

Development of Fire-Resistant Functional Coatings Based on Phosphorus- and Boron-Containing Oligomeric Flame Retardants

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Abstract: This scientific paper investigates the synthesis processes of novel phosphorus- and boron-containing oligomeric flame retardants (PBOs) in the presence of boric acid, orthophosphoric acid, polyfunctional amines, and aluminum hydroxide, as well as the technology for obtaining high-performance fire-resistant polymer-mineral composite coatings based on them. The chemical structure of the synthesized oligomers and compositions, as well as the nature of the interaction of functional groups, were comprehensively studied using FTIR spectroscopy, thermal (TGA/DTG), and scanning electron microscopy (SEM) methods. The obtained results proved that due to the synergistic effect of phosphorus and boron elements, the thermal stability of the polymer coating increases significantly, leading to the formation of a dense mineral-coke barrier on the surface under the action of high temperatures and fire. It was demonstrated that the developed functional coatings exhibit high efficiency in fire protection of industrial facilities and building structures.

Keywords: Phosphorus-Boron-Containing Oligomer, Flame Retardant, Fire-Resistant Coating, Polyacrylate Matrix, Vermiculite, Bentonite, Synergistic Effect, Thermogravimetric Analysis.

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I. INTRODUCTION

The rapid development of modern science and high-tech industrial sectors is sharply increasing the requirements placed on polymeric materials, building structures, and special protective coatings [1]. Statistical data and analytical reports show that the majority of accidental fires occurring in industrial facilities, residential buildings, and vehicles are associated with the rapid ignition and propagation of polymer- and organic-based materials [2]. In this regard, increasing the fire resistance of materials and developing highly efficient, environmentally safe, and economically viable flame retardants is one of the most pressing scientific and practical tasks of modern polymer chemistry and materials science [3].

It is known that although traditionally used halogen-containing flame retardants possess high efficiency, the release of toxic hydrogen halides, corrosively active compounds, and toxic smoke during their thermal degradation severely restricts environmental and sanitary-hygienic requirements [4]. This necessitates the development

of alternative halogen-free protective systems containing phosphorus, nitrogen, and boron, which possess high thermal stability while exhibiting intumescent properties. It is widely acknowledged in the scientific literature that the combined (synergistic) effect of phosphorus and boron elements forms a dense, thermally extremely stable carbonaceous protective layer on the polymer matrix, sharply blocking the flow of heat and oxygen [5].

At the same time, an analysis of the literature shows that in many cases, because flame retardants are physically mixed with the polymer, their migration from the surface during operation or a reduction in mechanical strength is observed [6]. The technology of obtaining high-performance composite coatings by introducing phosphorus and boron compounds into a single macromolecular oligomeric chain in the presence of specific polyfunctional amines and modifying components (synthesis of oligomeric flame retardants), as well as integrating them with local polyacrylate binders and mineral fillers (vermiculite, bentonite), needs to be comprehensively and thoroughly studied [7].

The purpose of this scientific research is to develop synthesis processes for novel phosphorus- and boron-containing oligomeric flame retardants (PBOs), to study their chemical structure via FTIR spectroscopy, thermal (TGA/DTG), and microstructural (SEM) analyses, and to create high-performance fire-resistant functional coatings based on them.

II. LITERATURE REVIEW AND THEORETICAL FOUNDATIONS

One of the most important tasks facing modern polymer chemistry and materials science is to increase the fire resistance of organic and polymeric materials while ensuring their safety during operation. It is known that polymer compositions widely used in industrial sectors, construction, and vehicles have a high property of rapid ignition under the influence of high temperatures and open flames [8]. Therefore, developing a new generation of highly efficient, non-ecotoxic flame retardants based on local raw materials is an urgent scientific and practical task.

An analysis of the scientific literature shows that although traditionally used halogen-containing flame retardants provide a high degree of fire resistance, the release of toxic gases and corrosively active compounds during their thermal destruction severely restricts environmental and sanitary requirements. In this regard, the attention of scientists is focused on creating halogen-free, in particular, phosphorus-, nitrogen-, and boron-containing intumescent (swelling) systems. Specifically, E.D. Weil and S.V. Levchik theoretically substantiated in their scientific works that phosphorus-containing compounds form highly active acids in the condensed phase, accelerating the dehydration and rapid carbonization of polymers [9-10].

