# EFFECT OF INORGANIC FILLER ON THE MECHANICAL AND TRIBOLOGICAL PERFORMANCE OF COMPOSITE MATERIALS

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*Abstract. The objective of the present work is the evaluation of the content of inorganic particles in the mechanical and tribological behaviour of polymeric matrix composites. In order to control easily the production of specimens, a polyester resin was used as matrix and silica particles were added as reinforcement. To understand the influence of reinforcement, composites with volumetric particle content ranged from 12 to 46 %,were produced and tested. There are several applications of inorganic particle reinforced composites where the volume percentage of the reinforcement is important, namely in dentistry. In posterior restorative resin materials the volume percentage of particles goes up to 50 or more. In the present study composite have fillers with irregular geometry therefore the connection between the matrix and the particles is more effective. Function of the shape, concentration degree and particle size of the filler its mechanical properties vary greatly. All of these factors influence the properties of the particle-reinforced composite, namely: wear resistance, hardness, flexural modulus, flexure strength and toughness.*

*Keywords: inorganic reinforcement, resin composite, tribological behavior, mechanical properties*

## 1. Introduction

In the last decade many filler systems, monomer systems and coupling agents have been tested with the aim of improving the mechanical and tribological properties of dental composites. The usage of particle reinforcement is done by economic and physical reasons, due to the low cost of the inorganic filler and/or to improve a specific characteristic of the resin composite. The filler characteristics, mainly, composition, size and percentage volume particles within the composite formulation have the potential to influence the performance of the composite.

There are several applications of composite materials where the inorganic fillers content is important, namely in dentistry. In posterior restorative resin materials their percentage in volume goes up to 50 or more. Function of the shape, concentration degree and particle size of the filler, the composite mechanical and tribological properties varies greatly, namely: wear resistance, hardness, flexural modulus, flexure strength and toughness. Some studies indicate that reinforcement by filler enhances the physical properties of hardness and elastic modulus (Ramalho and Antunes, 2005, Sabbaagh, Vreven and Leloup, 2002). The inclusion of inorganic filler doesn't improve all mechanical properties, for example, work-to-fracture and toughness decrease with filler content.

The role of the particles on the tribological behavior is not yet understood. While some authors achieved a rise of the wear for increasing filler content (Sole and Bole, 1996, Zou *et al.*, 2003), in other kind of applications inorganic particles are added to improve wear resistance, namely in abrasion wear (Ferracane *et al.*, 2002, Xing and Li, 2004, Luo, Lannutti and Seghi, 1998). Considering the fact that the increase of inorganic filler content, usually enhances the hardness and the elastic modulus, it could be expected an improvement of wear resistance. However, with the rise of inorganic filler the tension strength and the toughness diminish. Therefore, taking into account these contrary effects it is difficult to anticipate the wear behavior of composites with different filler content.

In the present work is evaluated the effect of the reinforcing particles in resin composite materials. The reinforcement particles used was silica and volume percentage was ranged from 12 to 46. For each one of the volume percentage of filler the tribological behavior is evaluated by abrasion, using the ball-cratering technique and reciprocating tests, with two distinct environments. In the case of the mechanical characterization the following tests were executed: hardness, bending and dynamic tests for elastic modulus evaluation.

All of the results attain for the composites were compared with the ones achieved with plain polyester resin. The microstructure of composites was analysed by scanning electron microscopy and the results were widely discussed.

## 2. Experimental procedures

### 2.1. Materials and specimen preparation

In the present work a commercial polyester resin was used, and as reinforcement particles of the composite material high purity silica particles with mean size of 5.65 μm was used. The particle content was ranged from 12 to 46 volume

percentage. Each one of the filler volume percentages was characterized by Mechanical and Tribological tests. The mechanical tests consisted in the determination of: hardness, flexural resistance, work-of-fracture, and finally elastic modulus evaluated by dynamic and static methods. Tribological tests involved two different wear techniques: micro-abrasion, by ball-cratering and reciprocating ball on plane tests. Besides the matrix without particles, in the present study the volume fractions of silica present in the composite specimens were of: 12, 16, 24, 30, 37 and 46 %. All the results attain for the composites were compared with the ones achieved with the polyester resin.

