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ORIGINAL ARTICLE

A novel synergistic phosphorus-nitrogen flame retardant for epoxy compositions and flame-retardant coatings

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ABSTRACT

The interaction of hexa methoxymethyl melamine with ammonium dihydrogen phosphate at 100°C was investigated. It is shown that under the action of an adduct of ammonium dihydrogen phosphate and hexa methoxymethyl melamine, homo condensation of the latter occurs and encapsulation of the unreacted part of ammonium dihydrogen phosphate occurs. The maximum polymer yield output corresponds to the threshold at the atomic ratio N:P=1:1 in the combined product. Encapsulated complex nitrogen-phosphorus-containing flame retardants were synthesized, which are used to determine fire resistance of epoxy resin cured with polyethylene polyamine. The optimal composition of complex flame retardants (atomic ratio close to 1:1) were found, which provides the fire resistance of the composite material V0 (UL 94 test) and the oxygen index of 32-36% with a 20% mass fraction of flame retardants in the composite material. The formation of protecting char on the surface of the substrate in the flame of a gas burner allows the composite material to be used as a flame-retardant coating for different constructions.

KEYWORDS

Flame retardant; Burning; Oxygen index; Epoxy resin; Hexa methoxymethyl melamine; Ammonium dihydrogen phosphate; Flame retardant coating

ARTICLE HISTORY

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Introduction

Epoxy resins (ER) are widely used in various industries due to their valuable properties - low shrinkage during curing, high adhesion to various materials, chemical resistance, good physical and mechanical and excellent dielectric properties. ER are used for the manufacture of filling and sealing compounds, putties, adhesives, lacquer films and coatings, binders for carbon, glass and basalt plastics, cast products and many other materials. However, the combustibility of epoxy-containing compounds and composite materials significantly limits their use in a number of areas.

Researchers pay a lot of attention to reducing the combustibility of ER. For this purpose, halogen-containing compounds were previously used (sometimes in combination with antimony oxide [1]. However, the possibility of the formation of toxic combustion products of such materials requires development and use of environmentally friendly flame retardants. Inorganic compounds (hydroxides, oxides, carbonates, etc.) provide a reduction in flammability with a sufficiently high content in composites, while negatively affecting their physical and mechanical characteristics. The main directions of research in the field of reducing the flammability of polymers and composite materials are presented in the review.

The most promising were organic phosphorus compounds in combination with a number of other compounds modified by heteroatoms (P, N, B, S) [2]. Phosphorus plays a key role in the development of new effective flame retardants, mainly due to its chemical versatility: it can act both in the condensed and in the gas phase, as additives or reactive components, in various degrees of oxidation and in synergy with numerous auxiliary elements without losing valuable properties. The attention of researchers is also attracted to polymer flame retardants, which have a higher temperature resistance compared to low-molecular weight analogues. In addition, the overlap of the temperature ranges of the destruction of flame retardants and polymer matrix, as a rule, aids reducing the flammability of composite materials.

Flame retardants containing heteroatoms, such as nitrogen, silicon, sulfur and boron in combination with phosphorus, provide a wide range of specific interactions compared to decomposition by purely phosphorus-containing compounds [3]. One of the main areas of research is the search for synergistic effects of reducing flammability due to a combination of compounds containing heteroatoms [4-9].

The combination of phosphorus and nitrogen (P-N) compounds is one of the most promising areas of research, since in some cases it has a synergistic effect due to the crosslinking of flame retardants with polymer chains of the matrix and contributing to the retention of phosphorus in the condensed phase [10-16]. This effect provides higher heat resistance and char residue. The two most well-known P-N structures are phosphoramide and cyclotriphosphazenes [18]. The main advantages of phosphoramides in comparison with similar phosphates are their high temperature resistance, low volatility and high viscosity due to hydrogen bonds. These properties make it possible to increase the density of the entire system and reduce mass loss during combustion, which increases the role of the condensed phase in the formation of a core residue after the decomposition of the entire system.

Markwart et al. [19] synthesized flame retardants with an exact ratio of phosphorus, nitrogen and oxygen atoms (phosphate ($POO(OR)_3$), phosphoramidate ($P{=}O(OR)_2(NHR)$), phosphordiamidate ($P{=}O(OR)(NHR)_2$), phosphoramide ($P{=}O(NHR)_3$). In the simulated fire scenario,

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phosphate demonstrated the highest efficiency in epoxy resins and was effective in both the gas and condensed phase. The flame-retardant activity in the gas phase is explained by the predominant mechanism of *cis*-elimination during combustion as a result of pyrolysis. When P–O bonds were replaced by P–N bonds, the *cis*-elimination process was slowed down, and the hydrolysis of P-N accelerated the decomposition of the matrix. An amide with three P-N bonds showed the highest activity in the condensed phase due to the rupture of P-N bonds during burning.

Schartel et al. [20] studied reactions in the condensed phase of seven structurally and chemically modified P and N containing flame retardants in cured epoxy resins. Mechanisms of reactions when using various flame retardants are proposed. According to the two-steps model the both steps are influenced and controlled by parameters including heating rate, decomposition and hydrolysis temperatures, and reactivity.

