SYNTHESIS AND PROCESSING OF POLYMERS AND POLYMERIC COMPOSITES

СИНТЕЗ И ПЕРЕРАБОТКА ПОЛИМЕРОВ И КОМПОЗИТОВ НА ИХ ОСНОВЕ

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RESEARCH ARTICLE

Projection of structure and compositions of resistance to burning polymer composite materials with flame retardants based on magnesium hydroxide

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Abstract

Objectives. *To identify general principles for the design of dispersed-filled polymer composite materials (DFPCMs) with different generalized and reduced parameters, as well as types of disperse structure with high fire resistance; to develop an algorithm for the creation of non-combustible polymer composites with flame-retardant fillers.*
Methods. *Scanning electron microscopy and laser diffraction were used to assess the shape, size, and particle size distribution of flame retardants. According to the presented classification of DFPCMs by structural principle, standard bar samples were obtained to determine the oxygen index (OI) and the fire resistance category.*
Results. *For the MFS-2 (medium filled system) and HFS (high filled system) structure types, the maximum resistance to burning (category V-0) is achieved with a generalized parameter of $\Theta \leq 0.40$ volume fractions; the OI value increases in 2 times (up to ~40%) in relation to the polymer matrix.*

Conclusions. *In order to obtain a flame retardant DFPCMs (OI = 40%, category V-0) based on ethylene vinyl acetate with OI = 20% and magnesium hydroxide (brucite), the amount of water vapor released during the decomposition of the flame-retardant filler should be at least ~250 mL/g with a coke residue ~32%. A developed algorithm for calculating compositions and generalized parameters for the creation of DFPCMs having a predetermined type of disperse structure and high resistance to burning is presented.*

Keywords: *composite materials, disperse structure, oxygen index, resistance to burning, cable composition, EVA, mineral flame retardants*

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НАУЧНАЯ СТАТЬЯ

Проектирование структуры и составов стойких к горению полимерных композиционных материалов с наполнителями-антипиренами на основе гидроксида магния

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Аннотация

Цели. *Установить фундаментальные закономерности для проектирования составов дисперсно-наполненных полимерных композиционных материалов (ДНПКМ) с разными обобщенными и приведенными параметрами и типами дисперсной структуры с высокой стойкостью к горению, а также разработать алгоритм создания негорючих полимерных композитов с наполнителями-антипиренами.*
Методы. *Оценку формы, размера и распределения частиц по размерам для наполнителей-антипиренов всех марок определяли на сканирующем электронном микроскопе и методом лазерной дифракции. Согласно представленной классификации ДНПКМ по структурному принципу были получены стандартные образцы брусков для определения кислородного индекса (КИ) и категории стойкости к горению.*
Результаты. *Установлено, что для структуры ДНПКМ типа СНС-2 (средне-наполненная система) и ВНС (высоконаполненная система) при обобщенном параметре Θ ≤ 0.40 об. д. достигается максимальная стойкость к горению (категория ПВ-0), а значение КИ возрастает в 2 раза (до ~40%) относительно полимерной матрицы.*
Выводы. *Показано, что для получения стойких к горению ДНПКМ (КИ = 40%, категория ПВ-0) на основе сэвилена с КИ = 20% и гидроксида магния (брусит),*

количество выделяющихся паров воды долно составлять не менее ~250 мл/г при разложении наполнителя-антипирена, а коксовый остаток ~32%. Представлен алгоритм расчета составов, обобщенных параметров и создания ДНПКМ с заданным типом дисперсной структуры и высокой стойкостью к горению.

Ключевые слова: *композиционные материалы, дисперсная структура, кислородный индекс, стойкость к горению, кабельная композиция, сэвилен, минеральные антипирены*

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INTRODUCTION

One of the urgent tasks in practical materials science consists in the creation of non-combustible polymeric and polymer composite materials (PCM) offering increased resistance to burning and low toxicity of gaseous substances emitted during burning.

The widespread use of dispersed-filled PCM (DFPCM) in industry is partly due to the large number of studies on flame-retardant substances of different chemical composition forming the basis for determining specific conditions for obtaining fire-resistant materials with reduced fire hazard [1–5].

Halogen-containing substances, which decompose when heated to release a halogen atom that inhibits the burning process, are actively used as flame retardants. However, their use is limited by the toxicity of combustion products and wastes involved in the production of halogen-containing polymer compositions, which both comprise significant environment pollutants [6–11].

In terms of halogen-free flame-retardant fillers, mineral powder fillers based on aluminum (Al), magnesium (Mg), and calcium (Ca) hydroxides, which form water vapors during decomposition, have proven most effective. In this case, the endothermic reaction of the filler decomposition with the release of water contributes to cooling, the isolation of the burning zone from available oxygen, and a reduction of gas exchange at the material surface, as well as reducing smoke formation [12]. In order to obtain burning resistant DFPCMs, the amount of mineral flame-retardant filler in them should be not less than ~45–60 wt % (22–30 vol % at density ~2.5 g/cm^3) according to the published data [11–13].

