ASEAN Journal for Science and Engineering in Materials

Journal homepage: https://ejournal.bumipublikasinusantara.id/index.php/ajsem

Synergistic Effects of Microspheres, Microfibers, and A Phosphorus-Boron Modifier in Fire- and Heat-Resistant Ethylene-Propylene-Diene Rubber Composites

V. G. Kochetkov, V. F. Kablov, N. A. Keibal, O. M. Novopolceva, D. A. Kryukova, D. A. Urzhumov, I. M. Myasnikov, S. V. Borisov, M. P. Spiridonova*

Volgograd State Technical University, Russian Federation
*Correspondence: E-mail: vg.kochetkov@mail.ru

ABSTRACT

This study investigates fire- and heat-resistant elastomeric composites based on ethylene-propylene-diene rubber containing functionally active microheterogeneous structures composed of microspheres, microfibers, and a synthesized phosphorus-boron organic modifier. The modifier was synthesized from aminotrimethylene phosphonic acid, diethylene glycol, and boric acid, while low-temperature plasma treatment was applied to enhance its interaction with the microdispersed components. The resulting three-component structures improved the mechanical, thermal, adhesive, and fire-protective performance of the elastomeric composites. Their incorporation increased the heating time of the unheated surface, reduced the linear burning rate, increased coke residue, and strengthened the resulting coke layer while maintaining material density. These findings demonstrate the synergistic role of microspheres, microfibers, and the phosphorus-boron modifier in developing multifunctional elastomeric composites with enhanced resistance to high-temperature and fire exposure.

ARTICLE INFO

Article History:
Submitted/Received 21 May 2026
First Revised 21 Jul 2026
Accepted 16 Aug 2026
First Available online 20 Aug 2026
Publication Date 01 Dec 2026

Keywords:
Ethylene-propylene-diene rubber;
Fire-heat protection;
Microfibers;
Microspheres;
Phosphorus-boron modifier.

1. INTRODUCTION

Fire- and heat-resistant polymeric materials are required in applications exposed to flame, high temperatures, thermal flux, and erosive environments. Their protective performance depends on limiting heat transfer, suppressing combustion, and forming a stable carbonaceous layer during thermal degradation. Flame-retardant systems containing phosphorus, nitrogen, boron, metals, or combinations of these elements have therefore been widely investigated to improve the thermal stability and fire resistance of polymers (Dogan *et al.*, 2021; Liu *et al.*, 2022; Afifah *et al.*, 2023a; Afifah *et al.*, 2023b).

Ethylene-propylene-diene rubber is attractive as a matrix for fire-heat protective materials because of its flexibility and applicability under demanding service conditions. However, improving fire resistance while maintaining low density, mechanical integrity, thermal insulation, and erosion resistance remains challenging. Hollow microspheres can reduce density and thermal conductivity, whereas microfibers can reinforce the material and the carbonized layer formed during high-temperature exposure. Their simultaneous use may nevertheless affect dispersion and interfacial compatibility.

This study investigates a three-component functional system consisting of microspheres, microfibers, and a synthesized phosphorus-boron-containing modifier in an ethylene-propylene-diene rubber matrix. The study further evaluates low-temperature plasma treatment as a means of improving interactions between the modifier and microdispersed components. The novelty lies in combining these components as functionally active microheterogeneous structures to improve fire-heat protection, mechanical performance, and structural stability without relying on a single protective mechanism.

2. LITERATURE REVIEW

Phosphorus- and nitrogen-containing flame retardants are particularly effective because they promote carbonization and the formation of thermally stable protective layers. During heating, phosphorus-containing species can promote dehydration and char formation, while nitrogen-containing products contribute to condensed- and gas-phase flame inhibition. The resulting char acts as a barrier against heat and mass transfer and can reduce the supply of combustible degradation products (Bogdanova *et al.*, 2023; Wang *et al.*, 2012).

The interaction between phosphorus- and nitrogen-containing components during thermal degradation is illustrated in **Figure 1**. Such multifunctional systems are of interest because flame retardants may also contribute to plasticization, surface activity, foaming, curing, or structural modification. Aminotrimethylene phosphonic acid is particularly relevant because its thermal transformation produces phosphorus- and nitrogen-containing species that can promote carbonization, while related phosphonic compounds have also been investigated in functional organic and corrosion-protection systems (Zhilin *et al.*, 2023).

Sacrificial fire-heat protective polymeric materials are used in oil and gas facilities, aviation, construction, and other applications where the substrate must be protected from intense thermal exposure. Their polymer matrices include ethylene-propylene, nitrile-butadiene, and silicone rubbers, as well as epoxy and chlorinated polymer systems (Hofmann *et al.*, 2024).