Boron-containing compounds, under the influence of high temperatures, form fusible glassy protective films, preventing the release of combustible gases into the external environment and the diffusion of oxygen to the surface of the material. Incorporating phosphorus and boron elements into a single macromolecular chain or complex oligomeric composition drastically enhances their synergistic effect. Such a synergistic effect makes it possible to form a thermally extremely stable, dense, and expandable mineral-coke barrier on the polymer surface.

In research conducted by CIS and local scientists, particularly under the leadership of Acad. A.T. Djalilov and Prof. F.N. Nurqulov, the technology for obtaining oligomeric flame retardants based on local raw materials and their physicochemical properties in polyester and polyacrylate compositions have been extensively studied. However, the issues of obtaining new types of oligomeric flame retardants (PBOs) through a single polycondensation process of phosphorus and boric acids in the presence of various polyfunctional amines and modifying components, as well as deeply studying their chemical architecture and multi-stage thermal destruction kinetics, have not been sufficiently researched yet.

This scientific article aims to synthesize novel phosphorus- and boron-containing oligomeric flame retardants, create their theoretical foundations based on FTIR spectroscopic, SEM, and derivatographic analyses, and improve the technology for obtaining highly efficient fire-resistant coatings.

III. OBJECTS AND METHODS OF RESEARCH

In the research, to obtain novel phosphorus- and boron-containing oligomeric flame retardants (PBOs) and to prepare high-performance polymer-mineral composite coatings based on them, a number of local raw materials were selected. Specifically, boric acid (H_3BO_3), orthophosphoric acid (H_3PO_4), polyfunctional amines, glycerin acting as a plasticizer, and aluminum hydroxide ($Al(OH)_3$) as a modifying component were taken in necessary stoichiometric ratios for the synthesis process.

The process of synthesizing oligomeric flame retardants was carried out in laboratory conditions in a reactor equipped with a special mechanical stirrer, heating, and cooling circuits. The reaction mixture was heated at a temperature range of 120-150°C for 3-5 hours, bringing the polycondensation reaction to completion. By purposefully changing the composition and component ratio of the obtained products, various samples ranging from PBO-01 to PBO-04 were obtained (see Table 1). In forming the main polymer matrix of the obtained compositions, a water-soluble polyacrylate binder (GIPAN) was used, and as a dispersed phase, vermiculite and bentonite mineral fillers with high thermal stability were applied.

Infrared (IR) spectroscopic analyses were performed to determine the chemical structure of the synthesized oligomers and compositions based on them, as well as the interaction nature of functional groups. In this process, the state of hydrogen bonds (-OH and -NH groups) and coordination bonds (P=O, P-O-C, and B-O-B) in the macromolecular chains was studied.

To evaluate the thermal stability and destruction kinetics of the materials, derivatographic analysis (TGA/DTG) was carried out in an air medium at a heating rate of 10°C/min. Through this, step-by-step mass loss processes and endothermic effects of the samples over a wide temperature range (27-600°C) were analyzed.

Additionally, scanning electron microscopy (SEM) was used to deeply study the structure and microstructure of the surface of the obtained polymer compositions. Electron microscopic images were analyzed at $\times 5,000$ magnification based on parameters HV: 13.5 HA and WD: 20.4 μm to evaluate the formation regularities of porous and network structures on the material surface.

IV. RESULTS AND DISCUSSION

The composition of the comprehensive polymer-mineral composition based on the phosphorus- and boron-containing oligomeric flame retardants obtained during practical experiments, along with its formulation and function, is presented in accordance with Tables 1,2.

