EFFECT OF TEMPERATURE AND ATMOSPHERE ON THE TRIBOLOGICAL BEHAVIOUR OF HIGH TRIBOLOGICAL PERFORMANCE PEEK (POLYETHER ETHER KETONE) COMPOSITE*

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Abstract

Polyether ether ketone (PEEK) is a high performance thermoplastic often selected for high temperature tribological applications under chemically aggressive environments. The present work evaluate the tribological behavior of a high performance PEEK composite under ambient and high temperature (30 and 80°C, respectively). The atmosphere was also varied (air or tetrafluorethane). An AMTI tribometer equipped with a hermetic chamber and a heating system was used to carry out sliding tests of PEEK cylinders on 304 stainless steel polished discs (Sq < 10 nm) with reciprocating movement and 175 N normal force. Surfaces roughness analyses were performed with a white light interferometer. As expected, there was a strong influence of temperature on the tribological behavior of the samples tested in ambient atmosphere (25% decrease in friction coefficient associated with a 100% increase in wear rate). On the other hand, samples tested in tetrafluorethane atmosphere showed no significant friction temperature dependence.

Keywords: Solid lubricant; Thermoplastics; Environment; Temperature.

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** Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.*

1 INTRODUCTION

Through the last decades, refrigerant industry has changed the used refrigerant fluid several times, generally driven by environmental issues [1-7]. More recently, refrigerant industry has shown interest in oil-less compressors [8,9]. This new generation of products, besides environmental benefits, reaches new levels of efficiency and allow the development of innovative refrigerators [10]. In this context, solid lubricant polymeric materials are a promising alternative to keep low friction and wear in lubricant-free systems. However, the harsh operation condition of compressors requires the use of high performance polymers, and compounds based on Polyether-ether-ketone (PEEK) are certainly some of the most promissory materials in current polymer tribology [11].

Few investigations of tribological behavior of polymeric materials in refrigerant atmospheres and dry conditions are available [2-7]. Cannaday & Polycarpou [3] found that tetrafluorethane refrigeration atmosphere resulted in tribological properties slightly superior than atmospheric air for several polymeric materials and composites. Moreover, MacCooK et al. [12] presented that neat PEEK showed lower friction coefficient and wear in dry and vacuum environments. However, the temperature effect on sliding wear of polymeric composites under refrigerant atmosphere is still unclear.

The main goal of the present work is to investigate the impact of high temperatures and refrigerant atmospheres on the tribological behavior of a wear resistance solid lubricated PEEK composite. On top of that, harsh cylinder-on-disc configuration and oscillatory movement were chosen as test conditions. White light interferometer, optical image analyses and Raman spectroscopy provide further insights about possible interactions between polymer composites and test environment.

2 MATERIAL AND METHODS

A commercially available 10% PTFE, 10% Graphite and 10% Carbon Fiber (CF) filled PEEK composite was selected due to its superior self-lubricating and wear characteristics [11]. Table 1 presents nominal mechanical properties of this PEEK composite. The material was provided as an 11 mm thick injection molded plate which was machined to 8 mm rods and then sliced into 4 mm height cylinders.

Table 1. Mechanical and tribological properties of PTFE+Graphite+CF filled PEEK

Modulus (GPa)	**Hardness (Rockwell M)**	**Tensile strength (MPa)**
11	80	150

These PEEK cylinders were analyzed in dry tribological tests under atmospheric air or tetrafluorethane atmosphere at low and high temperatures (30 and 80°C, respectively) in a custom-made AMTI tribometer. This apparatus is equipped with a hermetic chamber, a heating system and a two-channel load cell. Tribological tests were carried out with oscillatory linear movements in a cylinder-on-plate configuration (Figure 1), where the counter body is an AISI 304 stainless steel polished disc, with surface roughness (root mean square – S_q) lower than 10 nm. The tests had duration of 2 hours under 175 N normal load with frequency of 2 Hz and 10 mm stroke. Tests characteristics and parameters were chosen in order to closely reproduce operation conditions acting in hermetic compressors. Polymer wear rates were calculated using

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* *Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.*

wear volume measurements obtained by using a white-light interferometer (Zygo New View 7200). The results are the average of, at least, 3 tests for each condition.

