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TRIBOLOGICAL PROPERTIES OF UNSATURATED POLYESTER REINFORCED WITH GRAPHITE

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Abstract. *Polymer composites are materials that may combine mechanical and tribological characteristics that are not found in traditional engineering materials. In the present study, it was evaluated the tribological properties of an unsaturated polyester (UP) composite reinforced with graphite. For this purpose, unsaturated polyester matrix composite containing 0, 3, 7 and 15%wt of graphite were prepared by hand mixing. The tribological behavior of this composite was described under reciprocating dry sliding in a ball-on-plate contact against a tungsten carbide sphere. The friction and wear properties were studied as a function of normal load and frequency. Tests were performed with a combination of two loads and three velocities with a total sliding distance constant. Tribological test results show that the coefficient of friction (COF) decreases when adding graphite in unsaturated polyester. The presence of graphite decreases COF as a result of development of a tribofilm of graphite that lubricates the contact track. For this study the composite with 7% of graphite (UPG7%) presented the lowest COF values. However, for UPG15% there was a slight increase in friction compared to 7%wt of graphite indicating that higher concentrations of graphite might reduce mechanical resistance leading to higher wear track and COF.*

Keywords: *unsaturated polyester, tribology, coefficient of friction, graphite.*

1. INTRODUCTION

In the last decade, researchers had been using their efforts looking for polymeric materials to replace metals (Pitt, 2011). One of the most significant aspects is the endurance-weight ratio, where polymeric materials present performance is more competitive. In the tribological applications perspective, many polymeric families have interesting raw material costs, but no proper mechanical endurance. One way to overcome these material characteristics for tribological applications is to develop polymeric composites (Samyn, 2005).

According to ASTM D3878-95, composite is a material that consists from combining two or more materials, insoluble between themselves, with the objective to create a useful engineering composite with desired combined properties not encountered on the materials separately (Mano, 2004). Polymeric composites have polymer as matrix, which is combined by one or more materials with different properties, in a way that each one contributes to a desired property in the final product. The most common filler materials used on polymeric composites are fibers and particles (Bower, 2002).

The most used method to reduce friction and wear is using lubricants (Hutchings, 1992). However, some particulate materials, such as graphite, PTFE, MoS_2 and TiO_2, have as characteristics the self-lubrication. In the last decade, many researches have been looking to improve polymers tribological performance by introducing different kinds of solid lubricants (Larbi, 2013), because adding this materials on composites have been shown efficient in controlling friction, which could be an alternative for costs reduction.

The polyester family shows as an important characteristic its high geometric stability, however, it has low tenacity (Sperling, 2006) and crosslinking makes these materials brittle (Chakraborty *et al.*, 2014). According to Mark (2009), as main characteristics the polyester has low cost, easy moldability, can be manufactured under a large temperature zone and has appropriate mechanical endurance.

According to Materials Selection in Mechanical Design (2010), graphite is known to reduce coefficient of friction (COF) when used as a lubricant or combined with another material, such as unsaturated polyester. Graphite is brittle and soft, it has structure consisting of layers of carbon atoms, called graphene, arranged in hexagonal rings. The covalent bonds between carbon atoms are extremely strong, however, bonds between layers are weak. These weak bonds between graphenes gives the graphite the property of lubricant (Larbi *et al.*, 2013). Due to this property, graphite is commonly found as reinforced material in polymeric composites (Katiyar *et al.*, 2016). Graphite, as well as its allotropes, may be used as reinforcement in multifunctional engineering composites that combine high mechanical performance and reliability, as well as better wear behavior with high electrical and thermal conductivity, and with lower cost than other materials that have similar characteristics (Baptista *et al.*, 2016).

Previous works have studied the improvement on mechanical and tribological properties of unsaturated polyester through reinforcement particles as graphite (Chakraborty *et al*, 2014; Larbi *et al.*, 2013) and other types of particulate lubricant (Samyn, 2016; Katiyar *et al.*, 2016; Hashmi *et al.*, 2007). There are also a large number of studies that has shown the role of graphite fillers in polymeric composites as a solid lubricant enhancement to the tribological behavior in composites (Larbi *et al.*, 2013; Katiyar *et al.*, 2016; Baptista *et al.*, 2016)

