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FRICTION AND WEAR IN SLIDING CONTACT OF CAST IRON AGAINST PHENOLIC RESIN COMPOSITES REINFORCED WITH CARBONACEOUS FIBERS FROM PLANTAIN FIBER BUNDLES[1]

Santiago Betancourt D.[2]
Luis J. Cruz[2]
Alejandro Toro B.[3]

Abstract
The tribological behavior of novolac phenolic resin matrix composites reinforced with carbonaceous fibers was studied. The carbonaceous fibers were obtained from Colombian plantain crops residues by slow pyrolysis, through a process that allows retaining many morphological aspects of the natural fibers. The aim of this study is to determine the effect of this kind of carbonaceous fibers as a potential reinforcement or lubricant filler for tribological applications. Novolac phenolic resin with HMTA as curing agent and carbonaceous fibers obtained by slow pyrolysis of leaf sheaths plantain fibers from Urabá-Colombia, were used to obtain a composite material by compression molding process. Composite samples with different fiber volume fractions were tested in sliding contact against cast iron in a pin-on-disc wear testing machine equipped with a load cell for on-line measurement of friction force. At the end of the tests, the worn surfaces and the debris were analyzed in SEM. A decrease in friction coefficient and wear of composites was observed with the increase in fiber volume fraction, which was associated to a beneficial effect of the detachment of carbonaceous material from the worn surface. Under the tested conditions, this material remains at the interface between the composite and the cast iron, and acts as a solid lubricant. On the other hand, surface fatigue was identified as the dominant wear mechanism of the phenolic matrix.
Keywords: Sliding contact; Composites; Carbonaceous fibers; Cast iron.

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[2] *New Materials Research Group, School of Engineering, Pontificia Bolivariana University, Medellín, Colombia.*
[3] *Tribology and Surfaces Group, School of Materials Engineering, National University of Colombia, Medellín, Colombia*

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1 INTRODUCTION

Colombia is one of the world's most important producers of comestible fruits from Musa species, such as commercial plantain (Musa AAB, cv *''Dominico Harton''*), with cultivated areas of around 360000 ha. Nevertheless, since fruit only represents around of 12 wt% of the plant, after harvesting and fruit packing, the other parts become agricultural residues. Some of these residues are fibrous wastes composed by hemicelluloses, cellulose and lignin (lignocellulosic substances) forming vascular bundles as pseudo stem, leaf sheath or rachis.(1)

The thermal process to transform lignocellulosic materials into carbonaceous matter (char or charcoal), tar and gases is called pyrolysis. Slow heating rate pyrolysis process gives rise to a porous carbon frame with the morphology derived from its precursor(2-4) which can be used to ceramic synthesis such as silicon carbide, Alumina and Titania.(4)

It has been shown that this carbon frame has many favorable characteristics such as good electromagnetic shielding properties, excellent far infrared properties and high damping capacity.(5) Furthermore, the sliding friction coefficients of some carbon-based materials, either amorphous or crystalline, are among the lowest for any solids. Charcoal and carbonaceous substances, for instance, have good frictional characteristics even though they do not exhibit the basal slip properties of graphitic structures. Carbonaceous materials, including different types such as graphite, coke, black carbon and carbon fiber, are important ingredients of brake composite materials,(6) and are used in significant quantities (typically 5–20 vol.%) as additives for composite brake friction materials. Charcoal has also been reported as a potential replacement for graphite in composites for antifriction and antiwear applications, mainly in aluminum alloys.(5,7)

In addition, novolac phenolic resin is a common binder for resin-based friction materials.(8) Tribological applications of phenolic resins are usually limited due to their relatively poor stability and wear resistance. Therefore, it is imperative to incorporate various reinforcing and filling constituents such as reinforcing fibers, abrasives, binders, fillers, and friction modifiers (solid lubricants) into phenolic resin-based friction composites with the purpose of increasing their stability and wear resistance.(9-11)

Carbonaceous fibers obtained from Colombian plantain crops residues by slow pyrolysis, through a process that allows retaining many morphological aspects of the natural fibers are used as composite reinforcement for phenolic matrix composites. The aim of this study is to determine the effect on coefficient of friction, wear rate and wear mechanisms of this kind of carbonaceous fibers as potential additives for tribological applications.

