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Research Article

Synergic effect of oxidized polyacrylonitrile fibers and zinc borate on spark suppression in automotive brake pad composite materials

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ABSTRACT: The mechanical, physical, and thermal properties of composite friction material are key parameters influencing both the direct performance of automotive brake systems and secondary phenomena, such as spark and flame generation during braking. These properties are strongly affected by the composition and interaction of the raw materials used in the formulation. In this study, a novel friction material for automotive brake pads was developed with the aim of improving tribological and physical performance while reducing spark and flame generation. Oxidized polyacrylonitrile (PAN) fiber was incorporated into a reference formulation at volume ratios of 1:1, 1:2, and 1:4 relative to the aramid fiber conventionally used. In addition, zinc borate was introduced at 5, 10, and 15 vol%, replacing part of the conventional filler content. A hybrid formulation containing both PAN fiber and zinc borate was also evaluated to investigate possible synergistic effects. The samples were characterized by scanning electron microscopy, Gogan hardness, specific gravity, cold and hot compressibility, and thermal conductivity tests. Spark and flame generation tests were also performed under simulated braking conditions. The results showed that the incorporation of PAN fiber reduced material stiffness, whereas zinc borate increased it; their combined use resulted in a more balanced mechanical response. Compressibility and porosity were also affected by the additives, with noticeable variations among the formulations. Internal shear strength was significantly influenced, with one hybrid formulation showing a marked increase. In particular, the hybrid formulation exhibited a balanced performance, with reduced spark generation, indicating its potential for automotive brake pad applications.

Keywords: *Oxidized polyacrylonitrile fiber, Zinc borate, Brake pads, Spark suppression, Friction materials*

1. INTRODUCTION

The performance of braking systems critically depends on the ability of friction materials not only to provide stable coefficients of friction and adequate wear resistance but also to control adverse effects associated with heat generation, hot-particle detachment, and the risk of ignition. Automotive brake pads are complex, multi-phase composite materials, in which fibers, fillers, friction modifiers, and a polymeric binder are combined to achieve a tailored balance between mechanical integrity, thermal stability, and tribological performance. The strategic design of brake pad composites aims to optimize load transfer, energy dissipation, and durability, while simultaneously reducing the use of restricted substances such as copper and lowering production costs [1-3].

An increasingly important challenge involves spark and flame generation during braking, phenomena that are strongly influenced by both the intrinsic properties of the composite constituents and operating conditions such as contact pressure, sliding velocity, and temperature [4-7]. Experimental studies have

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demonstrated that hot sliding contacts can eject incandescent debris as a by-product of friction, which may act as a potential ignition source [5,7]. The propensity for spark formation depends on the reactivity and thermophysical properties of both counterface and pad constituents (e.g., copper, titanium, steel), as well as on the formation and stability of the tribo-layer, which governs energy dissipation at the sliding interface [5-8].

To mitigate these risks, recent research has explored the incorporation of functional additives and reinforcements capable of stabilizing the sliding contact under severe braking conditions. Zinc borate has been reported not only as a flame retardant additive but also as a promoter of tribo-layer formation, contributing to improved friction stability and reduced localized heating [9,10]. In parallel, oxidized polyacrylonitrile (PAN) fibers have emerged as promising alternatives due to their high oxidative stability and intrinsic flame-retardant characteristics at elevated temperatures, which may contribute to suppressing ignition-related phenomena [11-12].

Such effects have been investigated under conditions that closely resemble real-world braking scenarios, where brake pads and discs undergo significant surface heating, as demonstrated by Meyer, Beyer, and Krause [5]. Their findings showed that hot surfaces do not maintain direct contact with the surrounding atmosphere and that detached hot particles can be identified as friction by-products. Further analyses indicated that spark and flame generation is influenced by mechanical and physical brake conditions, including pressure, speed, contact configuration, and the composition of the friction material itself. Under these conditions, different raw materials exhibit distinct behaviors, with metallic constituents such as copper, titanium, and steel demonstrating varying propensities for spark and flame generation [5].

These findings are particularly relevant for materials used in commercial vehicle brake systems, given similarities in disc-pad contact mechanisms, temperature range, and tribological conditions. To address the challenges associated with particulate emissions and excessive heat generation, the present study investigates the incorporation of oxidized polyacrylonitrile fibers into a base brake pad formulation, aiming to enhance mechanical reinforcement and thermal stability. Additionally, zinc borate is introduced as a functional additive to retard flame ignition by promoting tribo-layer formation, while maintaining or improving the physical and mechanical properties of the composite, as suggested in the literature [5].

Although zinc borate has been previously investigated as a flame-retardant and tribological additive in brake friction materials, and oxidized polyacrylonitrile (PAN) fibers are recognized for their thermal stability and char-forming behavior, studies combining both materials in automotive brake pad formulations remain scarce. To the best of our knowledge, no previous study has systematically investigated the combined effects of zinc borate and oxidized PAN fibers on spark suppression behavior in automotive brake pad composites. In particular, there is still a lack of understanding regarding the synergistic relationship between flame-retardant additives and thermally stabilized organic fibers on spark and flame suppression under severe braking conditions. Therefore, the novelty of the present study lies not only in evaluating the individual effects of zinc borate and oxidized PAN fibers on the physical, mechanical, and thermal properties of friction materials, but also in systematically investigating their combined influence on spark generation behavior during simulated braking tests. This approach provides new insights into the design of safer and thermally stable friction materials capable of minimizing ignition-related phenomena while maintaining suitable mechanical and tribological performance for commercial vehicle brake applications.

2. MATERIALS AND METHODS

The oxidized polyacrylonitrile fiber was supplied by SGL Carbon Group. Zinc borate was purchased from Datiquim. The brake pad (BP) base formulation was designated as BP_PAN/0_ZB/0, and the other samples were prepared by modifying two raw materials from the original formulation: zinc borate (ZB) was used as a filler and replaced barium sulfide, and oxidized polyacrylonitrile fiber (PAN) replaced aramid fiber. The base formulation was defined based on the typical composition of a commercial brake pad material and comprised the main classes of raw materials commonly used in friction products. The fiber fraction was divided into organic and metallic fibers, given that this component was the primary focus of the present study. In this formulation, organic fibers accounted for 0.5–3.0 vol%, metallic fibers for 25.0–30.0 vol%, the polymeric binder for 12.0–16.5 vol%, friction modifiers for 45.0–50.0 vol%, and fillers for 2.0–6.5 vol%.