A number of phosphorus-nitrogen-containing epoxy resin hardeners with self-intumescence function [21-24], hyperbranched flame retardants with multifunctional properties in the process of polymer combustion [25-27], flame retardants modified with organosilicon compounds [28] and graphene [29] are proposed as new research directions.

The promising area of research is the creation of complex flame retardants containing phosphorus and nitrogen. A number of works show the synergistic effect of such flame retardants. The most commonly used are reactions of melamine and its derivatives with phosphorus-containing compounds. One of the most effective flame retardants for epoxy resins is melamine polyphosphate, especially in combination with synergistic additives, in particular with melamine poly (metal phosphates) [30], produced under the brand name "Safira".

Another approach to the problem of reducing the flammability of epoxy compounds is the use of ammonium polyphosphate encapsulated in melamine-formaldehyde resin. The properties of a modified 9,10-dihydroox-10-phosphaphenanthrene-10-oxide (DOPO) epoxy resin cured with phosphorus-containing amine with encapsulated ammonium polyphosphate were studied [31]. Various combinations of components were used in the work and more rigid, but relatively fragile materials with increased fire resistance (rating V_0 according to UL 94 standard), increased Young's modulus and tensile strength were obtained. At the same time, the glass transition temperature remained practically the same.

These data indicate the expediency of searching for and further studies of phosphorus-nitrogen-containing flame retardants with synergistic effect. The purpose of this work is to study nonstoichiometric interaction of the hexa methoxymethyl melamine resin with ammonium dihydrogen phosphate and to find the most effective ratio of components in the preparation of a complex flame retardant for cold-cured epoxy resin.

Experimental

Scanning electron microscopy (SEM) of the samples was performed using a JCM-6000 PLUS microscope equipped with an energy-dispersive spectrometer at accelerating voltages of 5-15 kV. The samples were applied in powder form to a conductive carbon adhesive tape.

Gel permeation chromatography (GPC) analysis was carried out on a chromatographic system consisting of a high-pressure pump STEYER series 2 (Aquilon, Russia), a refractometric detector Smart line RI 2300 (KNAUER, Germany) and a thermostat JETSTREAM 2 (KNAUER, Germany) at temperature of 40°C (± 0.1°C).

The eluents are tetrahydrofuran (THF) or toluene +2% THF, the flow rate is 1.0 ml/min. Columns with a length of 300 mm and a diameter of 7.8 mm (300x7.8 mm) are filled with Pheno gel sorbent (Phenomenex, USA), particle size is 5 microns, pore size varied from 103 to 105 A.

The analysis results were processed using the Multi Chrome 1.6 GPC software (Ampersand, Russia) when calculating MMD, or Uni Chrom 4.7 (Belarus).

Physico-mechanical tests of samples in the form of strips with a width of 10 mm and a thickness of 5 mm were carried out on a Shimadzu AGS-H tensile machine (Japan) at a tensile speed of 2 mm/min.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) measurements were carried out on the STA 449 F3 Jupiter (NETZSCH) instrument in air and argon atmosphere. IR spectra were recorded on a Nicolet device.

Ammonium dihydrogen phosphate (ADGP) of qualification "pure" and hexa methoxymethyl melamine resin ITAMIN HM-3 (Galstaff Multiresine, Italy) were used as received. The characteristics of the ITAMIN HM-3 resin are given in Table 1.

Table 1. Current commercially available ultrasound contrast agents.

Characteristics (reported by producer)	Description
Appearance	Clear or slightly muddy liquid
Theoretical solid content, %	100
Practical solid content, %	98-100
Esterifying alcohol	Methanol
Gardner Chromaticity	Max. 1
Free formaldehyde,%	Max. 0,2
Acid number, mg KOH/1 g	Max. 1
Brookfield viscosity at 25° C, MPa/s	2600-5800
Gardner viscosity at 25° C	Y-Z2
Density at 25° C, g/cm^3	1,2
Water solubility at 25° C	Min. 1/50
Solubility in xylene at 25° C	Min. 1/100
pH at 25°C	8,2

HM-3 resin was obtained by the interaction of melamine with formaldehyde in a methanol medium according to the scheme Figure 1.

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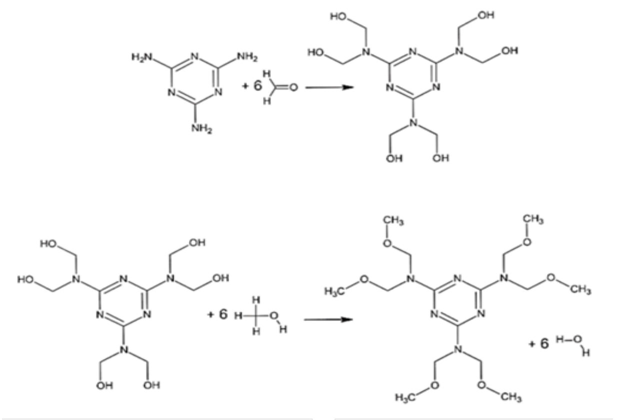

Figure 1. HM-3 resin synthesis scheme.

However, according to the GPC data (Figure 2), the HM-3 resin is a mixture of oligomers, with the following values of molecular weights: M_n=398, M_ω=625, polydispersity index M_ω/M_n =1.5709. The GPC data of HM-3 resin are given in Table 2.