This paper presents a tribological evaluation of neat polyester and polyester composite with unsaturated polyester matrix (UP) reinforced with graphite containing 3, 7 and 15 wt%-graphite. The tribological behavior of a polyester composite with graphite against a rigid body (tungsten carbide - WC) was evaluated through reciprocating tests.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

In the present study, the tribological setup in the tests was the ball-on-plate. The materials used in the tribological pair include a sphere of tungsten carbide (counter body) and the composite plate (body). The composite matrix was made of unsaturated orthophthalic polyester resin (Arazyn4.6) with the corresponding curing hardener and styrene monomer as a crosslinked agent. The mechanical properties, provided by the manufacturer, of the resin used are listed in Tab 1. Natural crystalline graphite platelets with average measured of ~3 µm were used as filler (Fig. 1). Four different compositions were prepared: matrix without graphite UPG0%, matrix with 3% (UPG3%), 7% (UPG7%) and 15% (UPG15%) in weight of graphite.

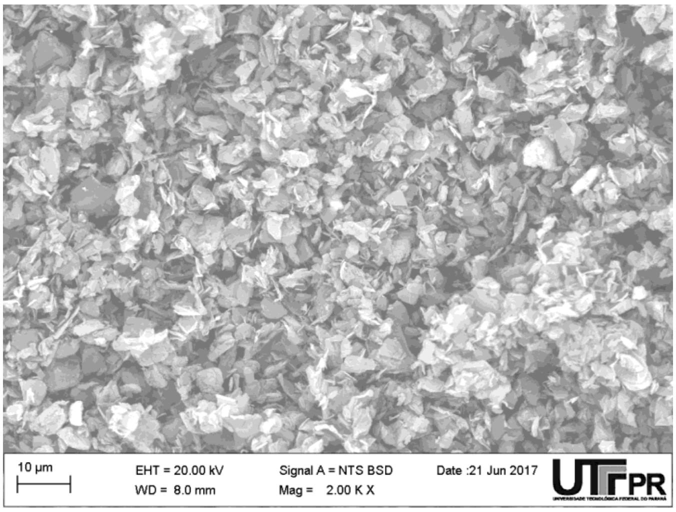


Figure 1 – Image of scanning electron microscopy (SEM) of the graphite platelets showing typical particle size and shape.

The graphite was supplied by MicroService (SP, Brazil) and for composite, a commercial unsaturated orthophtalic polyester resin, styrene and methyl ethyl ketone peroxide (MEK-P) were purchased from *Ideal resinas e silicones* (PR, Brazil).

The counter body of tungsten carbide was used as supplied, with no further process. The sphere with 4 mm in diameter had surface finish Sq of 14.4 µm. Carbide tungsten hardness is 1300 HV, with Young modulus of 670 GPa and ultimate tensile (UT) of 344 MPa (Bauccio, 1994).

Table 1 - Basic material properties for UP composites*.

Property	Unit	Unsaturated Polyester Resin (UPG0%)
Tensile strength	MPa	48
Young's Modulus	MPa	3400
Elongation	%	1.5
Flexural Strength	MPa	70

* *Information provided by the manufacturer*

2.2 Sample preparation

The samples of unsaturated polyester reinforced with graphite composite were prepared in laboratory. In the sample preparation processes the polyester resin and the styrene were homogenized by hand mixing. After homogenization, graphite powder was incorporate to the mixture. In order to decrease viscosity, to eliminate air bubbles, the mixture was placed in a laboratory stove for five minutes and then the hardener (MEKP) was carefully blended to cure the mixture. The prepared mixture was then poured into a mold and was cured for 24 hours at temperature of 40ºC degrees. After cure, the samples were machined, rubbed with 1200 sandpaper and polished with alumina. This process was made for the four compositions, Tab. 2 presents the percent for each material used.

Table 2 - Weight percent of UP resin, styrene monomer and graphite for each composite

	UPG0%	UPG3%	UPG7%	UPG15%
Unsaturated orthophthalic polyester resin	83	81	78	71
Styrene monomer	17	16	15	14
Graphite	0	3	7	15

2.3 Testing equipment and procedures

Microhardness Vickers (HV0.1) of the samples was measured using a Shimadzu-Micro hardness test, model HMV-2. At least three hardness measurements were carried out.

For the tribological tests it was used a tribometer of the manufacturer Bruker, model CETR-UMT (Comprehensive Materials Testing for Mechanical Tribological Properties). The test type realized were the reciprocating, which consists in applying a constant normal load while making sample in a tangential movement with the load. The composite plate was fixed and the counter face was placed into a ball holder.

