Rheological and Mechanical Characterization of Poly (methyl methacrylate)/silica (PMMA/SiO$_2$) Composites

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The search for new materials with properties suitable for specific applications has increased the number of research studies to fill the market demands. The development of polymer composites by the addition of inorganic fillers to the poly(methyl methacrylate) (PMMA) increases the potential use of this polymer in various application fields. The main objective of this work was to study the rheological and mechanical behavior of composites obtained from the addition of silica in two different types of PMMA matrix: a common (PMMAc) and an elastomeric copolymer (PMMAel). The results showed that the addition of silica particles to the PMMA matrix promoted an increase in torque, a decrease in the melt flow index of composites and an increase in hardness compared to pure polymers. The composites also showed a reduction of the maximum tensile strength for composites with PMMAc matrix and maintenance of tensile strength for composites with PMMAel matrix. The average width of scratch decreased due to a change in wear mechanism, attributed to the increase of hardness in the composites obtained.

Keywords: *polymer composites, poly (methyl methacrylate), silica, scratch, wear*

1. Introduction

The development of materials science has brought important contributions to the advancement of technology. The constant search for new materials with optimized performance and properties, for innovative applications and improvement of existing materials, is a challenge, and one of the reasons of technical and scientific development. The use of composites as engineering materials is gaining more space in various industry segments, since they provide good synergy in the interaction between the different components that form them, resulting in a range of properties inherent to the material, and attributions (economical and environmental) more interesting than their individual components[1,2]. This properties of a composite material depend not only upon the properties of the individual component phases (matrix, filler, interphase), but also upon their interaction[3].

PMMA has high stiffness and excellent dimensional stability, compared to other acrylic polymers widely used in the production of transparent artifacts to replace glass[4]. The incorporation of inorganic fillers into polymers can create materials with higher mechanical strength, thermal stability or with higher magnetic, optical or electrical properties. The use of silica as filler leads to improved properties such as increased rigidity, increased dimensional stability

and reduced flammability[5]. The interaction at the interface between them plays a crucial role in the properties and performance of composites used in a particular application.

Ferreira et al.[6] studied the mechanical behavior of a PMMA/SiO$_2$ mixture for applications in sanitary and kitchen equipment, varying the concentration of components and particle size of the silica used. The results showed that the material with higher silica content and finer grains exhibited higher mechanical properties (maximum stress and Young's modulus), compared to material with lower silica content and coarser grains. Fracture toughness was also evaluated, being higher for the latter. Wang et al.[7] evaluated the effect of the interface on the thermal stability of PMMA/SiO$_2$ hybrids by differential scanning calorimetry (DSC) and thermogravimetry (TGA) techniques. The results showed higher thermal stability for hybrids when compared to PMMA.

Brostow et al.[8] prepared nanocomposites of PMMA and montmorillonite clay (MMT) in a co-rotational twin-screw extrusion and injection molding, varying weight fraction of MMT Brazilian clays. Dynamic friction and wear rate of these composites were studied as a function of Brazilian clay concentration.

Sugimoto et al.[9] prepared reactive silica nanoparticles and copolymerized them with methyl methacrylate. The samples were analyzed by thermogravimetric analysis,

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dynamic mechanical analysis (DMA), Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). Results showed that the hybrids showed high transparency and increased Young's modulus, hardness and thermal stability.

Ito et al.[10] studied the incorporation of silica obtained from the controlled burning of *Equisetum arvense L.* stem in two kinds of PMMA polymer matrix with and without compatibilizer. The addition of these particles promoted improvements in thermal stability and viscosity of the composites produced. The mechanical properties of composites; however, showed small changes when compared to the pure polymer, probably due to the presence of large agglomerates which might be negatively affecting composites performance. The compatibilizer showed no effectiveness interaction, and should not be used for low silica concentrations.

Zou and Yoshida[11] studied the effect of the size of silica nanoparticles on the thermal decomposition of PMMA using the thermogravimetric technique. The author considered that the improvement of thermal stability depends on the size, on the state of dispersion and on the surface area of silica particles.