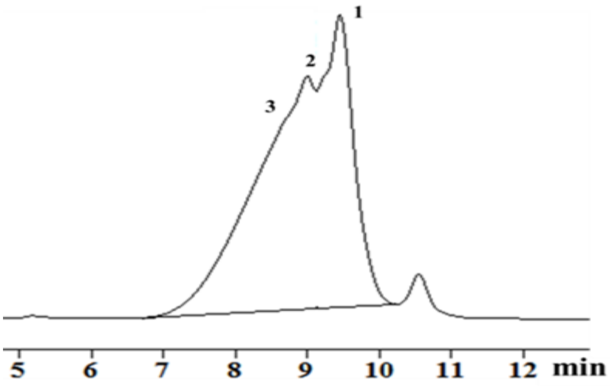

Figure 2. The GPC of HM-3 resin.

Taking into account approximately the same increment of molecular weights of oligomers, the predominant existence of monomers, dimers and trimers of hexamethoxymethylene melamine should be assumed. At the same time, the average functionality of the HM-3 sample was 5.2.

Table 2. The GPC data of the HM-3 resin.

Degree of condensation	Exit time, min	Molecule, Dalton	Concentration,%
>2	8,734	600	35,5
2	9,027	400	23,6
1	9,478	250	40,9
Total	-	-	100

The composition of the samples for the synthesis of HM-3 - ADGP adducts is presented in Table 3. The adducts were obtained in porcelain crucibles with preliminary mixing of the components, followed by heating to 100°C and exposure at this temperature for 5 hours. The exposure time is determined by bringing the samples to a constant mass at 100°C. The equivalent molecular weight of HM-3 is calculated taking into account the oligomeric composition of EHM-3 = 56.3. The functionality of ADGP is 2, therefore EADGP =61.5. All the products obtained are foamed clear solids (Figure 3).

Results and Discussion

Table 3. Composition of samples for obtaining HM-3 -ADGP adducts and mass loss in terms of HM-3 mass at 100°C for 5 h.

Sample	GP-1	GP -2	GP -3	GP -4	GP -6	GP -8	GP -10
HM-3, g	10	10	10	10	10	10	10
ADGP, g	1	2	3	4	6	8	10
HM-3, equ.	0,179	0,179	0,179	0,179	0,179	0,179	0,179
ADGP, equ.	0,016	0,032	0,048	0,064	0,096	0,124	0,160
N:P *	7,7	4.0	2,5	2,0	1,5	1,2	1,0
N:P **	7,3	3,7	2,2	1,7	1,2	0,88	0,69
Mass loss HM-3,%	20,4	21,8	22,6	23,9	24,4	24,6	23,8

*N:P- ratio to the sum of nitrogen atoms in sample; ** N:P- ratio to the sum of nitrogen atoms in HM-3

Figure 3. Appearance of adducts after exposure at 100° C for 5 hours.

The choice of adduction conditions in the hexamethoxymethylmelamine (viscous liquid)-ammonium dihydrogen phosphate (solid) system is based on thermogravimetry data. It is known that when ADGP is heated, the following reactions occur sequentially [33]:

-at 140°C: $2NH_4H_2PO_4 \rightarrow H_2P_2O_7 + H_2O$

-at 170°C: $3NH_4H_2PO_4 \rightarrow (NH4)_3H_2P_3O_{10} + H_2O$

-at 190°C: $NH_4H_2PO_4 \rightarrow NH_4PO_3$

DSC curve of ADGP (Figure 4), shows three endothermic peaks at 168, 177 and 206°C, while below 140°C thermal effects and mass loss are practically absent. DSC curve of the GP-4 sample shows two endothermic peaks at 139 and 197°C (Figure 5), accompanied by a stepwise loss of mass in the corresponding

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temperature ranges. The decrease in the temperature at the beginning of the mass loss of GP-4 in comparison with ADGP obviously indicates the interaction of reagents with the release of volatile products.

Hexa methoxymethyl melamine (HM-3) is a condensation product of melamine and formaldehyde in a methanol medium. Depending on the synthesis conditions, along with the formation of a monomer, dimers and trimers are present in the resin, which is confirmed by the above GPC data. During storage, the formation of dimers and trimers with the release of formaldehyde and methanol is also possible. The presence of dimers and trimers reduces the functionality of the HM-3 to some extent, so the equivalent mass should be calculated taking into account the reduced functionality.

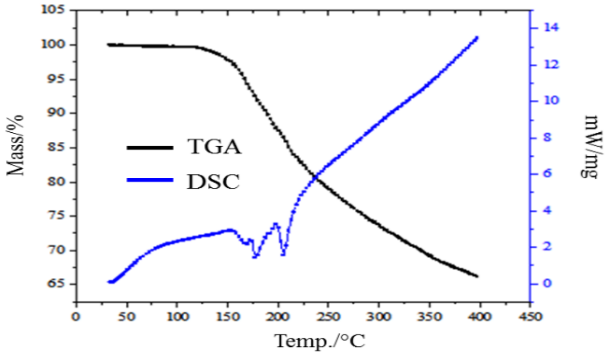

Figure 4. DSC and TGA of ADGP.