The percentage composition of each sample is shown in Table 1. Samples BP_PAN/0.6_ZB/0, BP_PAN/1.2_ZB/0, and BP_PAN/2.4_ZB/0 were prepared with percentages of 0.6%, 1.2%, and 2.4% by volume of oxidized polyacrylonitrile fiber, respectively. To evaluate the effect of zinc borate, 5% (BP_PAN/0_ZB/5), 10% (BP_PAN/0_ZB/10), and 15% (BP_PAN/0_ZB/15) by volume were added to the fraction of materials classified as friction modifiers. A combined formulation was also tested, using 1.2% by volume of oxidized polyacrylonitrile fiber and 5% by volume of zinc borate (BP_PAN/1.2_ZB/5). These percentages were selected based on a preliminary assessment of the influence of each individual component.

Table 1. Sample designations and material percentages.

Samples	Oxidized polyacrylonitrile (% vol)	Zinc borate (% vol)
BP_PAN/0_ZB/0	0	0
BP_PAN/0.6_ZB/0	0.6	0
BP_PAN/1.2_ZB/0	1.2	0
BP_PAN/2.4_ZB/0	2.4	0
BP_PAN/0_ZB/5	0	5
BP_PAN/0_ZB/10	0	10
BP_PAN/0_ZB/15	0	15
BP_PAN/1.2_ZB/5	1.2	5

For the brake pad production process, the raw materials were weighed and mixed in a 20 L Eirich laboratory mixer. The brake pads were then produced by pressing the friction mixture at a temperature of 160°C under a pressure of 300 kgf/cm^2 for 5 min. Subsequently, the samples underwent heat treatment in an oven at 270°C

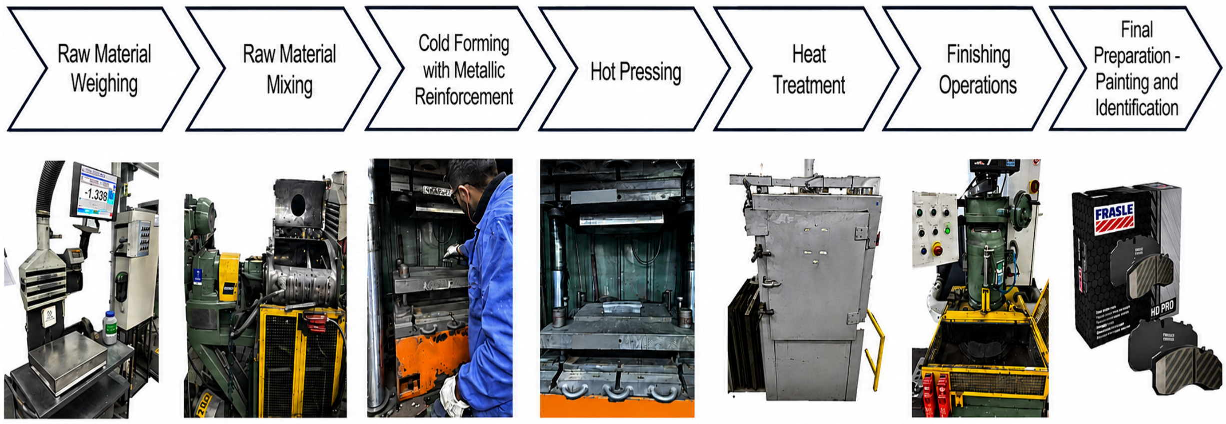

Figure 1. Representative image of a brake pad production process.

for 8 h. The final finishing step involved surface grinding to give the specified dimension followed by painting and identification. Figure 1 shows a representative image of the brake pad production process.

2.1. Characterization. ***2.1.1. Characterization of raw materials.*** Thermogravimetric analysis (TGA) of oxidized polyacrylonitrile fiber and zinc borate was performed under a synthetic air atmosphere (60 $ml.min^{-1}$) using Universal V4.5 TA instruments equipment. The analysis was carried out with a heating rate of 10°C.min^{-1} over a temperature range of 25°C to 950°C, using approximately 10 mg of each sample.

2.1.2. Characterization of brake pad friction materials.

The morphology of the samples was examined using a MIRA3 TESCAN scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS). For enhanced accuracy, selected samples were observed at a magnification of 5.000×. Prior to analysis, all specimens were cryo-fractured in liquid nitrogen and sputter-coated with gold.

The Gogan hardness test is a technique used to determine the stiffness of a material. The Gogan number is obtained by measuring the penetration depth of an indenter, expressed in units of 0.0064 mm. Tests were performed using a Model 911 durometer, with eight sampling cycles, applying a 1500 kgf load at specified points, in accordance with NBR 5520.

Specific gravity and porosity were measured according to ISO 15484. Three samples for each formulation were first weighed in air and then fully submerged in distilled water at room temperature to obtain the submerged weight. The average and standard deviation of the measurements were reported. Porosity was calculated using the information of sample volume (V), the theoretical mass expected (TME) and the experimentally measured specific gravity (EG). The porosity (P) was determined using the equation 1:

$$P = \left(1 - \frac{\frac{EG}{V}}{TME} \right) x100\% \quad (1)$$

Cold and hot compressibility were evaluated according to the ISO 6310 standard. Six samples were tested under each condition, and the average values along with their standard deviations were reported. These parameters reflect the combined physical effects associated with the material's elastic characteristics and plastic deformations. To assess the compressibility of the brake pad material, a load ranging from 0.5 to 8 MPa was applied for 1 s and maintained for an additional second after reaching the maximum pressure. Thermal transmission was also evaluated following ISO 6310. In this test, the friction material was placed on a heated plate at 400 ± 10°C for 15 min under a load of 0.5 MPa. Thermal transmission (T_t) was calculated using the equation 2:

$$T_t = T_2 - T_1 \quad (2)$$

Where T_2 is the final temperature of the component at the end of the test, and T_1 is the initial temperature. Internal shear strength was evaluated according to ISO 6311. Five specimens of each friction material, with dimensions of 20 x 20 x 10 mm, were tested. A force was applied with a rate of 4500 $N.s^{-1}$ to the specimens, and the result was recorded at the point of material displacement. The Analysis of Variance (ANOVA) test with one factor, a 95% confidence level, and a significance level of 0.05 was applied to verify significant differences between the mean values of the studied samples. Furthermore, the Tukey test was performed to identify which samples exhibited statistically significant differences. Statistical analysis was conducted using Past software version 4.03. The tests were applied to the Gogan hardness, density, cold and hot compressibility, internal shear strength, porosity, and thermal transmission measurements. Differences in averages were considered significant at $p \leq 0.05$. Identical letters were used to indicate statistically similar means.