The resin processing was done according to the manufactures information. A pre-determined volume of resin was put in a container, afterwards the hardener was added, 2 % of the initial volume of resin, and then the mixture was well stirred, finally, the volume of silica particles was progressively added and stirred again. The produced mixture was put in the PVC moulds. In order to attain a homogenous cure all the specimens were placed in a woven at 40ºC for 8 hours. The specimens, after being removed from the mould were polished until the surfaces did not have any imperfections, and the dimensions of the specimens were homogeneous. Because this type of resin tends to increase hardness in time, a previous study was done to determine the suitable number of days necessary to guarantee the stabilization of the hardness value. It was determined that after 20 days of storage in air laboratory conditions no noticeable change in the hardness was registered. The final specimen's geometry was rectangular bars (50 mm x 6 mm) with 4 mm thickness.

## 2.2. Mechanical tests

In the case of the mechanical characterization the following tests were executed: hardness, bending and dynamic tests for elastic modulus evaluation.

### 2.2.1. Hardness

Struers Duramin testing equipment was used to apply a load of 1.962 N for a period of 40 seconds. Ten indentations were made on the surface of each specimen.

### 2.2.2. Bending tests

Bending study was carried out by four-point-flexure tests performed according to standard ASTM C1161-94 (1996). Samples were loaded into an Instron machine at a speed rate of 0.5 mm/min using a support span of 40 mm and a loading span of 20 mm. The flexural strength is calculated using the Eq. 1, $P$ is the break load, $L$ the outer span and $b$ and $t$ respectively the width and the thickness of the specimen. The work-to-fracture was calculated by the area below the flexural curve that can be used as a comparative value of the toughness.

$$S = \frac{3PL}{4bt^2}$$
(1)

### 2.2.3. Dynamic tests

The elastic modulus was measured by the impulse excitation technique as described by Braem *et al.* (1986) and according to the standard ASTM C1259-96 (1996). Each specimen was set in free flexural vibration by a light mechanical impulse. A strain-gage is used to capture the flexural vibration signal. The fundamental frequency of the first flexural vibration mode was determined analyzing the vibration response by Fast Fourier Transform.

Elastic modulus was calculated as a function of the frequency of the first flexural vibration mode using Eq. 2.

$$E = 0.9465 \left( \frac{mf_t^2}{d} \right) \left( \frac{l^3}{t^3} \right) T_1$$
(2)

Where $l$ and $d$ are the length and width of the bar, $m$ their mass and $f_t$ is the fundamental frequency. According to ASTM standard, $T_1$ is a correction factor to take into account the finite dimensions of the bar. For the calculation of $T_1$ a constant Poisson ratio of 0.3 was used. Ten vibration spectra were measured on each specimen.

## 2.3. Wear tests

Two types of tests were performed. The first type of abrasion wear resistance was done using the ball-cratering technique. Another type of wear test selected was the reciprocating type, with geometry plane-sphere, and two types of environment conditions. On one hand, unidirectional micro-abrasion was used because it's an excellent procedure for determining the abrasion resistance of materials (Antunes and Ramalho, 2003), since it is a very reliable and expeditious technique. By the other hand, the reciprocating test, was selected due to similitude with the natural

movement occurred in the mouth, and because of the possibilities of the variations in the amplitude of movement and contact conditions, specifically environment solutions. An important advantage in the reciprocating tests is also the possibility of evaluating the wear of both materials in contact.