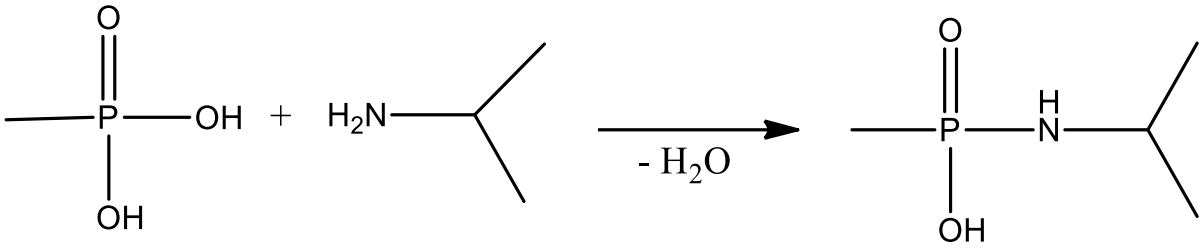


Figure 1. Interaction of phosphorus- and nitrogen-containing components associated with the formation of thermally stable structures during heating.

Density and thermal conductivity are critical characteristics of these protective materials. Hollow aluminosilicate microspheres are attractive fillers because of their low density and thermal conductivity and have been applied in fire-retardant coatings, lightweight composites, and thermal-insulating materials (Liu *et al.*, 2024; Inozemtsev and Korolev, 2013; Qiu *et al.*, 2024). However, fire-heat protective materials may also experience erosion under high-temperature gas flow. Microfibrous fillers can reinforce the polymer and carbonized layer, although their incorporation may increase density, thermal conductivity, and agglomeration while affecting polymer-filler interactions (Kablov *et al.*, 2018).

These limitations indicate that neither microspheres nor microfibers alone provide an optimal balance of thermal insulation, mechanical stability, and erosion resistance. A combined system in which microspheres reduce density, microfibers reinforce the structure, and a phosphorus-boron modifier promotes interfacial interaction and carbonization therefore provides a rational approach for developing multifunctional fire- and heat-resistant elastomeric composites.

3. METHOD

3.1. Synthesis of the Phosphorus-Boron Modifier

A phosphorus-boron-containing modifier, hexakis (2- (2 (boryl) ethoxy) ethyl) (nitrilotris (methylene)) triphosphonate (AFB), was synthesized from aminotrimethylene phosphonic acid, diethylene glycol, and boric acid, as illustrated in **Figure 2**.. In the first stage, aminotrimethylene phosphonic acid (95%, Sigma-Aldrich, No. 72568) was reacted with diethylene glycol (99.99%, Sigma-Aldrich, No. 8.03131) at a molar ratio of 1:6 for 3 h at 135 °C. Boric acid (99.5%, Sigma-Aldrich, No. B0394) was subsequently added at the same temperature at a molar ratio of 1:3, and the reaction was continued for 2.5 h. Reaction completion was evaluated from changes in viscosity, refractive index, and the volume of water collected using a Dean-Stark apparatus.

The resulting product was a yellow-orange viscous liquid containing 18% hydroxyl groups, with a refractive index of 1.4620 and a viscosity of 760 mm^2/s. It was soluble in water and insoluble in acetone. Its chemical structure was examined using a Nicolet-6700 Fourier-transform infrared spectrometer. The identified absorption bands included C-O, P=O at 2565-2570 cm^{-1}, $B(OR)_2$ at 1375-1380 cm^{-1}, and C-N at 1645-1660 cm^{-1}.