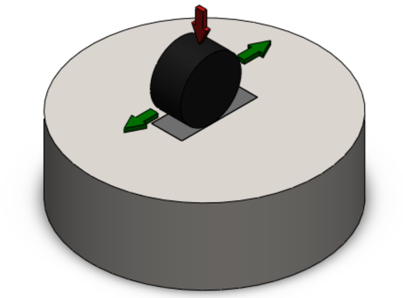

Figure 1. Cylinder-on-plate configuration. Red arrow indicates normal force. Green arrows indicate the sliding movement of PEEK cylinders.

Wear tracks were analyzed by white-light interferometry, optical image analyses and Raman spectroscopy (Renishaw 2000, equipped with 514nm argon laser) in order to access further information about wear mechanisms and tribolayer formation. A Gaussian filter (800 µm) where applied to surface roughness analysis in order remove waviness from samples surface.

3 RESULTS AND DISCUSSION

The wear that PEEK samples experienced through sliding tests followed the same trend in all tests conditions. The initial linear contact, with maximum Hertzian pressure of 290 MPa, evolved to large contact areas, with nominal pressure of around 40 MPa (Figure 2). Geometric data showed that the fiber-reinforced composites did not undergo long-range plastic deformation. Therefore, the enlargement of apparent contact area is assign, exclusively, to material removal, i.e. volumetric wear.

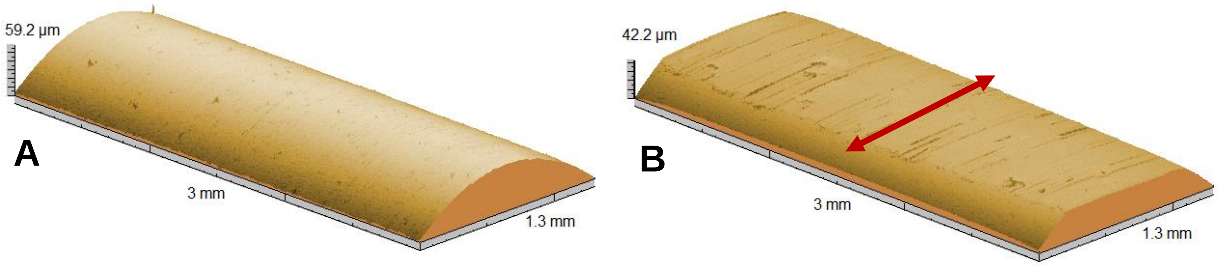

Figure 2. Geometry of PEEK cylinder before (A) and after (B) wear test at 30 °C and tetrafluorethane atmosphere. Red arrow indicates sliding direction

The wear rates resulting from these volumetric losses are show in Figure 3. Unlike coefficient of friction, wear rates showed no significant ambient atmosphere dependence. Cannaday & Polycarpou [3] reported that PEEK and PEEK composites showed a slight wear rate reduction when tested in tetrafluorethane atmosphere. On the other hand, temperature drove wear rates from $1.7\text{x}10^{-6}$ mm^3/N.m, at 30°C, to approximately $3.5\text{x}10^{-6}$ mm^3/N.m, at 80°C. The latter behavior is attributed to polymer thermal softening [13-15].

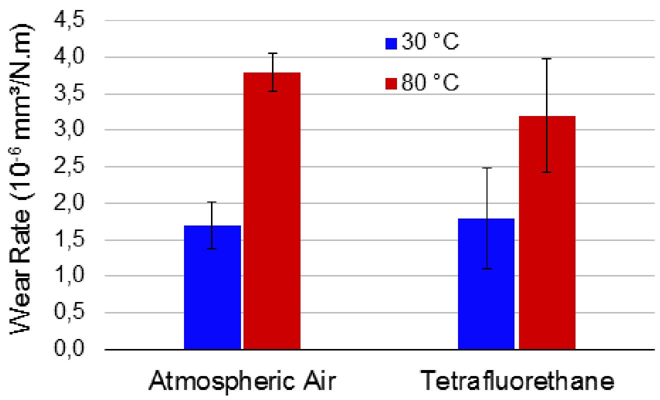

Figure 3. Wear rate of PEEK cylinders from sliding tests against 304 stainless steel discs

Likewise polymer cylinders, the wear on counter bodies followed the same trend in all tested conditions. Figure 4 reveals grooves aligned in the sliding direction on metallic surfaces after tribological tests.