### 2.3.1. Ball-cratering tests

A micro-abrasion test was performed to determine the abrasion resistance of the chosen materials. This technique is called ball-cratering, and consists of a sphere in rotation guided, with precise motion between points, solidary with a shaft. The sphere is kept in permanent contact with the vertical wear surface of a stationary specimen. A hanging weight is applied to guarantee a normal load. During these tests, abrasive slurry drops by gravity feed, keeping the contact area continuously covered with the slurry. The angular velocity of the shaft can be changed by means of a frequency inverter that feeds the electric motor. AISI 52100 steel spheres with 5 mm radius were used in the tests. This radius is similar to the curvature radius of molars. In order to ensure a good reproductivity the steel spheres where chemically etched (Allsop, Trezona and Hutchings, 1998). This provides an adequate roughness to sphere surface. A new ball was used for each specimen. The normal load $F_N$ applied to the contact was 0.5 N and the rotation velocity of the sphere was 100 r.p.m., corresponding to a linear nominal velocity of 0.052 m/s. The duration of the tests was 50, 100, 200 and 300 rotations. Two tests for each of the four numbers of rotations were carried out on each specimen, therefore each specimen was subjected to eight tests. The abrasive slurry used in the tests was an aqueous suspension of 0.35 g of glass micro-spheres per ml of distilled water. The diameter of the micro-spheres varied from 0.3 to 12 μm, with a mean value of 4 μm. The micro-spheres, with thick walls, are hollow silica-alumina ceramic with a hardness of 7 Mohs.

A Philips XL30 TMP Scanning Electron Microscope was used to measure the wear scars and examine the morphology of the crater in the wear surface. The wear scars were spherical in shape and their diameter was measured in two orthogonal directions, i.e., the direction of motion and the direction perpendicular to it. The average values of crater radius, $r$, as well as the sphere radius, $R$, were then used to calculate the depth, $h$, and volume, $V$, of removed material, using the Eq. 3 and 4.

$$h = R - \sqrt{R^2 - r^2} \tag{3}$$

$$V = \frac{\pi}{3} h^2 (3R - h)) \tag{4}$$

### 2.3.2. Reciprocating tests

The reciprocating tests were performed to determine the wear resistance of the chosen materials. This technique consists of a ball in reciprocating motion, in sliding contact, with a flat specimen of composite material. The ball is kept in permanent contact with the horizontal wear surface of the stationary specimen. A normal load of 5 N was applied to the ball, and the oscillatory movement was set a stroke length of 2 mm and frequency of 1 Hz. During the chewing process of human beings, the magnitude of mastigatory force in the oral cavity ranges from 3 to 36 N (Dowson, 1998). As in the current study, theoretically the surfaces interact by point contact; the normal load was fixed near the minimum referred values. In order to have contact conditions more similar to those that occurs in the mouth the reciprocating tests were performed imposing two environments: an artificial saliva solution and an abrasive solution. The duration of the tests differ, artificial saliva tests had 10.500 cycles while the ones with abrasive slurry only had 2.600 cycles.

The tests conditions were very similar for both environment solutions, excepting the number of cycles and the test environment. The artificial saliva is constituted with 0.7 and 1.2 g/l of NaCl and KCl respectively in distillated water. The abrasive solution is an aqueous suspension of 0.35 g of glass micro-spheres, with approximately 4 μm mean diameter, per milliliter of distilled water. In both cases the counterbody was a glass sphere with 10 mm diameter.

Respecting the number of cycles, for the tests with abrasive slurry the duration is smaller due to the fact that the associated damage is grater. The duration of 2.600 cycles allows the system to create sufficient wear volume in order to be visualized and measured on both the composites and the counterbody.

After testing the specimens were scanned by Roddenstock RM 600 laser stylus. The scanning done to all of the tested specimens were transversal to the sliding direction, the distance between profiles ranged from 20 to 30 μm, depending of the length of the wear scar. The areas of the 2-D profiles were integrated along the length of the wear mark allowing the determination of the volume removed by wear of composite material. The wear volume of the counterbody, glass sphere, has a spherical-caps shape and the diameter of their surface was measured in two orthogonal directions: the direction of motion and the direction perpendicular to it. The average values of crater radius, $r$, as well as the sphere radius, $R$, were then used to calculate the depth, $h$, and volume, $V$, of removed material, using Eq. 3 and 4.

The surfaces of the wear marks were examined by SEM. The images were attained allow to see the dimension and distribution of the particles and identifying the wear mechanisms occurred in the tests.

## 3. Results and discussion

### 3.1. Mechanical tests

Scanning microscope observation of polished surfaces of the composites allows concluding that the interface bond between the matrix and the particles is very effective. The performed composites display a good homogeneity as showed in Fig. 1, for 12 and 46 % particles content.

Table 1 presents the results of the micro-hardness tests. Observing the obtained results, one can see that there is a rise in the hardness with increasing percentage of particles.