The maximum content φ_{max} of a dispersed flame-retardant filler, which can practically be introduced into a PCM on a matrix of any nature, depends on the maximum packaging (k_p, φ_{max}), size (d), shape (k_e), fractional composition, and particle distribution in the volume of the polymer matrix (PM).

The following are generalized values of the maximum content (φ_{max}, vol fract.) of solid dispersed fillers with various particle sizes in DFPCMs, which are in good agreement with experimental data [14]:

– nanoparticles (1–100 nm) — $\varphi_{max} \approx$ ≈ 0.05–0.20 vol fract.

– ultradisperse particles (0.1–1.0 μm) — $\varphi_{max} \approx$ ≈ 0.20–0.255 vol fract.

– submicroparticles (1.0–3.0 μm) — $\varphi_{max} \approx$ ≈ 0.255–0.35 vol fract.

– microparticles (3–10 μm) — $\varphi_{max} \approx$ ≈ 0.35–0.45 vol fract.

– macroparticles (10–40 μm) — $\varphi_{max} \approx$ ≈ 0.45–0.62 vol fract.

– large particles (larger than 50 μm) — $\varphi_{max} \approx$ ≈ 0.62–0.64 vol fract.

Analysis of the above data showed that only large and macroparticles of flame-retardant fillers with a size of more than ~10 μm or their mixtures with nanoparticles and microparticles can be used to create burning-resistant DFPCMs [14]. When nano-, ultradisperse-, and submicro-particles are used, highly efficient dispersants must be used, which help to increase φ_{max} to allow the introduction of flame retardant in the required quantity (up to ~50–60 wt %).

Unfortunately, since data on the packaging and maximum content of dispersed flame-retardant fillers in DFPCM are virtually non-existent in the scientific and technical literature, it is not possible to determine the structural formation process in such systems.

New models, classifications, and calculations of DFPCM compositions, developed in recent years, generalized and reduced parameters of disperse structure relate dispersed structure types—diluted systems (DS), low-filled systems (LFS), medium-filled systems (MFS), medium-filled systems below the yield point (MFS-1), medium-filled systems above the yield point (MFS-2), and high-filled systems (HFS)—with a set of rheological, physical and mechanical, electrophysical, thermal, and optical characteristics [14]. However, there appear to be no data on burning resistance.

In [15], we considered the flammability of DFPCM flooring with silica inert filler with diameters of 500 μm and 160 μm in terms of the relationship of surface heat flux density (q) with generalized parameters, as well as providing a detailed disperse structure typology.

The aim of the present work is to establish fundamental regularities for the design of DFPCM compositions with different generalized and reduced parameters, as well as various disperse structure types offering high resistance to burning. This can provide the basis for the development of an algorithm for creating non-combustible polymer composites with flame-retardant fillers.

EXPERIMENTAL

DFPCM for cable insulation based on copolymer ethylene vinyl acetate – EVA 11306-075, with melt flow rate 8 g/10 min (*Kazanorgsintez*, Russia) and mineral antipyrine fillers from brucite EcoPiren® (EP) based on magnesium hydroxide $Mg(OH)_2$ (*RGKHO*, Russia) were used as a material basis for the study.

The shape, size, and particle size distribution for all grades of flame-retardant fillers were determined using a Hosokawa-Alpine scanning electron microscope (Germany) and a Malvern Mastersizer 2000 laser analyzer (*Malvern Panalytical*, UK).

Table 1 shows the main characteristics of the dispersed flame-retardant fillers (brucite) of the various EP grades.

Figure 1 shows the structure of the dispersed powder of EP flame-retardant filler.

As can be seen from Fig. 1, magnesium hydroxide particles have a scaly structure with a shape coefficient $k_e \approx 5$ [14]. Due to their shape often differing from lamellar, it is not possible to determine the shape coefficient of flame-retardant particles with the necessary accuracy from a study of micrographs (Fig. 1). The investigated EP dispersed flame-retardant fillers are characterized by a fairly wide particle size distribution. When constructing the structure of DFPCMs, the shape, size, particle size distribution, and the maximum content of the flame-retardant filler

Table 1. Characteristics of flame retardants based on magnesium hydroxide (brucite) of various EcoPiren® (EP) grades and particle sizes

Flame-retardant filler	Particle size change interval, μm	Average particle diameter d_{av}, μm	Specific surface area S_s, m²/g
EP 2SA	0.6–5.0	2.5	3.50
EP 3.5	1–10	5.0	2.63
EP 5.5	1–9	10.0	2.06
EP 10R	2–47	24.0	1.60
EP 20R	2–89	45.0	1.23

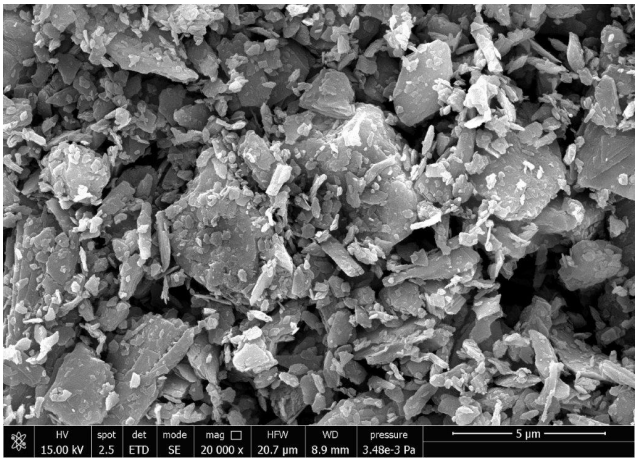


Fig. 1. Structure of the particles of the EP 3.5 flame-retardant filler.

in the PM takes into account the parameter φ_{max} (vol fract.), which can be determined using special experimental techniques [16]. The φ_{max} values for all investigated flame-retardant fillers (brucite) are given in Table 2.