The procedure for evaluating spark generation during braking in a disc brake system consisted of performing 20 brake events, with an initial application speed of 50 MPH and a final release speed of 15 MPH. Each brake was applied every 72 s with a deceleration of 9 fps2. This braking configuration and interval time promote rapid heating of both the brake disc and pad, leading to the release of overheated particles [13].

An adapted version of the Federal Motor Vehicle Safety Standards 121 (FMVSS121) procedure was conducted on an inertia dynamometer, recording data on torque, brake pressure and temperature, throughout cycles. Videos were also recorded during the test

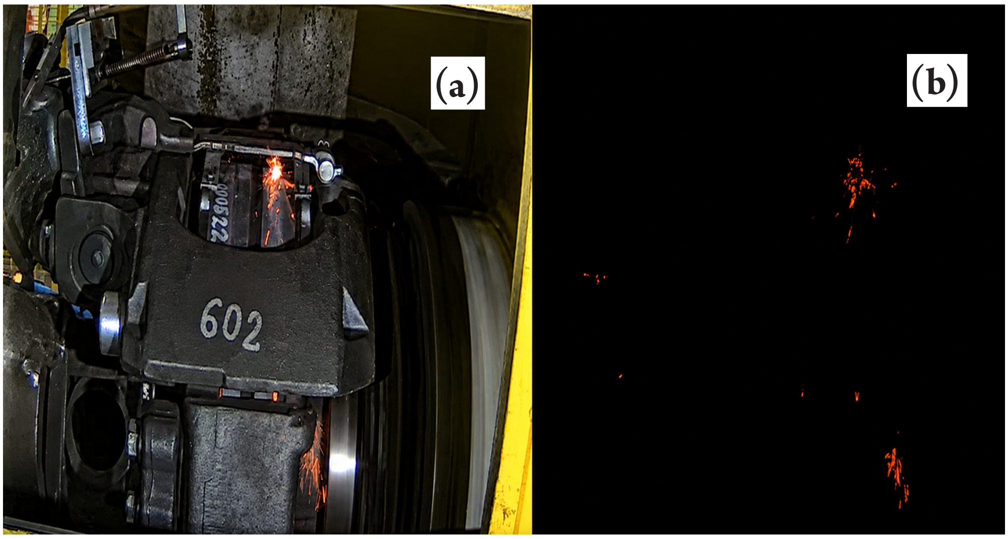

Figure 2. (a) Experimental apparatus used for spark generation and (b) representative image used to evaluate the amount of sparks and flames generated during the FMVSS-121 test procedure.

to verify the occurrence of sparks and flames. The results were statistically analyzed using Minitab software to compare outcomes and evaluate the responses obtained [1, 14]. The adapted FMVSS121 procedure used in this study evaluates the friction material under various conditions, such as speed, temperature (100°C and 300°C), and pressure (1.5 to 9 bar), to assess spark and/or flame generation (as illustrated in Figure 2), and well as the stability of friction [13, 15]. To evaluate the quantity of spark and flame during the FMVSS-121 test, a pixel method was applied to define in a quantitative way qualitative characteristics. It means the system records the brake system during the test, with a spark or flame appearing, this hot point is detected and the quantity of modified pixels using parts per million (ppm) to calculate it.

3. RESULTS AND DISCUSSION

Figure 3 presents the thermogravimetric analysis (TGA) and the derivative thermogravimetric (DTG) curves of zinc borate (a) and oxidized polyacrylonitrile fiber (b). For zinc borate (Figure 3a), two main mass loss events are observed, the first at ~ 315°C and the second close to 425°C, which are associated with the stepwise dehydration of hydrated zinc borate phases. A similar behavior was reported by Beltaci et al [16] and Schubert [17], who showed that zinc borate retains its water of hydration up to 300°C and undergoes endothermic dehydration at higher temperatures. This dehydration process is known to absorb heat and may locally attenuate flash temperatures at asperity contacts, which are responsible for the ignition of metallic wear particles during severe sliding [18, 19].

In Figure 3b, two main mass loss events are observed for the oxidized polyacrylonitrile fiber. The first, occurring near 50°C, is attributed to the maximum rate of degradation associated with moisture loss. The second event, starting at ~ 200°C and reaching a maximum degradation rate around 650°C, is associated with the thermal decomposition of the stabilized structure of oxidized PAN. According to Szepcsik and Pukánszky [20], this mass loss is

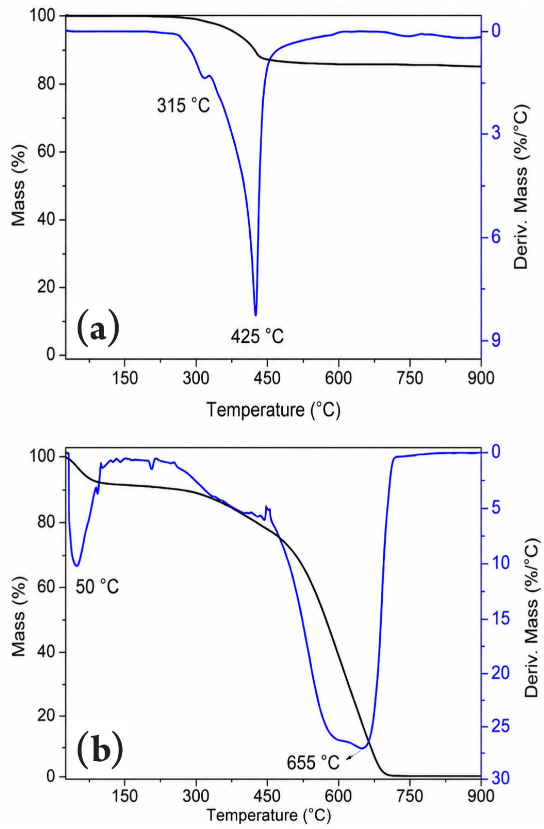

Figure 3. TGA and DTG of (a) ZB and (b) oxidized PAN fiber.

related to the elimination of non-cyclised nitrile groups and terminal imino groups, while the highly aromatized ladder structure promotes high char yield and thermal stability. Such a char-forming behavior is characteristic of oxidized PAN fibers and is associated with low emission of flammable volatiles and enhanced resistance to ignition [11].