Avolio et al.[12] synthesized PMMA nanocomposites with silica nanoparticles modified by *in situ* polymerization. NMR (nuclear magnetic resonance) experiments were performed to evaluate the nature of interactions between organic and the inorganic phases. The formation of an interphase consisting of PMMA chains grafted onto the silica surface was observed. The abrasion resistance and the glass transition temperature of these materials were also evaluated. The abrasion resistance of nanocomposites was improved due to changes in wear mechanism. The increase in the glass transition temperature was attributed to the strong interaction between polymer and the modified silica particles.

Wear can be defined as a progressive loss of material from the surface of a solid body due to mechanical action, that is, the contact and relative movement of this body against a solid, liquid or gaseous body[13]. Abrasive wear is related to some mechanisms, including microcutting, microploughing and microcracking (Figure 1). Microploughing and microcutting are dominant mechanisms in more ductile materials and the occurrence of one of them depends on the attack angle of abrasive particles. Microcutting occurs from a critical attack angle, which is a function of the material used and test conditions. The transition from microploughing to microcutting also depends on the friction coefficient. Microcracking is the wear mechanism most characteristic in brittle materials.

The main aim of this work was to study the rheological and mechanical properties of composites made with two types of PMMA and silica obtained by mechanical mixing in single screw extruder for new applications as engineering plastics.

2. Experimental

2.1. *Materials*

In this work, two types of PMMA (granules) were used: a polymer Acrigel® LEP100 (called PMMAc) and an elastomeric copolymer Acrigel® ECP800 (called PMMAel) with melt flow indexes (230°C/3.8 kg) of 3.8

and 1.1 g/10min (ASTM D 1238), respectively, acquired from Unigel Plásticos S/A. The inorganic filler used was precipitated silica particles ($10SiO_2.1H_2O$), TIXOSIL® 333, acquired from Rhodia.

2.2. *Methodology*

2.2.1. Particle

The laser diffraction particle size method was used for determining the average particle size of silica. Ultrasound was used before analysis to break up clumps for 10 minutes in the presence of a deflocullant (Triton X -100) from Aldrich. The equipment used was a Microtac, model S3500.

2.2.2. X-ray fluorescence (XRF)

Semi-quantitative analysis of powdered silica was performed in a Shimadzu XRF -1800 equipment to provide information about the chemical composition of this material.

2.2.3. Torque rheometry

Torque rheometry test was carried out in an internal mixer (Rheomix 600) operating with roller-type rotors coupled to a Haake-Büchler System 90 torque rheometer. Rotation speed of 50 rpm and temperature of 220°C were used, with mixing time of 10 minutes. Polymers and composites with 5 % silica were prepared directly in the rheometer without previous extrusion. The weight was kept constant at 50 g for all samples.

2.2.4. Sample preparation

Pure polymers and composites were processed on a single-screw extruder model AX 16 from AX Plásticos Máquinas Técnicas LTDA with screw diameter D=16mm and length/diameter ratio (L/D=26) and screw with Maddock-type dispersive element. Before mixing, the materials were previously dried in vacuum oven for 24 hours at 60°C. The temperature profile used during the extrusion was 220/240/230°C in the respective feeding/ mixing/matrix zones with rotation of 40 rpm. Table 1 shows the proportions of materials prepared by extrusion.
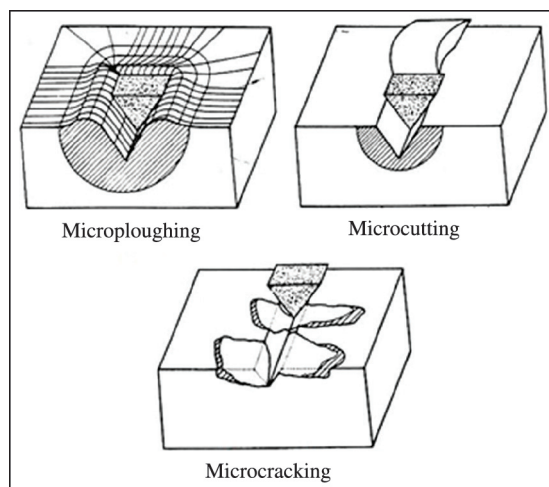

Figure 1. Wear mechanisms involved in abrasive wear[13].