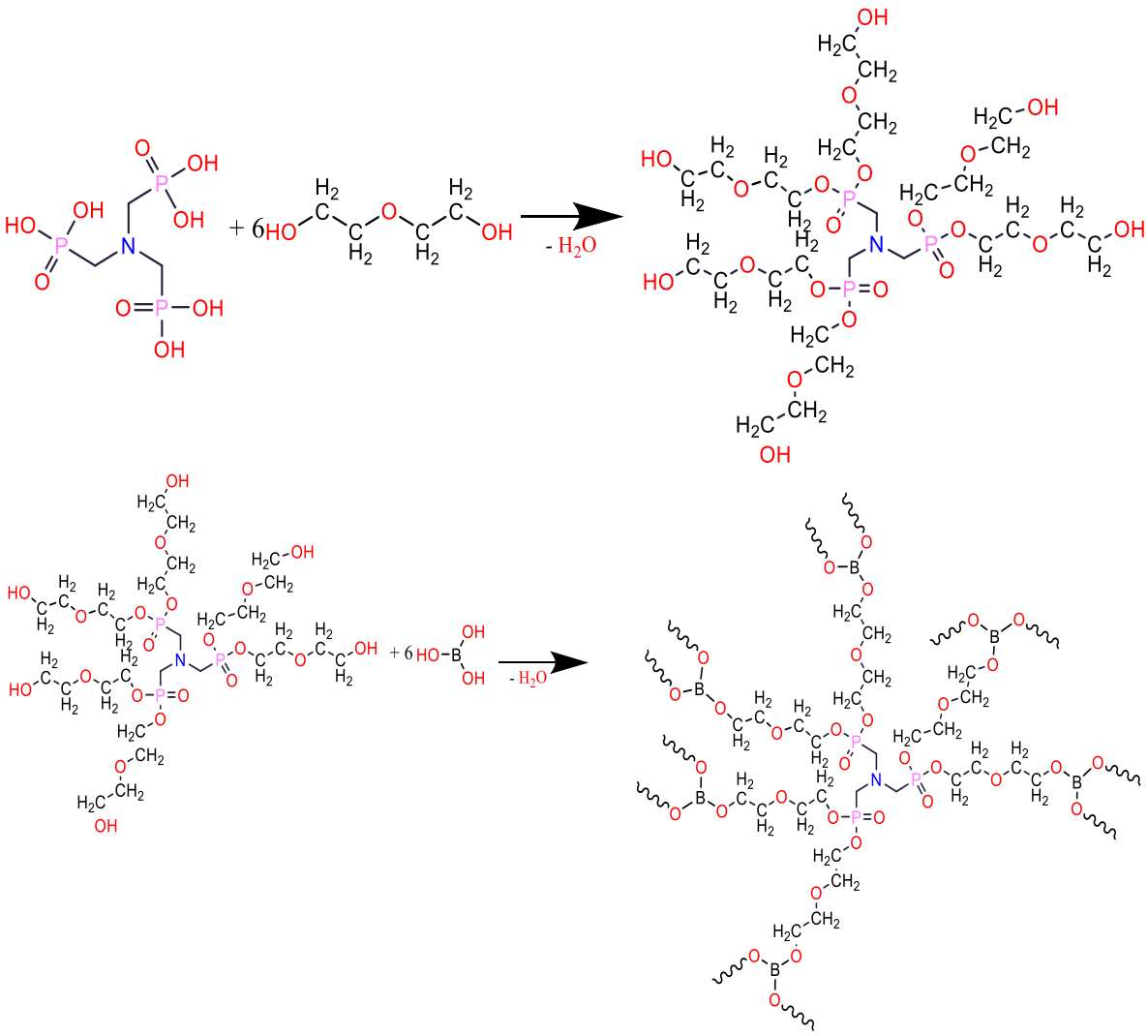


Figure 2. Synthesis route of the phosphorus-boron-containing AFB modifier from aminotrimethylene phosphonic acid, diethylene glycol, and boric acid.

3.2. Preparation of Functionally Active Microstructures

Microspheres and microfibers were introduced into the AFB modifier and thoroughly mixed. The mixture was then dried to constant weight with periodic stirring to obtain functionally active three-component microstructures. The microsphere-to-microfiber ratio was 3:10. To activate the surfaces of the microdispersed components, low-temperature plasma treatment was performed using an MD-20ST installation at a discharge power of 300 W for 7 min with filtered air as the working gas. In a separate treatment route, the AFB modifier was introduced directly into the plasma discharge (Kablov *et al.*, 2025). The formation and preservation of the functionally active microstructures in the rubber matrix and after high-temperature exposure are illustrated in **Figure 3**.

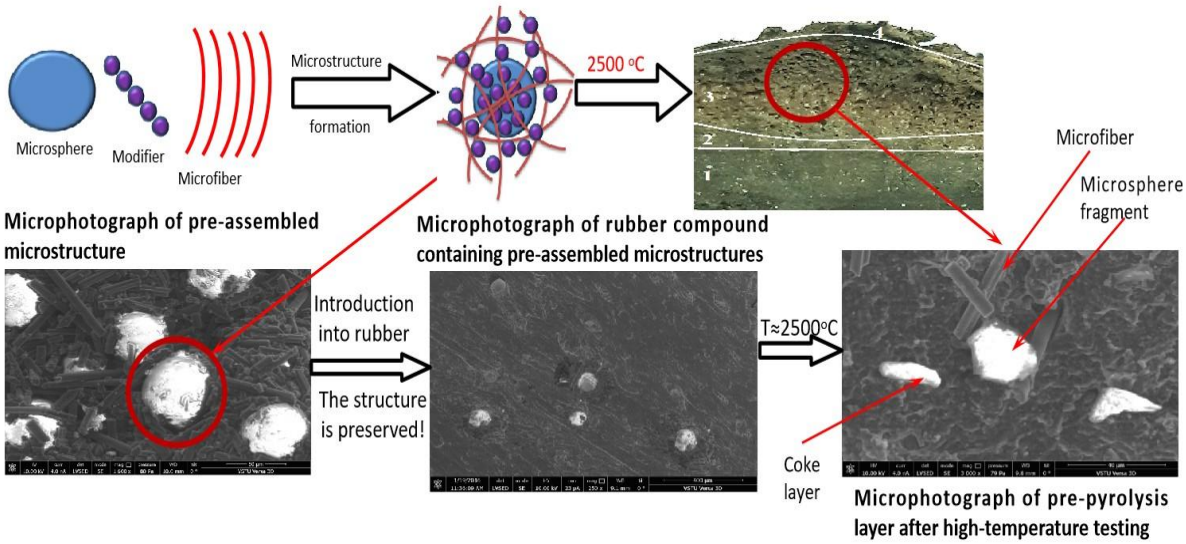


Figure 3. Formation, incorporation, and preservation of pre-assembled functionally active microstructures in the elastomeric matrix.

3.3. Preparation of Elastomeric Compositions

The resulting functionally active material was incorporated into an ethylene-propylene-diene rubber composition containing a sulfur vulcanization system and 30 parts by mass of BS-120 white carbon black. A composition without functionally active material was used as the control, while another composition containing the target additives introduced separately was prepared for comparison. The rubber compounds were mixed in a micro-rubber mixer and vulcanized in a Carver press at 165 °C for 40 min in accordance with GOST 30263-96.