2 MATERIALS AND METHODS

Carbonaceous fibers were obtained by pyrolysis of plantain fibers from leaf sheaths from Urabá, Colombia. A mechanical extraction process for plantain fibers was used according to the method described in Ganán et al.,(1) and fibers were further air-dried at least for 24 h. Once dried, fibers were then milled with a RETSCH SM 100 (Haan, Germany) to obtain a particle size lower than 5 mm length.

Fibers were pyrolyzed at slow heating rate, in an electrical tube furnace MTI GSL1600-80X. Samples were heated from room temperature up to 1000° C at 5 °C min^{-1}, held at this temperature for 90 min and then cooled down to room temperature

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at 5 °C min^{-1} until under N_2 atmosphere (99.9999% purity) using a flow rate of 200 ml l min^{-1}.
Phenolic resin powder 6600MC (Interquim - Azko Nobel Co. Medellin, Colombia) containing hexamethylenetetramine as curing agent was used as the matrix.

Composite manufacturing

Carbonaceous fibers and phenolic matrix were molded by compression molding process. Prior to that, both components were mixed for 5 min in a blender so as to improve the dispersion of the mixture. Contents of carbonaceous fibers were 2.5, 5.0, 7.5, 10 and 12.5 % in volume. Fully mixed raw material was loaded into a 140 mm diameter and 3.5 mm height steel mold and hot pressed at 200 bar and 165 °C for 15 min by using a thermo hydraulic pressing machine. Once the molding time was over the heating system was turned off while molding pressure was still applied for 10 min, then the pressure was released and molded composite discs were obtained.

Tribological tests

The tribological behavior of the phenolic resin and the composites with different amounts of carbonaceous fibers were evaluated using a pin-on-disc tribometer described in detail elsewhere.[12] Sample pins were glued to metallic pin supports and machined to obtain the final dimensions shown in Figure 1a. The detail of the assembly of the pin is given in Figure 1b. A commercial cast iron brake disc was used as the counter body in all the tests. The disc was properly machined to 220 mm in diameter and 8 mm in thickness and the testing surface was ground to a roughness of Ra = 0.495 ± 0.07 um.
Four tests were performed for each condition of normal load and tribological pair. In each test, the pin was fixed to a rigid arm and put in contact with a rotating ring under the application of a normal load by dead weights, as shown in Figire 1c. The test conditions are shown in Table 1, and Table 2 presents the main characteristics of the cast iron used as counter body.

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Figure 1. a) sketch of pin b) assembly detail c) detail of load application system

Table 1. Tribological test conditions

Environmental Temperature	25 ± 2 °C
Atmosphere	Air, no lubrication
Testing length	1000 m
Relative speed	1 m s^{-1}
Load	1.541 kgf (15.11 N)

Table 2. Main characteristics of cast iron brake discs used as counter bodies

Characteristic	**Values**			
Hardness	170 – 217 HB			
Chemical composition (% wt)	C Si S P Mn	3.65 -3.85 2.15 -2.795 Max 0.15 Max 0.10 0.5 – 0.9	Cr Sn Cu Mo Ni Fe	Max 0.25 Max 0.10 Max. 0.60 Max. 0.10 Max 0.20 Balance
Metallurgical characteristics	Type1- 1A (sheets) Size 3 -4		Pearlite: 90% min Ferrite: 5% Max Cementite: 5% Max	

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Friction force was registered at a rate of 10 Hz with the aid of a system composed of a load cell, data acquisition card and Labview 5.1 software provided by National Instruments under an educational contract.
After the tribological tests, the pins were cleaned in alcohol in ultrasonic bath for 5 min, dried in air flow and then weighted in an analytical balance Sartorius CPA225D. Stereomicroscopy and scanning electron microscopy were used to study the worn surfaces and wear mechanisms.

3 RESULTS AND DISCUSSION

Figure 2 shows the average values of friction coefficient and wear rate obtained after the pin-on-disc tests. Phenolic resin without addition of carbonaceous fibers is represented as the 0.0% sample.