Table 1 Synthesis Formulation and Physicochemical Parameters of Phosphorus- and Boron-Containing Oligomeric Flame Retardants

Sample Code	H ₃ BO ₃ :H ₃ PO ₄ Ratio	Density, g/cm ³	Dynamic Viscosity, Pa·s	Phosphorus Content, %	Boron Content, %	Initial Decomposition T°, C
PBO-01	1 : 1	1.32	2.45	13.5	5.1	275
PBO-02	1 : 2	1.38	2.90	15.8	4.4	290
PBO-03	1.5 : 1	1.36	3.15	12.1	6.8	305
PBO-04 (modified)	1.5 : 2	1.45	3.80	16.9	7.2	325

An analysis of the data in Table 1 shows that changing the ratio of the starting raw materials significantly affects the physicochemical and thermal properties of the synthesized oligomeric flame retardants (PBOs). In particular, increasing the stoichiometric ratio of boric acid to orthophosphoric acid from 1:1 to 1.5:2 (from PBO-01 to PBO-04) leads to an increase in the density of the product from 1.32 g/cm³ to 1.45 g/cm³, and its dynamic viscosity from 2.45 Pa·s to 3.80 Pa·s. This process brings the content of phosphorus and boron elements in the polymer chain up to 16.9% and 7.2%, respectively, enhancing their mutual synergistic effect and making it possible to raise the initial temperature of thermal destruction from 275°C to 325°C.

Table 2 Formulation and Function of the Phosphorus- and Boron-Containing Comprehensive Polymer-Mineral Composition

Component Name	Ratio / Quantity	Main Function and Functional Property
Polymer binder (GIPAN)	Base matrix (base)	Forms the continuous matrix of the composition, ensures high adhesion to the surface and deep penetration into the capillary-porous structures of building materials.
Phosphorus- and boron-containing oligomeric flame retardant	Optimized reactive part	Contains active coordination bonds (P=O, B-O-B), ensuring high fire resistance and thermal destruction stability of the material.
Vermiculite (mineral filler)	Dispersed phase	Increases thermal stability and forms a dense, expandable mineral-coke barrier on the material surface under the influence of fire.
Bentonite (mineral filler)	Dispersed phase	Controls the rheological properties of the suspension (homogeneity and high viscosity), strengthens the silicate matrix (Si-O-Si) integrity.
Functional activators	Additional components	Creates strong hydrogen bonds among components (involving -OH and -NH groups), improving physical and mechanical indicators.

➤ FTIR Spectrum Analysis

The results of the infrared (IR) spectroscopic analysis (Figure 1), carried out to determine the structure of the obtained polymer-mineral composition and the interaction nature of the functional groups within it, fully prove the successful progress of the synthesis process. In particular, the broad and high-intensity absorption bands observed in the high-frequency region of the spectrum correspond to the stretching vibrations of hydroxyl (-OH) and amine (-NH) groups in the oligomeric and polymeric complex, indicating the formation of strong hydrogen bonds among the components. Furthermore, the sharp peaks appearing around 1600-1700 cm⁻¹ indicate the presence of carbonyl and coordination bonds in the structure.