3.4. Characterization and Testing

Vulcanization characteristics were measured using an MDR 3000 Professional rheometer according to ASTM D 2084-79. Cohesive strength was determined according to ISO 9026:2007, and tensile properties were measured according to GOST ISO 37-2020. Thermal aging resistance was evaluated according to GOST 9.024-74. Fire- and heat-resistance performance was assessed from the temperature increase on the unheated surface during plasma-torch exposure, thermo-oxidative degradation resistance according to OST 92-0903-78, and linear burning rate according to GOST 12.1.044-2018. During short-term high-temperature exposure, the sample surface temperature reached approximately 2000°C.

Dispersion of the modifying additive in the elastomeric matrix was evaluated using a Disper Tester 3000 Plus. Adhesive properties were determined according to GOST R 57834-2017 using a polychloroprene-based adhesive grade 88CA.

Differential thermal analysis and thermogravimetric analysis were performed using a Derivatograph HQT 1. Coke residue was determined in an STQ-8-12 muffle furnace according to OST 92-0903-78. Contact angle and adhesion work were measured using a DSA25E instrument.

Erosion resistance was evaluated by rotating the sample while applying tangential plasma-torch heating. The onset of combustion, coke-layer detachment time, sample diameter after exposure, and thickness of the remaining non-disrupted layer were determined.

The tear propagation strength of the carbonized layer was calculated from the centrifugal force acting at the interface between the coke layer and the non-degraded material during sample rotation under high-temperature exposure (Equation (1)):

$$\sigma = \frac{2(\pi\omega)^2\left(R_0^2 - R^2\right)\rho_k}{(R_0 - R)} \quad (1)$$

where ω is the angular velocity, R_0 is the initial radius, R is the radius to the pyrolysis-layer boundary, and ρ_k is the coke density.

4. RESULTS AND DISCUSSION

The synthesized phosphorus-boron modifier showed only a limited influence on the basic rheometric characteristics of the ethylene-propylene-diene rubber compounds. The minimum and maximum torque, induction period, and vulcanization rate changed only slightly at moderate modifier contents. A noticeable decrease in maximum torque and optimal vulcanization time occurred only when the modifier content exceeded 10 parts by mass, indicating that excessive addition may interfere with the development of the elastomeric network during vulcanization.

At lower concentrations, the modifier produced a more favorable balance between processability and mechanical performance. Tensile strength previously reached a maximum at 3-5 parts by mass of the modifier, corresponding to an increase of approximately 60-70% relative to the control material. The accompanying 5-15% increase in elongation at break suggests that the modifier does not act solely as a rigid flame-retardant component but may also contribute to increased molecular mobility within the elastomeric matrix. This behavior is consistent with the plasticizing effect proposed for the synthesized organoelement compound.

The rheometric characteristics of the compositions containing microspheres, microfibers, and the AFB modifier remained close to those of the control material, as shown in **Table 1**. The torque difference varied from 1.52 to 1.75 N·m compared with 1.63 N·m for the control, while the vulcanization rate remained 0.02 min^{-1} for all compositions. The optimal vulcanization time also remained within a relatively narrow range of 28.52-29.65 min. These results indicate that incorporation of the functional components did not substantially disrupt the vulcanization process under the selected formulation and processing conditions.

A clearer distinction was observed in the Payne effect. The value increased from 85.87 kPa for the control to 106.56 kPa when the components were introduced additively. In contrast, the compositions containing the modifier in the functionally active system exhibited lower values of 87.27 and 88.01 kPa. The higher Payne effect observed for the additive formulation indicates stronger filler-filler interactions or less homogeneous distribution of dispersed components. By contrast, the lower values obtained for the AFB-containing systems suggest that the modifier improves the organization and distribution of microspheres and microfibers within the rubber matrix. This interpretation is also consistent with the observed improvement in mechanical properties.

Table 1. Influence of microspheres, microfibers, and the phosphorus-boron modifier on vulcanization, physical-mechanical, thermal-aging, and fire-heat protective characteristics of ethylene-propylene-diene rubber compositions.

INDICATORS	SAMPLE CODE			
	CONTROL SAMPLE	SM	AFB	AFB-P
Content of MSF, mass parts per 100 mass parts of rubber	0	3	3	3
Content of MKV, mass parts per 100 mass parts of rubber	0	10	10	10
Content of AFB, mass parts per 100 mass parts of rubber	0	5	5	5
Characteristics of Rubber Mixtures				
Difference between Maximum and Minimum Torque ΔM, N·m	1.63	1.75	1.62	1.52
Induction Period τS, min	1.90	1.91	1.82	2.00
Optimal Vulcanization Time τ90, min	28.52	29.65	29.13	29.54
Vulcanization Rate Indicator Rv, min-1	0.02	0.02	0.02	0.02
Payne Effect, kPa	85.87	106.56	87.27	88.01
Cohesive Strength of the Composition, kN/m	0.836	0.853	0.884	0.879
Properties of Vulcanizates (Vulcanization at 165 °C for 40 min)				
Conditional Tensile Strength fp, MPa	12.3	15.63	17.34	17.00
Relative Elongation at Break ε, %	630	580	600	610
Relative Residual Elongation after Break, %	20	14	15	16
Density, kg/m³	1060	1031	1032	1030
Changes in Indicators after Thermal Aging (125 °C for 72 h)				
Δfp, %	-12.4	2.15	-2.75	-1.65
Δε, %	-49.55	-46.65	-54.11	-53.14
Thermal Protection and Thermophysical Properties of Vulcanizates				
Time for Unheated Surface of Sample to Reach 100 °C, s	140	180	215	225
Linear Burning Rate, mm/s	0.688	0.470	0.439	0.430
Coke Residue, %	19.68	28.14	29.90	29.37
Time for Delamination of Coke Layer, s	24	38	43	45
Strength of Coke Layer Adhesion, mPa	36.8	40.1	43.6	44.5

