

## RESPONSE OF PEEK TO EXTERNAL STIMULI

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**Abstract.** *It was investigated the experimental response of a set of stationary plane surfaces of polyetheretherketone and polytetrafluorethylene (PEEK and PTFE) polymers submitted to the sliding contact of an AISI 4140 steel rotating cylinder. The heating, mass transfer due to contact, self lubrication evidences and wear rate determinations during and after the experiments (seven repetitions) are presented and discussed. The tests were performed under ambient conditions using a specially designed tribometer, under normal loading, sliding velocity and sliding distance conveniently specified to satisfy demands of the petroleum engineering. The tribological behaviour of the two studied polymers was discussed in terms of wear rate, wear mechanisms and especially transfer film that included some tribochemical responses.*

**Keywords:** *Polymer; Self Lubrication; Wear; Transfer film; Smart materials*

### 1. INTRODUCTION

Nowadays, polymers have been used in several tribological applications such as seals, plastic gears, artificial joints, guide rails, sliding bearings. This is because polymer materials have advantages in their light weight, damping, self-lubrication and noise reduction properties.

Polymer surfaces, when used as bearing materials are worn by a harder counterface. The application of the hard metallic counterface rubbing against the polymer surface is dictated by mechanical design requirements and also by the fact that polymers are more effective against a metallic counterface than when sliding against themselves (Stakowiak and Batchelor). Has been a major concern of petroleum engineers minimize environment impacts caused by leakage of petroleum during the processes of production and refining of petroleum. Several systems of these processes use tribological pairs constituted of polymer-metal. In this scenario the components are involved with friction, lubrication, wear. In such situation the ultimate performance of materials depends not only on their bulk properties, but also on their surface microstructure and interfacial behavior.

Thus, currently the focus of research has moved to the design of materials with ‘smart’ or ‘intelligent’ surface behavior. In concept, the intelligent polymers are also known as “stimuli responsive” or “environmentally sensitive” polymers, which will undergo relatively large and abrupt, physical or chemical changes as responses to small external stimuli in the environmental conditions. Among the environmentally stimuli can detach temperature, mechanism stress, strain, specific ions, chemical agents etc (Li *et al.* 2009). Luzinov *et al* (2004) present a review about research on adaptive and environmentally sensitive polymer surfaces designed to respond to external stimuli in a controlled and predictable manner where they detached process of modification in surface behavior of polymer by chemical/physical treatment. Flame and plasma treatments are generally applicable methods that serve to introduce oxygen, nitrogen, and other functionalities. Oxidation of low-density polyethylene (PE) film with chromic acid resulted in the material (PE-COOH) bearing hydrophilic carboxylic acid and ketone groups in a thin oxidative functionalized surface (Luzinov *et al* (2004)).

The presence of ketone groups is evidenced in the Polyether ether ketone (PEEK), aromatic polymer that present symmetry of the benzene rings along the polymer backbone giving mechanical strength and young modulus. Flexibility and crystallizing ability of the chain is provided by ether par ligation (—O—) (Figure 1).

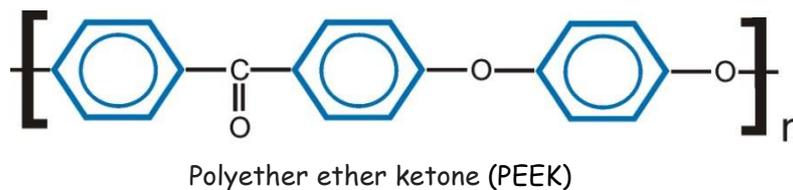


Figure 1. Chemical formula of polyether ether ketone (PEEK)

Friedrich *et al.* (1999) deals chemical interactions between evaporated chromium on surface oxygen-plasma-modified of polymers where a chemical reaction between plasma introduced carbonyl groups ( $>C=O$ ) and  $Cr^0$  was detected and interpreted as a redox reaction where chrome oxide species are formed and a reduction of carbonyl groups occurs. The general character of this redox reaction was suggested by an investigation of a number of different polymer-metal combinations. The redox reaction at metal/polymer is function of the redox potential of the metal component ( $K > Al > Cr$ ). These authors also emphasize the occurrence of reaction between chromium and aromatic rings in polymers.

Tribochemical wear arises of chemical reactions that occurring between contact bodies or polymer and environment. Instances include oxidation, hydrolysis and dissolution. Stachowiak and Batchelor (1996) commented the effects of surface films, for example, oxide film on surface temperature in sliding contacts. When the oxide formed have high thermal conductivity the temperature in the contact zone will decrease. However Hutchings (1992) emphasizes that the contact temperature decreases with the oxide film formation because the shear resistance of the film is less than the substrate reducing the friction coefficient.