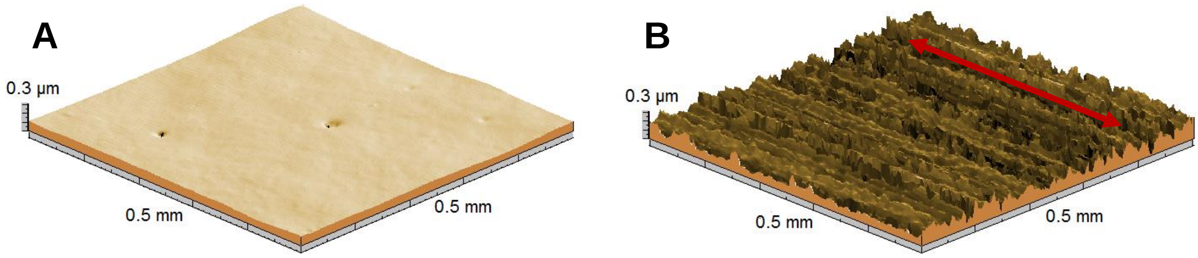

Figure 4. Topography of 304 stainless steel disc before (A) and after (B) wear test at 30 °C and Atmospheric air. Red arrow indicates sliding direction

As a result of grooves formation, all samples showed wear tracks with increased root mean square roughness (Rq) as ilustrated in Figure 5. Nevertheless, the resulting roughness inside wear tracks, and consequently grooves dimensions, seems to be independent of evaluated temperatures and atmospheres.

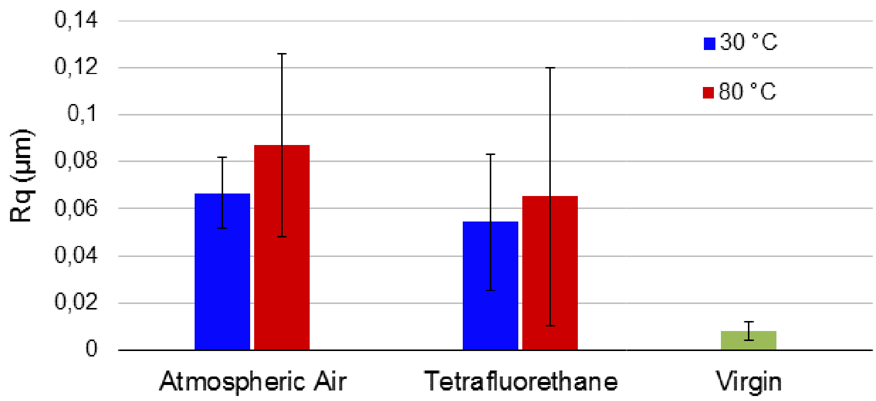

Figure 5. Wear tracks root mean square roughness (Rq) extracted from profiles transverse to sliding direction. Average Rq from virgin regions is also displayed.

Profile analyses on wear tracks were performed in order to evaluate the nature of the groves displayed in Figure 4. As well as exemplified in Figure 6, peaks and valleys were defined from the mean height of the virgin region and their areas were calculated. The difference obtained from peaks and valleys areas was 15 ± 20 µm², i.e. it was statistically equal to zero. Therefore, significant volumetric changes did not

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occur and it is possible to attribute the grooves formation to abrasive mechanisms of microploughing [16]. Since successive ploughing leads to microfatigue wear mechanisms [16], one can consider these grooves were produced, mainly, in the earlier stages of tribological contact.