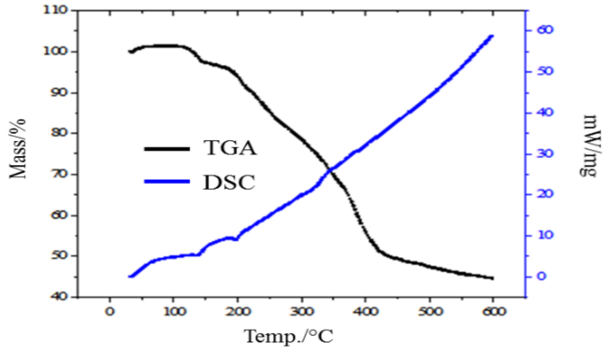

Figure 5. DSC and TGA of GP-4.

When heating HM-3 to 130°C, the mass loss was about 2%, which indicates the absence of a homo condensation reaction under these conditions. It has been shown that this occurs at 150°C in the presence of p-toluene sulfonic acid with the release of methanol (17%) and formaldehyde (83%) or in the presence of basic catalysts, with a mass loss of 29% [33]. At 100°C in the presence of p-toluene sulfonic acid, mass loss is not significant even after 73 hours of exposure.

Taking into account the data obtained, insignificant side reactions of individual components are practically absent at 100-120° C. The kinetics of the adduction process was studied at 100° C (Figure 6 and b). The mass loss of all samples reaches a plateau after a 4-hour exposure. For all samples, the values of mass loss are comparable (Figure 7 a and b) regardless of the mass fraction of ADGP, which indicates partial homo condensation of HM-3 under these conditions. Nevertheless, based on the magnitude of the mass loss, the degree of homo condensation of HM-3 is maximal at approximately the same atomic ratio of N and P (Figure 6 a). At the same time, the threshold is reached, when a further increase in the mass fraction of ADGP leads to a decrease in the degree of homo condensation.

The role of ADGP as a catalyst for the polycondensation

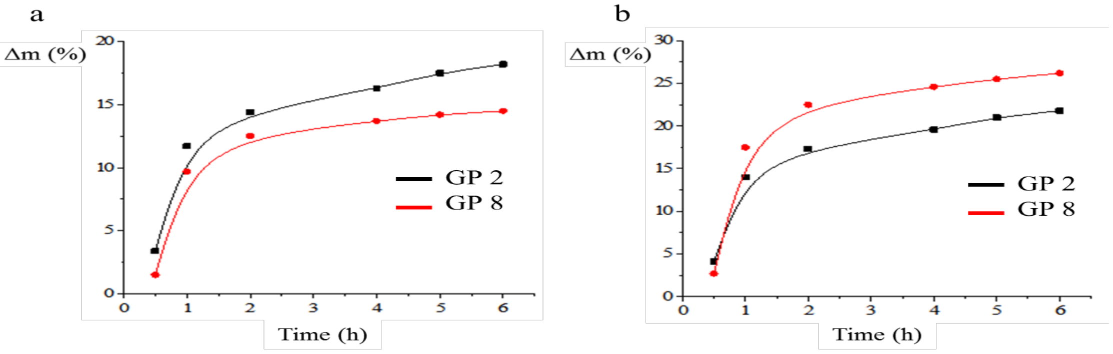

Figure 6. The dependence of the mass loss(Δm_1) of the sum of the components of samples GP-2 and GP-8 (a) and the mass loss (Δm_2) of HM-3 in samples GP-2 and GP-8 (b) on the exposure time at 100°C.

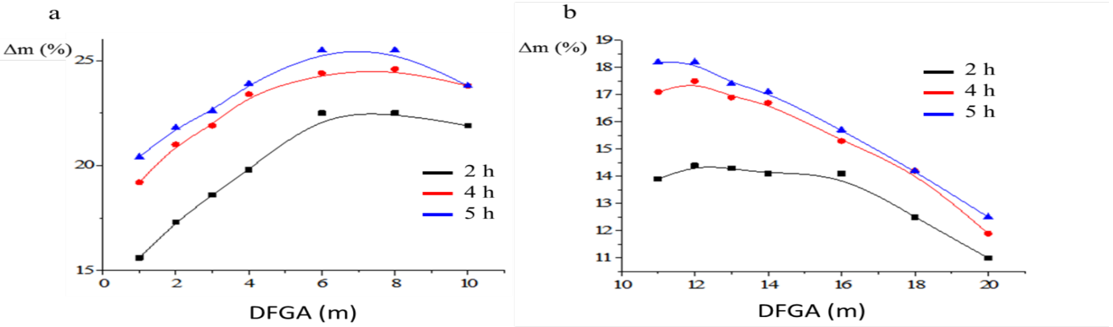

Figure 7. The dependence of the mass loss of the samples on the mass of DGFA (a) and the dependence of the mass loss of the samples on the total mass (b).

process can be explained based on the following data. Diammonium hydrophosphate (DAGP), whose functionality, unlike ADGP, is equal to 1, does not catalyze the HM-3 homo condensation reaction at 100°C. Consequently, ammonium nitrogen in this case does not exhibit catalytic activity, and monofunctional DAGP in the case of interaction with HM-3 acts as a telogen, thereby limiting the growth of the molecular weight of HM-3. But when ADGP interacts with HM-3, it is possible to form secondary amines - bridging bonds between ADGP and HM-3. Therefore, the catalysts of HM-3 homo condensation seem to be the adducts of ADGP with HM-3 formed at the initial stage of the reaction. The absence of adduct formation in the HM-3 - DAGP system may also be due to the lower reactivity of the hydroxyl group of DAGP compared to the hydroxyl groups of ADGP. Catalysis by secondary amines present in HM-3 dimers and trimers can be explained by certain increase in the viscosity of HM-3 during its storage. The partial interaction of the components at the initial stage is indicated by the presence of weak endothermic peaks during subsequent heating of GP-4 above 100°C (Figure 5), which can be explained by the transition of the system from the diffusion to the kinetic regime and an increase in the reaction rate of ADGP with HM-3.