2.2.5. Injection molding

Specimens (ASTM D 638 Type I) were injection molded in an Arburg machine model Allrounder 270S. The processing conditions were: injection temperature profile of 210/220/230/240/240°C, mold temperature of 40°C and cooling time of 35 seconds.

2.2.6. Melt flow index (MFI)

The melt flow index of unprocessed polymers and processed materials was determined in a CEAST extrusion plastometer, standardized according to ASTM D 1238 using temperature of 230°C and weight of 3.8 kilograms.

2.2.7. Tensile test

Tensile tests were performed in a universal Shimadzu testing machine model AG - X 300 kN using type I specimen of ASTM D 638. The test speed was 5 mm/min until specimen rupture.

2.2.8. Scratch test

Scratch test was performed with a device made for this task, based on the Hoffman scratch test equipment. The equipment consists of a cart having a standard weight of 200g applied on the sliding surface with commercial steel scriber brand Cortag. Three scratches were performed in each sample, which were subsequently analyzed by light microscopy in Olympus equipment, GX 51, and the average widths (15 measurements for each scratch) were measured with the aid of the Image J software. After assembly, the entire apparatus had a weight of 214.7 g on the samples assayed. The contact angle of the scriber of 85° was measured using a Mitutoyo profile projector model PH- R14.

2.2.9. Hardness

The Rockwell M hardness measurements were performed using a steel ball with diameter of ¼ inch, pre - load of 10 kgf and load of 100 kgf on a Durometer brand Pantec model RASN. Five measurements were performed on each sample, in accordance with ASTM D 785.

3. Results and Discussion

3.1. *Silica characterization*

3.1.1. Silica FRX

The X-ray fluorescence analysis (Table 2) aimed to provide quantitative information on the composition of precipitated silica used in this work.

The results show the chemical composition of compounds present in the test material containing silica in greater amounts and compounds such as sulfur trioxide and copper oxide in smaller amounts, probably from the inefficient filtration and washing process carried out in the industry to remove all traces of chemical salts and by-products of the precipitation process.

3.1.2. Laser diffraction

Figure 2 shows the accumulated and discrete particle size distribution curve of the silica used. The analysis showed that the measures ranged from 2.7 to 74 μm, with a mean diameter of 13.4 μm.

According to Jillavenkatesa et al.[17], knowing the size and distribution of particles is a prerequisite for many processing and manufacturing operations involving particulate systems. Therefore, particle size has a significant effect on the mechanical strength of composites, which generally increases with smaller size of particles[18-20].

3.1.3. Silica morphology

SEM analysis (Figure 3) was performed not only to characterize the morphology of precipitated silica but also for carrying out measures related to particle size.

Figure 3 shows that the particles do not have well-defined shape. The results of particle size characterization and scanning electron microscopy indicate the need to perform a processing step with higher shear rate in order to achieve greater efficiency in silica dispersion. For particle size measurement, the measurement of about 200 particles was performed using image analysis software (Image J), obtaining an average size of 11.5 ± 2.7 μm, approaching the value obtained by laser diffraction.

Lau[21] showed that the mechanical properties of composites and nanocomposites are affected by particle size, particle type and in particular, by the particle/matrix interfacial adhesion. Sumita et al.[22] reported the importance of substituting microscale silica by particles in nanometric scale, giving greater stiffness and resistance to polymers.

3.2. *Characterization of composites*

3.2.1. Torque rheometry

In the processing of polymers, the rheological properties depend on operating (temperature, pressure, flow, etc.) and

Table 1. Materials processed by extrusion.

Materials	% Weight fraction
PMMAc/SiO$_2$ PMMAel/SiO$_2$	100
	99.5/0.5
	99/1
	95/5

Table 2. FRX of precipitated sílica.