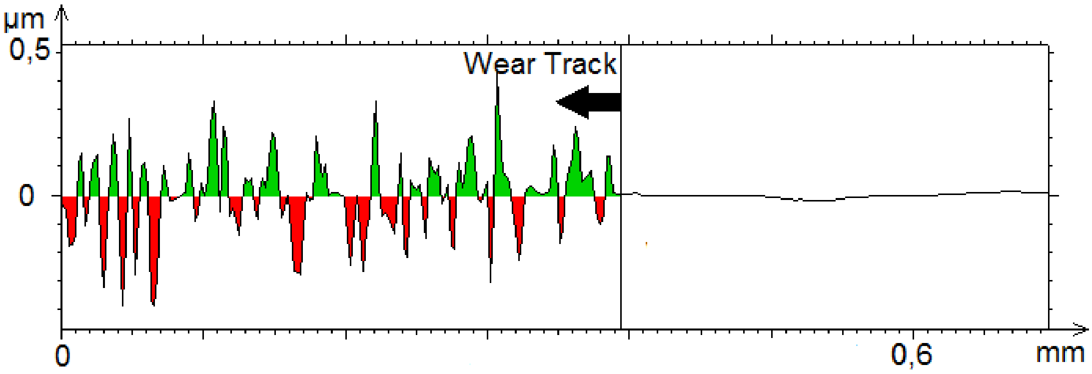

Figure 6. Topography profile (transverse to sliding direction) extracted from wear track boundary of counter body tested under atmospheric air at 80 °C. Green and red areas show wear track peaks and valleys, respectively, in relation to the mean height from the virgin region.

Figure 7 presents typical results from image analyses of worn samples. Micrographs from PEEK wear regions revealed grooves aligned in the direction of sliding, typical from microploughing wear mechanisms, and shear induced plastic flow regions in the boundary of worn surfaces, attributed to smearing [11,14,16]. Additionally, as cylinders wear out, one can observe carbon fibers being exposed to tribological contact. These hard spots are able to plough counter bodies surface, forming the grooves showed in Figure 4 [17,18]. In return, the abraded metallic surfaces, filled with sharp asperities, are able to plough polymers surface and wear out carbon fibers edges. On the other hand, although topography analyses did not evidenced significant material deposition on wear tracks, micrographs from counter bodies surfaces revealed the formation of a tribo-layer. It worth noting that free carbon fibers were not observed on counter body surface

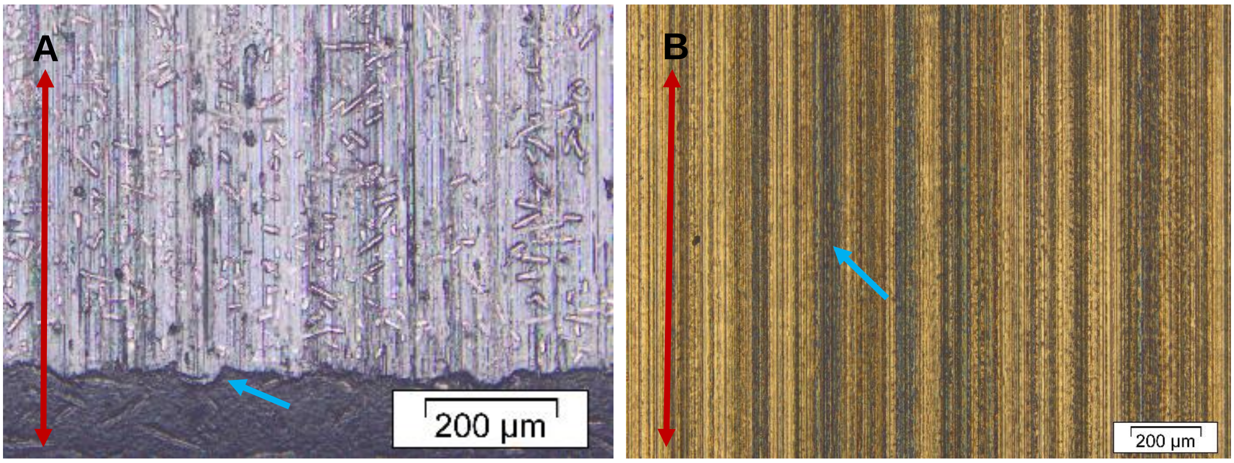

Figure 7. Optical micrographs of polymer (A) and counter body (B) worn regions from samples tested under atmospheric air at 80 °C. Red arrows indicate sliding direction. Blue arrows indicate regions of shear induced plastic flow (left) and material deposition (right)

Raman spectroscopy analyses (Figure 8) from counter bodies wear tracks showed D (~1360 cm^{-1}) and G (~1580 cm^{-1}) bands, which are common to graphite-based structures [19,20]. The low bands intensity obtained from samples tested at 30 °C