Both materials exhibit thermal stability above 300°C, with the maximum mass loss occurring at temperatures exceeding 400°C. Considering the temperature range reached during the adapted FMVSS-121 braking tests, these results indicate that neither zinc borate nor oxidized PAN fibers undergo significant thermal decomposition under service-relevant conditions. Moreover, the endothermic dehydration of zinc borate and the char-forming nature of oxidized PAN fibers may contribute synergistically to heat absorption, stabilization of the tribo-layer, and reduction of hot particle detachment, which are key factors governing spark and flame generation in friction materials [19, 21]. The morphology of three representative formulations was analyzed by scanning electron microscopy (SEM): BP_PAN/2.4_ZB/0, containing 2.4% oxidized PAN fiber; BP_PAN/0_ZB/10, containing 10% zinc borate; and BP_PAN/1.2_ZB/5, the hybrid formulation containing 1.2% oxidized PAN fiber and 5% zinc borate. These formulations represent, respectively, the systems with oxidized PAN fiber substitution, zinc borate substitution, and combined PAN fiber/zinc borate incorporation, as shown in Figure 4.

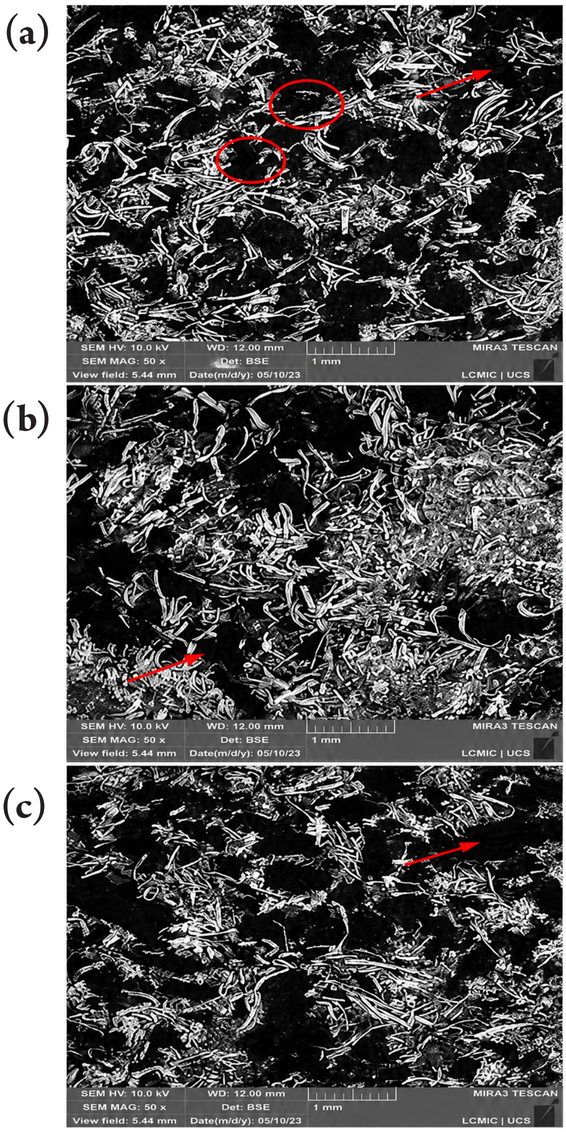

Figure 4. SEM micrographs of friction material sample containing (a) 2.4% oxidized polyacrylonitrile fiber, (b) 10% zinc borate (c) 1.2% oxidized polyacrylonitrile fiber and 5% zinc borate samples.

In general, the fibers were well distributed, and no evidence of fiber pull-out was observed, as the detached fibers remained embedded in the matrix. However, voids were observed in some regions of the fractured surface, as highlighted by the red circles, along with some matrix cracking, as indicated by the arrows. The voids were correlated to the material porosity. The partial replacement of aramid fiber with PAN did not significantly alter the morphology of the samples when comparing Figures 4a and 4b, nor did the presence of zinc borate.

It is important to note that these components were added in low amounts, and the high quantity of visible fiber is due to the iron-containing fibers, as confirmed by the EDS analysis (Figure 5), in which the primary elements detected were carbon (C), oxygen (O), and iron (Fe), along with other elements present in smaller proportions.

In BP_PAN/2.4_ZB/0 sample (a), the presence of zinc (Zn) was not detected; however, in the BP_PAN/0_ZB/10 (b) and BP_PAN/1.2_ZB/5 (c) samples, the presence of zinc borate was confirmed by the detection of this element, which was uniformly distributed throughout the matrix without signs of agglomeration. A high proportion of steel fibers (Fe) was also observed. This feature is relevant because the metallic constituents of friction materials may influence spark generation and ignition propensity during sliding contact, as reported by Li et al. [7], who showed that mechanically generated friction sparks and their incendivity depend strongly on the type of metal alloy involved. In the BP_PAN/1.2_ZB/5 sample, the presence of zinc borate (Zn) was confirmed, whereas the polyacrylonitrile fiber could not be clearly identified due to its organic nature.

Figure 6 presents the results for specific gravity and Gogan hardness of the studied samples. Figure 6a shows a decrease in specific mass with increasing oxidized polyacrylonitrile fiber content. Samples containing zinc borate exhibited lower specific mass compared to the control sample and to those containing only oxidized polyacrylonitrile fibers. The BP_PAN/1.2_ZB/5 sample, which combines materials with higher density, showed values similar to those of the samples containing equivalent zinc borate content. The Gogan hardness test is a non-destructive method related to material stiffness, where lower Gogan hardness values correspond to higher stiffness. In the Gogan hardness analysis (Figure 6b), replacing aramid fiber with oxidized PAN increased hardness, indicating reduced stiffness, whereas the addition of zinc borate led to increased stiffness. The BP_PAN/1.2_ZB/5 sample showed a significant decrease in hardness (~ 39 ± 1 GC) compared to the base material BP_PAN/0_ZB/0 (~ 67 ± 2 GC).