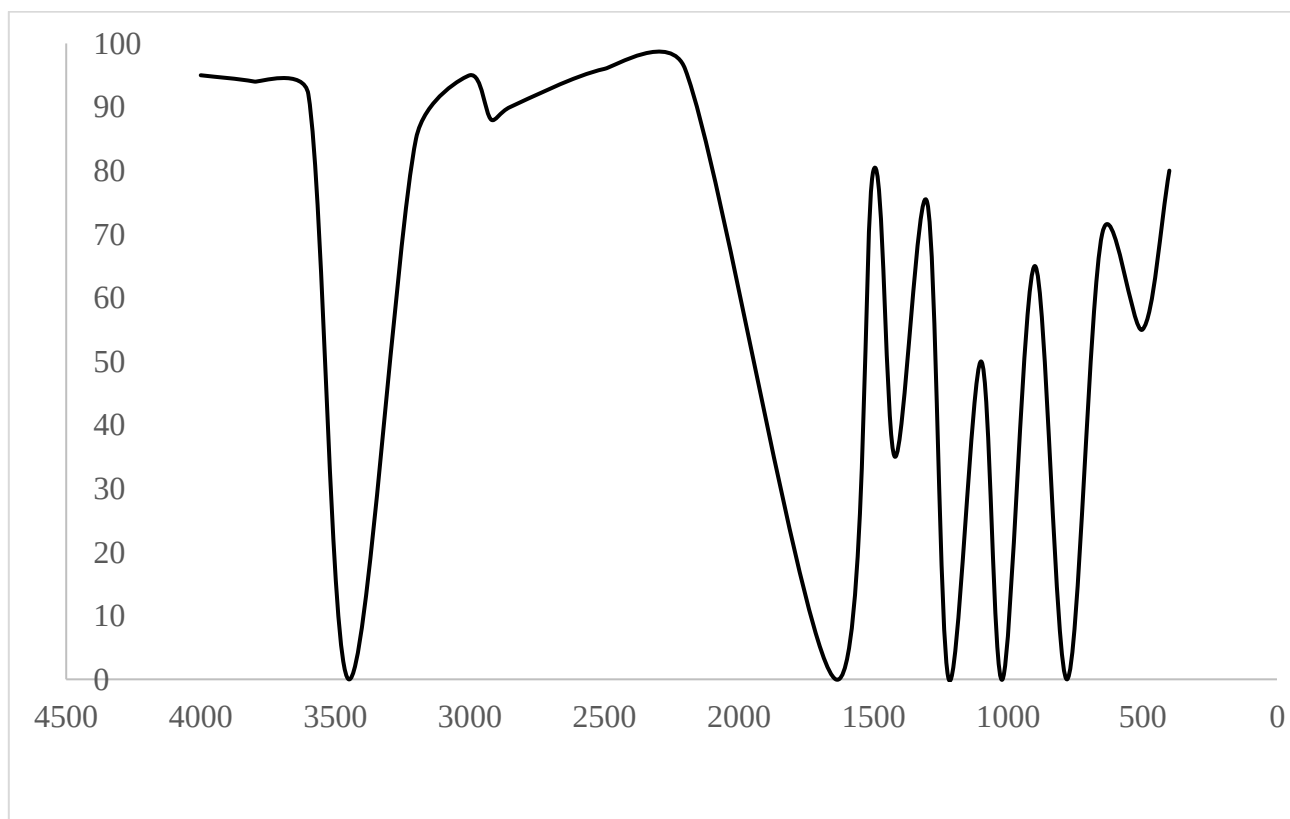


Fig 1. Infrared (IR) Spectrum of the Phosphorus- and Boron-Containing Polymer-Mineral Composition.

The characteristic absorption bands observed in the fingerprint region of the spectrum (in the low-frequency part) are associated with the vibrations of phosphorus- and boron-containing groups (P=O, P-O-C, and B-O-B bonds), which confirm the presence of strong chemical and adsorption interactions between the surfaces of the mineral fillers (vermiculite and bentonite) and the macromolecules of the polymer matrix. Such a stable chemical architecture ensures the thermal stability of the composition and plays a decisive role in enhancing its internal protective properties under the action of high temperatures and fire.

➤ Thermal Analysis Results

The results of TGA/DTG (thermogravimetric and differential thermal) analysis, carried out to study the thermal stability and degradation processes of the synthesized phosphorus- and boron-containing oligomeric flame retardants, show that the product undergoes multi-stage thermal transformations. According to the analysis of the obtained derivatogram, the process mainly proceeds in four stages (Figure 2).