From the above data follows the incorrectness of determining the parameter φ_{max} by bulk density for investigated flame retardants.

The maximum content of the flame-retardant filler in DFPCM (φ_{max} ~ 0.62 vol fract.) is achieved for macroparticles of EP-10R and EP-20R grades with a particle size of 25 and 45 μm, respectively. With a decrease in the particle size to 2.5 μm, φ_{max} decreases to 0.25 vol fract. (EP 2SA).

The design of a disperse structure having different types and various generalized parameters, as well as DFPCM compositions based on EVA and flame retardants of various EP grades, was carried out according to the algorithm developed earlier [14].

The content of a dispersed flame-retardant filler (φ_f) with a known parameter φ_{max} ensures the formation of a given type of structure in the DFPCM (classified according to the generalized parameter Θ), was calculated by Eq. (1) [14]:

$$\varphi_f = (1 - \Theta) \times \varphi_{max}, \text{ vol fract.} \quad (1)$$

where Θ is the PM fraction for the formation of interlayers between filler particles in DFPCM.

Figure 2 shows the dependencies of $\varphi_f = f(\Theta)$ for the design of DFPCM compositions with a given type of disperse structure based on EVA and flame-retardant fillers of various EP grades.

The presented data on DFPCM compositions show that when using flame-retardant fillers with a particle size of 2.5–10 μm (EP 2SA grade with φ_{max} = 0.25 vol fract., EP 3.5 with φ_{max} = 0.35 vol fract., and EP 5.5 with φ_{max} = 0.43 vol fract.), it is almost impossible to introduce a sufficient amount of dispersed filler (up to ~60 wt %) to obtain materials resistant to burning [14].

In [17], it is shown that the amount of water vapor released from the flame-retardant filler

Table 2. φ_{max} values for dispersed powders of flame-retardant fillers of various EP grades

No.	Flame-retardant filler	Particle diameter d_{av}, μm	φ_{max}, vol fract.			
			By oil capacity	By the sealing graph	By three concentrations	By bulk density
1	EP 2SA	2.5	0.27	0.24	0.23	0.157
2	EP 3.5	5.0	0.36	0.34	0.35	0.168
3	EP 5.5	10.0	0.47	0.43	0.42	0.195
4	EP 10R	25.0	0.61	0.6	0.59	0.231
5	EP 20R	45.0	0.63	0.62	0.61	0.291

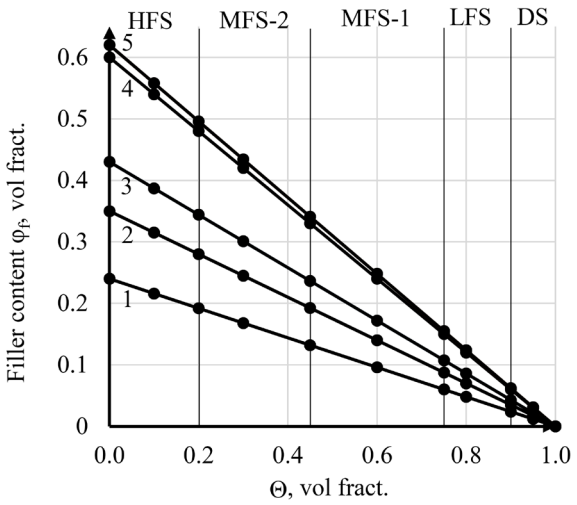


Fig. 2. Dependence of the flame-retardant filler content (φ_f) in DFPCM on the generalized parameter Θ for various EP grades:
1 – EP 2SA (φ_{max} = 0.25); 2 – EP 3.5 (φ_{max} = 0.35);
3 – EP 5.5 (φ_{max} = 0.43); 4 – EP 10R (φ_{max} = 0.60);
5 – EP 20R (φ_{max} = 0.62).

(brucite). Depending on the particle diameter, this reaches its maximum value (V_{H_2O} ~ 430 mL/g) with a particle diameter of more than 10 μm.

Considering the maximum packing (φ_{max}) and the amount of water vapor emitted during decomposition, the EP 10R flame-retardant filler (d_{av} = 25 μm and φ_{max} = 0.60 vol fract.) was used to investigate the effect of structure type and parameters and create the burning-resistant DFPCM.