The porosity of each friction material in Figure 7 ranges from ~17 to 27%. Brake pads should have a certain amount of porosity to minimize the effect of water and oil on the friction coefficient. Increasing porosity by more than 10% could reduce the brake noise. Mutlu et al [22] reported values from 7 to 18% in brake pads porosity, and the authors observed that the specimens with high porosity tend to exhibit high friction coefficient. Magnier et al [23] also reported that a porosity level of 10% or higher is commonly

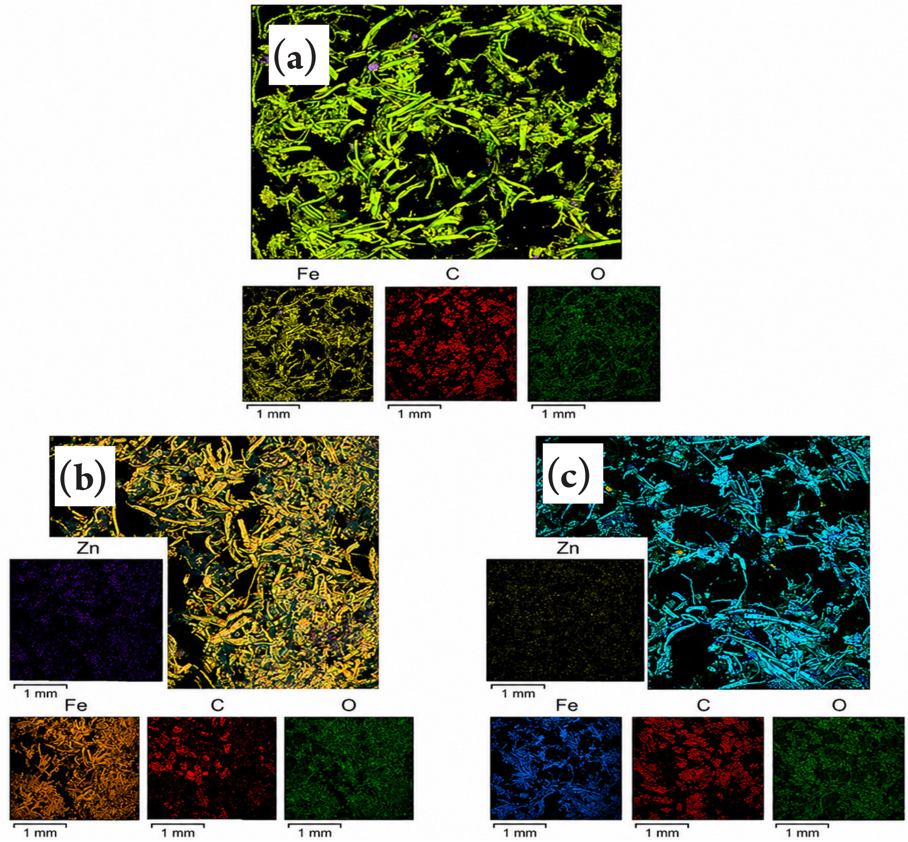

Figure 5. EDS for (a) 2.4% oxidized polyacrylonitrile fiber (BP_PAN/2.4_ZB/0), (b) 10% zinc borate (BP_PAN/0_ZB/10) and (c) 1.2% oxidized polyacrylonitrile fiber and 5% zinc borate (BP_PAN/1.2_ZB/5) samples.

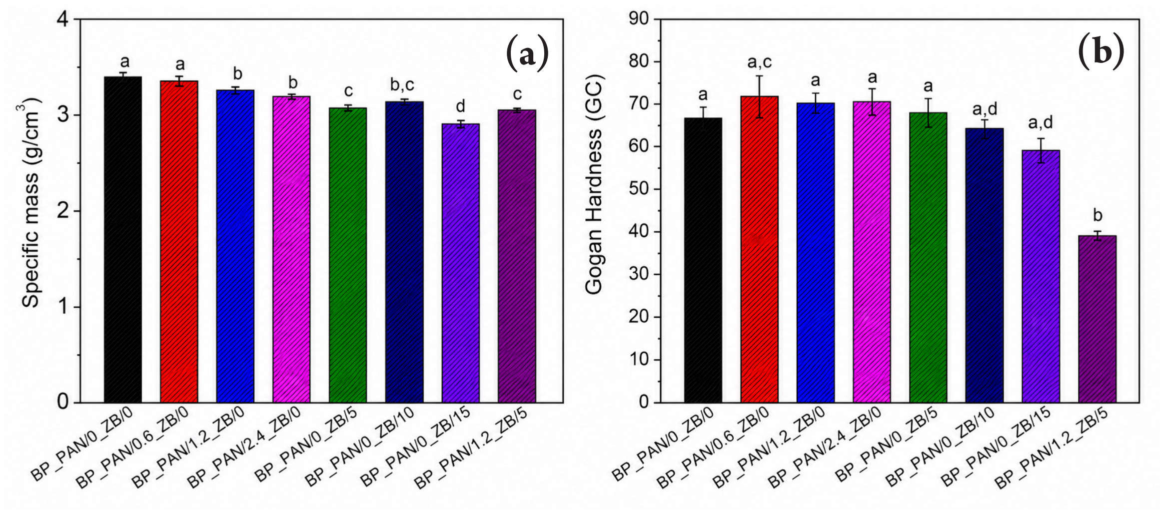

Figure 6. Results for specific mass (a) and Gogan hardness (b) of the studied samples. Different letters indicate statistically significant differences among mean values according to Tukey's multiple range test ($p \leq 0.05$).

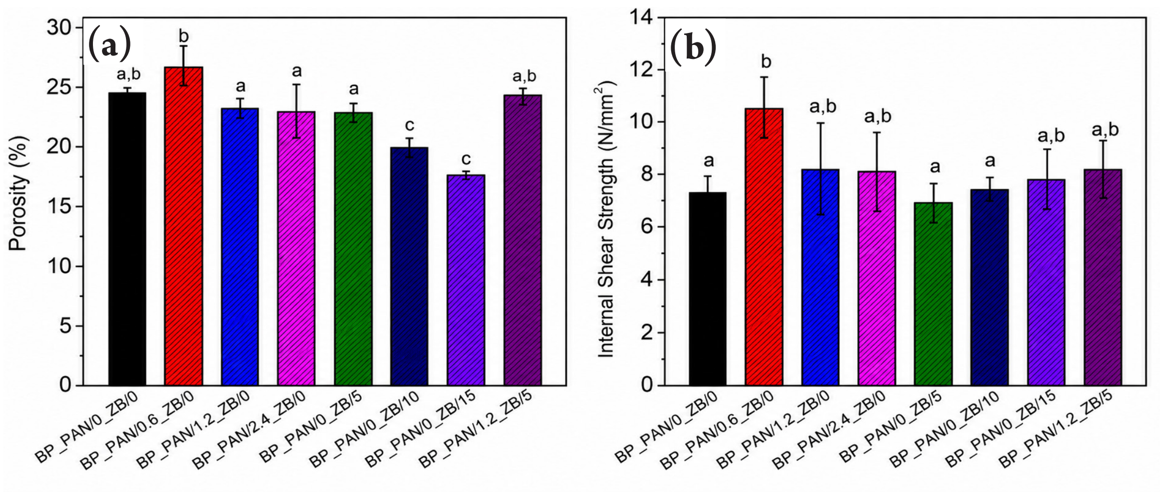

Figure 7. Porosity (a) and (b) internal shear strength results for the studied samples. Different letters indicate statistically significant differences among mean values according to Tukey's multiple range test ($p \leq 0.05$).

observed in friction materials. This characteristic is usually associated with other properties, such as friction coefficient and wear rate. Indeed, porosity affects the braking mechanism, as it can lead to variations in the contact pressure during the braking process. In this study, no direct relationship was observed between porosity and the specific mass shown in Figure 6a. Although a reduction in specific mass was expected to result in higher porosity values, this behavior was not confirmed.