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indicates that the tribo-layer formed in these test conditions is too thin. This behavior is in agreement to Sheiretov et al. [2], who reported that higher temperatures enhance the formation of uniform tribo-layers. On the other hand, the higher intensity ratio between D and G bands (ID/IG) from samples tested under atmospheric air at 80 °C (0.97, against 0.70 from tetrafluorethane at 80 °C) indicates a higher disorder on graphite structure [19,20]. However, the origin of these graphite-based layers remains undiscovered, since it can be attributed to different carbon sources such as: i) graphite fillers from polymer composition; ii) degraded polymers (PEEK and PTFE); iii) degraded carbon fibers.

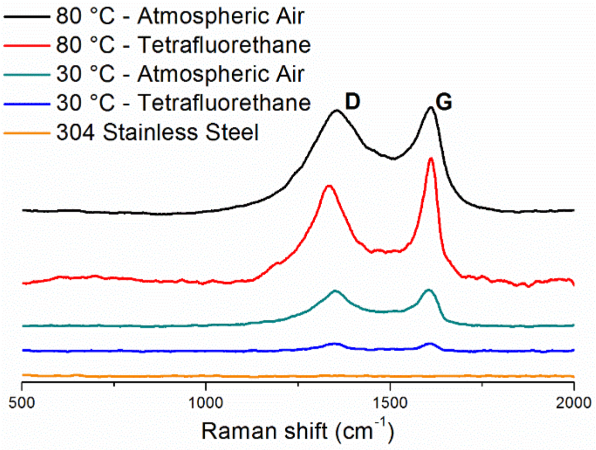

Figure 8. Wear tracks Raman spectrums. Raman spectrum from virgin AISE 304 stainless stell is also displayed

Figure 9 presents typical evolution of the friction coefficient with test time and the average coefficient of friction (COF), calculated in the steady state regime, for each studied condition.

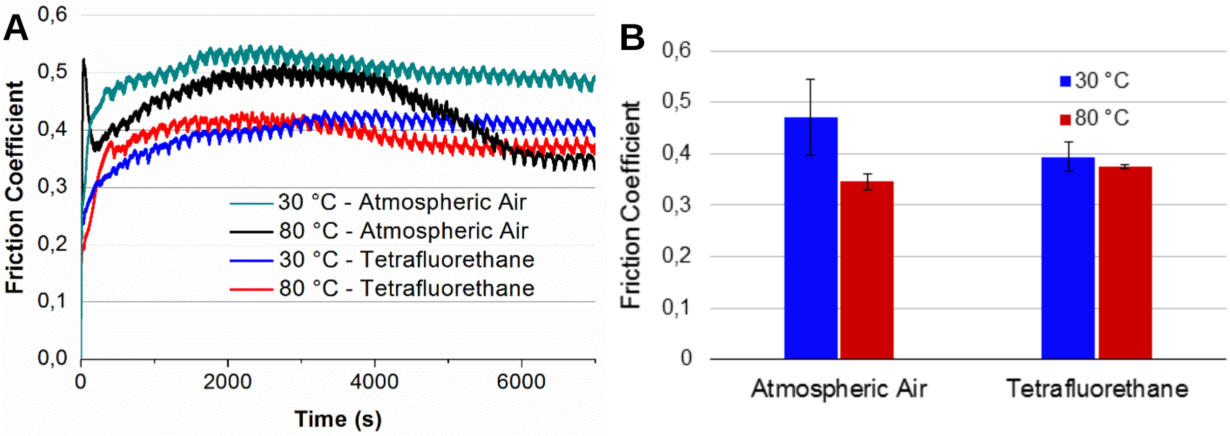

Figure 9. Friction behavior (A) and steady state friction coefficients (B) of PEEK composites sliding against 304 stainless steel discs

Figure 9(A) shows how the evolution of COF during the test duration is influenced by the chamber atmosphere and temperature. All results present similar behavior. Initially, there is a gradual increase followed by a maximum, and them, after a drop, a steady state is reached. At maximum point, samples tested in atmospheric air exhibited COF 40% higher than samples tested in tetrafluoretane atmosphere. After this point, samples tested at 80 °C exhibited a friction coefficient drop of 30%, under atmospheric air, and of 14%, under tetrafluorethane atmosphere. Samples tested at

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30° showed slopes of 9%. Thus, the steady state COF was drastically affected by temperature under atmospheric air, going from 0.47 at 30 °C to 0.34 at 80 °C. On the other hand, samples tested under tetrafluorethane atmosphere showed no significant temperature dependence, with friction coefficients varying around 0.38.