Table 1. Hardness values of for all materials particle percentage.

| Particles content [%] | Hardness [MPa] |
|---|---|
| 0 | 217.2 ± 0.9 |
| 12 | 253.2 ± 1.3 |
| 16 | 282.0 ± 0.5 |
| 24 | 304.7 ± 0.4 |
| 30 | 330.6 ± 1.2 |
| 37 | 374.1 ± 2.2 |
| 46 | 418.3 ± 0.7 |



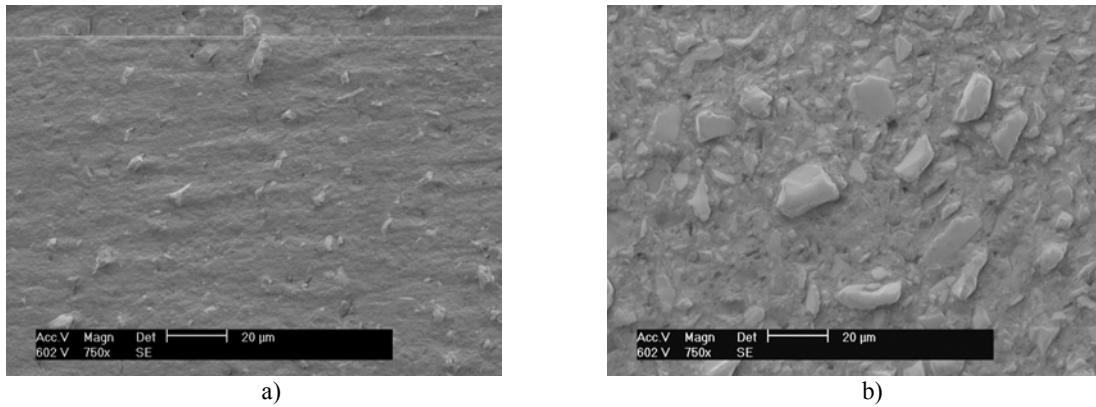a)                                                          b)

Figure 1. SEM views of the polished surfaces for composites with, a) 12 and, b) 46 % of particles.

Bending tests allows three different results, namely: flexural resistance, elastic modulus and work-of-fracture (the energy required to fracture the specimen, obtained from the area under the load-displacement curve divided by the specimens' cross-section area). The first result is presented in Fig. 2, representing the evolution of Flexural Stress *vs*. Crosshead displacement. The slope of the curves load-displacement is a measure of the elastic modulus although for higher strain than the value obtained by dynamic tests. The values of the elastic modulus obtained by bending tests, called, static, in opposition, to the achieved by dynamic method, are presented in Tab. 2, their relative evolution is very similar to the dynamic elastic modulus, although the dynamic are higher. Similar results were obtained by Sabbagh *et al.* (2002). The high values obtained with the dynamic method are due to the high strain rate on the specimen during testing (Braem *et al.,* 1986). The displayed results show that with increasing values of particles the values the ultimate breakload displacement are smaller and the flexural resistance diminishes. Therefore, although the raise in the static elastic modulus increases, the particles content leads to a reduction in the work-to-fracture, Tab. 2.

Table 2. Values for the flexural resistance, work-of-fracture, and static elastic modulus for each one of the volume fractions of the reinforcement particles of the composite materials studied.

| Particles content [%] | Average Flexural resistance [MPa] | Work-of-fracture [J/m²] | Static Elastic Modulus [GPa] |
|---|---|---|---|
| 0 | 54.2 | $4.3 \times 10^3$ | 2.93 |
| 12 | 44.05 | $1.8 \times 10^3$ | 4.38 |
| 16 | 36.69 | $1.4 \times 10^3$ | 4.52 |

| 24 | 36.01 | $1.1 \times 10^3$ | 5.24 |
| 30 | 27.05 | $2.9 \times 10^2$ | 5.72 |
| 37 | 23.61 | $1.3 \times 10^2$ | 7.3 |
| 46 | 24.93 | $3.5 \times 10^2$ | 9.52 |