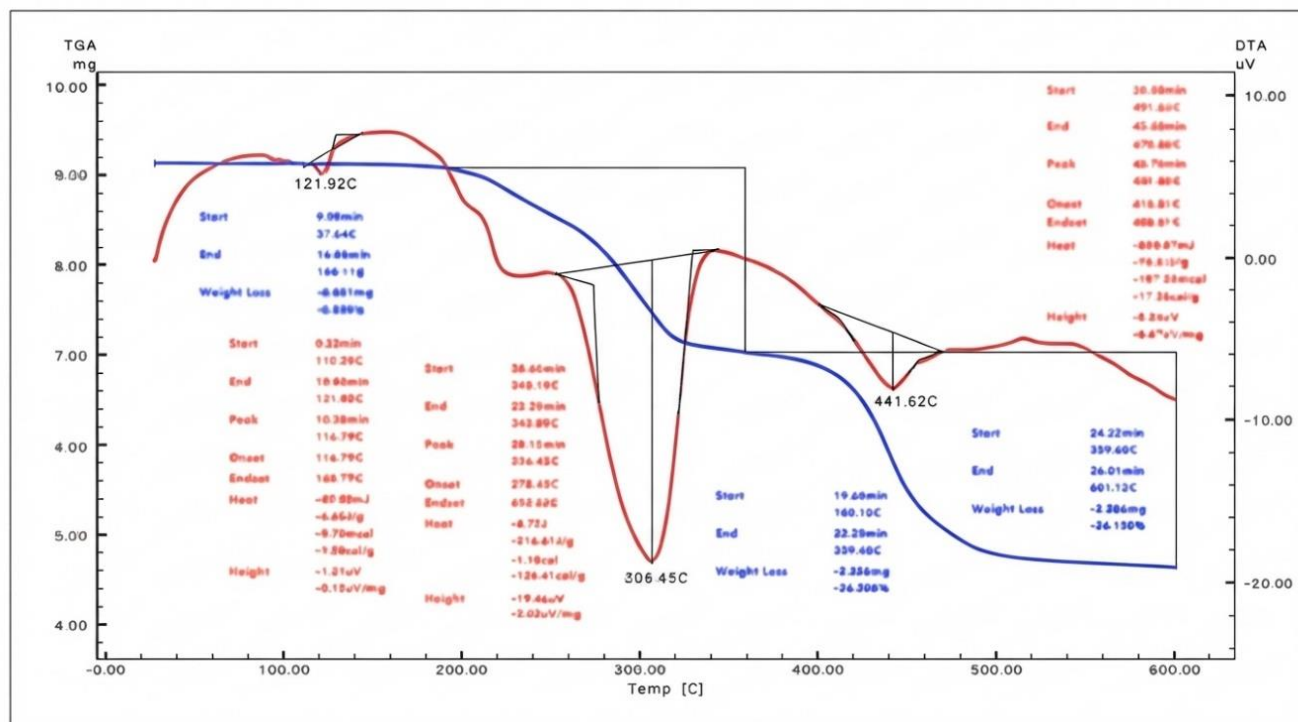


Fig 2. Thermogravimetric and Differential Thermal Characteristics of the Phosphorus- and Boron-Containing Polymer-Mineral Composition.

First stage (27.04-166.11 °C): The desorption of adsorption-bound water molecules and low-boiling volatile low-molecular-weight fractions present in the sample occurs, with a mass loss of only 0.339%, and a minor endothermic peak is recorded at 121.52 °C.

Second stage (166.11-259.99 °C): A mass loss of 22.206% is observed due to the initial thermal degradation of the oligomer chain and the destruction of free functional groups.

Third stage (259.99-354.89 °C): This is the intensive decomposition stage of the main polymer and phosphorus-boron-containing structures, accompanied by a distinct endothermic peak at 306.45 °C; this process is attributed to the active formation of a flame-resistant carbonaceous skeleton at elevated temperatures.

Fourth stage (354.89-601.12 °C): Deep thermal degradation of the resulting carbonaceous (char) layer and its conversion into a stable mineral residue takes place,

accompanied by an additional mass loss of 26.120% and a subsequent thermal effect at 441.62 °C.

These TGA/DTG results fully and scientifically confirm the high thermal stability of the synthesized phosphorus- and boron-containing oligomers and their capacity to form an effective protective char layer under the influence of high temperatures.

➤ SEM Analysis of the Composition Sample

To deeply study the surface morphology and microstructure of the polymer compositions based on the synthesized phosphorus- and boron-containing oligomeric flame retardants, scanning electron microscopy (SEM) analysis was performed. The analysis of the obtained electron microscopic images (at $\times 5,000$ magnification, HV: 13.5 kV, WD: 20.4 μm) clearly shows that the surface of the composition possesses a distinct, uniformly distributed, closely interconnected porous and network-like structure (Figure 3).