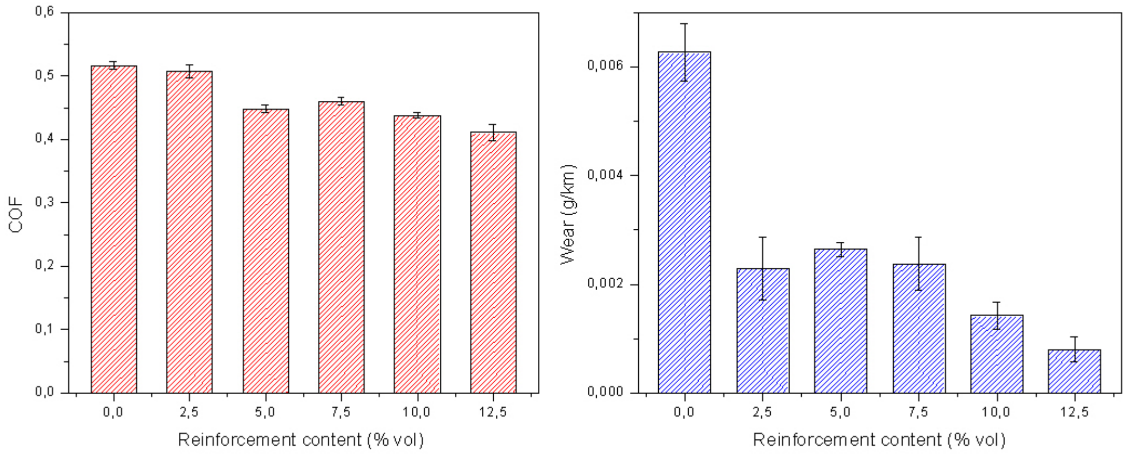

Figure 2. a) Coefficient of friction vs Reinforcement content, b) Wear rate vs Reinforcement content. Pin-on-disc tests performed against a gray cast iron counter body.

Figure 2a shows that composite materials with carbonaceous fibers present a lower friction coefficient when compared to fiber-free phenolic resin samples, being observed a reduction of 20% for samples with 12.5% carbonaceous fiber content. A stable friction behavior was observed in all cases as can be verified in the Friction force vs. testing time curves shown in Figure 3. It can be seen that after the running-in period the friction force suffered only minor changes and the curves found for the different replicas were very similar.

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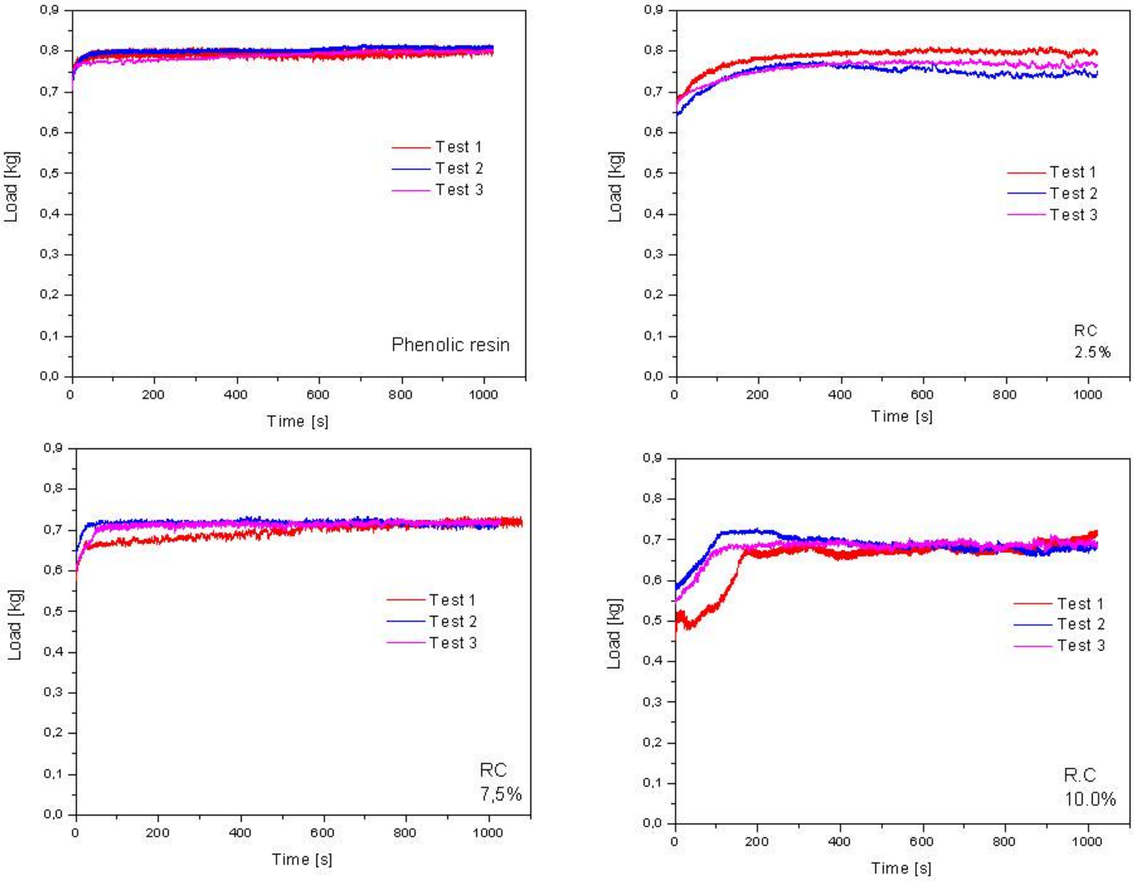