Therefore oxide film presence can be useful to reduce the friction in systems applications with interfaces polymer/metal as seals, bearings and sliding materials. The present study investigated behavior of the PEEK and PTFE (polytetrafluoroethylene) polymers in contact with AISI 4140 steel in laboratory sliding tests using measure of temperature near the contact zone and scanning electronic microscopy (SEM) and Energy Dispersive Spectroscopy X-Rays (EDS microanalysis) of polymer surface.

## 2. Experimental

### 2.1. Materials and sample preparation

Two polymers were used in this work, PEEK and PTFE, Figure 2. The polymeric sample had 13 mm of diameter and 12 mm of length. The counterbodies were cylindrical axis of AISI 4140 steel ( $27 \pm 1$  HRC) with 12 mm of diameter and 18 mm of length. The chemical composition of the steel is presented in the Table 1. Additional data are furnished by Lima da Silva, 2010.

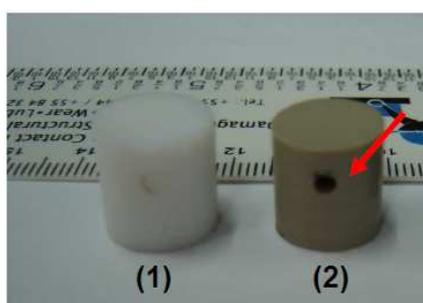


Figure 2. Polymeric sample (1) PTFE (2) PEEK. The arrow indicates the hole for inserting the thermocouple

Table 1. Chemical composition of AISI 4140 alloy steel used in this investigation

%C	%Cr	%Mn	%Mo	%P	%Si	%S	%Fe
0.38 - 0.43	0.80 - 1.10	0.70 - 1.0	0.15 - 0.25	$\leq 0.03$	0.15 - 0.30	$\leq 0.04$	balance

Before each testing, the surfaces of the samples were smoothed with abrasive papers of #80, #150, #280, #320, #400, #600 mesh. While the counterbodies of #80, #150, #280 mesh obtaining roughness of  $R_a = 0.300 \pm 0.05 \mu m$ . Bodies and counterbodies were then cleaned with distilled water in an ultrasonic bath during ten minutes.

## 2.2. Tribological test

The tribometer used had two unlubricated journal bearings that supported the counterbody cylindrical shaft. A frequency inverter was used to vary the sliding velocity. The tests were carried out in the scheme cylindrical shaft – flat sample (Figure 3). In the sliding wear tester, the counterbody cylindrical shaft was fixed at the ends and was driven by an electric motor. A polymeric flat sample was mounted vertically on a pivoted arm and was loaded against the shaft by a dead weight.

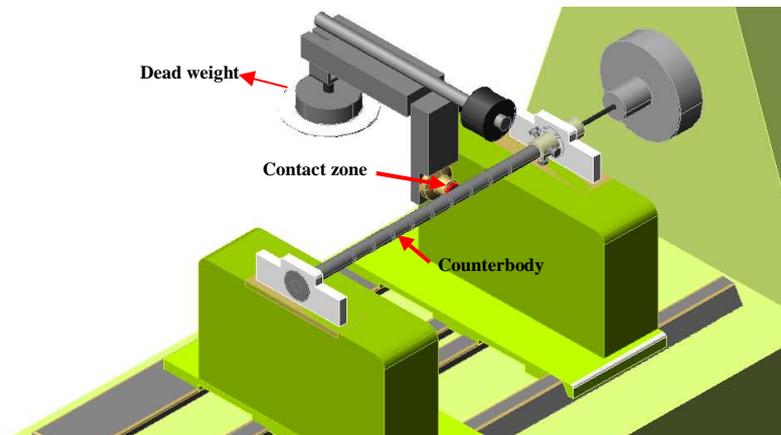


Figure 3. Schematic diagram of the sliding wear tester

In this research was disregarded the deflection of the counterbody cylindrical shaft formed by action of the transversal force (from normal load) and the reactions in the ends (bearings) due to supports. Since the shaft length was small, having negligible effect on friction and wear of the polymer.

During the tests, parameters as normal load, sliding velocity and sliding distance were fixed at 5.0 N, 1.0 m/s and 1000 m. The relativity humidity was  $50 \pm 10$  %. The temperature (at  $3.0 \pm 0.5$  mm of the contact) was acquired at 0.05 Hz rate (Figure 4).