To conduct experimental studies, the following compositions of DFPCM with an EP 10R flame-retardant filler (d_{av} = 25 μm, φ_{max} = 0.60 vol fract.) and different types of structures were used: DS with Θ = 0.95 vol fract., φ_f = 0.03 vol fract.; LFS with Θ = 0.75 vol fract., φ_f = 0.15 vol fract.; MFS-1 with Θ = 0.60 vol fract., φ_f = 0.24 vol fract. and with Θ = 0.50 vol fract., φ_f = 0.30 vol fract.; MFS-2 with Θ = 0.45 vol fract., φ_f = 0.33 vol fract. and with Θ = 0.30 vol fract., φ_f = 0.42 vol fract.; HFS with Θ = 0.20 vol fract., φ_f = 0.48 vol fract.

DFPCMs based on EVA and EP 10R fillers with different disperse structure types were produced by mixing the raw components on a LabTech LZ80/VS twin-screw extruder (*Labtech Engineering*, Thailand) with a screw diameter of 16 mm at 200°C and a screw speed of 150 rpm.

In order to determine the oxygen index (OI)[1] and the category of resistance to burning (method B)[2], standard samples in bar form were obtained from DFPCMs with different types of disperse structure using injection molding.

Samples in the form of standard bars were cast on the ARBURG injection molding machine (Germany) at a pressure of 50 MPa, a melt temperature of 200°C, a mold temperature of 30°C, a holding time under pressure of 5 s, and a cooling time of 24 s.

The testing of DFPCMs with different types of disperse structure for resistance to burning and determination of OI was carried out in the Center of Scientific and Technical Department No. 3 of the G.S. Petrov Plastics Research and Testing Institute (Russia).

For determining the burning resistance of DFPCM, the burning and smoldering times of a vertically mounted bar specimen were recorded; based on the test results, the material was assigned a burning resistance category whose parameters are shown in Table 3.

DFPCMs of the V-0 category are characterized by the greatest resistance to burning. Samples that do not conform to the presented categories of resistance to burning are assigned a category—out of category (–), which corresponds to the lowest resistance to burning. For the initial PM EVA the flammability parameters were determined: OI = 20.5% and flammability category—(–).

RESULTS AND DISCUSSION

The results on burning resistance and OI parameters for all investigated samples of DFPCMs based on EVA 11306-075 grade with EP 10R flame-retardant filler are given in Table 4.

According to the results of the experiment, DFPCM with a magnesium hydroxide content of EP 10R not less than ~0.36 vol fract. (~0.59 wt fract.), which corresponds to the disperse structure types MFS-2 (Θ ≤ 0.40 vol fract.) and HFS (Θ ≤ 0.20 vol fract.), has the highest category of resistance to burning (V-0).

Polymer materials with the specified category of resistance to burning are approved for the manufacture of electrical products in the cable industry [18]. According to works of A.V. Filina [18] and A.A. Frik[3], DFPCM used as electrical insulation materials should have an OI of at least ~32%.

[1] GOST 21793-76. Gosstandart of the USSR. Plastics. Method for determination of the oxygen index. Moscow: State committee for standards of the council of ministers of the USSR; 1976.

[2] GOST 28157-2018. Interstate standard. Plastics. Methods for determining the resistance to burning. Moscow: Standartinform; 2018.

[3] Frik A.A. *Research and development of fire-resistant cables using halogen-free materials*: Cand. Sci. Thesis. Moscow: VNIIKP; 2016. 20 p. (in Russ.).

Table 3. Criteria for the category of resistance to burning DFPCM

Test indicators	Category of resistance to burning		
	V-0	V-1	V-2
Burning time after application of flame, no more than, s	10	30	30
The total burning time of 5 samples after two-fold application of flame, s	50	250	250
Does not burn and smolder before clamping	+	+	+
Ignition of hygroscopic cotton wool located 300 mm from the sample	–	–	+
Burning and smoldering of the sample after the second removal of the flame, no more than, s	30	60	60

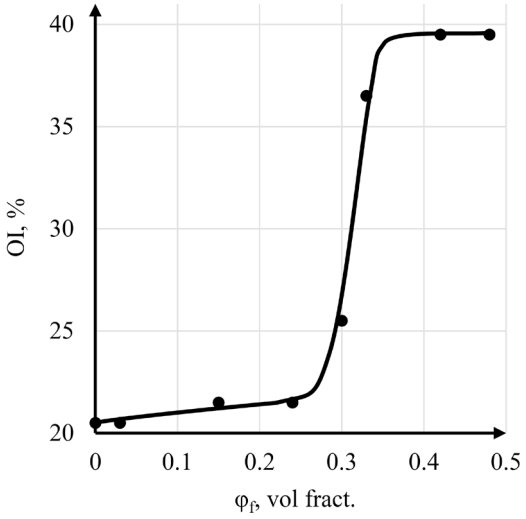
Note: "+" – the indicator is achieved; "–" – the indicator is not achieved.