Figure 3. Friction force vs. Testing time for pure phenolic resin and composites with different reinforcement contents (RC of 2.5, 7.5 and 10%). Pin-on-disc tests performed against a gray cast iron counter body.

The reduction in wear rate with the addition of carbonaceous fibers was much more dramatic, with relative variations up to 85% with respect to pure phenolic resin, as can be seen in Figure 2b. The results did not reveal statistical differences among the wear rates of samples with 2.5, 5.0 and 7.5 % of carbonaceous fibers.

According to friction coefficient and wear rate results, the addition of carbonaceous fibers to phenolic resin led to an improvement in tribological behavior due to significant reduction in wear rates while the friction coefficient values remained quite stable. This behavior can be attributed to the presence of graphite layers into the amorphous structure of carbonaceous material, and also to the beneficial effect of the detachment of carbonaceous fibers that remain trapped between the composite and the cast iron during the tests.

Images of the general aspect of the worn surface of pins and discs are shown in Figure 4a and b. Carbonaceous fibers with different sizes and random distribution are observed in pin's surface. Evidences of sliding wear can be identified on the surfaces although no cracks or signs of brittle fracture are observed. Darker zone corresponding to sliding track present over cast iron disc surface after tribotest (Figure 4b).

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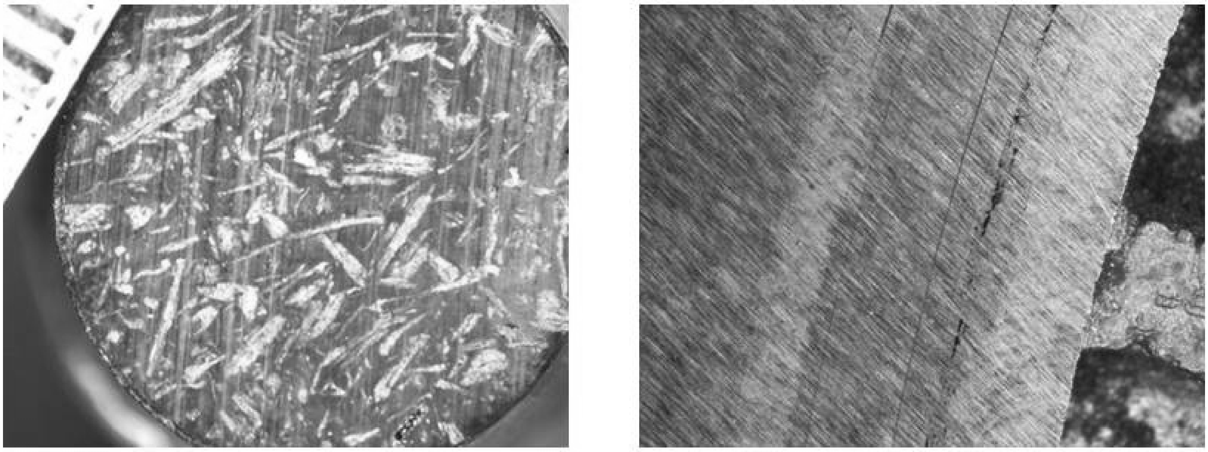

A B

Figure 4. Typical aspect of worn surfaces, a) pin surface (12.5 % reinforcement content) and b) disc surface.