The cohesive strength increased from 0.836 kN/m for the control to 0.853, 0.884, and 0.879 kN/m for the modified compositions. Although the differences are moderate, they indicate that the presence of the functional modifier does not weaken the internal integrity of the elastomeric system. The tensile strength increased more substantially, from 12.3 MPa for the control to 15.63 MPa for the additive composition and to 17.34 and 17.00 MPa for the AFB-containing compositions. These results show that the combined use of the modifier and microdispersed fillers can improve strength without a substantial loss of extensibility.

The relative elongation at break remained between 580 and 610% for the modified materials compared with 630% for the control. This moderate reduction is accompanied by a marked increase in tensile strength, indicating that reinforcement was achieved without severe embrittlement. The residual elongation after break also decreased from 20% for the control to 14-16% for the modified compositions. Taken together, these changes indicate that

the functionally active microstructures affect the balance between reinforcement, deformability, and elastic recovery rather than simply increasing stiffness.

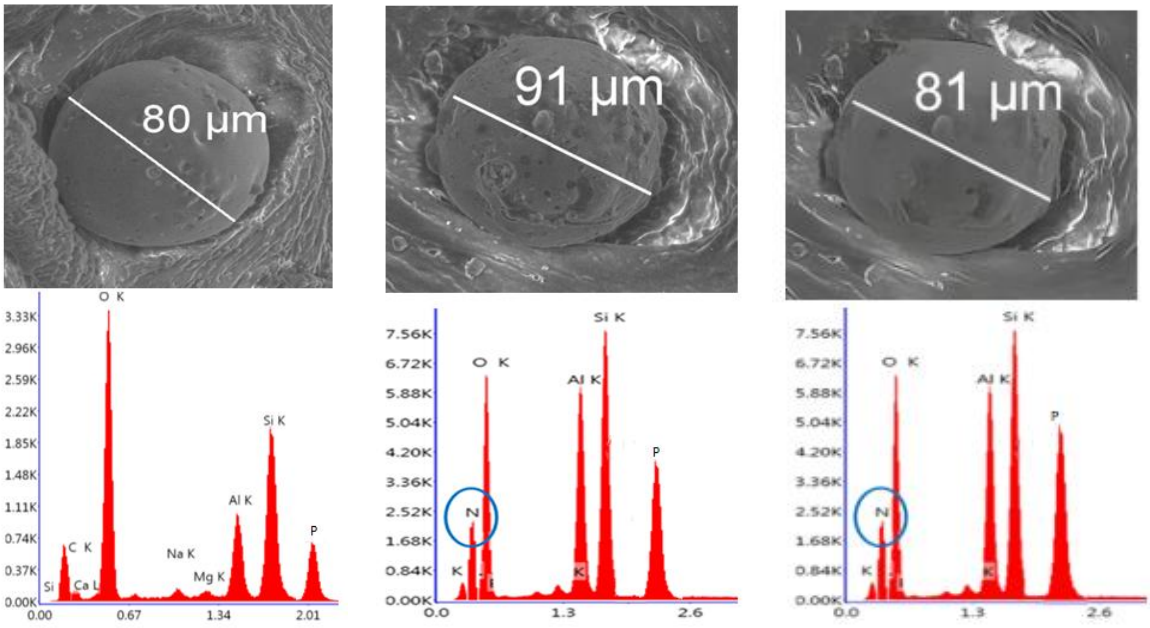
The density of the modified materials remained close to that of the control. The control density was 1060 kg/m³, whereas the experimental formulations showed values between 1030 and 1032 kg/m³. This result is important because microfibrous reinforcement can increase density and thermal conductivity, which is undesirable for fire-heat protective materials. The presence of hollow microspheres compensates for this effect and allows reinforcement to be introduced without increasing the overall density of the material. This complementary function of microspheres and microfibers is one of the advantages of the combined microheterogeneous system.

The behavior after thermal aging further demonstrates that the modifier influences the stability of the elastomeric network. After aging at 125 °C for 72 h, the control showed a 12.4% reduction in tensile strength. In contrast, the changes in tensile strength for the modified compositions ranged from +2.15% to −2.75%. Thus, the modified materials retained their strength more effectively after thermal exposure. The effect was especially evident in the composition in which the modifier was introduced separately from the microspheres and microfibers. The elongation at break decreased for all samples after aging, indicating that thermal exposure still affected elastomeric mobility, but the improved retention of tensile strength confirms a stabilizing contribution of the functional additive.