The unreacted part of ADGP is enveloped by the resulting polymer by analogy with encapsulation (Figure 8) and at elevated temperature, as it transitions from the diffusion to the kinetic regime, it can also react with HM-3 and accelerate the process of homo condensation.

According to IR spectroscopy data (Figure 9), the GP-8 sample the narrow intense absorption band of HM-3 ($\delta_s CH_3$) at 1505 cm-1, present in the individual HM-3 spectrum, is practically absent. This means the formation of an almost completely cross-linked polymer due to the formation of bridging bonds by secondary amines (a very weak peak in the region of 3111 cm^{-1}). A narrow intensive peak at 1542 cm^{-1} (triazine ring) and 1073 cm^{-1} (ADGP0) indicate the presence of both precursors in the flame-retardant composition. Absorption bands in the IR spectra of phosphorus-containing compounds are usually difficult to identify due to overlapping signals of P=O, P-O, P-N bonds in the region of 1200-900 cm^{-1}. In addition, the absorption bands of these bonds are usually present in the form of doublets. In this regard, the most intense signal at 1072 cm^{-1} is represented by a superposition of at least five absorption bands, that are very difficult to isolate.

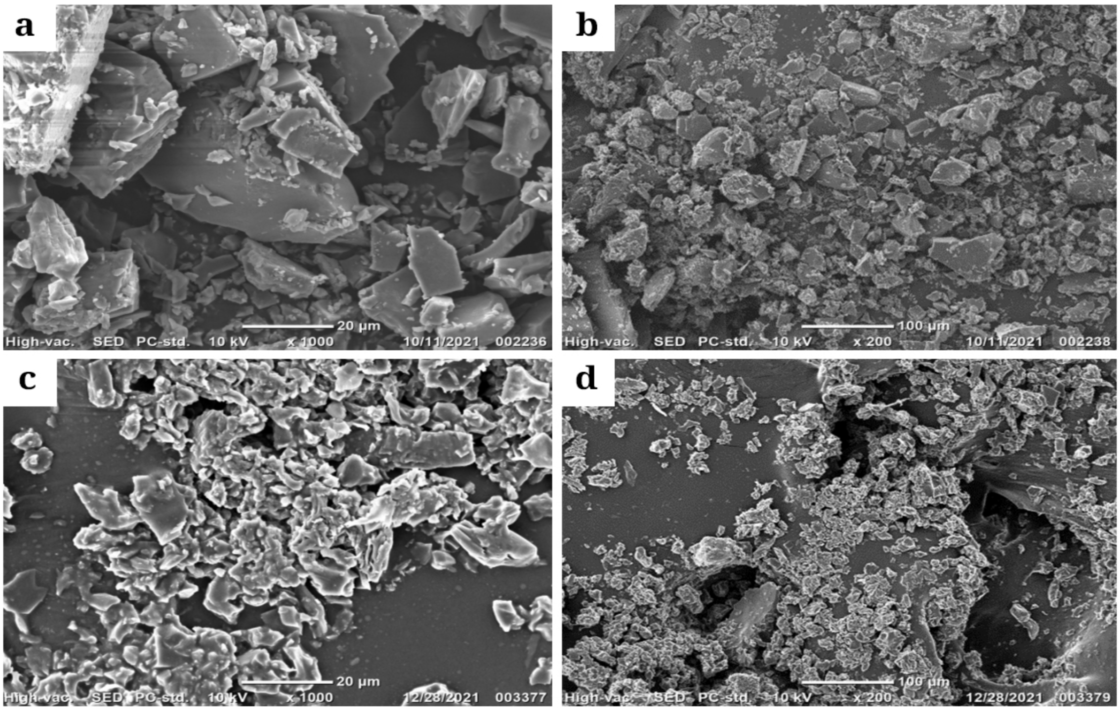

Figure 8. Microphotographs of DGFA (a,b) and GP-8 (c,d).

According to SEM data, the ratio of nitrogen and phosphorus atoms of encapsulated ADGP samples is approximately 10:1, which indicates a sufficiently high degree of encapsulation (Figure 10).

The paper presented the results of comparative tests of fire

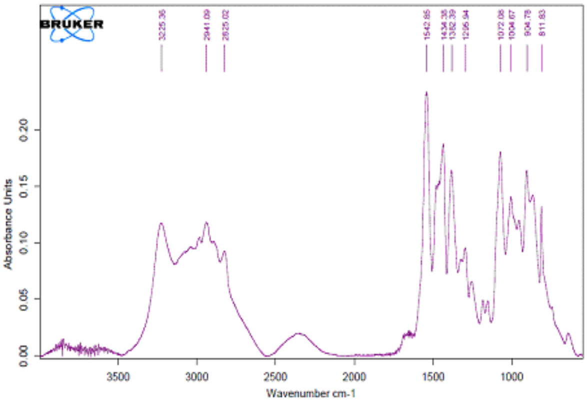

Figure 9. IR spectra of GP-8 sample.