The tests were conducted without lubrication at room temperature. Sliding tests were done with a combination of two normal loads of 2.5 and 5 N and three sliding frequencies of 5, 10 and 20 Hz with a constant value of total sliding distance of 30 m in stroke of 5 mm. The parameters for reciprocating tests are presented in Tab. 3

The coefficient of friction values (COF) were calculated using the Eq. (1)

$$\mu = \frac{F}{F_n} \tag{1}$$

where F is the frictional force and F_n is the applied load on the sample. The friction force readings were taken as the average of 70 readings per second during testing time.

Table 3 - Parameters for tribological tests

Test Condition	Normal Load (N)	Frequency (Hz)	Stroke Size (mm)	Covered distance (m)	Maximum velocity (m/s)	Time (min)
1	2.5	5	5	30	0.05	10
2	2.5	10	5	30	0.10	5.0
3	2.5	20	5	30	0.20	2.5
4	5	5	5	30	0.05	10
5	5	15	5	30	0.10	5.0
6	5	20	5	30	0.20	2.5

2.4 Microstuctural and Surface Analysis

The surfaces of the composites were analyzed using a scanning electron microscope (SEM) to observe fillers distribution and occurrence of pores. The surface, scars and wear mechanisms resulting after wear test were also examined using SEM.

The samples surfaces, before tribological tests, were submitted to a white light interferometry (WLI), process to a better analysis of the surface morphology and 3D roughness. The analysis were conducted by a Taylor Hobson Talysurf CCI Lite, provide by the LAMEQ (*Laboratório de Metrologia e Qualidade*) of the UTFPR. The 3D roughness parameters measured are shown in Tab. 4. Besides that, depth measurements on the wear tracks of the worn surface were made.

Table 4 – 3D roughness parameters of UP samples composites.

3D Parameter	Unit	Description
Sq	µm	Root mean square height
Ssk	-	Skewness
Sku	-	Kurtosis

3. RESULTS AND DISCUSSION

3.1 Microstructure

Figure 2 shows a SEM micrograph of polished surface showing homogeneously distributed graphite in the matrix and no porosity. The uniform distribution of the reinforcing particles and the absence of pores show an important role to improved mechanical and tribological properties of composites (Wang *et al.*, 2012; Mosleh-Shirazi *et al.*, 2016; Baptista *et al.*, 2016). The homogeneously distribution of the fillers and no porosity is important because represents a consolidated fabrication method. The presence of pores in composites, as well as in metals or other types of composites, may cause a stress concentrator, moreover, for polymer composites porosity might indicate that the reinforced material is not completed wetted by the resin or the fillers are agglomerated.

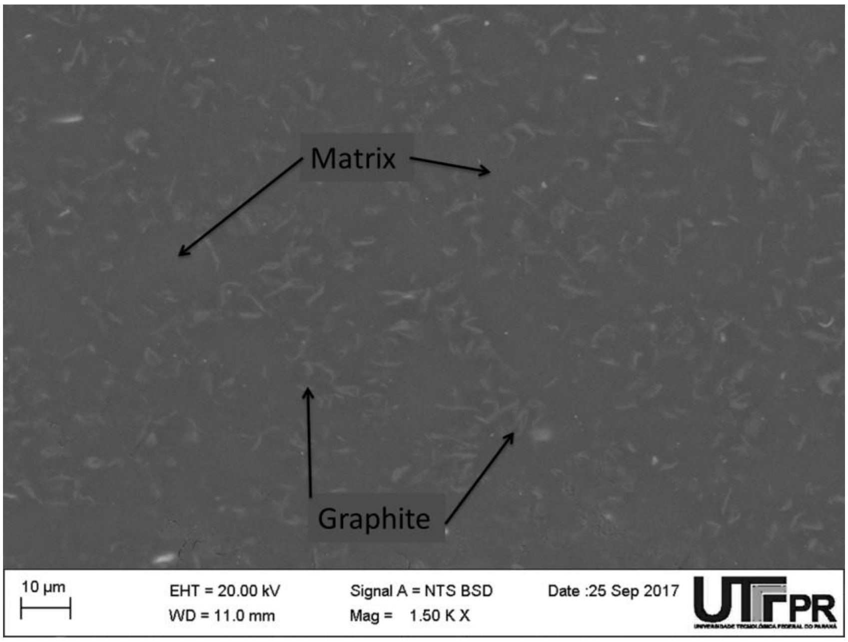


Figure 2 – Typical microstructure of the manufactured composite showing a homogeneous graphite distribution and absence of pores in the matrix (Example of surface of UPG7%)