An important factor controlling these improvements is the interaction between the modifier and the surfaces of the dispersed components. Low-temperature plasma treatment was therefore used to activate the surfaces of the microspheres and microfibers. Plasma treatment can modify the outer surface of polymeric and particulate materials through surface cleaning and the formation of oxygen- and nitrogen-containing functional groups, including carbonyl, alcohol, peroxide, and amine species. These groups can increase surface energy and improve interaction with surrounding phases (Gilman *et al.*, 2017; Provotorova *et al.*, 2014).

The effect of the modifier introduction method on the microsphere surface is shown in **Figure 4**. Compared with untreated particles, preliminary plasma treatment and direct introduction of the modifier into the plasma discharge resulted in a more uniform surface layer. Elemental analysis also indicated an increase in phosphorus content at the microsphere surface. At the same time, the contact angle decreased from 79° for the untreated surface to 43° after modification. The decrease in contact angle indicates improved wettability, supporting stronger interaction between the modified dispersed phase and the elastomeric matrix.

The improvement in surface interaction provides a plausible explanation for the reduced Payne effect and increased tensile and cohesive strength. A more uniform modifier layer can reduce direct filler-filler contact, improve dispersion, and promote stronger interfacial interaction between the microdispersed components and the rubber matrix. The modifier therefore performs more than one function: it contributes to fire protection through phosphorus- and boron-containing groups while simultaneously improving interfacial compatibility.



(a) (b) (c)

Figure 4. Appearance and elemental composition of microsphere surfaces depending on the AFB modifier introduction method: (a) without preliminary low-temperature plasma treatment; (b) with preliminary low-temperature plasma treatment; and (c) modifier introduced directly into the low-temperature plasma discharge.

These structural effects are directly related to the fire-heat protective performance presented in **Table 1**. The time required for the unheated surface to reach 100 °C increased from 140 s for the control to 180 s for the additive system and to 215 and 225 s for the AFB-containing compositions. At the same time, the linear burning rate decreased from 0.688 mm/s for the control to 0.470, 0.439, and 0.430 mm/s for the modified materials. The progressive improvement indicates that the protective effect cannot be attributed to a single component alone. Instead, microspheres, microfibers, and the phosphorus-boron modifier contribute through complementary mechanisms involving thermal insulation, structural reinforcement, and enhanced carbonization.

The improvement in fire-heat protection was accompanied by substantial changes in carbonization behavior. As shown in **Table 1**, coke residue increased from 19.68% for the control to 28.14% for the additive formulation, 29.90% for AFB, and 29.37% for AFB-P. At the same time, the linear burning rate decreased from 0.688 mm/s for the control to 0.470, 0.439, and 0.430 mm/s, respectively. These results indicate that the modified systems favor carbonaceous residue formation while reducing the rate of combustion.

The increase in coke residue is consistent with the role of phosphorus- and nitrogen-containing flame-retardant systems in promoting condensed-phase protection. During thermal degradation, phosphorus-containing species can support dehydration and carbonization, while nitrogen-containing products contribute to the formation and stabilization of protective structures. The resulting carbonized layer restricts heat and mass transfer between the flame and the underlying polymer, thereby limiting further degradation (Bogdanova *et al.*, 2023; Wang *et al.*, 2012).

The effectiveness of the coke layer also depends on its mechanical stability. The coke-layer delamination time increased from 24 s for the control to 38 s for the additive formulation and to 43 and 45 s for AFB and AFB-P, respectively. Coke-layer adhesion strength increased from 36.8 mPa for the control to 40.1, 43.6, and 44.5 mPa for the modified compositions. These results show that the functionally active systems not only increase the amount of carbonized residue but also delay its separation from the underlying material.

Microfibers are likely to contribute directly to this behavior by reinforcing the carbonized structure formed during high-temperature exposure. Fibrous fillers can create a reinforcing network within elastomeric fire-protective materials and improve resistance to structural disruption under thermal and erosive loading (Kablov *et al.*, 2018). In the present system, this reinforcing effect complements the carbonization promoted by the modifier, allowing the protective coke layer to remain intact for a longer period.

The hollow microspheres provide a different but complementary function. Their low density and thermal conductivity make them suitable for thermal-protective composites where reduced heat transfer must be achieved without substantially increasing material density (Inozemtsev and Korolev, 2013; Qiu *et al.*, 2024). In the investigated compositions, the density remained between 1030 and 1032 kg/m³ compared with 1060 kg/m³ for the control. Thus, the microspheres compensate for the density increase that may otherwise accompany microfiber reinforcement.

The combined functions of the three components explain the observed improvement in fire-heat protection. The modified compositions showed a substantial reduction in linear burning rate and an increase in coke residue compared with the control. The pre-assembled functional systems provided better fire-heat protective performance than both the control and the formulation in which the components were introduced additively. These results support the concept that the three-component system operates through complementary rather than isolated mechanisms.