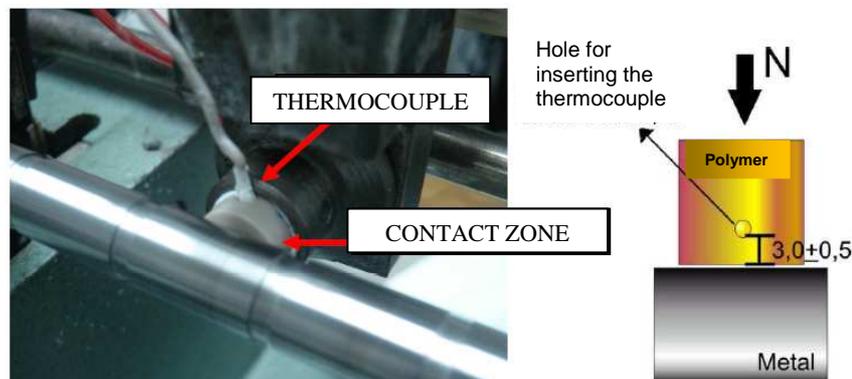


Figure 4. Detail of the contact area with the thermocouple to measure the temperature

The width of the wear track on the polymeric samples was measured using a scanning electronic microscope. Then, the wear volume loss,  $V$ , and wear rate,  $k$ , of the samples was calculated conform (Wang *et al.* 2009; Zhang , 2008; Chen, 2003; Khedkar *et al.* 2002) as observed in Eq. (1) and (2).

$$V = B \left[ r^2 \arcsen \frac{b}{2r} - \frac{b}{2} \sqrt{r^2 - \frac{b^2}{4}} \right] \quad (1)$$

$$k = \frac{B}{PxL} \left[ r^2 \arcsen \frac{b}{2r} - \frac{b}{2} \sqrt{r^2 - \frac{b^2}{4}} \right] \quad (2)$$

where  $B$  is the width of the sample (mm),  $R$  is the radius of the steel cylinder (mm), and  $b$  is the width of the wear track on the specimens (mm). In Eq. (3),  $k$  is specific wear rate ( $\text{m}^2/\text{N}$ ),  $L$  is the sliding distance (m) and  $P$  is the load (N). Seven repeat (discordant or confirmatory) tests were conducted for each set of frictional pairs, and the average of the seven repeat tests is reported in this article.

Morphologies of the worn surfaces were examined using a Shimadzu scanning electron microscope (SEM) and an Energy Dispersive Spectroscopy X-Rays (EDS microanalysis). To increase the resolution of SEM observation, the polymer samples were plated with gold coating to render them electrical conductivity

### 3. RESULTS AND DISCUSSION

#### 3.1 Wear mechanism

Particularly to polymers, different wear mechanisms are cluster in two categories: cohesive and interfacial process. In the cohesive process, the friction work is dissipated in a volume relatively great adjacent to interface. The cohesive wear is controlled by mechanical properties of the bodies that are interacting. Several mechanical wear mechanisms can be inserted in this category as abrasive, fatigue and fretting.

Interfacial wear process involves dissipation of friction work in a region much closer, generating a great increase of local temperature. Beyond mechanical properties, the surface chemical should be taken into consideration to determine the extent of damage due to wear. Transfer film and corrosive or chemical wear belongs to this category.

*Fatigue wear*: occurs in polymers probably as result of the formation of cracks associated with elastic deformation at high tension cycles generating spalling (propagation of subsurface cracks) and delamination (Dong and Bell, 1999). This wear mechanism was identified in the PTFE as delamination and PEEK as crater probably due to spalling (Fig. 5).

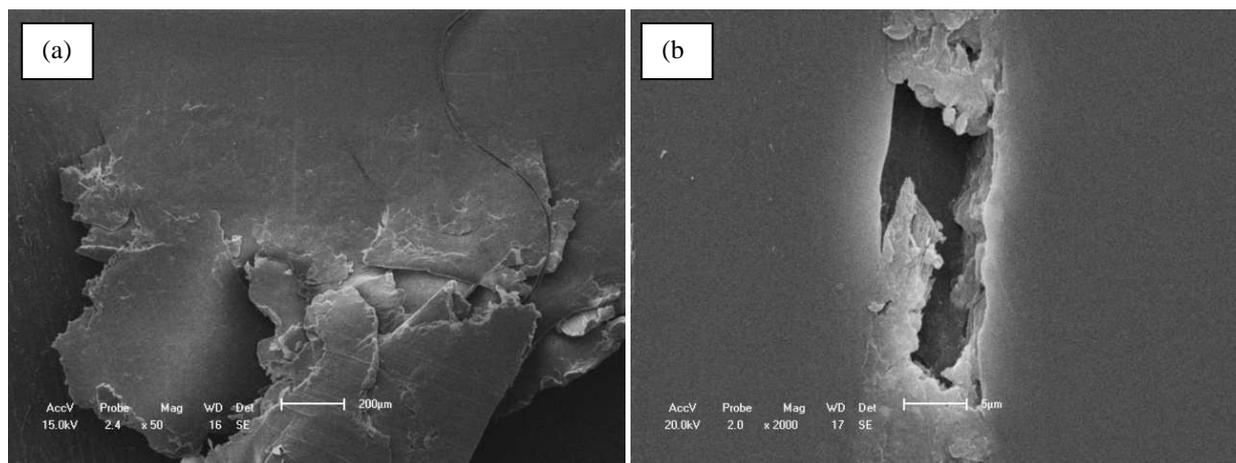


Figure 5. SEM images (a) PTFE detaching the delamination (b) PEEK detaching crater by spalling

PTFE delamination is associated, probably, to phenomenon known crazing that precedes the fracture of thermoplastic polymers. In accordance with Callister (2000) and Canevarolo (2006) regions of high local flow favor the formation of microvoids interconnected by fibrillar bridges. Traction tensions leads to elongation and rupture of this bridges and coalescence of microvoids starting the cracks formation. Crazes were observed in the SEM image as presented in the Fig. 6. The continuation of tension action after the crack formation leads to release of a lamina triggering to delamination.