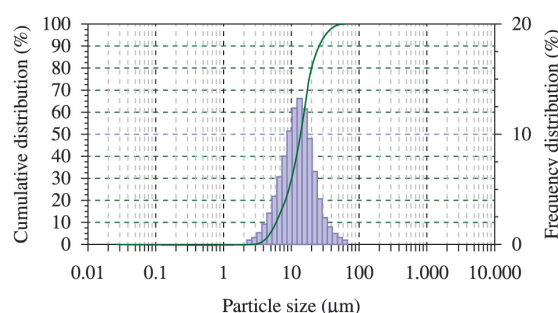| Content	(%)
SiO$_2$	96.73
SO$_3$	2.93
CuO	0.34

Figure 2. Silica particle size characterization.
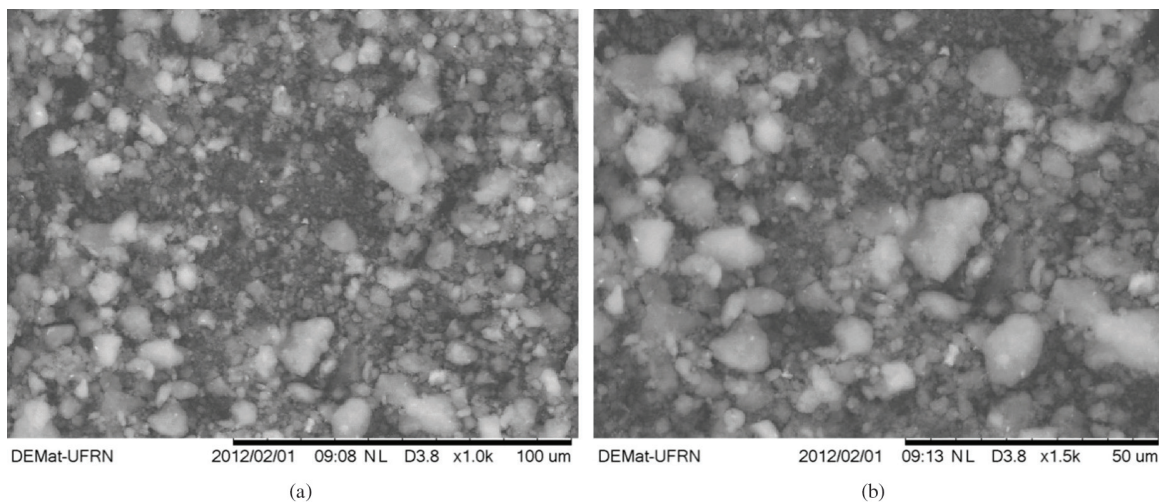
(a)   (b)

Figure 3. SEM images of silica with magnification of: a) 1000x; b) 1500x.

structural parameters (molecular weight, molecular weight distribution, etc.). Thus, it is recommended to measure rheological properties such as viscosity under conditions closer or similar to processing conditions[23]. The torque rheometer results are shown as a torque *versus* time curve for polymers and for composites with 5 % silica without prior extrusion, as can be seen in Figure 4.

Torque peak at the beginning of processing is called the load peak, which refers to the torque required to maintain rotation speed programmed in the rheometer, while the material is flowing into the camera. Initially, PMMA polymer samples were tested to identify the polymer behavior in relation to the processing conditions. It was found that much of the mass added to the equipment was melted 2 minutes after processing began. It was also observed that the PMMAc/SiO2 (95/5) curve is shifted to the right due to a delay in the supply of this sample into the rheometer.

The results showed that although PMMAel has higher torque after 10 minutes when compared to PMMAc, the increase in torque promoted by SiO_2 addition was minimized for PMMAel, indicating that much of the silica may have been attracted by the rubber phase of copolymer, thus reducing the effect of interaction of PMMA with silica particles. After 10 minutes of mixing, the increase in torque promoted by the addition of silica particles into the PMMAc matrix was about 20%. According to Marconcini et al.[24,] the increased torque during test is indicative of increased viscosity of the composite compared to the pure polymer, showing an interaction between the system components, similar to those presented in this work, except that the sample used the compatibilizer. Clearly, the rheological evidences presented are not sufficient to prove the nature of the interactions between the copolymer and silica, requiring complementary investigative techniques.