The thermal-barrier effect is also evident from the time required for the unheated surface to reach 100 °C. This time increased from 140 s for the control to 180 s for the additive formulation and to 215 and 225 s for the AFB and AFB-P compositions. The delayed heating can be associated with the combined effects of reduced heat transfer through the hollow microspheres and the development of a carbonized protective layer during exposure. Stable char structures are widely recognized as physical barriers that restrict heat transfer to the polymer and reduce the release of combustible degradation products (Bogdanova *et al.*, 2023; Wang *et al.*, 2012).

The improvement obtained with the pre-assembled functional structures was greater than that achieved when the same components were introduced additively. This difference suggests that spatial organization and interfacial interaction are important for the performance of the system. Surface modification by low-temperature plasma can increase surface activity and improve adhesion between dispersed phases and elastomeric matrices through the formation of polar functional groups (Gilman *et al.*, 2017; Provotorova *et al.*, 2014). The reduction in contact angle and the increased phosphorus content observed on the modified microsphere surface in **Figure 4** support this interpretation.

Mechanical retention at elevated temperature is another important requirement for fire-heat protective elastomers. The results are summarized in **Table 2**. At 75 °C, the conditional tensile strength was 3.44 MPa for the control and 3.85, 4.03, and 3.87 MPa for SM, AFB, and

AFB-P, respectively. At 150 °C, the corresponding values were 2.06, 2.18, 2.79, and 3.00 MPa. The AFB-P formulation therefore retained the highest tensile strength at the highest testing temperature.

Table 2. Conditional tensile strength and elongation at break of the ethylene-propylene-diene rubber compositions at elevated testing temperatures.

SAMPLE CODE	CONDITIONAL TENSILE STRENGTH, MPa			ELONGATION AT BREAK, %		
	75 °C	125 °C	150 °C	75 °C	125 °C	150 °C
Control Sample	3.44	2.51	2.06	278	188	123
SM	3.85	**3.08**	2.18	245	**179**	130
AFB	**4.03**	2.01	**2.79**	**269**	131	**161**
AFB-P	3.87	2.87	3.00	203	138	146

At 150 °C, elongation at break was 123% for the control, compared with 130, 161, and 146% for SM, AFB, and AFB-P, respectively. The modifier-containing compositions therefore maintained greater deformability than the control under the highest testing temperature. This result is consistent with the previously observed ability of the modifier to improve the balance between reinforcement and elastomeric mobility.

The modifier also influenced adhesive performance. Adhesion strength increased from 0.63 MPa for the control to 0.74 MPa for SM, 0.85 MPa for AFB, and 0.88 MPa for AFB-P. This improvement is relevant for multilayer fire-protective materials, where insufficient interfacial adhesion can lead to premature separation of protective layers during thermal exposure.

The enhanced adhesion can be related to the improved surface interaction produced by the functional modifier and plasma treatment. Low-temperature plasma modification can alter the chemical composition of material surfaces and promote the formation of polar functional groups that increase wettability and adhesive interaction (Gilman *et al.*, 2017; Provotorova *et al.*, 2014). The decrease in contact angle from 79 to 43° after modification is consistent with this mechanism and provides a direct link between surface activation and the improved adhesive behavior of the composite.

The phosphorus- and nitrogen-containing structure of the modifier also contributes to the development of an intumescent protective layer. A more uniform distribution of the modifier within the elastomeric matrix favors formation of a denser and finer porous region before complete pyrolysis. Such structural development can increase the effectiveness of the protective layer by reducing direct heat transfer and stabilizing the carbonized phase during thermal exposure. The formation of thermally stable protective structures is a characteristic feature of phosphorus- and nitrogen-containing flame-retardant systems (Bogdanova *et al.*, 2023).

The DTA and TGA results provide additional support for this interpretation. Incorporation of the modifier increased the area of the endothermic peak and reduced mass loss. The endothermic response was associated with physicochemical processes occurring during degradation, including cyclization and sublimation processes. Under conditions without rapid thermal flux, the thermogravimetric curves of AFB and AFB-P remained above that of the control, indicating greater mass retention during heating. These thermal-analysis results are

consistent with the increased coke residue and reduced burning rate. Greater retention of material in the condensed phase allows a larger fraction of the composite to participate in formation of the protective carbonized structure. The modifier promotes carbonization, the microfibers reinforce the resulting coke, and the microspheres contribute to thermal insulation while limiting density. The combined action of these components therefore produces a more stable thermal barrier than the individual additives acting independently. The improved performance of the developed elastomeric composites can be attributed to the integration of chemical, interfacial, and structural mechanisms. The phosphorus-boron-containing modifier promotes carbonization and improves interfacial interaction, the microfibers reinforce the carbonized layer, the hollow microspheres contribute to thermal insulation and density control, and low-temperature plasma treatment enhances interaction among the dispersed components. This combined mechanism explains the higher coke residue, lower burning rate, delayed heat transfer, increased coke-layer stability, improved adhesion, and better retention of mechanical properties at elevated temperature.