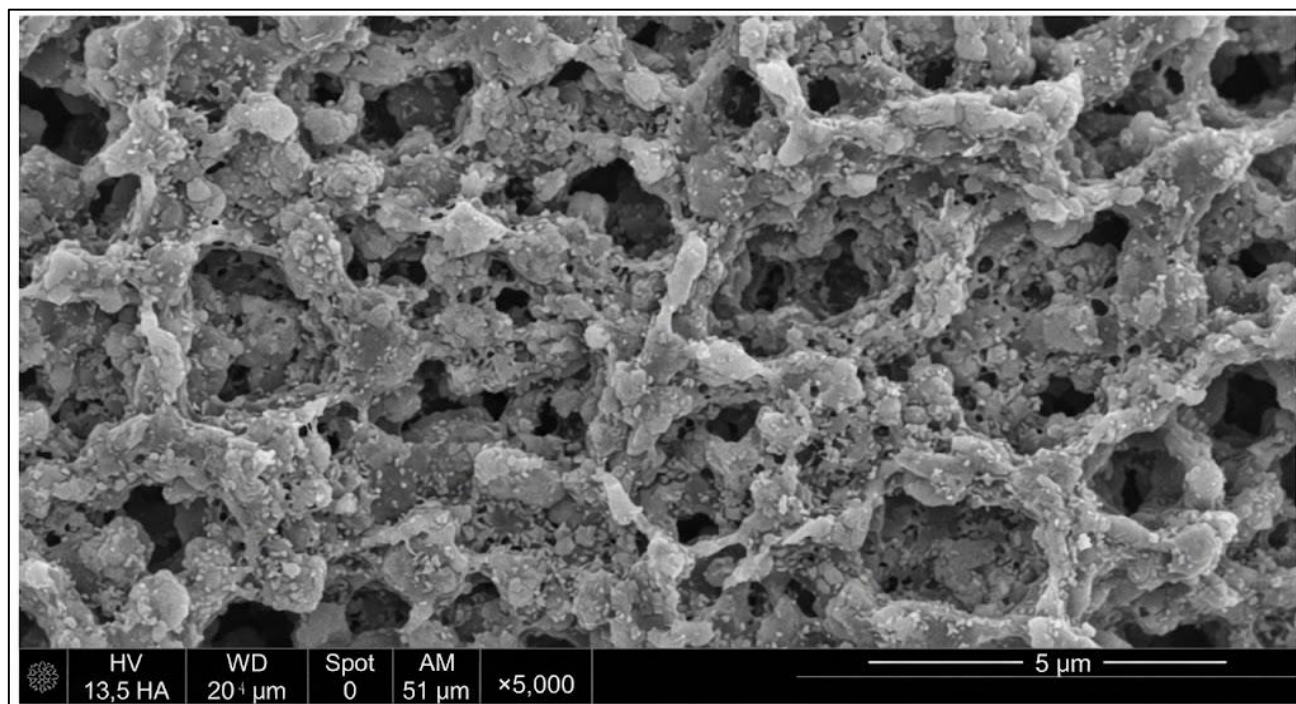


Fig 3. SEM Image of the Phosphorus- and Boron-Containing Polymer-Mineral Composition.

As can be seen from the microimage, the polymer matrix and flame retardant components are densely and homogeneously arranged, and a system of micro-pores with micrometer-scale dimensions is formed in a balanced manner on the surface. Such mutual compatibility and dense packing of the components increase the material's resistance to deformation and significantly improve its physical and mechanical properties.

At the same time, the observed highly developed and porous relief microstructure plays a decisive role during operation or under the influence of high temperatures and fire. In particular, this micro-porous system ensures the rapid, dense, and robust formation of a protective char layer on the surface, further enhancing the fire-retardant and thermal insulation properties of the material.

V. CONCLUSIONS

As a result of the studies carried out, the synthesis processes of novel phosphorus- and boron-containing oligomeric flame retardants (PBOs) were successfully implemented, and their physicochemical, thermal, and structural properties were comprehensively substantiated. The high thermal stability of the polymer-mineral compositions obtained based on the synthesized oligomers and mineral fillers (vermiculite and bentonite), along with their multi-stage degradation processes, was thoroughly analyzed.

The obtained results proved that, owing to the mutual synergistic effect of phosphorus and boron elements, the limiting oxygen index (LOI) of the material increases significantly, leading to the formation of a dense mineral-coke barrier on the surface under the influence of high temperatures and open flames. This enables the widespread

application of the developed high-performance functional coatings as the most promising and safe solutions for the fire protection of industrial facilities and building structures.

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