of epoxy composites modified by bromine-organic compounds (ceramic pipe test method)

Table 2

Fire safety properties of ECM with brominated fire retardants

Type of fire retardant	T_c, K	LOI, %	c_l, %	V_{FS}, for $[O_2]$=45%, mm/s	D_m, m^2/kg, for	
					pyrolysis	combustion
No fire retardant	573	21.6	34.0	0.41	410	570
Pure hexachlorobenzene	563	27.2	37.4	0.35	470	580
Hescabromobenzene	553	28.8	36.1	0.31	440	1000
Decabromodiphenyl oxide	543	28.2	36.8	0.25	460	900
Tetrabrom P-xylene	543	27.9	37.9	0.33	490	890
2,4,6-Tribromaniline	573	28.4	36.0	0.33	480	820
N (2,4,6-tribromophenyl)-maleimide	563	28.5	36.1	0.48	430	830
Pentabromophenol	553	28.4	38.4	0.24	460	360
3,5,3', 5'-tetrabromo-4,4'-diamidiphenylsulfone	568	28.1	36.1	0.35	470	810
2,4,6-tribromophenol	563	28.7	39.4	0.23	550	820
Tetrabromodiphenylpropane	563	27.2	39.6	0.45	–	–
Tetrabromphthalic anhydride	543	28.1	38.9	0.36	490	900

Table 3

Thermal stability, combustibility and fume evolution of epoxy matrix composites

Properties	Type of fire retardant			
	Redant 1-2	Redant 2-1	Redant 2	Redant 1
LOI, %	32.3	33.2	30.5	33.7
Temperature, K				
beginning of decomposition	557	525	526	537
maximal rate of decomposition for:				
• stage 1	590	595	595	606
• stage 2	720	718	720	713
Flame spread rate for oxygen concentration, mm/s				
• 40 %	–	0.27	–	0.27
• 50 %	0.48	0.5	0.56	0.46
Heat of combustion, kJ/kg	29900	–	29030	31570
Fume evolution, m^2/kg, for				
• pyrolysis	770	870	760	850
• combustion	650	730	690	630

With the increase of the content of additive brominated fire retardants, the flammability and combustibility of epoxy composites decrease. For example, with an increase of the tetrabromodian content to 9.8 % the T_i of EMC decreases from 573 to 553 K, T_{si} increases from 733 to 763 K, and LOI increases from 21.6 to 29.2 %. D_m in pyrolysis mode is practically independent of the content of fire retardants and its value is 420–440 m^2/kg. In the combustion mode D_m increases from 570 to 990 m^2/kg. The dependence between LOI of ECM and amount of bromine in the composite is shown in Fig. 3.

Influence of Redant bromine-organic fire retardants on the heat resistance and fire hazard of EMC is shown in Table 3 (amount of fire retardants is 8.6 % by mass, amount of marshalite is 47.2 % by mass). EMC modified with Redant 1-C have a higher thermal conductivity (the specific heat of combustion of the composition containing 20 wt. parts of Redant 1 is 31570 kJ/kg, while for materials modified with Redant 2 and Redant 1-2 these values are 29030 and 29900 kJ/kg, respectively) and they are also characterized by reduced heat resistance. The mass burnup rate of composites modified with 20 wt. parts of Redant 1 and Redant 2-1 are 32, 17 and 30.59 g/(m^2·s), respectively, with a heat flux density of 10.58 kW/m^2.

Considering that additive brominated fire retardants are crystalline or amphoric powders, it was suggested to use them in a form of solution in *N*,*N*-dimethyl-2,4,6-tribromoaniline. It was revealed that as the concentration of Redant 1 in *N*,*N*-dimethyl-2,4,6-tribromoaniline increases up to 50 %, the LOI of composites increase from 25.8 to 30.1 %, mass burnup rate at a warm flux density of 10.58 kW/m^2 is reduced from 29.1 to 23.4 g/(m^2 s), and the heat of combustion decreases linearly from 34400 to 30150 kJ/kg (Fig. 4). The maximum values of D_m were observed for composites with 20–30% solution of Redant 1 in *N*,*N*-dimethyl-2,4,6-

tribromoaniline (Fig. 5). The use of Redant fire retardants in form of solution in *N*,*N*-dimethyl-2,4,6-tribromanyline makes it possible to produce low-combustible EMC and eliminate flame propagation over the surface.