Table 4. Type of structure, generalized parameters, compositions of DFPCM based on EVA + EP 10R and their resistance to burning

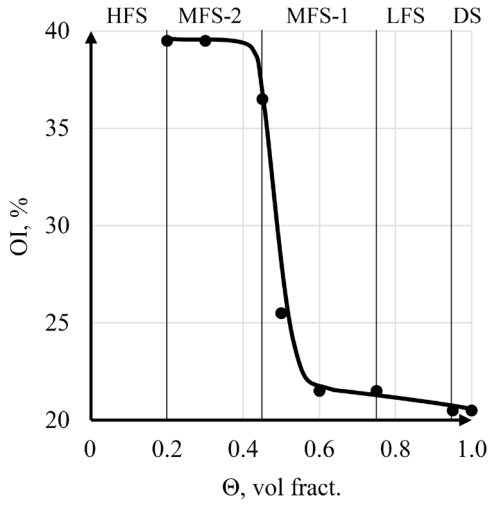
DFPCM composition	Type of structure	Θ, vol fract.	EP 10R (φ_f) content		Category of resistance to burning GOST 28157-2018
			vol fract.	wt fract.	
EVA 11306-075	–	1.0	–		(–)
EVA 11306-075 + EP 10R	DS	0.95	0.03	0.07	(–)
	LFS	0.75	0.15	0.31	(–)
	MFS-1	0.60	0.24	0.45	V-2
		0.50	0.30	0.52	V-2
	MFS-2	0.45	0.33	0.56	V-1
		0.40	0.36	0.59	V-0
		0.30	0.42	0.65	V-0
	HFS	0.20	0.48	0.70	V-0

Figure 3 shows the dependence of OI = $f(\varphi_f)$ and, for the first time, the OI dependence for DFPCMs on the generalized parameter (Θ) of the disperse structure, forming a basis for relating the disperse structure types with the OI parameter and the burning resistance. Here it should be noted that the traditional OI dependence on φf does not allow the classification of DFPCMs according to the structural principle (DS, LFS, MFS-1, MFS-2, and HFS).

The dependence OI = f(Θ) for DFPCMs has an S-shaped form and characteristic areas that correspond to different types of disperse structure.



(a)



(b)

Fig. 3. OI dependence for DFPCM based on EVA: (a) on the EP 10R flame-retardant filler content, (b) on the generalized parameter Θ.

In area 1, the OI value increases by only ~10%, amounting to ~22% when the EP 10R is introduced into the EVA. These are the DS, LFS, and MFS-1 structure types (up to Θ ≥ 0.60 vol fract.).

In area 2, there is a sharp jump in the OI value from 22 to 37% in the formation of DFPCM with the MFS-1 structure type at Θ ≈ 0.60–0.45 vol fract.

In area 3, the OI reaches its maximum value of 40%, which is associated with the formation of MFS-2 (Θ < 0.40–0.30 vol fract.) and HFS (Θ ≤ 0.20 vol fract.) structures in DFPCMs, along with a corresponding increase in the flame-retardant filler (brucite) content.

Thus, for DFPCMs based on EVA with OI = 20.5% and EP 10R flame retardant, it is possible to achieve the OI value in ~2 times higher than the OI value characteristic for an unfilled PM at the creation of disperse structures of MFS-2 and HFS types. In this case, the maximum value Θ ≈ 0.40 vol fract., EP 10R flame-retardant filler content ≈0.36 vol fract. (0.59 wt fract.), an OI of ≈40%, and a category of resistance to burning—V-0.

At OI ≈ 32% (the recommendation given in works of Filina [18] and Frik (Footnote 3)), the cable insulation from DFPCM based on EVA + EP 10R can have a structure like MFS-1 with Θ ≈ 0.50 vol fract.; the filler content will decrease and amount to $\varphi_f \approx 0.30$ vol fract. (0.52 wt fract.).

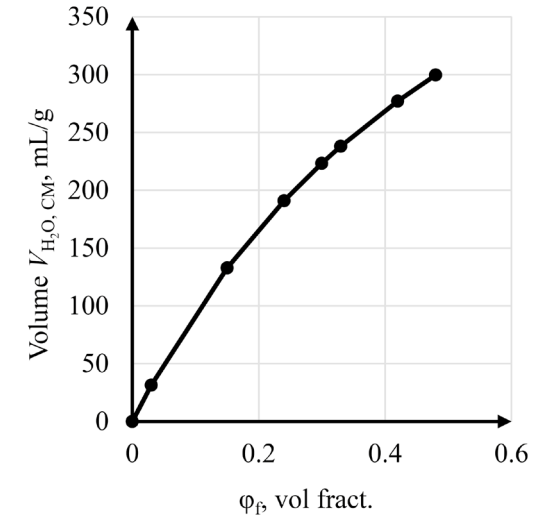
For the first time, data on the influence of disperse structure type on the OI and burning resistance for DFPCM based on EVA and dispersed flame-retardant filler are presented, allowing the purposeful design of compositions offering a predetermined resistance to burning.

The increase in the OI value when EVA is added to the PM with EP 10R flame-retardant filler is due to the decomposition of magnesium hydroxide and the release of water vapor. Water vapor and coke residue formation are the main factors increasing the OI and burning resistance of DFPCMs.