4. CONCLUSION

The developed ethylene-propylene-diene rubber composites demonstrated improved fire-heat protective performance through the combined action of microspheres, microfibers, and a phosphorus-boron-containing modifier. The functional system increased coke formation, delayed heat transfer, reduced linear burning rate, and improved coke-layer stability while maintaining low density and mechanical integrity. Low-temperature plasma treatment further enhanced interfacial interaction and surface wettability. The modified materials also showed better strength retention at elevated temperatures and improved adhesion. These results confirm that integrating thermal insulation, carbonization, reinforcement, and interfacial modification within a single microheterogeneous system is an effective strategy for developing multifunctional fire- and heat-resistant elastomeric composites.

5. ACKNOWLEDGMENTS

Financial support was provided by the Ministry of science and higher education of Russian Federation. The research was carried out at the expense of financial support for the implementation of the VSTU development program within the framework of the strategic academic leadership program "Priority 2030", a research project No. 45/055-26.

6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper is free from plagiarism.

7. REFERENCES

Afifah, S., Mudzakir, A., and Nandiyanto, A. B. D. (2023a). Empirical demonstration of fire-retardant bamboo to junior high school students for improving understanding of physicochemical properties of organic material. *Journal of Engineering Science and Technology*, *18*(1), 136-146.

Afifah, S., Mudzakir, A., Nandiyanto, A. B. D., Ragadhita, R., Maryanti, R., Al Husaeni, D. F., Al Husaeni, D. N., and Fiandini, M. (2023b). Sustainability literacy to vocational students through distance learning with experimental demonstration: Ionic liquid experiment and its application as fire retardant. *Journal of Technical Education and Training*, *15*(1), 55-72.

Bogdanova, V. V., Kobets, O. I., Platonov, A. S., and Perevoznikova, A. B. (2023). Optimization of fire-resistant and fire-thermal protective properties of intumescent composites using mathematical experimental planning. *Gorenie i vzryv*, *16*(3), 62-72.

Dogan, M., Dogan, S. D., Savas, L. A., Ozcelik, G., and Tayfun, U. (2021). Flame retardant effect of boron compounds in polymeric materials. *Composites Part B: Engineering, 222*, 109088.

Gilman, A. B., Kuznetsov, A. A., and Ozerin, A. N. (2017). Modification of ultra-high-molecular-weight polyethylene fibers and powders using low-temperature plasma. *Russian Chemical Bulletin, 66*(4), 577-586.

Hofmann, T., Giesen, R. U., and Heim, H. P. (2024). High consistency silicone rubber foams. *Polymers, 16*, 1181.

Inozemtsev, A. S., and Korolev, E. V. (2013). Hollow microspheres are an effective filler for high-strength lightweight concretes. *Industrial and Civil Engineering, 10*, 80-83.

Kablov, V. F., Keibal, N. A., Kochetkov, V. G., Motchenko, A. O., and Antonov, Yu. M. (2018). Research of the influence of carbon microfiber on the properties of elastomer fire-protective materials. *Russian Journal of Applied Chemistry, 91*(7), 1160-1164.

Kablov, V. F., Kochetkov, V. G., Keibal, N. A., Novopoltseva, O. M., Kryukova, D. A., Urzhumov, D. A., Shesternin, M. I., and Myasnikov, I. M. (2025). Adjusting the properties of heat- and fire-resistant elastomers by low-temperature plasma treatment of reinforcing microparticles. *Russian Engineering Research, 45*, 1516-1520.

Liu, G., Yu, H., Zhu, T., Chen, J., Dong, X., Jia, H., Sun, J., Gu, X., and Zhang, S. (2024). Constructing flame retardant microspheres for safe and stable poly(ethylene oxide)-based all-solid-state batteries at high voltage. *Chemical Engineering Journal, 485*, 149756.

Liu, J., Qi, P., Meng, D., Li, L., Sun, J., Li, H., Gu, X., Jiang, S., and Zhang, S. (2022). Eco-friendly flame retardant and smoke suppression coating containing boron compounds and phytic acids for nylon/cotton blend fabrics. *Industrial Crops and Products, 186*, 115239.

Provotorova, D. A., Kablov, V. F., Ozerin, A. N., Gilman, A. B., Yablokov, M. Y., Aksenov, V. I., and Keybal, N. A. (2014). Modification of unsaturated rubbers in low-temperature plasma as a method to improve their adhesion properties. *Polymer Science Series D*, *7*(2), 99-101.

Qiu, S., Su, F., Zhou, Y., Li, Y., Wang, X., and Zhang, L. (2024). Multi-scale ceramic self-extinguishing fire retardant coating based on scale armor layer. *Chemical Engineering Journal, 499*, 156137.

Wang, Z., Zhang, X., Bao, C., Wang, Q., Qin, Y., and Tian, X. (2012). The synergistic effect of aluminum hypophosphide and nanosilica on flame-retarded ethylene-propylene-diene monomer rubber. *Journal of Applied Polymer Science, 124*(4), 3487-3493.

Zhilin, I. A., Chausov, F. F., Lomova, N. V., Kazantseva, I. S., Isupov, N. Y., and Averkiev, I. K. (2023). Impact of the chelate complex of nitrilotris (methylenephosphonic acid) with copper on the corrosion-electrochemical behavior of carbon steel in an aqueous medium. *Russian Journal of Applied Chemistry*, *96*(2), 176-189.