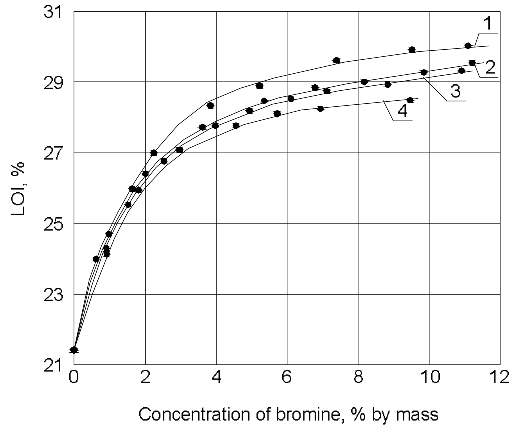

Fig.3. Dependence between concentration of bromine in the material and LOI for epoxy composites with additive bromine-organic fire retardants: hexabromobenzene (1); decabromodiphenyl oxide (2); 2,4,6-tribromanylene (3) and *N*-(2,4,6-tribromophenyl)maleimide (4)

Thus, the use of industrial grades of additive brominated fire retardants allows to produce EMC with LOI of 31–33 % for bromine concentration of 6–8 % by mass. The optimal amount of such fire retardants is 8–10 % by mass. For such concentration, the strength of EMC is only slightly reduced. The mechanism of action of bromine-containing fire retardants was considered in detail in [23-25].

The effect of the content of reactive bromine-containing epoxy compounds on the combustibility of cured binders is shown in Fig. 6. As it follows from Fig. 6, bromine-containing epoxy oligomer UP-631 is more effective than aniline-modified diglycidyl ether of tetrabromodiamine and brominated ED-22 epoxy oligomer. This is due to different concentration of bromine in these epoxy compounds. This conclusion is confirmed by the experimentally observed linear dependence between the LOI epoxy polymers and bromine concentration (Fig. 7).

It should be noted that reactive bromine-containing compounds are significantly less efficient than additive fire retardants. For example, to obtain composites with LOI equal to 27 %, the concentration of bromine in the composition with pentabromophenol must be 8.3 %, while the concentration of bromine-containing UP-631 oligomer must be 20 %. This is due to higher concentration of bromine in additive brominated fore retardants (58–86 %) compared to bromine-containing epoxy compounds (bromine concentration is 25.0–48.8 %).

A promising direction of reducing the combustibility of EMC is the use of microencapsulated fire retardants. Microcapsules containing fire retardants explosively break down when exposed to elevated temperatures or flames, throwing the vaporized flame-extinguishing agent into the flame zone. As an example, Fig. 8 illustrates the effect of the content of microencapsulated fire retardants on the combustibility of EMC. In this case, the microencapsulated DBDFO is inferior to the ordinary DBDFO. The efficiency of microencapsulated fire retardants depends mainly on the diameter of the microspheres, chemical nature of the fire retardant used and, to a lesser extent, on the chemical nature of the microcapsule shell. The effects of microencapsulated DBDFO (5.85 % by mass) on the combustibility of epoxy composites filled with marshallite (41.8 % by mass) are summarized in Table 4.

The effective smoke suppressor of polymeric materials is ferrocene (Fig. 9).

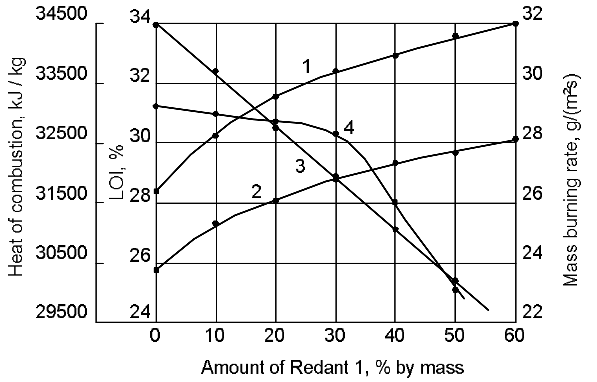

Fig. 4. Dependencies between combustibility of epoxy matrix composites and the amount of Redant 1 in *N*,*N*-dimethyl-2,4,6-tribromoaniline: LOI (1, 2); heat of combustion (3); mass burning rate (4). For 1 – amount of fire retardant in the composition is 8.6 % by mass; for 2, 3, 4 – 4.5 % by mass

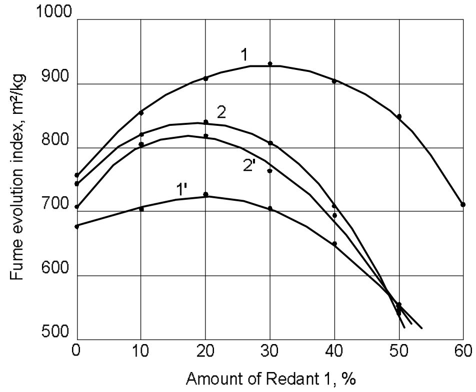

Fig. 5. Dependencies between fume evolution of epoxy matrix composites and the amount of Redant 1 in *N*,*N*-dimethyl-2,4,6-tribromoaniline: pyrolysis mode (1, 2); flaming combustion (1' 2'). For 1, 1' – amount of fire retardant is 4.1 % by mass; for 2, 2' – 7.9 % by mass