Figure 7b presents the internal shear strength results, with the minimum required value for brake pads being 2.50 $N.mm^{-2}$. All samples exceeded this safety requirement. Chen and Lam [24] investigated shear strength under different conditions, including raw materials, cure rate and other processing parameters. In their study, different raw materials exhibited more than a 100% variation in shear strength. In this study, a significant increase in internal shear strength was observed with fiber replacement, particularly in sample BP_PAN/0.6_ZB/0, which showed an increase of more than 40% compared with the reference sample. This improvement may be associated with better mechanical anchoring of the fibrous phase and enhanced load transfer within the phenolic matrix. Similar behavior has been reported in fiber-reinforced brake friction composites, in which the incorporation of reinforcing fibers contributes to improved structural integrity and resistance to shear failure [25-27]. However, the increase in oxidized PAN content did not lead to a proportional increase in shear strength, indicating that the reinforcing effect depends on an adequate balance between fiber content, matrix continuity, and porosity. The hybrid BP_PAN/1.2_ZB/5 formulation showed an intermediate shear strength, indicating that the combined addition of oxidized PAN fiber and zinc borate maintained adequate composite cohesion while contributing to a balanced mechanical response.

Figure 8 presents the cold and hot compressibility results. For cold compressibility, all samples exhibited similar behavior compared to the base material (BP_PAN/0_ZB/0). Among the tested formulations, sample BP_PAN/0_ZB/10 showed a significantly higher compressibility than samples BP_PAN/0.6_ZB/0 and BP_PAN/2.4_ZB/0. In the hot compressibility test, the

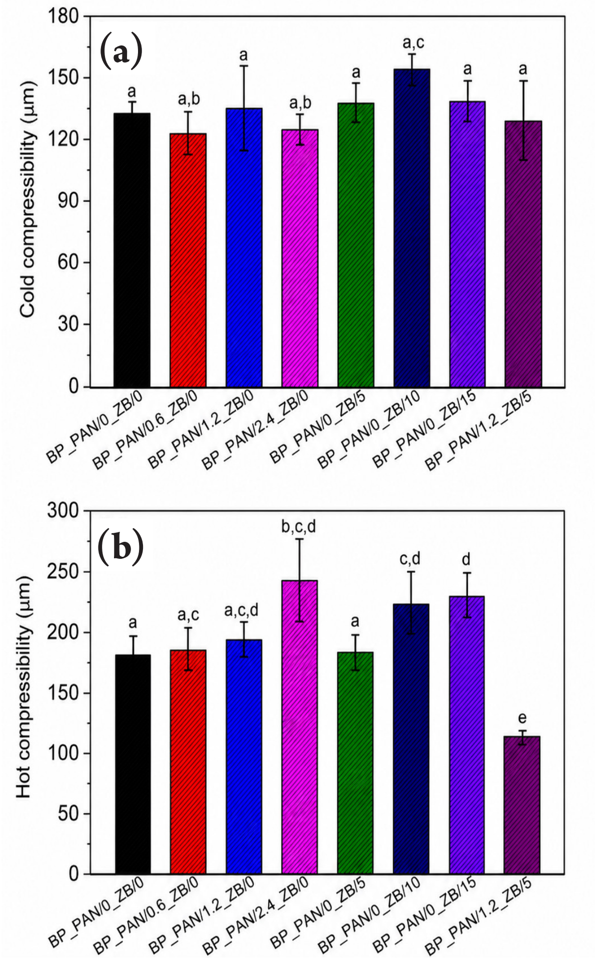

Figure 8. Cold compressibility (a) and hot compressibility (b) results for the studied samples. Different letters indicate statistically significant differences among mean values according to Tukey's multiple range test ($p \leq 0.05$).

highest values were reported for samples BP_PAN/2.4_ZB/0, BP_PAN/0_ZB/10, and BP_PAN/0_ZB/15. The hybrid sample BP_PAN/1.2_ZB/5 demonstrated the most stable performance, maintaining compressibility values even under elevated temperatures.

By comparing the results obtained from the cold and hot compressibility tests, it is evident that cold compressibility exhibits lower values (~120 to 150 µm) than those observed for hot compressibility (~115 to 240 µm). When the material is heated, the phenolic resin matrix is affected and its chains can get molecular mobility, increasing the deformation of the pad (hot compressibility). Such behavior can significantly influence the performance of friction materials in terms of wear, friction coefficient, spark generation, vibration, and other characteristics that are frequently investigated. Dadkar et al. [25] studied the performance of friction materials with fiber combinations and highlighted compressibility as a key parameter. However, for an accurate evaluation of friction material performance, compressibility should be interpreted in conjunction with other test results, as isolated analysis may lead to misleading conclusions. For instance, the sample BP_PAN/1.2_ZB/5 demonstrated very stable compressibility values under both cold and hot conditions, in contrast to the others, including the base material.

Figure 9 presents the thermal transmission values, which did not exhibit a correlation associated with the type or percentage of the new raw materials added to the formulation. An exception was observed for sample BP_PAN/1.2_ZB/5, which also exhibited stable compressibility values, including under hot compressibility conditions. Brezolin and Soares [26] demonstrated that friction materials can influence the behavior of adjacent materials, and that certain combinations of friction material properties may enhance or reduce this influence. These findings reinforce the importance of correlating physical properties to properly interpret the results. Thermal transmission can be affected by differences in specific mass, hardness and other physical characteristics [26].