3.2.2. Melt flow index measurements

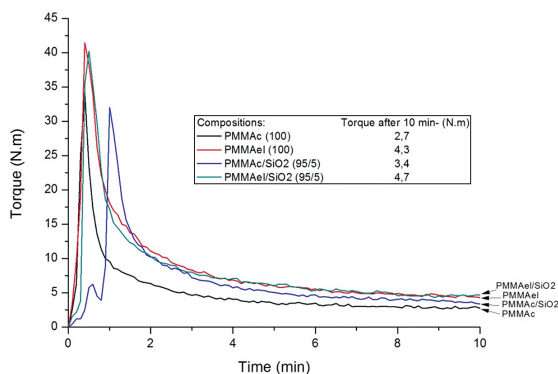The melt flow index (MFI) of processed unprocessed polymers is shown in Figure 5.

Figure 4 . Torque rheometry of polymers and composites with 5 % silica.

These results show a reduction in the melt flow index of composites in both matrices with increasing silica concentration, since the addition of fillers increases the viscosity. The melt flow index is an empirically defined parameter, inversely proportional to the viscosity of the material at specific temperature and shear rate[25]. Unlike PMMAc, PMMAel has rubber particles present as dispersed phase in its matrix, which contributed to a lower melt flow index (higher viscosity). In MFI, the flow to pass through the die is elongational and needs to direct the molecules in the flow direction. This directing is hindered in the presence of the silica particles, and even more in the presence of elastomeric phase, providing a higher decrease in MFI for composites with PMMAel. Results also indicate that there was a slight increase in the melt flow index of polymers after processing, indicating the occurrence a small degradation of these materials during this step. MFI results should be cautiously interpreted due to the fact that the method of analysis may present several flaws as the results are very sensitive to measurement procedure details, especially for low MFI polymers. It should also be mentioned that MFI values are not truly useful to predict the actual processing conditions, since many commercial thermoplastic are
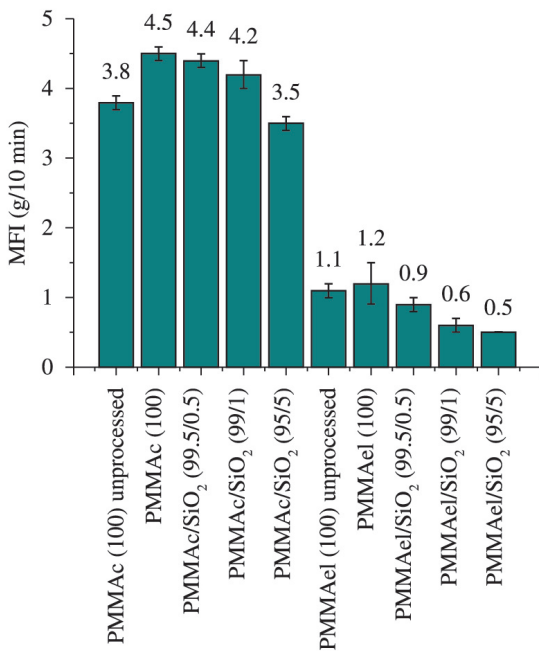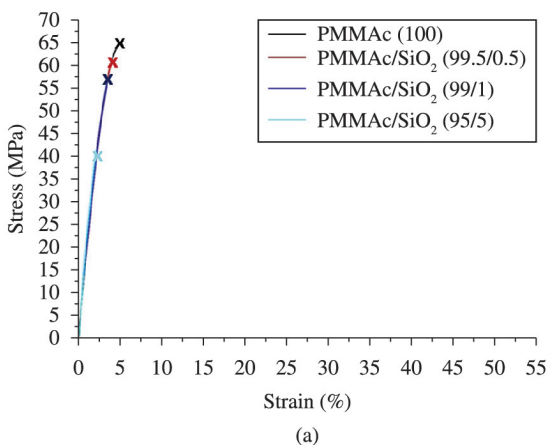
Figure 5. Graph comparing the melt flow index of polymers and processed composites.

Table 3. Tensile strength results of polymers and composites.

Composition (% mass)	Maximum tensile strength (MPa)
PMMAc (100)	64.2 ± 0.6
PMMAc/SiO$_2$ (99.5/0.5)	57.7 ± 2.3
PMMAc/SiO$_2$ (99/1)	55.2 ± 1.6
PMMAc/SiO$_2$ (95/5)	37.9 ± 2.6
PMMAel (100)	32.9 ± 0.8
PMMAel/SiO$_2$ (99.5/0.5)	34.2 ± 0.2
PMMAel/SiO$_2$ (99/1)	34.2 ± 0.1
PMMAel/SiO$_2$ (95/5)	34.6 ± 0.3

pseudoplastics or have decreased viscosity with increasing shear rate, being usually processed at much higher rates than those imposed during the measurement of this property[26].