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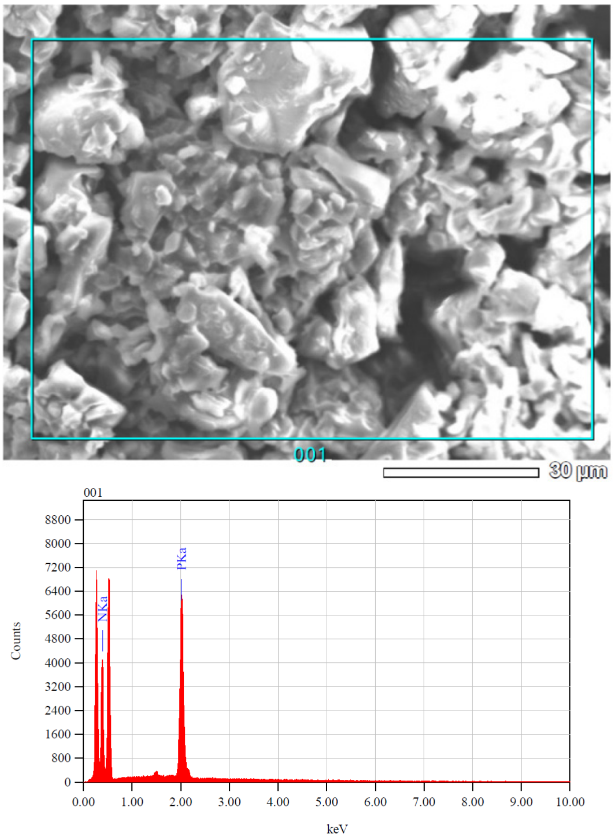

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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.5795
Element         (keV)    Mass%    Sigma    Atom%   Compound    Mass%   Cation          K
 P K            2.013    22.24     0.13    11.46                                 19.5713
 N K            0.392    77.76     0.42    88.54                                 80.4287
Total                   100.00            100.00
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Figure 10. GP-8 microphotograph and the results of elemental analysis.

resistance of composite materials based on epoxy resin and dicyandiamide at 20% content of some commercial flame retardants. In this work, a composition based on epoxy resin and polyethylenepolyamine (12%) with a 20% content of some GP brand adducts was used as a model (Table 3) [30].

The test samples were prepared by mixing all the components and thoroughly grinding in a porcelain mortar to a homogeneous consistency. The curing took place for 24 hours at room temperature in fluoroplastic molds of the corresponding configurations, followed by heat treatment at 100°C for 1 hour. Thus, the appearance of the EGP-36 sample (Figure 11) is an opaque yellow surface with visible dispersed particles of complex flame-retardant GP-8. The appearance of the samples of the entire test series of samples is the same (Figure 11).

According to the TGA and DSC data of the EPG-36b (air) and EPG-36a (argon) samples (Figure 12), the exothermic peak at 262°C should be attributed to the post-curing of epoxy resin, since it is present on the DSC curve in the argon atmosphere and is not associated with thermal oxidation processes. At this temperature, the transition of reactions in the material from the diffusion to the kinetic regime probably occurs. Thermooxidation processes in the EPG-36b sample begins around 300°C, and thermolysis of the EPG-36a sample starts at 350°C. The explosive nature of this process leads to a greater loss of mass compared to the loss of mass of the sample in air, when thermal oxidative degradation takes place under milder conditions and conditions are created for pyrolysis with the formation of difficult-to-burn polyaromatic compounds or elemental carbon. The course of pyrolytic reactions is facilitated by repeated foaming, as evidenced by the formation of a foam-coke rod when processing a small sample of composite material with a gas burner flame (Figure 13).

The data of TGA and DSC of some composite material

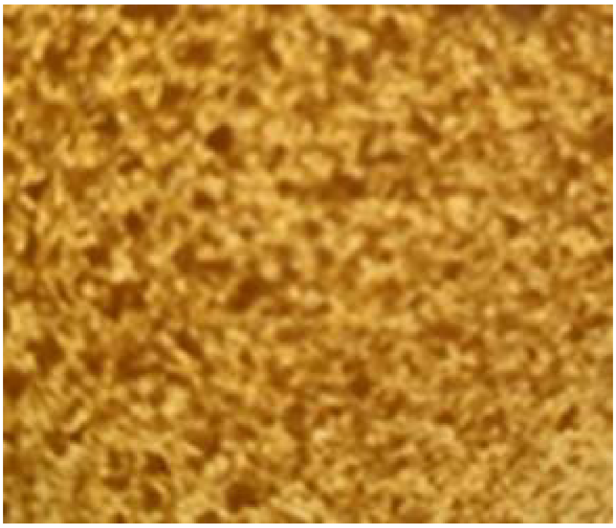

Figure 11. Microphotograph of the cured sample EGP-36.