3.2 Tribological and mechanical properties

Figure 3 shows that addition of graphite resulted in decreased hardness for unsaturated polyester composites. Similar results have also been reported elsewhere (Mosleh-Shirazi *et al*., 2016; Katiyar *et al*., 2016). This is explained by the presence of graphite particles, known as a soft material, within composites that contribute lowering their hardness. These results also imply that addition of graphite might have influence the mechanical properties of the composite. For UPG15% the results of hardness had more dispersion, probably because larger amounts of graphite are more difficult to obtain a homogeneous mixture which may cause variation of the microhardness values.

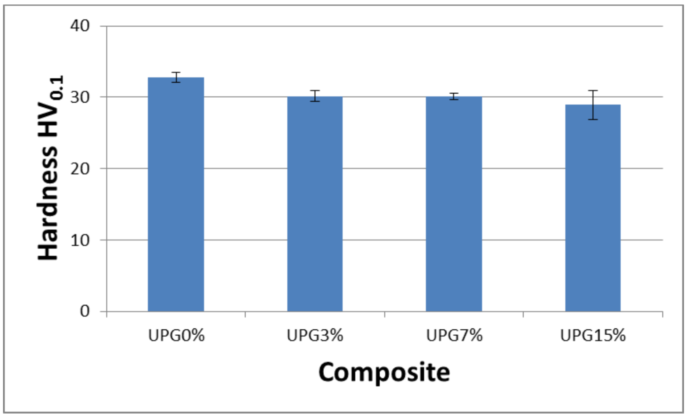


Figure 3 - The variation in the microhardness of unsaturated polyester composite with their graphite contents.

The tribological behavior of the composites containing 3, 7 and 15wt% graphite and the neat polyester were analyzed in order to understand the role of the graphite concerning COF and wear resistance. Figure 4 (a) and (b) shows average values of coefficient of friction calculated for the last 10 m of the test in a steady-state condition. The COF is presented as a function of the amount of graphite and load for the six conditions, Fig 4a present COF for normal load of 2.5N and Fig. 4b 5N.

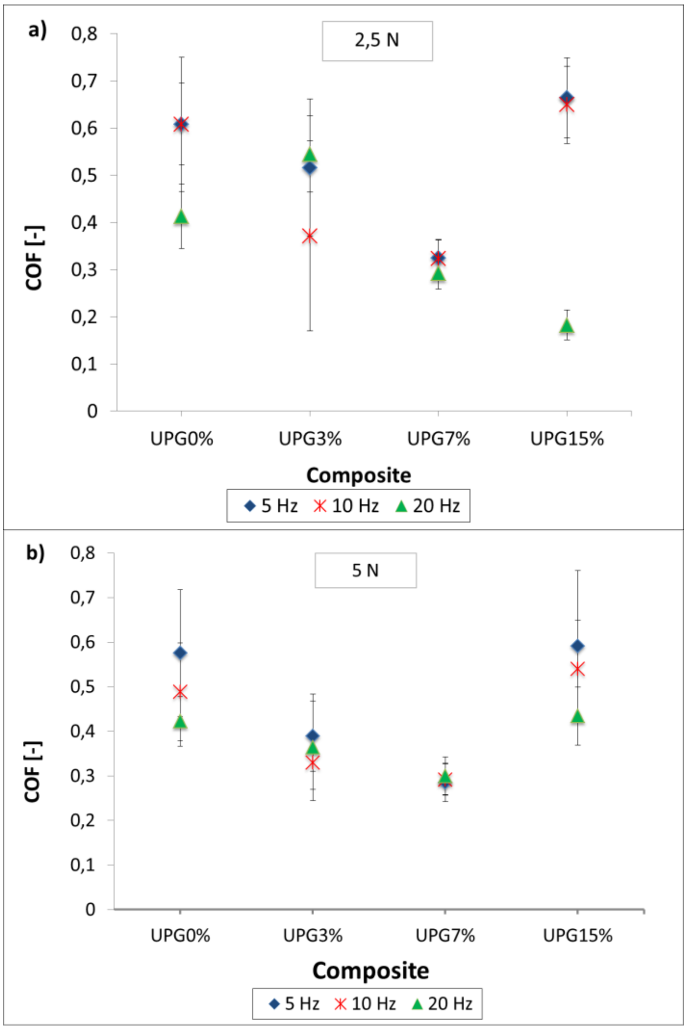


Figure 4 - Coefficient of friction versus the percentage of graphite and frequencies for a) 2.5N and b)5N