The aspect of the worn surface of fiber-free phenolic resin samples is shown in Figure 5. Although plastic deformation is observed up to some extent (Figures 5a and b), evidences of fatigue-related wear mechanisms are clearly identified as can be seen in Figure 5c, where a particle of material is about to be detached as a result of the joining of cracks that grew parallel to the contact surface. The characteristic pattern consisting of regularly spaced cracks perpendicular to the sliding direction (Figure 5d) has been previously observed in thermoset polymers sliding against smooth surfaces,[13,14] and is typically associated to surface fatigue. Crazing evidences can also be observed in Figure 5d, which are normally expected in polymers submitted to sliding wear conditions.

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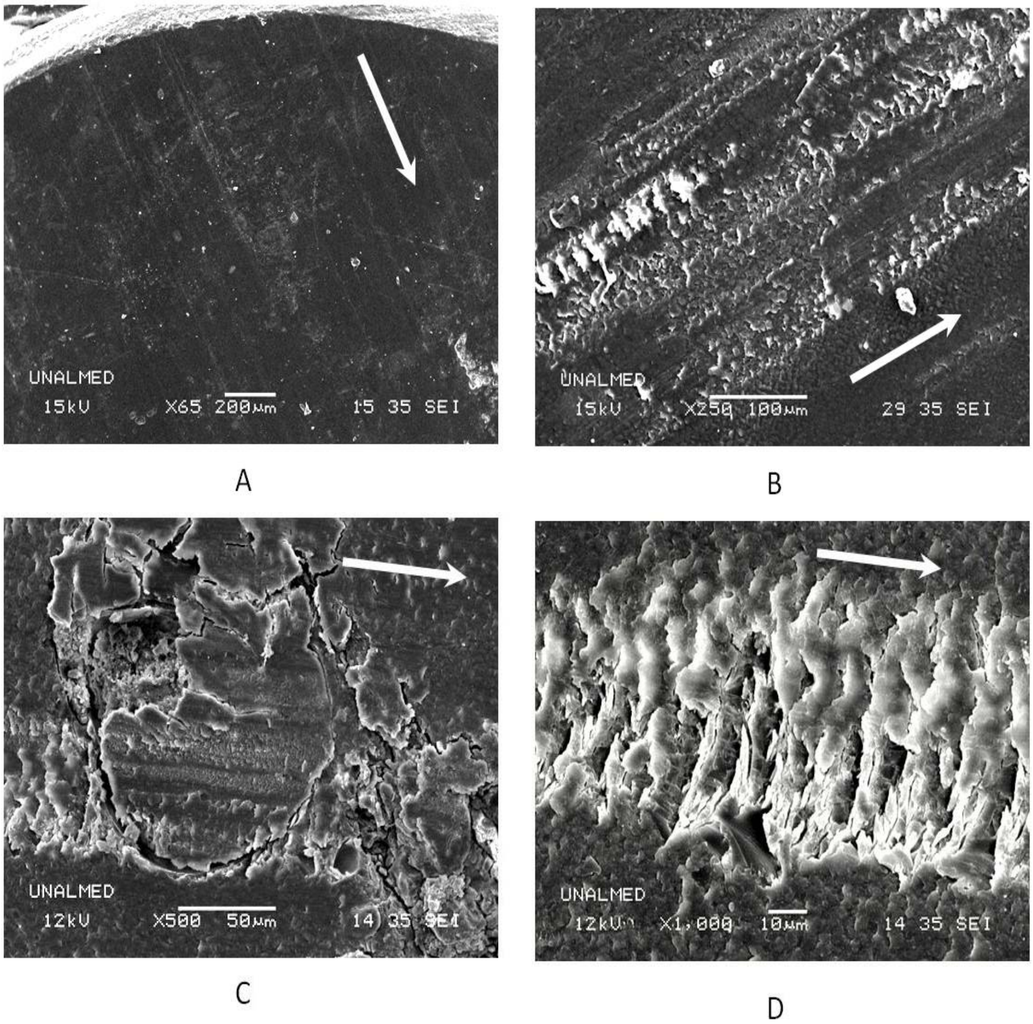

Figure 5. Aspect of the worn surface of phenolic resin samples after pin-on-disc tests. SEM A) 65X, B) 250X, C) 500X, D) 1000X. (Arrow represents sliding direction).