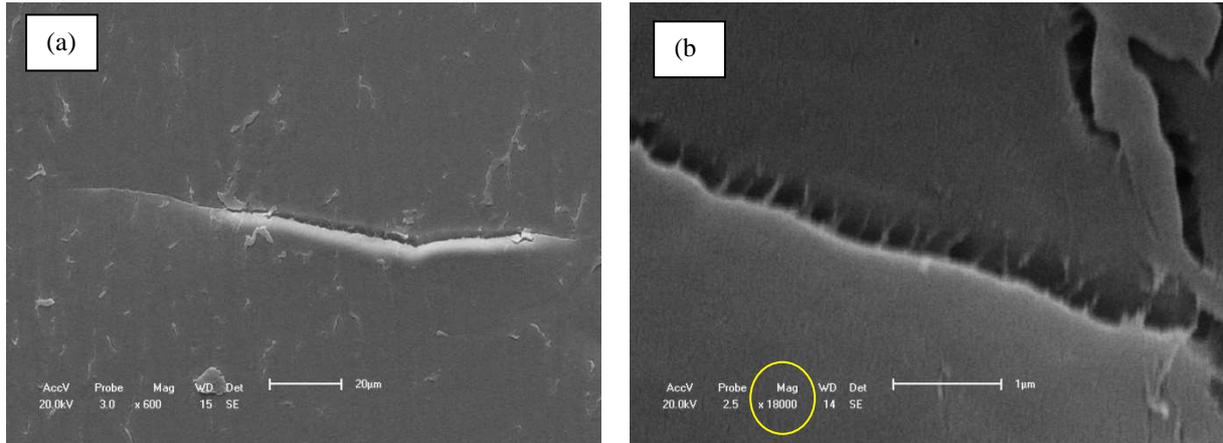


Figure 6. SEM images of a crack identified in the wear surface of PTFE emphasizing the possible occurrence of crazes

**Abrasive wear:** arise by hard asperities of the counterbody (two bodies) or by hard particles (referred as three) bodies between the surfaces. These asperities or particles penetrate in the polymer and remove material by micro-cutting or shearing process (Dong e Bell, 1999). The scratches observed in the sliding direction in the PEEK and PTFE surface after tests against the steel are indication of abrasion at two bodies, Fig. 7.

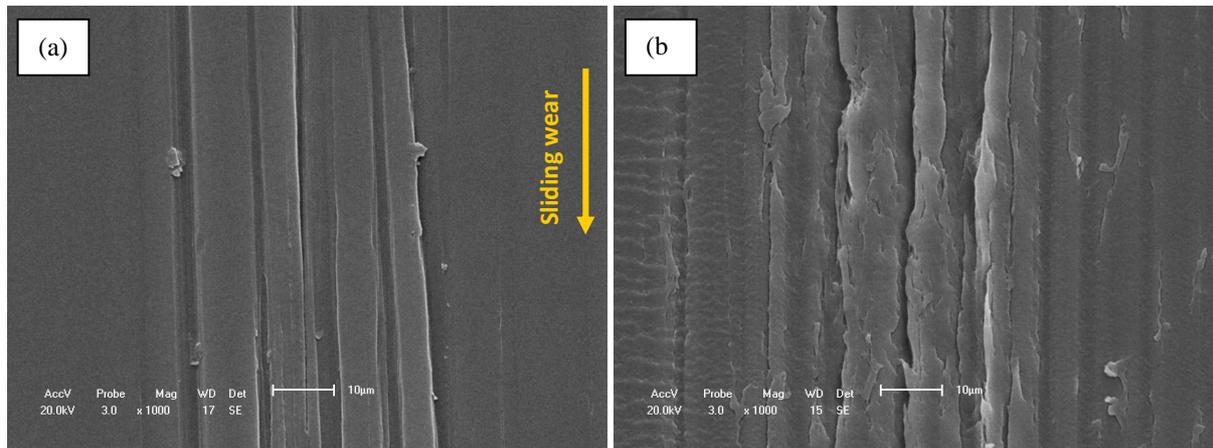


Figure 7. SEM image of the surfaces (a) PEEK and (b) PTFE

**Tribochemical wear:** occurs by chemical reactions between bodies in contact or between polymer and environment. Examples include the polymer oxidation, hydrolysis and dissolution. These reactions can lead to break of chains and polymer degradation. Presence of particles and film oxide on the surface of the PEEK, after the tests in this research characterize this wear mechanism, as presented in the Fig. 8. Magnification of the region delimited by circle in the Fig. 8 was shown in the Fig. 9 evidencing EDS microanalysis of the A and C points.