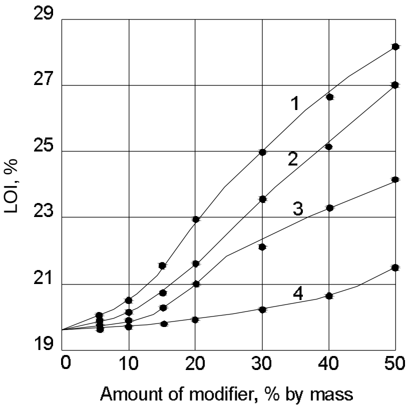

Fig. 6. Dependence between flammability of cured ED-20 epoxy resin and concentration of halogen-containing modifiers: bromine-containing UP-631 oligomer (1); modified diglycidyl ether of tetrabromodian at 1:1 molar ratio between UP-631 and aniline (2); brominated ED-22 oligomer with a bromine concentration of 25 % by mass (3) and chlorine-containing Oxylin-6 oligomer (4)

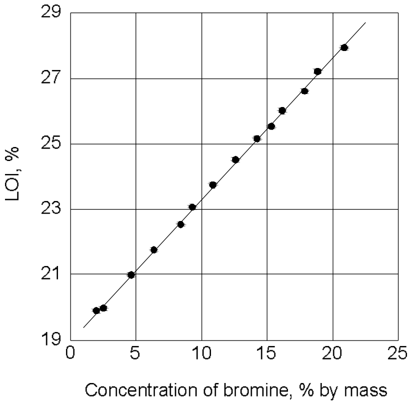

Fig. 7. Dependence between concentration of bromine and LOI of cured epoxy binders

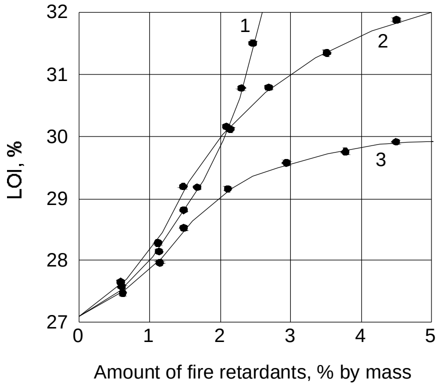

Fig. 8. Dependence between content of microencapsulated fire retardants and LOI of epoxy materials: ammonium polyphosphate (2); Chladon-114V2 (2) and carbon tetrachloride (3)

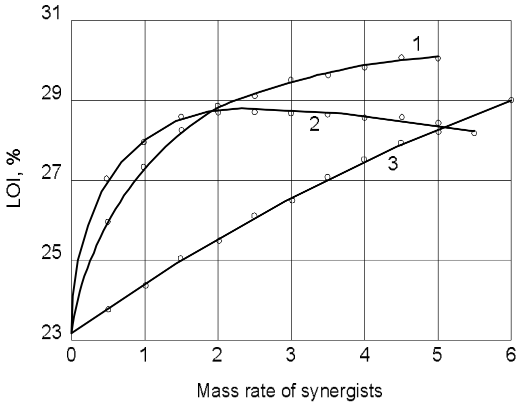

Fig. 9. Dependencies between LOI of epoxy matrix composites and amount of synergists: ferrocene (1); boron (2) and Sb_2O_3 (3)

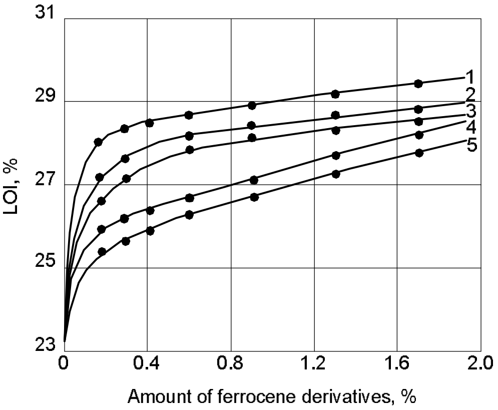

Fig. 10. Dependence between LOI of epoxy matrix mortars and amount of ferrocene derivatives: α-oxyethylferrocene (1); ferrocene (2); diacetylferrocene (3); ferrocenedicarboxylic acid (4) and acetylferrocene (5)