All of the various specimens of the several percentages of reinforcement particles were measured and weighted. The fundamental frequency of bending vibration modes was achieved by FFT analysis of the free vibration response and the elastic modulus was calculated according to Eq. 2. Table 3, presents the mean values obtained for the material tested. There is a clear rise in the values of the dynamic elastic modulus for an increase in the percentage of reinforcement particles.
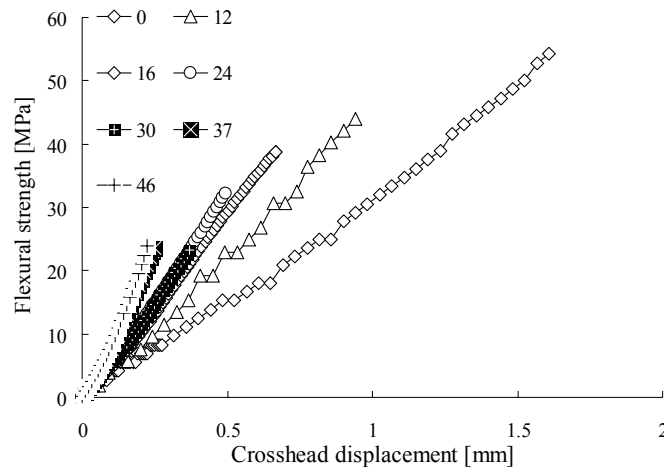


Figure 2. Flexural stress *versus* crosshead displacement for all the particle contents.

Table 3. Dynamic elastic modulus determined by impulse excitation of vibration.

| Reinforcement particles [%] | Dynamic Elastic Modulus [GPa] |
| --- | --- |
| 0 | 4.5 |
| 12 | 6.2 |
| 16 | 6.9 |
| 24 | 8.6 |
| 30 | 9.2 |
| 37 | 12.5 |
| 46 | 15.8 |

The Elastic modulus of the material tested results from a complex interaction between the mechanical properties of the two phases of the composite components.

### 3.2. Tribological tests

In the micro-abrasion tests, using the ball-cratering technique, craters vary proportionally to the number of rotations, maintaining a constant spherical geometry. For each material, test condition and number of rotations, a certain wear volume, expressed in $mm^3$, was obtained and the mean value of wear volume for every distance covered was determined. For each material a graph was plotted showing the corresponding mean wear volume for each of the four distances covered. After this, a numerical linear regression was carried out so as to allow the calculation the specific wear rate, confirming that there is a linear dependency between the wear volume and the distance covered. The specific wear rates obtained were calculate dividing the slope of the graph, wear volume in function of the distances covered, for the load applied, 0.5 N (Ramalho and Antunes, 2005). Figure 3 shows the performance of each specimen of composite material relative under abrasion contact. The higher the specific wear rate the smaller is the wear resistance. Thus, composites with silica volume fractions of 16 % show the best wear resistance. The values of wear volume increase from 16 to 46 %. The specific wear rate values of the resin and specimens with volume fractions of 12 % are very

similar to the ones obtained by the specimens of 37 %. Therefore, from the results displayed by this type of test the ideal value of particle content should be 16 % to maximize the abrasion resistance.
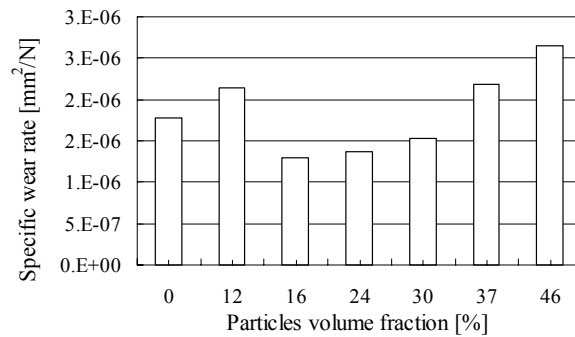


Figure 3. Evolution of the specific wear rate factor as a function of particle volume fraction.

For the reciprocating tests two type of environment were investigated, artificial saliva and abrasive slurry. The graph of Fig. 4 a), shows the values of wear obtained for the different composite, note that the wear volumes of composites with 37 and 46 % particle content are enormously bigger than the rest, their values are respectively of 0.38 mm$^3$ and 1.48 mm$^3$.The wear volume for the 46 % composite is: 16 times the value obtained for the resin, 0%, 3 times the value of wear volume of the composite with 37 % and 400 times the value of the composite with 24 % content. The composite with particle content that register the smaller value of material removed by wear was the 24 % content.