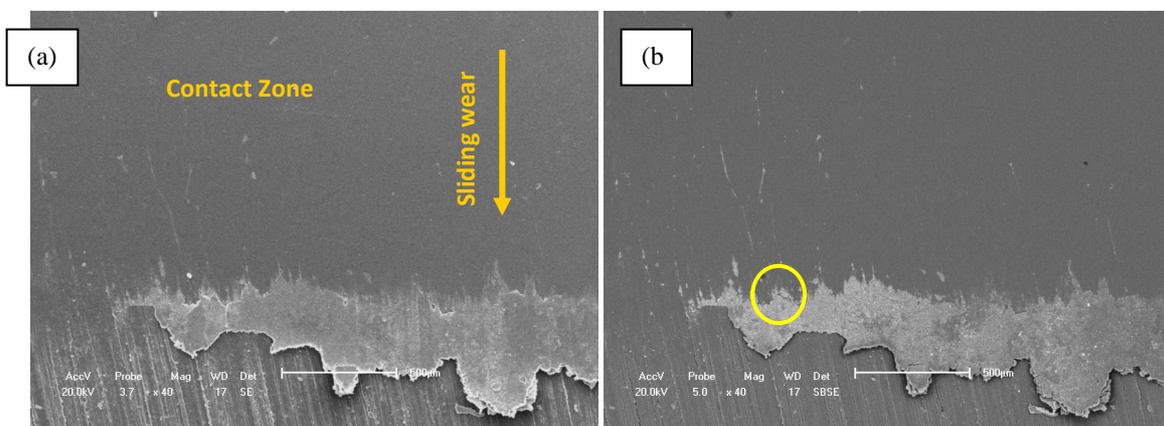


Figure 8. SEM images (a) SE and (b) BSE of the PEEK surface after test. In (b) clearer areas are chrome and iron oxides, constituents of the AISI 4140

Iron and chrome presence was evidenced in the microanalysis originated from counterbody of alloy steel. PEEK has oxygen in its chemical structure molecular, from ether groups ( $-\text{O}-$ ) and ketone ( $\text{RC}(=\text{O})\text{R}'$ ), such presence along with interfacial heat caused by friction, may have favored the intense formation of particles and films oxide resulting in break of the polymeric chains as commented by Dasari *et al.* (2009). Friedrich *et al.* researches in 1999 about chemical interactions polymer-metal indicate occurrence of redox reactions between functional polymeric groups containing oxygen and metals with redox potential as potassium, aluminum and chrome. After tests with this material, it is important to assert that the oxide formation was not seen on the PTFE surface.