For majority of cases the effect of load was not decisive on the COF, but it tends to be slightly higher for 2.5 N. At first, the small variation on COF as fuction of load, may be explained by the fact that the range of the load on this study was subtle, however, there is a tendency, observed in previous polymer composites works, that increased normal loads results in lower COF (Sudheer *et al.*, 2014; Hashmi *et al*., 2007). A possible cause might be that detached material aligned on the sliding direction, due to the thermo-mechanical effect, enhanced the COF (Hashmi *et al*., 2007). The only configuration that does not follow the pattern is for UPG15% with frequency of 20Hz. In this case there was an increase of COF with load increase. For this result, the raise of COF might be related with graphite amount and formation of tribofilm. From Fig. 4 it is also possible to perceive that COF reduces up to 7%. Other studies (Mosleh-Shirazi *et al.*, 2016) have shown that when graphite exceeds a certain level, the mechanical properties debase and graphite may weaken the matrix causing fatigue delamination, and the presence of a nonuniform layer increase COF (Baptista, 2016).

The value of COF for the UPG0% increase with a load increase and its values is in agreement with the literature (Chakraborty *et al.*, 2014). The graphite exhibit significant effect as self-lubrification for UP composites mostly for conditions of 5 and 10 Hz for both loads. During the slinding tests, graphite particles detached from the sample, forming a layer between the body and counter body reducing contact among asperities and thereby causing reduction on COF.

3.3 CHARACTERIZATION OF SURFACES

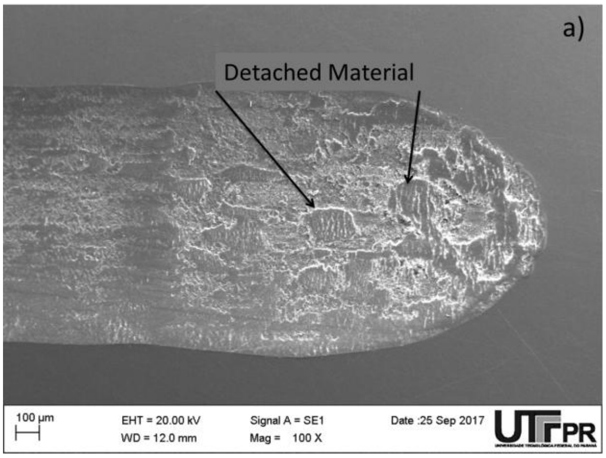
The average results with the standard deviation of the 3D roughness are presented in Tab 5. The *Sq* parameter is an overall texture of comprising the surface (Michigan Metrology, 2014) that is related with how further of the average the profile is. From the results, it is possible to observe that the parameter *Sq* increases with the increase of graphite. Less amount of graphite leads to more regular surfaces.

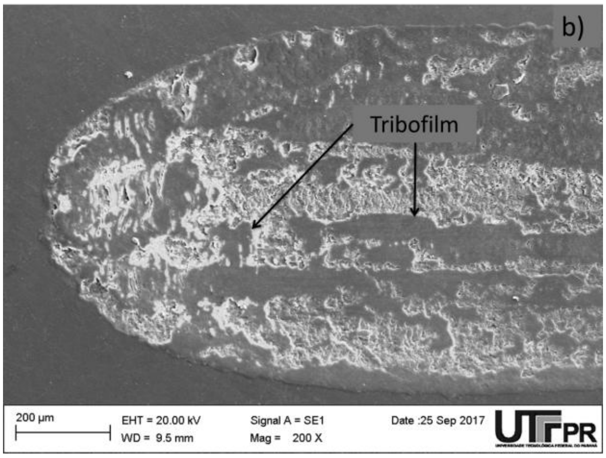
Table 5 – 3D roughness average for neat polyester and UP composites.