Regarding the composite samples, the microstructure examination revealed a random distribution of carbonaceous fibers, with no preferred orientation with respect to the sliding direction. Figure 6a shows a low magnification image of the surface of a typical sample, where a number of features such as holes and incomplete carbonaceous fibers can be observed. Typical vascular plant morphology of carbonaceous fibers can be observed in Figure 6b, in a region where the fibers were broken and the inner part was exposed. Similarly to what was found in fiber-free phenolic resin samples, crazing and surface fatigue of the polymer are the dominant wear mechanisms, although some cracks, pores and small holes were observed along the fibers too. The holes correspond to interconnection canals for plant food transport, which were enlarged by carbonization process.

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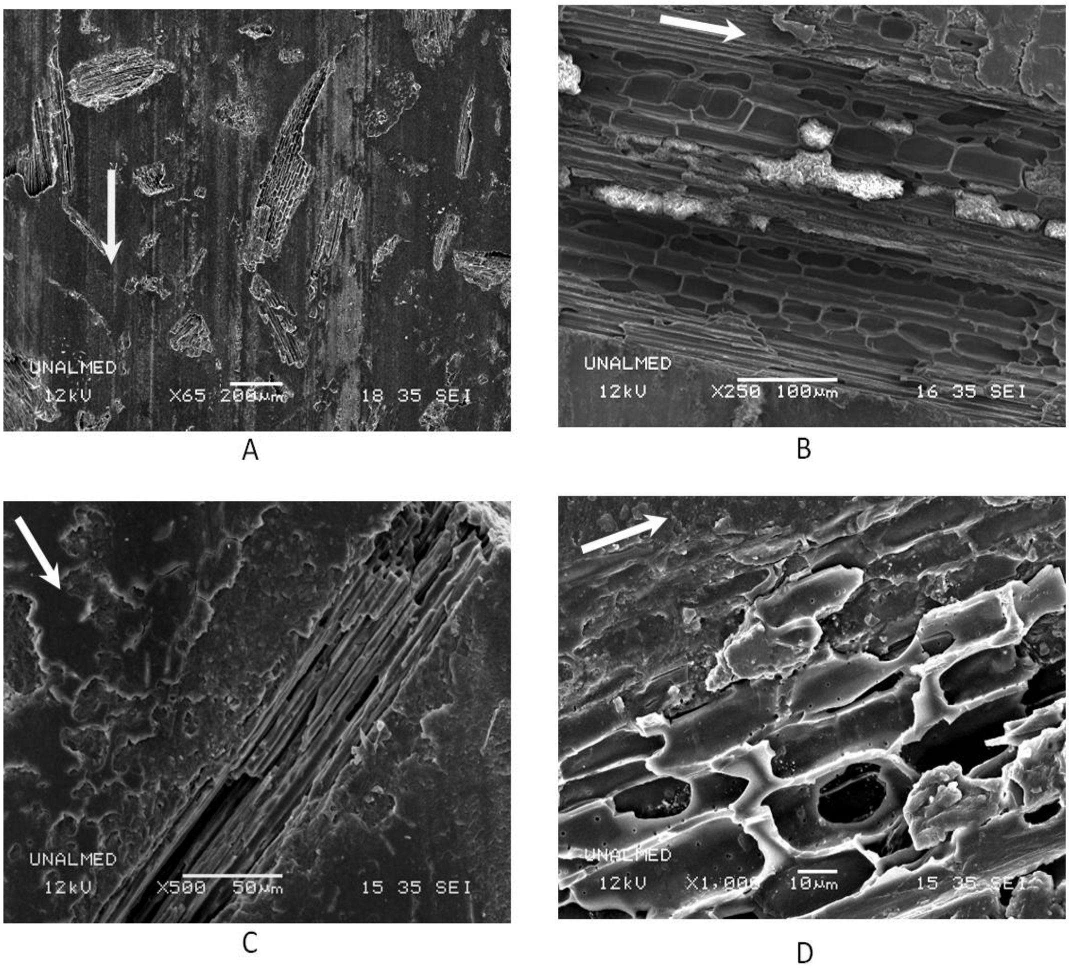