Friction behavior observed in Figure 9 was a result from the addition of adhesive interfacial forces, ploughing on polymeric samples and ploughing on counter bodies surfaces. Moreover, the intensity of each of these portions is a function of contact pressure, contact topography and tribo-layer characteristics. Therefore, based on observed wear characteristics, it is possible to delineate the following assumptions regarding to observed friction behavior.

In the beginning, the linear contact pressure, which is higher than polymer tensile strength, readily worn the cylinder surface, exposing sharp carbon fibers to the tribological contact. As the composite cylinder wears out, more fibers are available to plough the counter body surface, leading to a fast increase COF as observed in Figure 9.

Besides, this harsh abrasive environment could prevent the formation of a protective tribo-layer, which would explain the higher transient COF observed at samples tested in atmospheric air in Figure 9 [12]. Without a protective tribo-layer the interfacial adhesive forces would be attributed to interactions between PEEK matrix and metallic surface. Thus, according to McCook et al. [12], the relative humidity around 40% present in atmospheric air increases the COF of PEEK matrix running against metallic surfaces.

With the increase of contact area, eventually, the contact pressure reduces to values below the polymer tensile strength and microploughing and adhesive mechanisms, observed in Figure 7, prevail. Reducing polymer wear rate, few new fibers got exposed to tribological contact. On top of that, carbon fibers edges wear out. As a result, the gradual increase of COF starts to slow down.

An attenuation of abrasive mechanisms could also enhance the formation of a protective tribo-layer as the graphite based structure observed in Figures 7 and 8, which could drop the COF as observed in Figure 9. Lower temperatures as 30 °C prevents or slows down the formation of an uniform tribo-layer, which results in a small drop in transient COF [2]. According to Yen et al. [21] “The presence of vapors, such as water, is required for graphite to lubricate”. Thus, the water vapor present in atmospheric air reduces the bonding energy between the hexagonal planes of graphite structures which could explain the lower steady state COF observed in samples tested in atmospheric air at 80 °C.

At last, the steady-state COF prevail indicates that contact pressure, contact topography and tribo-layer stabilized.

4 CONCLUSION

Table 2 summarizes the observed tribological behavior. PEEK composite wear rates were drastically influenced by test temperature, but no significant atmosphere dependence was detected. AISI 304 counter bodies wear lead to increased surface roughness (R_q) in all testing conditions, but no volumetric losses were detected. Samples tested in atmospheric air showed higher COF through transient regime. However, at steady state regime, samples tested in atmospheric air at 80 °C showed the lowest COF. On the other hand, samples tested in tetrafluorethane atmosphere showed no significant friction temperature dependence.

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Table 2. Summary of tribological behavior

Test Condition	Max. transient COF	Steady state COF	Wear rate (10^{-6} mm/Nm)	Wear track Rq (nm)
Atm. air at 30 °C	0.52 ± 0.07	0.47 ± 0.07	1.7 ± 0.3	66 ± 15
Atm. air at 80 °C	0.49 ± 0.02	0.34 ± 0.01	3.8 ± 0.2	87 ± 39
R134a* at 30 °C	0.44 ± 0.02	0.39 ± 0.02	1.8 ± 0.7	54 ± 29
R134a* at 80 °C	0.43 ± 0.02	0.37 ± 0.01	3.2 ± 0.7	65 ± 55
none	-	-	-	7 ± 3

** R134a is the commercial name for tetrafluorethane refrigerant fluid.*

Graphite based tribo-layers were observed on counter bodies surface after sliding tests. Higher test temperatures enhanced the tribo-layers formation and the presence of atmospheric air resulted in graphite structure with higher disorder.

Acknowledgments

The authors wish to thank CNPq and Capes/Proex for financial support.

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