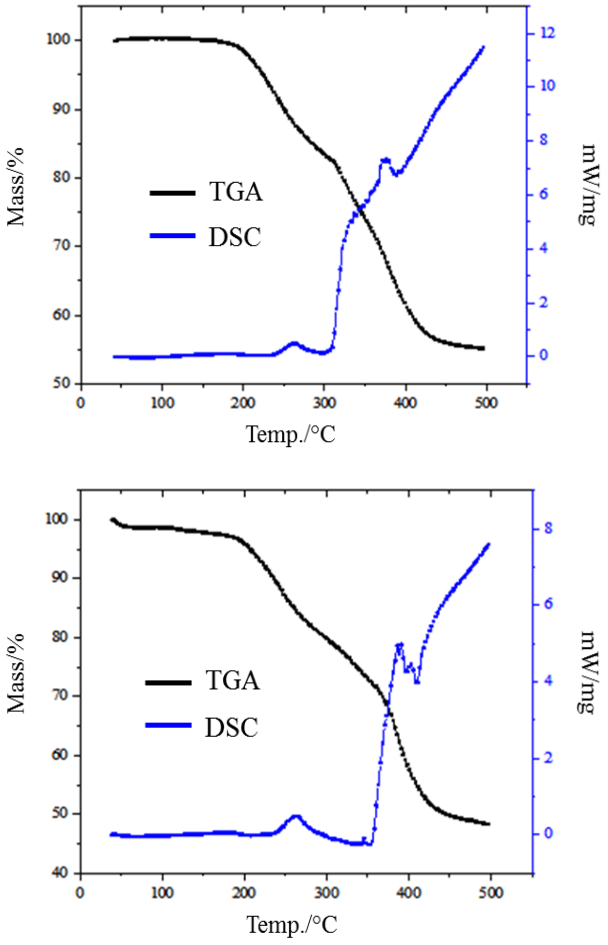

Figure 12. TGA and DSC curves of the EPG-36 sample in air (a) and argon atmosphere (b).

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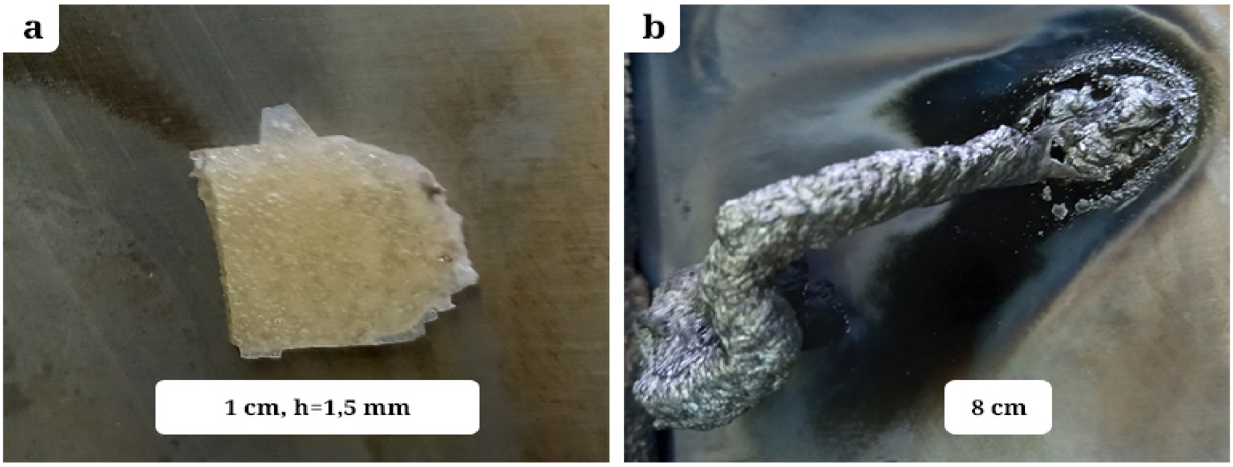

Figure 13. Sample EPG-36 (a) and its foaming in the flame of a gas burner (b).

samples, depending on the mass fraction of ADGP in the flame retardant, are given in (Table 4). As the mass fraction of ADGP increases, the temperature of post-curing decreases, which indicates the catalysis of ADGP not only of the HM-3 homo condensation process in flame retardants, but also of the process of post-curing of the epoxy composition at elevated temperature. However, with an equivalent excess of ADGP to HM-3, the thermal effect of the curing reaction decreases and its temperature significantly decreases. This state of the sample corresponds to the threshold in obtaining adducts HM-3 and ADGP (Figure 8). Value of the oxygen index of EPG samples depending on the mass fraction of ADGP in flame retardant also correlated with previously described regularity (Table. 5).

Resistance to burning of composite materials EPG samples

Table 4. Data of TGA and DSC composite materials with 20% flame retardant content.

Sample No.	Mass fraction of DGFA in flame retardant, %	$t/\Delta m_{5}$	$t/\Delta m_{15}$	$t/\Delta m_{30}$	$t/\Delta H$, J/g	The residue at 500° C, %
EPG-31	10	69	186	338	304/-35	38
EPG -32	20	69	186	338	267/46	40
EPG -33	28,5	70	186	338	267/41	41
EPG -36b	44	71	185	339	262/53	55
EPG -36a	44	71	187	338	262/78	48
EPG -37	50	70	186	338	248/31	57

Table 5. Fire resistance assessment of composite materials.