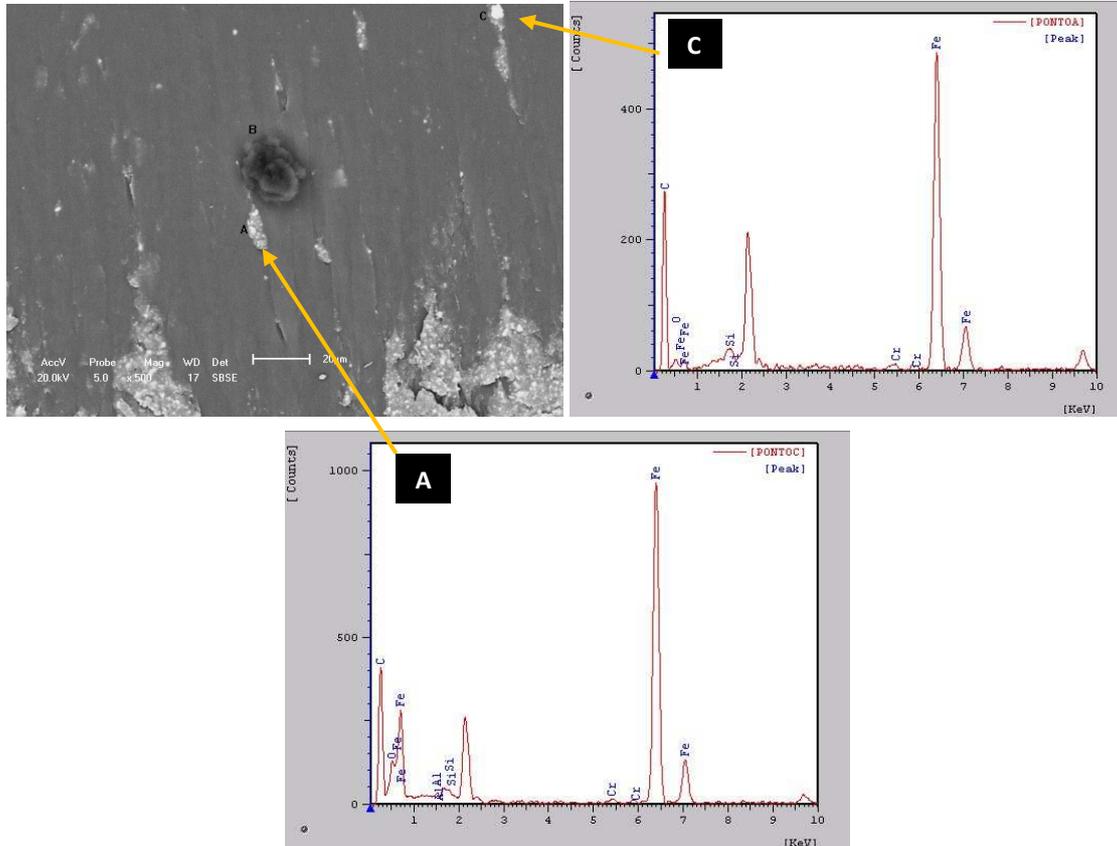


Figure 9. SEM images SE and BSE and EDS microanalysis of the PEEK surface after test. Proving the formation of chrome and iron oxides, constituents of the AISI 4140

Adhesive wear: characterized by presence of wear particles that detached and remained in the contact a polymeric film on the metallic counterbody (Fig. 9), aging on the friction and wear. In the case of polymers, junctions are formed by physical and chemical interactions that can include Van der Waals bond or hydrogen bridges that, according to Briscoe *et al.* (1993), occur probably due to heating in the interface can melting or soften the polymer. Some theories were developed to explicate the adhesive wear, as presents by Dasari *et al.* (2009):

- 1) Thermodynamic theory: adhesion occurred due best wettability of a solid surface by melted polymer;
- 2) Chemical theory: credits to adhesion the formation of chemical bonds in the interface;
- 3) Theory of the weak cohesion layer: explain the rupture of the intermediate layer between solids.



Figure 9. Image of the test PTFE – AISI 4140, arrow show the PTFE on the counterbody

Thus it is possible say that tribological processes produce change in both, geometry and material composition on the contact surface. This changes were identified in the present research, where the predominant tribological mechanism was influenced by composition and molecular structure of the polymer submitted to contact as recommended by Holmberg *et al.* (2007).

### 3.2 Wear rate

Fig. 10 present wear rate of the PTFE and PEEK after tests. Can be observed that the PTFE wear rate was  $1,5 \times 10^{-12} \text{ m}^2/\text{N}$  and to PEEK was  $1,7 \times 10^{-14} \text{ m}^2/\text{N}$ . Thus PEEK presented higher wear resistance than PTFE. This difference of almost two magnitude order in the wear rate is associated to wear mechanism of each polymer as identified by SEM images. PTFE suffers delamination in function of its molecular structure that favors formation and breaking of transfer films of low shear strength during sliding resulting in high wear rate. In the PEEK occurred tribochemical reactions with film oxide formation acting as protection against wear posterior.

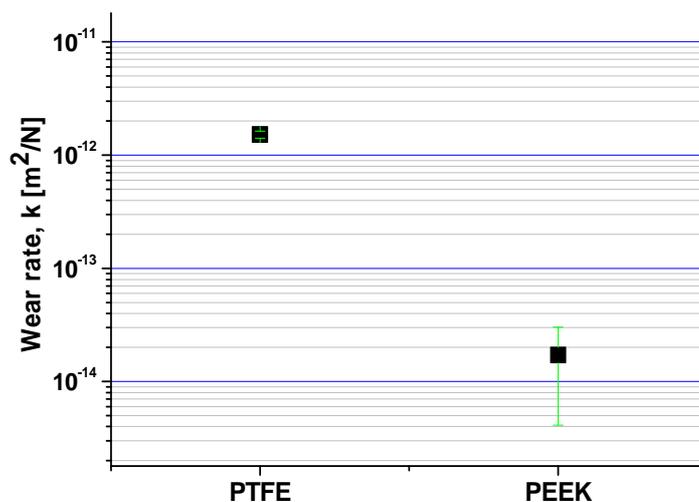


Figure 10. Wear rate of the PTFE and PEEK after tests

In Table 1 was presented wear rates values of the PTFE and PEEK found in the literature. Observed that although different conditions of tests in the refereed works, wear rates values are approximated of the obtained in the present research, with  $9 \times 10^{-13} \text{ m}^2/\text{N}$  to PTFE and  $3 \times 10^{-14} \text{ m}^2/\text{N}$  to PEEK.