From the evaluation of the wear volumes of the glass ball tested against the various composite materials the difference between them is not so grate as for the composites. Again, the values of the antagonist wear tested against composites with 46 and 37 particle content is higher then the rest. Now, the difference between 46 % and 0 is 10 times, while, for the antagonist with less volume the value is of about 30 times. The glass ball with less wear volume was the one tested against the composite with 12 % particle content, however, the difference registered between the antagonists tested against composites of: 12, 16, 24 and 30 % is very small, Fig. 4 b).
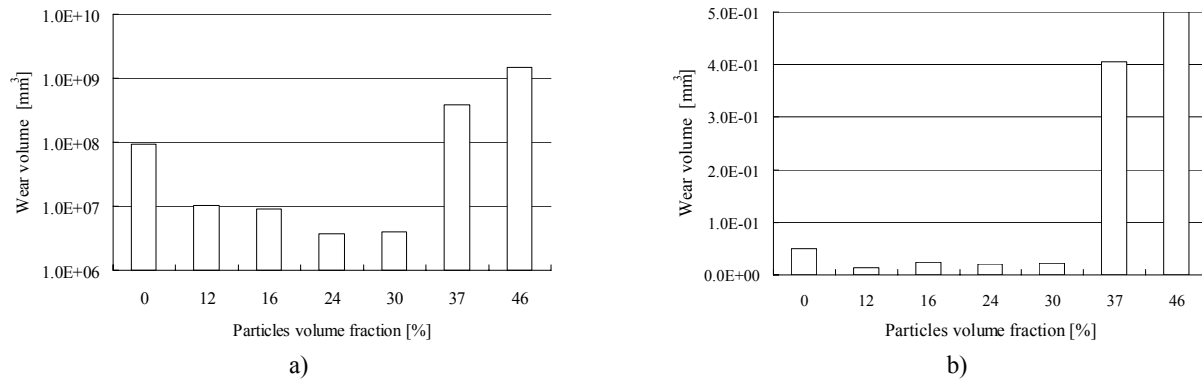


a)



b)

Figure 4. Reciprocating test with artificial saliva, wear volumes of: a) composite materials and b) antagonist.

Figure 5, presents the results of the reciprocating tests with abrasive slurry. In general, occurred a rise in the wear volumes for increasing particle content, the wear values of composites with 37 and 46 are very similar. The smaller value occurred for the resin specimens. From the comparison of the wear values for the saliva and for the abrasive slurry the specimens with particle content of 12, 16, 24 and 30 %, present higher values for the abrasive solution.

From the analysis of the wear volumes of the antagonist body, one can say that there is a gradual increase in the wear volumes for increasing particle content. The smaller value was registered in the case of the tests against the resin specimen, Fig. 5 b). Comparing the wear volume of tests with saliva and with abrasive slurry, again the antagonists tested against composites with 12, 16, 24 and 30 register higher wear volumes.
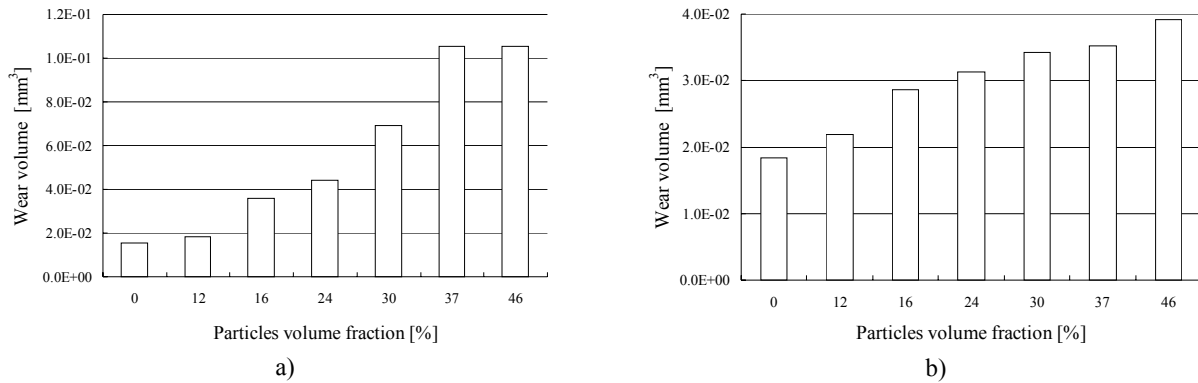
Figure 5. Wear volumes of: a) composite materials and b) antagonist, for the reciprocating test with abrasive slurry.