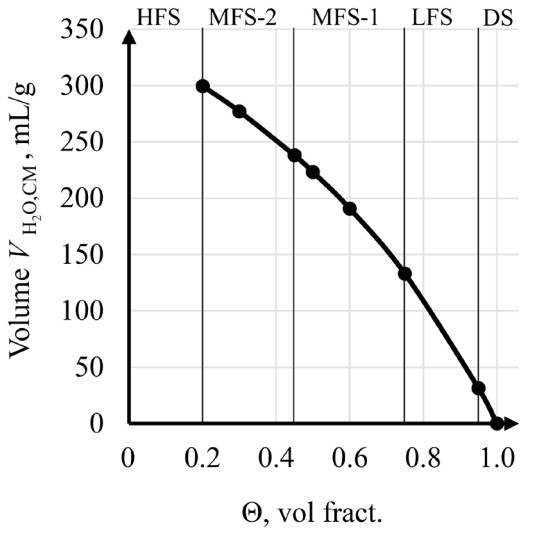
According to thermogravimetric analysis (TGA) [17], we determined the amount of water vapor emitted from 1 g of EP 10R flame-retardant filler (brucite) to be ~425 mL/g; the corresponding coke residue value was 32%.

Figure 4 shows the dependencies of the volume of water vapor emitted during brucite decomposition in DFPCM on the flame-retardant filler content and the generalized parameter Θ, which determines the type of DFPCM disperse structure.

According to the general pattern, the volume of water vapor increases with an increase in the content of the flame-retardant filler and a decrease in the generalized parameter; this however depends on the DFPCM structure type. From the above, it can be concluded that the higher the content of

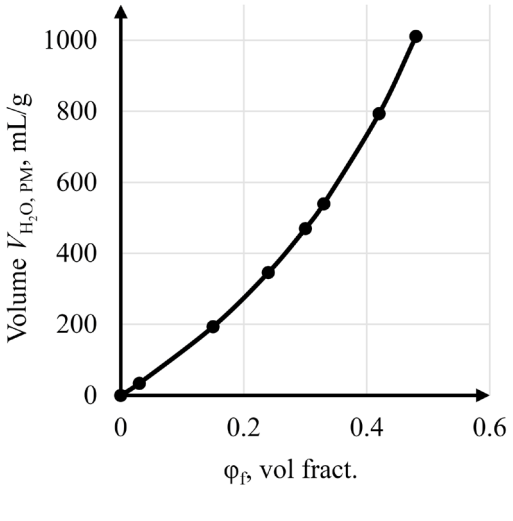


(a)

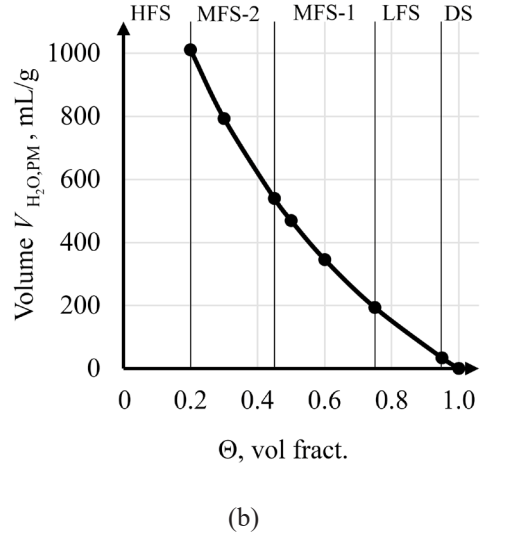


(b)

Fig. 4. Dependence of the volume of water vapor released during the decomposition of brucite in DFPCM: (a) on the content of the flame-retardant filler, (b) on the generalized parameter Θ.



(a)



(b)

Fig. 5. Dependence of the volume of water vapor released during the decomposition of brucite per 1 g of polymer matrix: (a) on the content of the flame-retardant filler, (b) on the generalized parameter Θ.

water-releasing flame retardant during the decomposition reaction, the higher water content in the polymer composite material during burning.

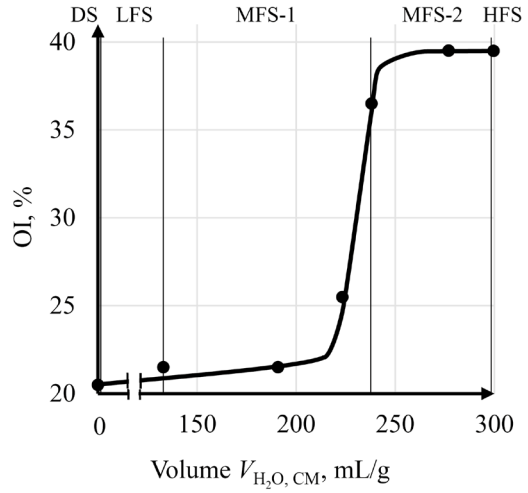
Since the burning of DFPCM is due to the exothermic depolymerization of EVA, it is of interest to determine the volume of water vapor per 1 g of PM needed to inhibit the burning process.

Figure 5 shows the dependencies of the volume of water vapor emitted during brucite decomposition per 1 g of PM ($V_{H_2O,PM}$, mL/g) on the flame-retardant filler content and generalized parameter Θ, which determines the DFPCM disperse structure type.