3.2.3. Tensile test

The maximum tensile strength of pure polymers and of composites obtained at concentrations of 0.5, 1 and 5% by weight was determined through tensile tests by evaluating the effect of silica concentration on this property. Table 3 presents the average maximum tensile strength values of injection molded samples.

The mechanical properties of composites suffered some variations in relation to pure polymers. This table shows a significant decrease in the tensile strength for PMMAc/SiO$_2$ composites with increasing silica concentration. This reduction may be related to the presence of silica particles of irregular shape, which can act as stress concentrators, thus weakening the material. For PMMAel/SiO$_2$ composites, the addition of silica particles not provide any change in tensile strength of these materials, probably indicating that the interaction of the particles with this type of matrix should have been decreased due to interactions with the rubber phase of the copolymer. These results were also observed by Marconcini et al.[24], who used silica particles obtained from the controlled burning of *Equisetum arvense L.* stem using conditions similar to those described by De Souza et al.[27].

Figure 6 shows comparative stress versus deformation curves of a representative sample of polymers and their composites, constructed with maximum tensile strength values that came closest to the average. The deformation values presented for comparative purposes were determined from the displacement of the machine's movable head.

Based on the curves shown, no significant change with respect to stiffness was observed for both PMMAc and PMMAel matrices. For PMMAc and their composites the value of Young's modulus was approximatelly 2.5 GPa and to PMMAel and their composites was 1.4 GPa. Thus, there is evidence that the amount of reinforcement may not have directly influenced this property, which is most strongly affected by the type of reinforcement than by the added content[18].
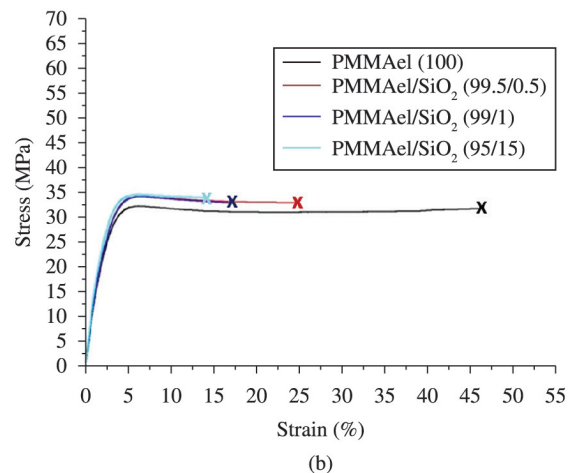

(a)

(b)

Figure 6. Comparative stress *versus* deformation curves: a) PMMAc matrix; b) PMMAel matrix.

With respect to the elongation at rupture observed in the graphs of Figure 6, there is a reduction due to the increase in the silica concentration for all composites studied, being more significant for PMMAel/SiO$_2$, reducing about 3 times its deformation. This behavior can be explained by the fact that silica particles have different geometries, and may act as stress concentrators, which can be seen in the micrographs shown in Figure 3.

3.2.4. Rockwell M hardness

The hardness test results are shown in Table 4.

With respect to surface hardness, the results show that the silica particles were effective in increasing this property to PMMAc, about 20% to PMMAc/SiO2 (95/5) composite, while for PMMAel no significant variation was observed. Although there is evidence that the particles are attracted into the copolymer elastomeric phase, the amount of filler

Table 4. Hardness results the samples obtained by injection molding.

Injected specimens	Rockwell Hardness (HRM)
PMMAc (100)	68.0 ± 0.7
PMMAc/SiO$_2$ (99.5/0.5)	71.0 ± 0.7
PMMAc/SiO$_2$ (99/1)	76.2 ± 1.9
PMMAc/SiO$_2$ (95/5)	80.2 ± 0.8
PMMAel (100)	40.4 ± 2.7
PMMAel/SiO$_2$ (99.5/0.5)	41.6 ± 2.1
PMMAel/SiO$_2$ (99/1)	44.6 ± 1.5
PMMAel/SiO$_2$ (95/5)	45.2 ± 1.3

Table 5. Average width of scratch.