Table 1. Wear rate values of the PEEK and PTFE found in the literature

	Wear rate (literature)	
	PTFE	Chen <i>et al.</i> $9 \times 10^{-13}$ (Aço inox; 0,1 m/s; 200 N; 100m)
PEEK	Zhang <i>et al.</i> $3 \times 10^{-14}$ (AISI 52100; 0,2 m/s; 9 N; 1 km)	

### 3.3 System Heating

During the tribological tests occur friction between polymer and steel resulting in contact heating that was measured by thermocouple near the contact zone. The system heating, considered as temperature near the contact ( $T_c$ ) minus environment temperature ( $T_a$ ), was presented in the Figs. 11 and 12 to PTFE and PEEK, respectively, to seven test repetitions.

Heating in the tests with PTFE reached around 10 °C haven test where this values not arrived 6 °C (Fig. 11). PTFE is known as solid lubricate material, characteristic originated by molecular structure with linear chain joined by Van der Waals bond that due to weak nature confer to polymer low shear strength. Moreover, fluorine atoms involve the chains difficult its interactions making lower shear strength.

System heating in the tests with PEEK reached around 9 °C. This result is similar to PTFE heating, however, the PEEK not is consider solid lubricate by literature.

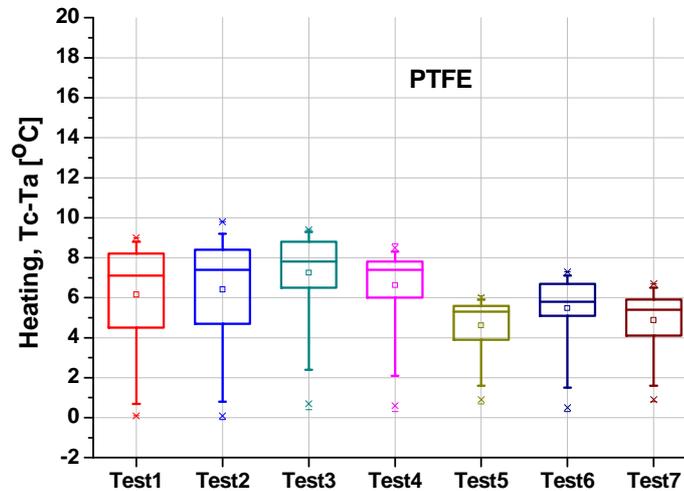


Figure 11. System heating in the tribological tests with PTFE

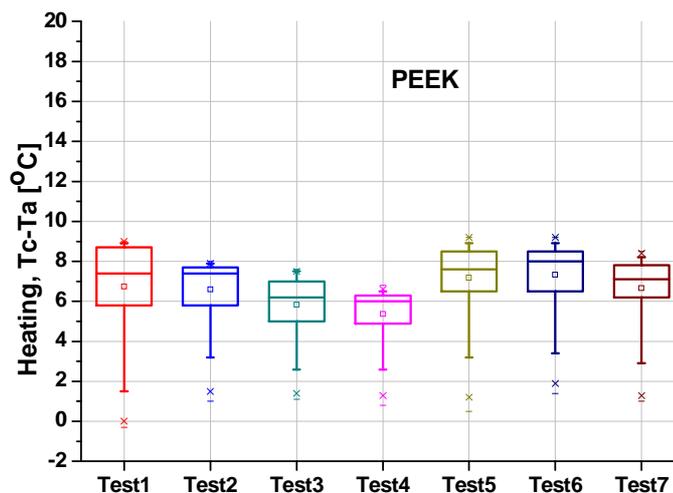


Figure 12. System heating in the tribological tests with PEEK

#### 4. CONCLUSIONS

Tribological tests were accomplished with PTFE and PEEK sliding against AISI 4140 steel in the configuration of a stationary polymeric flat sample – rotational cylindrical metallic shaft. Wear mechanisms identified on the PTFE surface were delamination and adhesive wear, as evidenced in the SEM image, Fig. 5(a) and photography of contact zone, Fig. 9. These wear mechanisms configure a solid lubricant behaviour because the laminas originated by delamination detached by the polymer wear and adhered to the steel contact surface shown a self lubrication action of the interface – identified in real-time by the heating response next of the contact. The PTFE presented its classic transfer film formation due to molecular and crystalline structure. The crystalline structure consisted of layers of crystalline material between relatively weak layers of amorphous material and this favors deformation of the PTFE in a series of discrete laminas. A block of PTFE in contact with a harder counterface loses material as a series of laminate resulting in low friction but a high wear rate (Stackowiak and Batchelor, 1996). High wear rate and low system heating (evidencing low coefficient of friction) were observed in this work. The delamination of the PTFE is mentioned also by Li *et al.* (2001), Khedkar *et al.* (2002), Lima da Silva *et al.* (2007) and Lima da Silva (2010).