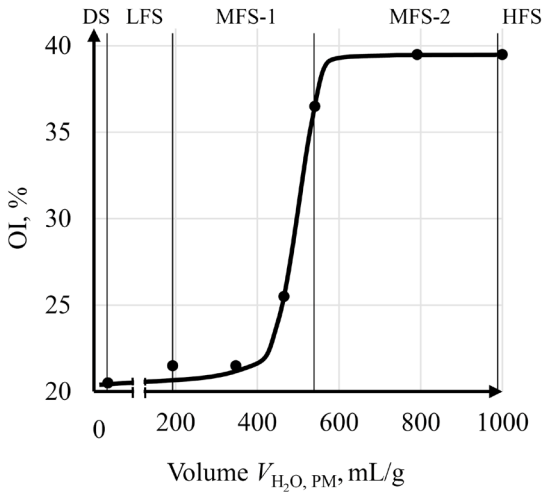
As can be seen from the obtained data, in order to obtain DFPCM with high OI (~40%) and the category V-0, the water vapor content per 1 g of PM should be at least 600 mL/g.

On the basis of the dependencies, which were obtained for the first time, it became possible to relate the OI of DFPCM with the volume of water vapor emitted during the decomposition of the EP 10R flame-retardant filler and the type of disperse structure (Fig. 6).

For the structure types of DS, LFS, and MFS-1 up to Θ ≥ 0.60 vol fract., the OI for EBA-based DFPCM is practically not increased (from 20.5 to 22%). A sharp increase in the OI (~2.0 times) occurs when more than 220 mL/g of water vapor is released in the area of change in the generalized parameter Θ from 0.60 to



(a)



(b)

Fig. 6. Dependence of the oxygenation index for DFPCM on the volume of water vapor released during the decomposition of EcoPiren® brucite: (a) by 1 g of PCM, (b) by 1 g of the polymer matrix.

0.40 vol fract., which corresponds to the transition of the MFS-1 structure to MFS-2 and HFS. The maximum OI value of 40% for the EVA-based DFPCM is reached at Θ ≈ 0.40 vol fract. and a water vapor emissionof 250 mL/g and $V_{H_2O,PM}$ = 600 mL/g. Further, as the volume of emitted water vapor increases [more than 250 (600) mL/g], the OI value for DFPCM with MFS-2 and HFS structures remains almost constant.

Thus, the optimum amount of water vapor to create a DFPCM with high OI value and resistance to burning is $V_{H_2O,CM}$ ≈ 250 mL/g and $V_{H_2O,PM}$ ≈ 600 mL/g, flame-retardant filler content of 0.36 vol fract., structure types are MFS-2 and HFS (Θ ≤ 0.40 vol fract.).

For the recommended OI value of ≈32% ([18] and Footnote 3), the cable insulation of DFPCM based on EVA + EP 10R can have an MFS-1 structure with Θ ≈ 0.47 vol fract. and a water vapor amount of $V_{H_2O,CM}$ ≈ 230 mL/g and $V_{H_2O,PM}$ = 512 mL/g.

Table 5 summarizes the OI and burning resistance as well as the characteristics of DFPCM based on EVA and EP 10R magnesium hydroxide (d_{av} = 25 μm and φ_{max} = 0.60 vol fract.) with different types of disperse structure.

The obtained results and new disperse structure model representations form a basis for designing the structure type, compositions of DFPCM with maximum value of OI and high burning resistance at known values of φ_{max}, coke residue, and amount of water vapor (V_{H_2O}) emitted from 1 g of dispersed flame-retardant filler.

It was shown in [19] that extruded and cast DFPCM are well processed into products if the condition Θ ≈ 0.50–0.60 vol fract. and the disperse structure of MFS-1 type (up to yield strength) is fulfilled.

Thus, in order to create high-tech and burning-resistant extrusion and injection-molded DFPCM, it is necessary to create an MFS-1 structure with ≈0.50–0.60 vol fract. and a flame-retardant filler content of at least 0.36 vol fract.

The main problem of increasing the generalized parameter Θ to 0.50–0.60 vol fract. at a constant value of φ_f (not less than 0.36 vol fract.) is related to the creation of a new dispersed flame-retardant filler with a given fractional composition, in which the packing parameter φmax should reach the value of 0.70–0.75 vol fract. (increasing from 0.60 to 0.75 vol fract.). However, we do not consider these issues in the present work.

The following is an algorithm for the design of DFPCM formulations using a flame-retardant filler based on EVA (OI = 20.5%) and magnesium hydroxide (EP) with a high OI value and resistance to burning.

Based on the research carried out and the fundamental dependencies established, a general algorithm for the design of compositions and a given type of DFPCM structure with flame-retardant fillers with high OI and resistance to burning can be proposed:

1. To select of PM with a determination of OI, burning resistance according to GOST, and TGA test.

2. To choose a flame-retardant filler, study it by differential thermal analysis and TGA and determine the main characteristics: the temperature of the decomposition start (T_{start}), the temperature of the loss of 10% of the mass (T_{10}), the temperature of the decomposition end (T_{end}), the temperature

Table 5. Structure parameters and resistance to burning DFPCM based on EVA and EP 10R (d_{av} = 5 μm, φ_{max} = 0.60 vol fract.)