Figure 6. Aspect of the worn surface of composite samples after pin-on-disc tests. SEM A) 65X, B) 250X, C) 500X, D) 1000X. (Arrow represents sliding direction).

Evidences of adhesive wear of phenolic resin were found after SEM examination of the worn surface of cast iron discs. Fragments of polymeric matrix are adhered to the disc's surface, whose asperities also promote abrasion of the composite samples. Figure 7 shows the typical aspect of the wear track left in the disc as a consequence of adhesion of polymeric material (darker zones), where the arrow marks the sliding direction

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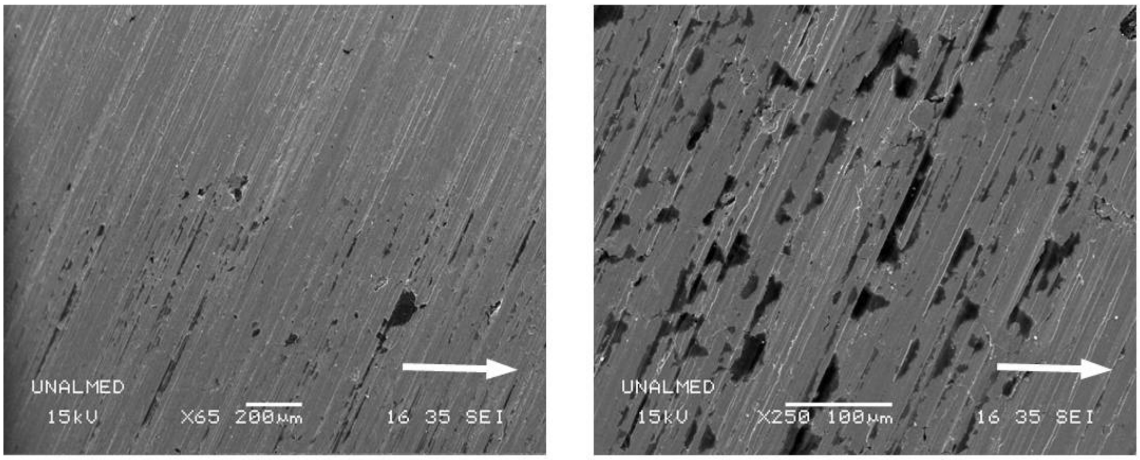

A B

Figure 7. Aspect of the worn surface of composite samples after pin-on-disc tests. SEM A) 65X, B) 250X. (Arrow represents sliding direction)

A suggested sequence of events leading to mass loss during sliding of composite samples against cast iron is as follows:

- Phenolic resin matrix is first removed, adhesive and surface fatigue wear mechanisms occur while carbonaceous fibers are exposed.
- Cracks form and propagate through the carbonaceous fibers.
- Small portions of carbonaceous fibers break down and are detached from the surface of the composite sample, but remain at the contact interface.
- Carbonaceous debris is gradually disintegrated due to a milling effect at the pin-disc interface.
- A fine distribution of carbonaceous particles is spread over the contact interface acting as a solid lubricant, which is consistent with the stable friction coefficient and reduced wear rate observed.

4 CONCLUSIONS

The tribological behavior of phenolic resin composites reinforced with carbonaceous fibers sliding against cast iron was studied.
A reduction in wear rate of composites was observed with the increase in fiber volume fraction, which was initially associated to prevention of adhesive effects and a possible beneficial effect of carbonaceous material detach as a solid lubricant.
Friction coefficient also showed a trend to reduce with the increase of fiber volume fraction, although the measured values were close to those found in pure phenolic resin samples.
Surface fatigue and crazing were identified as the dominant wear mechanisms of the phenolic matrix, while brittle fracture was the main cause of detachment of carbonaceous fibers.

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