In agreement with this interpretation, Abbasi et al. [27] reported that the elastic compression modulus and thermal conductivity of polymer-based composite friction materials are key parameters governing the thermal interaction between the pad and the counterface. According to the authors, minimizing temperature rise at the contact interface depends on a balance between mechanical conformability and heat dissipation. Softer materials, with lower elastic modulus, can increase the real contact area and dissipate part of the frictional heat through deformation, whereas stiffer materials require higher thermal conductivity to promote heat conduction through the pad. Therefore, thermal transmission should not be interpreted as an isolated property, since it is affected by specific gravity, hardness, compressibility, elastic modulus, and heat dissipation capacity during braking.

The adapted FMVSS121 dynamometer procedure considered pressure, torque, temperature, and spark/flame generation. FMVSS121 tests monitor the torque of the brake system during the braking cycle, as well as the system pressure and brake system temperature [13]. In this study, the three main parameters, torque, pressure, and temperature, were monitored during the tests. The basic principle of the brake system was to adjust the brake pressure in order to maintain the braking torque, with heating of the brake

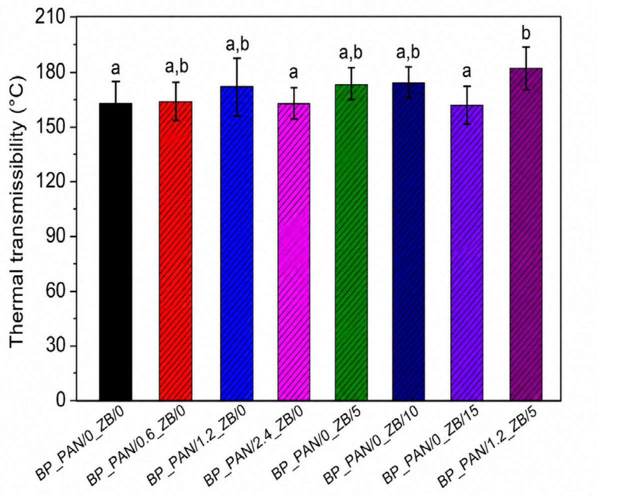

Figure 9. Thermal transmission results for the studied samples. Different letters indicate statistically significant differences among mean values according to Tukey's multiple range test ($p \leq 0.05$).

system being one of the resulting phenomena.

Figure 10 shows the spark-generation behavior of the studied brake-pad formulations during the adapted FMVSS-121 dynamometer test. For each formulation, the x-axis is divided into three test regions: the first region corresponds to the 20 successive braking sequences recorded during the standard spark-evaluation stage; the second region corresponds to six braking cycles performed with the brake system heated to 100 °C; and the third region corresponds to six braking cycles performed at 300 °C. The y-axis represents the spark intensity quantified by the image-analysis method, expressed as the sum of modified pixels in parts per million (ppm × 10^4). Therefore, lower values indicate lower spark and/or flame generation during braking. In this study, values below 300 × 10^4 ppm were considered acceptable for the friction material under the tested conditions.

The reference formulation, BP_PAN/0_ZB/0, showed relatively low spark generation throughout the test, with most values below the 300 × 10^4 ppm threshold. However, a gradual increase in spark intensity was observed during the first 20 braking sequences, reaching values close to 200 - 250 ppm. This behavior indicates that, although the reference material remained within the acceptable range, the repeated braking cycles promoted progressive changes at the friction interface, probably associated with surface heating, debris formation, and the evolution of the third-body layer.

The incorporation of oxidized PAN fiber alone did not eliminate spark generation and, in some cases, increased the spark response. For BP_PAN/0.6_ZB/0, BP_PAN/1.2_ZB/0, and BP_PAN/2.4_ZB/0, the spark intensity generally increased during the standard braking sequence, especially after approximately the 10th to 12th braking event. The formulation containing 2.4% oxidized PAN fiber reached values around or above the acceptance limit, indicating that higher PAN contents may contribute to a more severe frictional contact condition. This behavior may be associated with changes in the mechanical and physical response of the material.