Criteria conditions	UL94 Vertical Burning Test								
	V_0	V_1	V_2	EGP-31	EGP-32	EGP-33	EGP-35	EGP-36	EGP-37
Total flaming combustion for each specimen, $t_{\text{г}}$, c	<10	<30	<30	>10	>10	>10	7	5	>10
Total flaming combustion for all 5 specimens of any set, $t_{\text{сг}}$, c	<50	<250	<250	<250	>250	>250	76	42	>250
Flaming and glowing combustion for each specimen after second burner flame application $t_{\text{зг}}$, c	<30	<60	<60	>60	>60	>60	4	3	>60
Glowing or flaming combustion of any specimen to holding clamp	-	-	-	+	+	+	-	-	+
Cotton ignited by flaming drips from any specimen	-	-	+	-	-	-	-	-	+
Test results				-	-	-	V_0	V_0	-
Oxygen index, %	-	-	-	16,7	18,4	20,8	31,9	34,4	31,6
Mass fraction of ADGP in flame retardant, %	-	-	-	10	20	28,5	37,5	44	50

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(Figure 14) were evaluated for compliance with the requirements of standard UL 94 (Table. 5).

After the first application of the flame, all test samples were extinguished within 1-5 seconds. After the second application of the flame, all samples, with the exception of EPG-35 and EPG-36, burned to clamps, but without the formation of burning droplets. The V_0 category corresponds to the EPG-35 and EPG-36 samples. The ratio of phosphorus and nitrogen atoms in the flame retardant is close to 1:1. In this case, the maximum yield of nitrogen-containing phosphorus compounds in the form of a strong heat-resistant ceramic-like structure is expected. Obviously, these structures play a key role in creating an effective barrier in the form of foam, limiting oxygen access to the substrate surface and creating favorable conditions for pyrolysis of the organic component of the composite material.

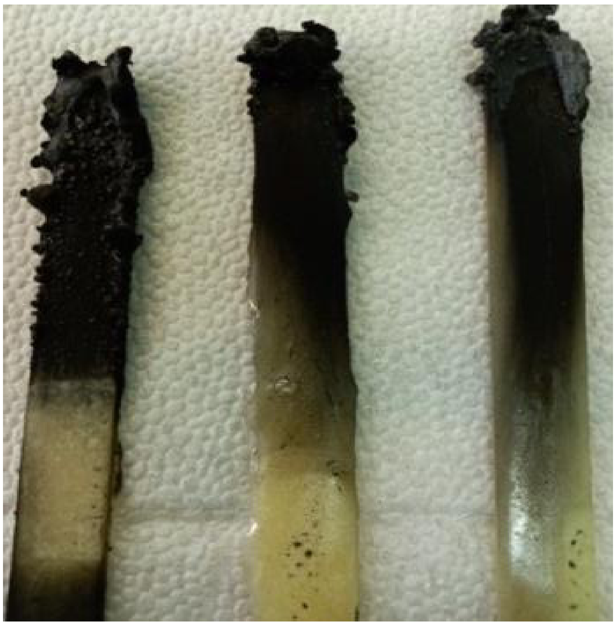

Figure 14. Appearance of samples after testing according to UL 94 standard: from left to right - EPG-32; EPG-36; EPG-37.

The results of physical and mechanical tests of EPG-36 sample are presented in (Table 6). According to the results, the stiffness of EPG-36 samples is significantly lower compared to the samples without flame retardant. The introduction of flame retardant increases the elongation at break 5-6 times and has a plasticizing effect on the cured composite material. The tensile stress at break, which is most reduced in EPG-36, can be increased by using other cold curing hardeners, for example, triethylenetetramine.

Table 6. Physical and mechanical properties of EPG-36 sample.

Sample	$б_{P}$, MPa	$\varepsilon_{p, \%}$	E_{o}, MPa	$б_{сж,}$ MPa	$\varepsilon_{сж.\%}$
EPG-36	14,0	11,5	345	82,5	34
Without fire retardant	50	2	-	113	-

Conclusions

The properties of hexa methoxymethyl melamine and ammonium dihydrogen phosphate as precursors for the synthesis of a complex phosphorus-nitrogen containing flame retardant have been studied. A method was developed for obtaining encapsulated complex flame retardants at 100°C with a different ratio of phosphorus and nitrogen atoms. Data on the kinetics of mass loss over time of samples with different component ratios indicate that the reaction of hexa methoxymethyl melamine homo condensation was catalyzed by HM-3 and ADGP adducts. A threshold value for reducing mass loss with an increase in the mass fraction of ADGP has been found, which corresponds to the ratio P:N =1:1.

The addition of the complex flame retardants with a ratio of HM-3: ADGP = 10:(7-9) by weight into the epoxy resin - polyethylene polyamine model system provides epoxy materials with the rating V_0. The oxygen index values are also maximal for these ratios. The conclusion is made about the optimal atomic ratio of phosphorus and nitrogen in a complex flame retardant, which provides the maximum yield of ceramic-like phosphorus-nitrogen-containing structures as one of the key thermo- and fire-resistant components of the foam formed when exposed to flame.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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