PMMA/SiO$_2$ (% mass)	Width of scratch (µm)	
	PMMAc/SiO$_2$	PMMAel/SiO$_2$
(100/0)	129.7 ± 9.0	197. 4 ± 10.6
(99,5/0,5)	122.5 ± 10.1	168.8 ± 12.0
(99/1)	118.5 ± 3.9	164.7 ± 6.1
(95/5)	137.6 ± 5.7	158.6 ± 12.9

and dispersion of these particles may not be sufficient to promote better hardness results.

3.2.5. Scratch assay

The average width of scratch is shown in Table 5.

These results show a decrease in the average scratch width with increasing silica concentration, except for PMMAc/SiO$_2$ (95/5), which showed an increase in the average width of the tear, which may have been caused by the pullout of part of the polymer with the silica during scratch, which is typical of the microcracking wear mechanism.

A visual difference was also observed between scratch produced in each polymer and composite studied, as illustrated in Figure 7.

Figure 7 shows the transition from microploughing to microcutting wear mechanisms in composites with PMMAel matrix with increased silica concentration. Normally, the mechanism shifts from microploughing to microcutting with increasing hardness of the material, and even greater increases in hardness result in shift from microcutting to microcracking[13]. Composite with PMMAc matrix only show the microcutting wear mechanism, typical of brittle materials of high hardness.

4. Conclusions

The effects of adding silica particles to two types of PMMA matrices were evaluated in terms of the mechanical and rheological properties of these materials. With respect to the tensile mechanical properties, it was observed that there was a reduction in tensile strength for composites with PMMAc matrix and a maintenance of this property for composites with PMMAel matrix as a function of increasing silica concentration. There was a significant increase in hardness for both types of PMMA matrices, being more significant for polymer with PMMAc matrix, changing the wear mechanism of composites studied. The torque rheometry and melt flow index results showed that increasing the silica concentration in the PMMA matrices resulted in general increase in the system viscosity and hence in a decrease in the melt flow index. The incorporation of silica particles into the PMMA matrix is feasible and promising to obtain composites with thermoplastic matrix.
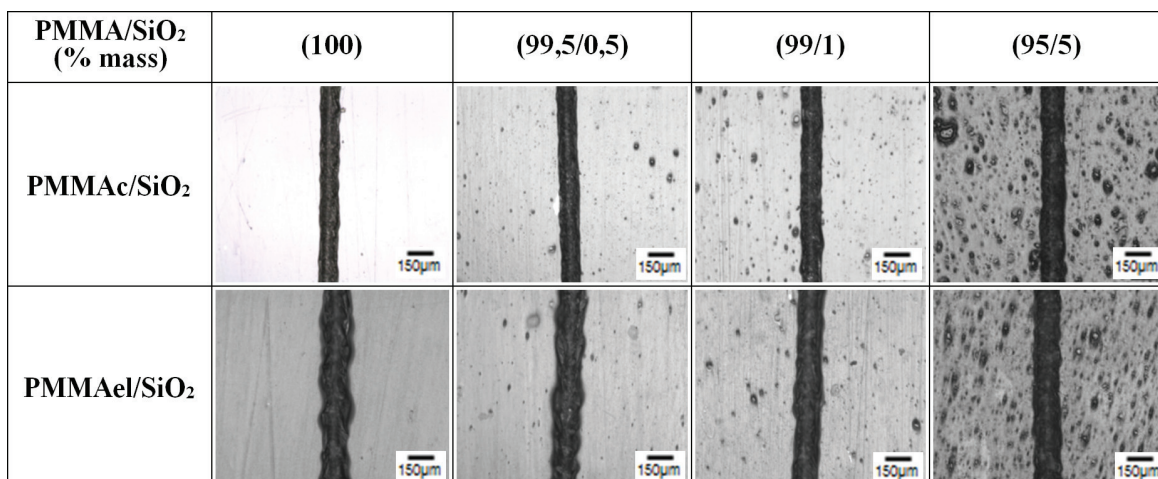

Figure 7. Optical microscopy images of scratch.

Acknowledgements

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