Sample	Sq	Ssk	Sku
UPG0%	0.074 ±0.001	-0.4 ± 0.2	4.5 ± 0.6
UPG3%	0.12 ± 0.01	-0.6 ± 0.9	4.1 ± 0.4
UPG7%	0.20 ± 0.07	-1.0 ± 0.4	4.8 ± 1.1
UPG15%	0.21 ± 0.05	-0.7 ± 0.6	7.7 ± 1.4
Sphere	14.4 ± 0.1	-0.5 ± 0.01	2.8 ± 0.06

The *Ssk* parameter is a measure of surface symmetry (Michigan Metrology, 2014) relating peaks and valleys. All the samples showed negative *Ssk*, that represents the dominance of valleys over peaks. The samples with more graphite showed a lower *Ssk*, which represents that the surface tends to be more asymmetry. The *Sku* parameter indicates the presence and distribution of peaks and valleys. Values above 3 indicate higher amounts of peaks and surfaces with predominance of peaks have a propensity to experience more wear. The samples presented *Sku* above 3, which could indicate that neat polyester and UP composites tends to wear.

Figure 5 shows SEM micrograph of worn surface for the four materials studied. Figure 5a is neat polyester at 5 N normal load and 20 Hz frequency. From the image is possible to observe compressed detached material in the rim extremities. An addition of graphite - UPG3% (Fig. 5b) at 5 N normal load and 10 Hz frequency – showed an irregular worn surface with formation of tribofilm on the entire track. UPG7% (Fig. 5c) at 5 N normal load and 10 Hz frequency, showed a better wear resistance, with a smoother worn surface and formation of tribofilm. At this compositions were observed the greater amount of transfer film, the development of graphite film is commonly associated with decrease COF and this result is in agreement with the tribological tests (Fig. 4). UPG15% (Fig. 5d) at 5 N normal load and 10 Hz frequency presents an expressive quantity of compressed layers formed from the wear debris, indicating that more material was detached. Incorporation of higher quantities of graphite might reduce mechanical properties of the material generating less resistance and consequently causing fatigue delamination with greater amount of material removed or moved to the rims. Changes of worn surfaces and wear mechanisms are consistent with the results of tribological tests.





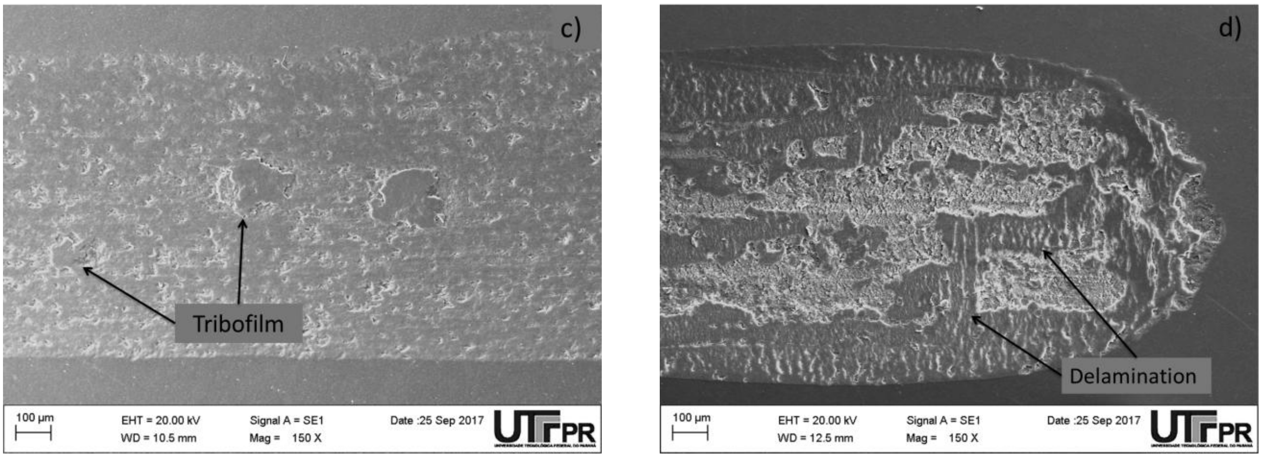
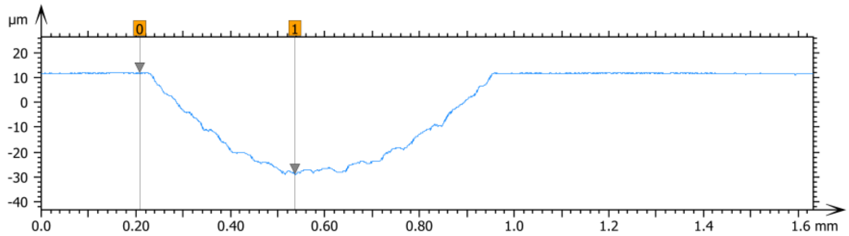


Figure 5 – Typical SEM micrograph of worn surfaces after testing a) UPG0%, b) UPG3%, c) UPG7%and d)UPG15%.