Table 4

LOI of epoxy compositions with decabromodiphenyl oxide

Type of decabromodiphenyl oxide	LOI, %
DBDPO with a particle diameter of 240 μm	36.9
DBDPO with a shell of epoxy resin with a particle diameter of 150–400 μm	32.1
DBDPO with a shell of epoxy resin with a particle diameter of at least 150 μm	33.5
DBDPO with a shell of a copolymer of styrene and *N*-(2,4,6-tribromophenyl)-maleimide with a particle diameter of at least 150 μm	32.1
DBDPO with a shell of a copolymer of styrene and *N*-(2,4,6-tribromophenyl)-maleimide with a particle diameter of not more than 150 μm	32.8
DBDPO with a shell of an aromatic polyamide with a particle diameter of 150-400 μm	32.1
DBDPO with a shell of an aromatic polyamide with a particle diameter of at least 150 μm	32.1
Chladon-II4B2 with a shell of polyvinyl alcohol with a particle diameter of 125-250 μm	28.6

Table 5

Thermal stability and combustibility of filled epoxy matrix composites (amount of filler is 35 % by mass) with 0.29 % by mass of ferrocene derivatives

Properties	No admixtures	Ferrocene	α-oxyethyl ferrocene	Acetylferrocene	Ferrocene dicarboxylic acid	poly-di(α-oxyisopropylenyl) ferrocene	Sb_2O_3
Temperature, K:							
• ignition	493	513	503	493	493	493	–
• start of decomposition	557	549	558	546	557	555	557
• maximal rate of decomposition							
* on the first stage	577	574	578	573	578	579	579
* on the second stage	758	773	741	732	756	754	769
self ignition	758	563	743	753	753	753	–
Maximal rate of decomposition, %/min,							
• on the first stage	19.9	19.9	20.0	21.2	18.4	21.4	22.2
• on the second stage	18.9	24.2	24.5	20.8	18.8	16.0	22.9
Specific heat of decomposition, kJ/kg	4070	4300	3960	4300	4300	3300	4360
LOI, %	23.3	27.6	28.3	25.6	26.1	25.8	27.9

It has been established that the cyclopentadienyl sandwich-like derivatives of iron do not affect the ignition temperature (493–503 K) and decomposition of epoxy compositions in the low-temperature region (Table 5), but significantly affect pyrolysis at temperatures above 573 K. In later case, the higher the efficiency of the ferrocene derivatives, the higher the decomposition rate of the epoxy composites in the second stage. The LOI of EMC with ferrocene derivatives can also be increased (Fig. 10).

The high efficiency of acetyl- and α-hydroxyethylferrocene in comparison with ordinary ferrocene is due to the ease of formation of ultradispersed catalytically active iron oxides (Fe_2O_3, Fe_3O_4) during pyrolysis of derivatives. This affects the mechanism of pyrolysis of carbonizing polymers, increases the probability of formation of carbonized layer on the surface of the polymer, and suppresses formation of benzene and smoke. Optimal concentration of ferrocene derivatives in EMC is 0.3–0.5 % by mass.

4. Conclusions

In the present work, we summarized and discussed the results of several laboratory tests. The tests were carried out to answer the question concerning the suitability and effectiveness of different measures that allow to reduce fire hazards of EMC. Considerable amount of experimental data concerning properties of EMC was obtained. Influence of the type and content of different fillers and fire retardants to the heat resistance, ignitability, flammability and smoke-forming ability of EMC was examined. The compositions of EMC that are characterized by elevated performance properties, including low combustibility, are determined. The developed composites can be successfully used in the construction industry.

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ВОГНЕСТІЙКІ КОМПОЗИТИ НА ОСНОВІ ПОЛІМЕРНОЇ МАТРИЦІ

Анотація. *Вивчено термостабільність і пожежно-технічні параметри епоксидних композитів з різними затвердниками, наповнювачами, пластифікаторами та ретардантами. Показано, що вміст мінеральних наповнювачів до 45 % мало впливає на займистість. Формування диму зменшується лінійно з підвищенням ступеня наповнення. Показано, що для отримання низькогорючих матеріалів кисневий індекс повинен перевищувати 31 %. Встановлено, що оптимальна концентрація промислових бромованих вогнетривких речовин становить 8–10% за масою. Для зменшення горючості епоксидних композитів запропоновано використовувати бромвмісні ретарданти у вигляді розчину в N, N-диметил-2,4,6-трибромоаніліні. Показана висока ефективність ацетил- та α-гідроксиетилферроценових додатків для зменшення диму.*

Ключові слова: *бромвмісні ретарданти, займистість, горючість, епоксидні композити, наповнювач, пластифікатор, похідні ферроцену.*