Tribochemical reactions were the main interaction observed in the PEEK surface involving interatomic forces with oxide production in the form of film and particles. According to Friedrich *et al.* (1999), chemical interactions polymer-metal can involve *redox* reactions between functional polymeric groups containing oxygen and metals with *redox*

potential as chrome favoring oxide formation. The oxide film remained on the polymer surface resulting in heating similar to presented in the test with PTFE, which is low since this polymer is a solid lubricant. Two hypotheses can be associated to this phenomenon: (1) thermal conductivity of the oxide an order of magnitude higher than polymer as suggested by Stackowiak and Batchelor, 1996; (2) low friction coefficient as result of interfacial film of shear resistance lower than polymer as proposed by Hutchings (1992). Thus the PEEK after suffer external stimulus of friction (that result in an initial heating) in the presence of metal with *redox* potential responds with a film formation and respective stabilization of the system heating in the range of that achieved by PTFE, a solid lubricant. This phenomenon can justify a tribochemical characterization of the PEEK as a smart polymer.

## 5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the CAPES, Petrobras and PPGEM-UFRN. Helpful discussion with professors Antonio Moreira dos Santos (Heating response) and Efrain Pantaleon Matamoros (Tribochemical aspects) were greatly appreciated.

## 6. REFERENCES

- Briscoe, B.J., Stuart, B.H., Sebastian, S., Tweedale, P.J., 1993, The failure of poly (ether ether ketone) in high speed contacts. *Wear*, **162-4**, pt.A, pp.407-17.
- Callister, W. D., 2000, *Materials Science and Engineering: An Introduction*. 5 ed. New York: John Wiley & Sons.
- Canevarolo Jr, S. V. , 2006 *Ciência dos polímeros*. 2. ed. São Paulo: Artliber Editora. 275p.
- Chen, W.X.; Li, F.; Han, G.; Xia, J.B.; Wang, L.Y.; Tu, J.P.; Xu, Z.D., 2003 Tribological behavior of carbon-nanotube-filled PTFE composites. *Tribology Letters*, **15**(3). pp. 275-8.
- Dasari, A.; Yu, Z.-Z.; Mai, Y.-W. Fundamental aspects and recent progress on wear/scratch damage in polymer Nanocomposites. *Materials Science and Engineering R*, **63**, p. 31–80, 2009.
- Dong, H.; Bell, T. State-of-the-art overview: ion beam surface modification of polymers towards improving tribological properties. *Surface and Coatings Technology*, **111**, p. 29–40, 1999.
- Friedrich, J.F.; Unger, W.E.,S; Lippitz, A.; Koprinarov, I.; Kühn, G.; Weidner, St., Vogel, L. Chemical reactions at polymer surfaces interacting with a gas plasma or with metal atoms — their relevance to adhesion. *Surface and Coatings Technology* **116–119** (1999). pp.772–782.
- Holmberg, K., 2007, Friction and wear of coated surfaces — scales, modelling and simulation of tribomechanisms. *Surface & Coatings Technology*, **202**, pp. 1034–1049.
- Hutchings, I.M. *Tribology - Friction and Wear of Engineering Materials*. Cambridge: British Library Cataloguing in Publication Data, 1992. 273p.
- Khedkar, J. Negulescu, I. Meletis, E. I., 2002, Sliding wear behavior of PTFE composites, *Wear*, **252**, pp. 361–369.
- Li, D.; He, Q.; Li, J., 2009, Smart core/shell nanocomposites: Intelligent polymers modified gold nanoparticles. *Advances in Colloid and Interface Science*, **149** (1-2) pp. 28–38.
- Li, F.; Hu, K.; Li, J., Zhao, B.-Y., 2001 The friction and wear characteristics of nanometer ZnO filled Polytetrafluoroethylene, *Wear*, **249**, pp. 877–882
- Lima da Silva, R. C. (2010) Desgaste de Polímeros Estruturais de Engenharia em contato de deslizamento com cilindro metálico. Natal-RN, UFRN, Programa de Pos-graduação em Eng. Mecânica. *Tese de Doutorado*. 160 p.
- Lima da Silva, R. C.; Silva, J. B.; Medeiros, J. T. N. Wear rate fluctuation of a sliding system polymer-steel under the effect of fixed and free journal bearings. Brasilia-DF, Proceedings (CD-ROM) of the 19<sup>th</sup> International Congress of Mechanical Engineering, *COBEM 2007*
- Luzinov, I.; Minko, S.; Tsukruk, V.V., 2004 Inverse and Reversible Switching Gradient Surfaces from Mixed Polyelectrolyte Brushes. *Prog. Polym. Sci.* **29**, pp. 635–698.
- Stachowiak, G. W.; Batchelor, A. W., 1996, *Engineering Tribology*, Ed Butterworth Heinemann, 744p
- Zhang, G. *et al.* Temperature dependence of the tribological mechanisms of amorphous PEEK (polyetheretherketone) under dry sliding conditions. *Acta Materialia*, 2008.

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