## 4. Morphology

Scanning microscope observation of polished surfaces of the composites allows concluding that the interface bond between the matrix and the particles is very effective. The performed composites display a good homogeneity as showed in Fig. 6, for 12 and 46 % volume of particles percentages of filler.
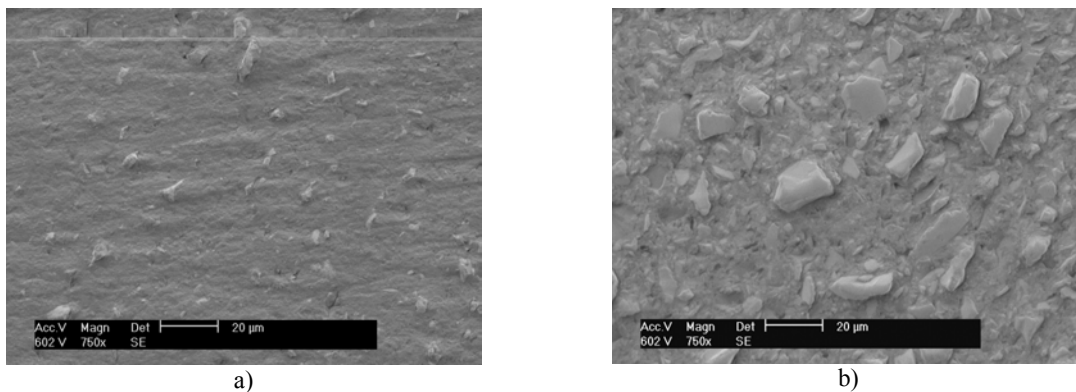


Figure 6. SEM views of the polished surfaces for composites with, a) 12 and, b) 46 % of particles.

Regarding the morphology, all wear tested samples were observed by SEM. In what concerns the ball-cratering tests, there was no relevant difference in the wear mechanisms and in the morphology of the abraded surfaces of the various composite specimens. Two-body abrasion occurs in all tested specimens; peaks and valleys caused by the debris are clearly visible abrading both the polymeric matrix and the reinforcement particles. No preferential detaching of reinforcement particles was observed, meaning that the particles were abraded together with the matrix material. Figure 7 shows two abraded surfaces, composites with 0 and 12 % particle content, where it can be seen some abrasive particles, micro-glass balls, attached to the composites.