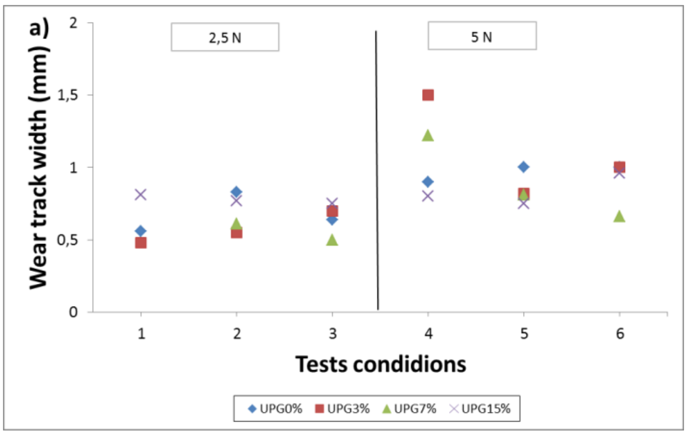
After the tribological tests, the maximum depth and width of the wears tracks were measure through the roughness profile (Fig. 7). Figure 6 shows an example of the wear tracks for UPG15%. Figure 4 summarized the wear tracks width/depth *vs.* tests conditions for the four material compositions. Overall, the neat polyester was the material with most worn surface. This may be explained by the fact that polyester presents a brittle behavior and when submitted in a condition of dry sliding might cause micro fractures on the surface, causing a severe wear (Chakraborty *et al.*, 2014).



Parameters	0-1	Unit
Horizontal distance	0.328	mm
Height difference	-41	µm

Figure 6 - Typical worn surface profile

The UPG7% and UPG3% presented the best results to wear resistance except for test condition 4. The condition 4 is 5 N normal load, 5 Hz frequency with 0.05 m/s of maximum velocity. In these conditions the low velocity causes wear mostly by plastic deformation, thereby increasing wear and COF. This condition also presents the higher COF for all composites (Fig. 4b).



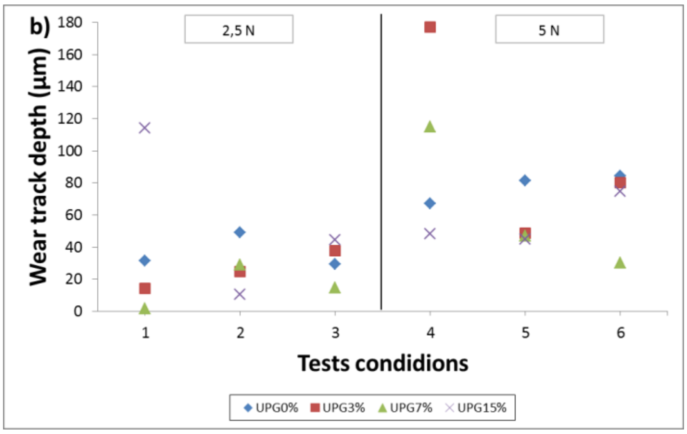


Figure 7 – a) Width and b) depth of wear tracks for all compositions.

4. CONCLUSIONS

The tribological behavior of unsaturated polyester matrix composite reinforced with graphite was investigated as a function of graphite contents, under reciprocating tests. From experimental results, the following conclusions can be drawn from the experimental study on wear behavior of UP composite:

- Adding graphite in UP enhance wear resistance, in comparison with neat polyester, for sliding velocities above 0.05m/s;
- The addition of graphite in UP reduces COF for 3 and 7%wt graphite;
- At 7% graphite contents was obtained the lowest COF and the greater amount of graphite films;
- Low velocity causes high values of wear and COF for UP composites;
- Adding graphite in UP reduces wear and increases the formation of graphite films up to 7% of graphite;
- Graphite reduces UP hardness; however the amount of filler has little influence on hardness of graphite/UP composites.

5. ACKNOWLEDGEMENTS

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