Parameters	Types of DFPCM dispersed structure based on EVA + EP 10R								
	DF	LFS	MFS-1			MFS-2			HFS
Θ, vol fract.	0.95	0.75	0.60	0.50	0.47	0.45	0.40	0.30	0.20
φ_f, vol fract.	0.03	0.15	0.24	0.30	0.32	0.33	0.36	0.42	0.48
φ_f, wt fract.	0.07	0.31	0.45	0.52	0.55	0.56	0.59	0.65	0.70
$V_{H_2O,CM}$, mL/g	31.3	132.9	190.8	223.3	230.0	238.0	251.8	277.0	299.9
$V_{H_2O,PM}$, mL/g	33.7	192.6	346.9	465.2	512.2	540.9	614.1	791.4	999.7
OI, %	21.5	21.5	21.5	25.5	32	36.5	39.5	40.0	40.0
Category of resistance to burning	–	–	V-2	V-2	V-2	V-1	V-0	V-0	V-0

range of decomposition (ΔT), coke residue, and the volume of water vapor released from 1 g of flame-retardant filler (V_{H_2O}).

3. To determine the main characteristics of the dispersed flame-retardant filler: average particle diameter (d_{av}), particle shape ratio (k_e), specific surface area of particles (S_s), particle size distribution, density, and porosity.

4. To experimentally determine the packing parameter (k_p) and the maximum dispersed filler content φ_{max} according to the known methods for flame-retardant filler [17, 18].

5. To calculate the value of the generalized parameter Θ for DFPCM at a known value of φ_{max} for a flame-retardant filler with its various contents, provided $\varphi_f \leq \varphi_{max}$, according to Eq. (2):

$$\Theta = (\varphi_{max} - f^3\varphi_f) / \varphi_{max} \ , \qquad (2)$$

where Θ is the share of PM to form a layer between the dispersed particles in the DFPCM; φ_{max} is the maximum content of the dispersed filler; φ_f is the content of the dispersed filler; $f^3 = (1 + 2\delta / d)$ is the ratio of the boundary layer thickness (δ) to the diameter (d) of the dispersed particles. For large, macro, and microparticles, the coefficient $f^3 \approx 1$.

6. To classify DFPCM according to the structural principle and determine the type of disperse structure of DFPCM (DS, LFS, MFS-1, MFS-2, and HFS) according to the values of the generalized parameter Θ at different contents of φ_f.

7. To calculate the flame-retardant filler content ($\varphi_{vol\ f}$, vol fract.) for each type of DFPCM disperse structure by Eq. (3):

$$\varphi_{vol\ f} = (1 - \Theta) \cdot \varphi_{max} \ . \qquad (3)$$

8. To calculate the flame-retardant filler content in mass units ($\varphi_{wt\ f}$, wt fract.) and determinate the compositions for each type of DFPCM disperse structure by Eq. (4):

$$\varphi_{wt\ f} = \frac{\varphi_{vol\ f}}{\varphi_{vol\ f}\left(1 - \frac{\rho_p}{\rho_f}\right) + \frac{\rho_p}{\rho_f}} \text{ wt fract.} \ , \qquad (4)$$

where ρ_f and ρ_p are the densities of the flame-retardant filler and PM.

9. To calculate the volume of released water vapor ($V_{H_2O,CM}$ and $V_{H_2O,PM}$) during the decomposition of the flame-retardant filler in DFPCM with

different structure types and flame-retardant filler content according to Eqs. (5) and (6):

$$V_{H_2O,CM} = V_{H_2O} \cdot \varphi_{wt\,f}, \quad (5)$$

$$V_{H_2O,PM} = V_{H_2O} / \varphi_{wt\,p}, \quad (6)$$

where $\varphi_{wt\,p}$ is the PM content in mass units.

10. To determine the optimum DFPCM composition and structure with high OI and resistance to burning (V-0) under the conditions:

$$V_{H_2O,CM} \geq 250 \text{ mL/g},$$
$$V_{H_2O,PM} \geq 600 \text{ mL/g}.$$

CONCLUSIONS

For the first time, the fundamental dependencies on OI and burning resistance of DFPCM based on EVA with flame-retardant fillers on the case study of EcoPyrene® magnesium hydroxide (brucite) were obtained. This forms the basis for determining the construction, type and parameters of disperse structure with the main characteristics of resistance to burning and OI.

The introduction of magnesium hydroxide (brucite) in the optimal amount in the EVA allows the OI to be increased from 20.5 to 40% (~2 times). The critical water vapor content for maximizing the OI value (up to ~40%) for DFPCM, which is at least $V_{H_2O,CM} \approx 250$ mL/g and $V_{H_2O,PM} \approx 600$ mL/g, was established.

The maximum burning resistance and OI are achieved for DFPCM based on EVA + EP 10R with a generalized parameter $\Theta \leq 0.40$ vol fract. for the MFS-2 structure type and the flame-retardant filler content $\varphi_f = 0.36$ vol fract. (0.59 wt fract.).

Authors' contributions

K.A. Brekhova – conducting experiments, processing experimental data;

I.D. Simonov-Emel'yanov – the research concept, processing experimental data;

A.A. Pykhtin – correction of the research concept.

The authors declare no conflicts of interest.

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