On reciprocating tests, composites reveal bigger marks when tested with saliva. The scratches abrade both particles and matrix, Fig. 8 a). Also, in several specimens tested with saliva there is a formation of a thin layer by agglomeration of resin debris. This is noticed especially in the specimens without reinforcement particles, Fig. 8 b). In fact, the main difference, in terms of morphology of the surfaces for the two type of environment, is the existence, or not, of the layer of resin. In the case of the reciprocating tests with abrasive slurry this layer is probably destroyed, and removed by the debris in the contact.
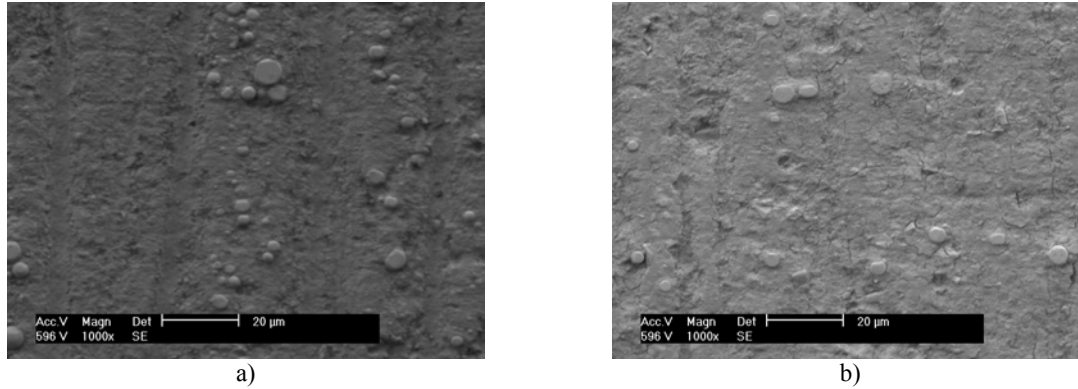
Figure 7. Wear mark of ball-cratering for: a) resin specimen, b) composite specimen with 12 % particle content.
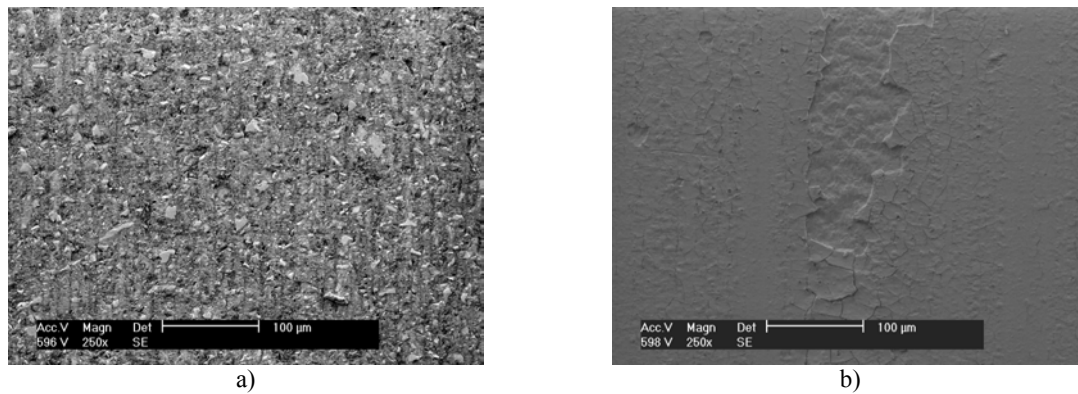


Figure 8. Morphology of the wear surfaces after reciprocating tests with saliva, a) 46 % particle content, abrasion of the particles along with the matrix, b) 0 % particle content, with an adherent thin layer.

## 5. Conclusions

In what concerns the mechanical properties, hardness, dynamic and static tests there is an increase in mechanical properties that corresponds to a rise in the volume percentage of reinforcement particles. However, the increasing of particle content leads to lower flexural resistance and smaller break load displacement. Therefore, in spite of higher elastic modulus, the work-to-fracture diminishes with the rise of particle content.

For the case of the tribological behavior, the wear of resin composites was investigated on reciprocating and micro-abrasion contacts against glass and steel balls respectively. Reciprocating experiments have been carried out with two environmental solutions: artificial saliva and aqueous abrasive slurry. This study made it possible to conclude that:

- o   In what concerns the ball-cratering tests there is an increase in the wear factor for particle contents above 16 %. The wear factor of the resin and composites with volume fractions of 12 % is very similar to the ones obtained by the specimens of 37 %. In this type of tests the ideal value of particle content is about 16 %;
- o   From the evaluation of the reciprocating wear with saliva the composite tested specimens reveal minimum wear for the particle percentages of 24 and 30 %. The worst results were achieved for 0, 37 and 46 % of particle content;
- o   From the analysis of the wear volumes of the antagonist body tested under saliva, the minimum wear volumes were obtained when the particle content on the composite range from 12 to 30 %;
- o   The reciprocating tests with abrasive particles leads to severe contact conditions. On this case the resin shows the best behavior and the addition of particles always increase the amount of wear in both composite and antagonist ball;
- o   In spite of the results observed for reciprocating tests with abrasive particles, it seems that the best wear behavior considering all the wear test results, could be achieved for reinforcement particle content approximately between 16 and 24 %.

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