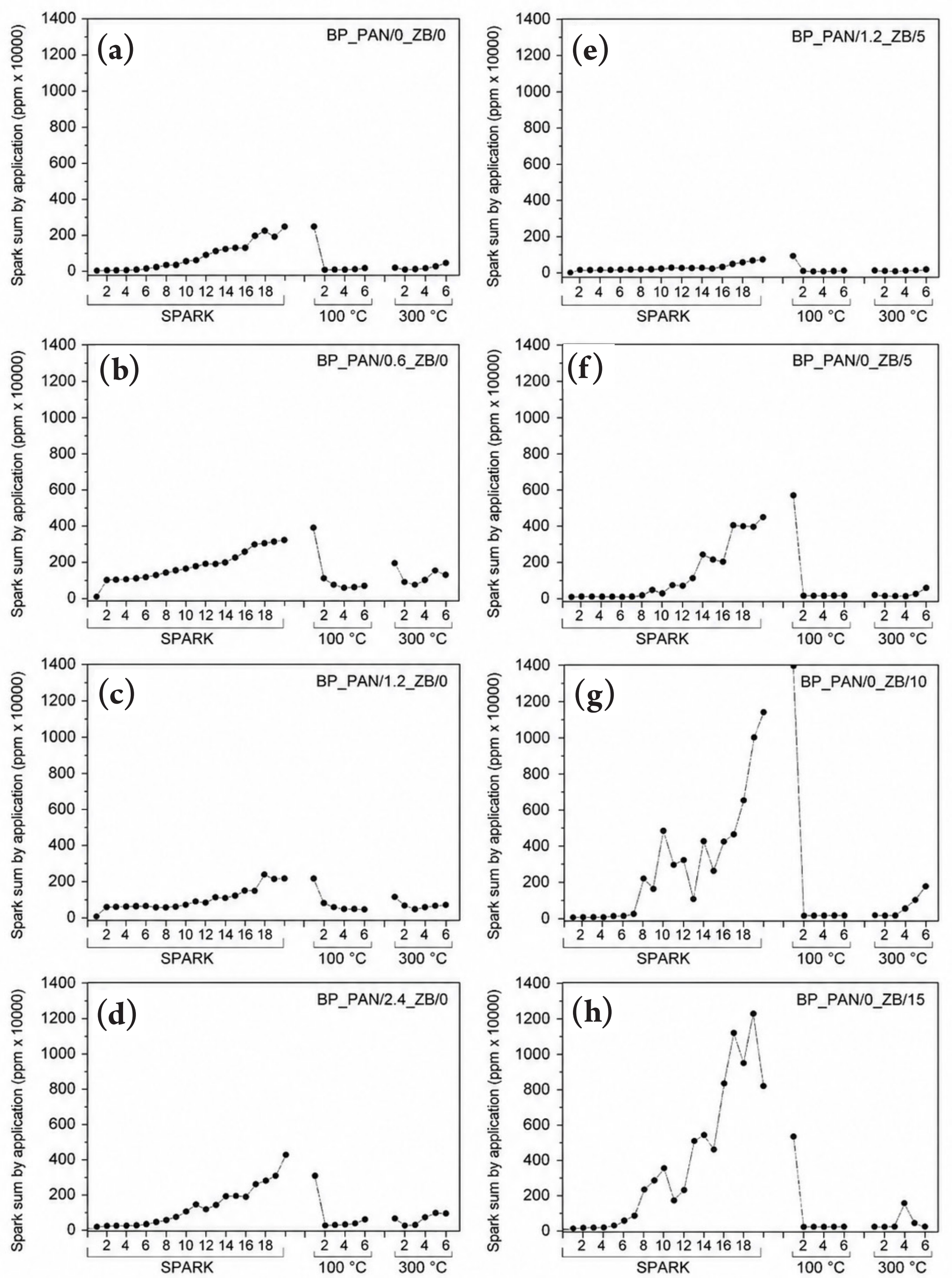

Figure 10. Spark generation of the studied brake-pad formulations during the adapted FMVSS-121 dynamometer test. The x-axis is divided into three regions: 20 successive braking sequences under the standard spark-evaluation condition, followed by six braking cycles at 100 °C and six braking cycles at 300 °C. Spark generation was quantified by image analysis and expressed as the sum of modified pixels in ppm × 10000.

The Gogan hardness results indicated that PAN-containing formulations tended to present higher Gogan hardness values, which correspond to lower stiffness. In addition, changes in porosity and hot compressibility may have affected the stability of the contact surface during repeated braking. Under these conditions, a less stable friction layer may favor the detachment of overheated particles and increase spark generation, even though the PAN fiber itself has good thermal resistance.

In contrast, the addition of zinc borate strongly affected spark generation. The formulation containing 5% zinc borate, BP_PAN/0_ZB/5, showed an intermediate response, with spark values increasing during the standard braking sequence and reaching values above 300 ppm in some cycles. However, when the zinc borate content was increased to 10 and 15%, a much more pronounced spark generation was observed. BP_PAN/0_ZB/10 and BP_PAN/0_ZB/15 exhibited the highest spark intensities among all compositions, with values largely exceeding the 300×10^4 ppm limit during the standard braking sequence. This result indicates that the excessive addition of zinc borate did not improve the stability of the friction material under the conditions evaluated. Although zinc borate is commonly associated with flame retardancy and may contribute to the formation of a protective tribological layer [10, 28], excessive contents may alter the compactness, wear behavior, and integrity of the friction film, increasing the release of hot particles during braking. This behavior is consistent with the findings of Öztürk and Mutlu [21], who reported that the mechanical and tribological performance of brake friction composites was strongly dependent on the relative contents of zinc borate and fly ash. In their study, formulations containing low zinc borate contents (0-5 wt%) showed better friction stability and fade resistance than those containing higher zinc borate levels (10-35 wt%), with the best friction response observed for the composite containing 5 wt% zinc borate.

A different behavior was observed for the hybrid formulation BP_PAN/1.2_ZB/5. This sample presented the lowest and most stable spark-generation response among the modified formulations. During the standard braking sequence, the spark intensity remained well below the 300×10^4 ppm threshold, with only a slight increase at the end of the sequence. In the cycles performed at 100 °C and 300 °C, the spark generation was also very low, indicating good stability under different thermal conditions. This result indicates a synergistic effect between oxidized PAN fiber and a moderate zinc borate content. The PAN fiber may contribute to maintaining the structural integrity of the friction material, while zinc borate at 5 vol% may assist in stabilizing the tribological layer and reducing the detachment of incandescent debris. This interpretation is supported by the previous characterization results: the hybrid formulation showed a marked reduction in Gogan hardness value, indicating increased stiffness; stable cold and hot compressibility; adequate porosity; and one of the highest thermal transmission values. Together, these properties suggest that BP_PAN/1.2_ZB/5 developed a more stable friction interface, reducing localized instabilities responsible for spark and flame generation.

It is also noteworthy that, for most formulations, the highest spark intensities occurred during the first 20 successive braking events, whereas the cycles at 100 °C and 300 °C generally produced lower values. This indicates that spark generation was governed not only by the imposed temperature, but mainly by the dynamic evolution of the friction layer during repeated braking. Therefore, the spark response appears to be controlled by the combined effects of formulation, contact stability, debris detachment, and thermal dissipation. Overall, the results show that neither oxidized PAN fiber nor zinc borate alone guaranteed spark suppression. Instead, the best performance was achieved by the balanced hybrid formulation BP_PAN/1.2_ZB/5, which combined reduced spark generation with suitable physical, mechanical, and thermal behavior for automotive brake-pad applications.

4. CONCLUSION

The results obtained through various analyses highlighted the effects of incorporating oxidized polyacrylonitrile fiber and zinc borate into friction materials. Both oxidized polyacrylonitrile fiber and zinc borate exhibited adequate thermal stability for use in friction materials, as confirmed by TGA. SEM and EDS analyses revealed the distribution and interaction of the additives within the material. The oxidized polyacrylonitrile fiber displayed organic characteristics, while zinc borate was identified by its zinc composition. The addition of oxidized polyacrylonitrile fiber reduced the stiffness of the materials, while zinc borate increased it. The combination of the two additives resulted in a balance of properties. The compressibility and porosity of the materials were influenced by the addition of the additives, with noticeable variations observed across the samples. Internal shear strength was significantly influenced by the additives, with sample showing a significant increase. The results of this study provide relevant insights into the mechanisms governing spark and flame generation in friction materials. The suppression of sparks appears to be closely linked to the stabilization of the tribological interface, as well as to a reduction in the detachment of hot particles during friction. From this perspective, spark generation cannot be attributed to a single isolated factor, but rather to the combined interaction of thermal behavior, mechanical properties, and the stability of the friction layer formed during operation. Finally, FMVSS tests confirmed the distinct behavior of the materials under simulated braking conditions, with sample BP_PAN/1.2_ZB/5 exhibiting a balanced performance and potential for automotive brake appli-

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DECLARATIONS

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AVAILABILITY OF DATA

The data that support the findings of this study are available from the corresponding author upon reasonable request.

AI DISCLOSURE STATEMENT

The authors declare that no Generative AI tools were used in the preparation, writing, analysis, or editing of this manuscript.

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