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Nanocomposites of poly(methyl methacrylate) (PMMA) and montmorillonite (MMT) Brazilian clay: A tribological study

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Abstract. Nanocomposites of PMMA+MMT Brazilian clays were developed by mechanical mixing in co-rotational twin-screw extrusion and injection molding with varying weight fraction of MMT Brazilian clays. The clays were purchased in crude form and then washed and purified to extract the organic materials and contaminants.

Dynamic friction and wear rate of these composites were studied as a function of concentration of the Brazilian clay. With an increase in the amount of MMT Brazilian clay, the dynamic friction of the nanocomposites increases, a clear but not large effect. It can be explained by sticky nature of clay; clay in the composite is also on the surface and sticks to the partner surface. The wear rate as a function of the clay concentration passes through a minimum at 1 wt% MMT; at this concentration the clay provides a reinforcement against abrasion. At higher clay concentrations we see a dramatic increase in wear – a consequence of clay agglomeration and increased brittleness. The conclusions are confirmed by microscopy results.

Keywords: *nanocomposites, poly(methyl methacrylate), montmorillonite, dynamic friction, wear*

1. Introduction

Most of the work on tribology to date, in particular at the micro- and nano-scale, is focused on metals and ceramics used for nano-electronics industry and microelectro-mechanical systems (MEMS). Although polymers and polymer nanocomposites, owing to their adequate strength, lightness, versatility, ease of processing and low cost, have been widely employed to replace the traditional metals and ceramics in microelectronic packaging, coatings, aerospace, automotive, food packaging and biomedical applications, not much research has been done on them in this regard. This may be due to their viscoelastic properties, which makes the processes and analysis complicated. Additionally, in the case of polymer nanocomposites, detailed knowledge of the role of nano-fillers during the tribological processes, and the precise relationships between structures, properties and processing are required [1].

Nanostructured materials promise fruitful development for applications in the aerospace sector due to their high strength, low density and thermal stability. These applications include equipping aircrafts, rockets, space stations and platforms for planetary or solar exploration [2]. Nanotechnology has

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attracted the interest of numerous research groups around the world due to its potential for application in various industries [3].

Poly(methyl methacrylate) (PMMA) is an important amorphous thermoplastic with desirable properties, including clarity (the transparency is close to the ultraviolet region and also the infrared), chemical resistance, good moldability, protection against ultraviolet radiation, good weatherability, high strength, and dimensional stability [4–6]. Moreover, PMMA has good resistance to both acidic and alkaline environments. PMMA is resistant to many inorganic reagents, aliphatic hydrocarbons, nonpolar solvents and acidic and alkaline solutions [7]. However, PMMA has limitations in its thermal stability and mechanical-dynamical properties at high temperatures. One way to improve the performance of polymers is the addition of nanoparticles such as clays, silica or carbon nanotubes to the polymer matrix [8–11]. Nanocomposites based on layered smectite clays as the reinforcing part of the matrix often exhibit improved mechanical properties [6]. Usually, PMMA nanocomposites offer a potential for reduced gas permeability, improved physical performance, and increased heat resistance – often without a sacrifice in optical clarity [6].

Understanding the physical nature of friction, the definition of wear, its consequences, its mechanisms and ways to control its effects are fundamental to modern engineering. The purpose of this study was to evaluate the tribological performance of nanocomposites consisting of PMMA and montmorillonite (MMT) Brazilian clay.

2. Experimental

2.1. Materials

Neat PMMA Cristal 01-DH-ECL used was kindly donated by the Unigel SA (Sao Bernardo Do Campo, Brazil) company. Its melt index is 2.5 g/10 min (ASTM D 1238). MMT Brazilian clay from the company Bentonisa was used as a filler. There is no significant difference between the clay we have used and clays from other countries.

2.2. Preparation of clay

The clay was purchased in crude form and was washed and purified to extract the organic materials and contaminants. It was subsequently dried in an oven with circulating air for 48 h at 60°C to remove any excess water remaining after washing.

2.3. Processing

Initially, before the steps of extrusion mixing and injection molding, all materials were kept in vacuum at 60°C for 15 h to remove any humidity absorbed by the materials.

Table 1 shows the formulations of nanocomposites mixed in a twin-screw extruder, B&P Process Equipment, model MP19-TC (d = 19 mm and L/D = 25), using a temperature profile of 180°C in the feed zone and 200/210/220/210°C in the subsequent areas. The extruder was used in co-rotating configuration.

The samples were injection molded in an Arburg Allrounder model 270V machine using the following temperature profile: 210/220/230/230/240°C and mold temperature of 50°C.

Table 1. Formulations of nanocomposites

#	Composition	% Weight fraction
1	Neat PMMA	100
2	PMMA/MMT	99/1
3	PMMA/MMT	97/3
4	PMMA/MMT	95/5

2.4. Friction determination

Nanovea pin-on-disc tribometer from Micro Photonics Inc., was used for determining dynamic friction. A SS 302 grade stainless ball with diameter 3.20 mm was used as the pin. The pin was loaded onto the test sample with a precisely known weight of 5.0 N. The highly stiff elastic arm insures a nearly fixed contact point and thus a stable position in the friction track. Dynamic friction is determined during the test by measuring the deflection of the elastic arm by direct measurement of the change in torque [12]. The rotation speed of the disc was 100.0 rpm and the radius of wear track was 2.0 mm. The test was performed for 5000 revolutions under room temperature conditions. The results reported are averages from 3 runs.

2.5. Wear rate determination

Wear rate was determined through the wear track resulted due to the pin-on-disc friction test after 5000 revolutions. The wear track width was determined using a Veeco Dektak 150 profilometer. A profilometer measures the vertical depth of a horizontal material and is often used for determination of relative surface roughness of a material. It amplifies and records the vertical motions of a stylus (in contact with the test material) which is slowly dragged along the surface of the material at a constant speed. As the stylus moves, the stylus rides over the sample surface detecting surface deviations; i.e., the vertical deflection of the stylus measures the change in step height [13].

A stylus with tip radius of 12.5 µm was used. The force applied to the sample was 1.0 mg, and scan rate was 26.7 µm/s. The scan length was 800 µm and the measurement range was 65.5 µm.

Seven values of wear track width were measured at different locations on each sample and averaged for the purpose of accuracy. All samples were cleaned by high pressure air to remove all debris before each test.

Volume loss due to wear V_m was then calculated using the Equation (1) as suggested by the ASTM G99-05 standard:

$$V_m = 2\pi R A^2 \tag{1}$$

where V_m is the volume loss in mm^3, R is the wear track radius in mm (2.0 mm in this case), and A is the wear area width in mm^2.

Wear rate Z was then calculated using Equation (2):

$$Z = \frac{V_m}{WX} \tag{2}$$

where Z is in mm^3/Nm, V_m is the volume loss due to wear in mm^3, W is the load in N, and X is the sliding distance in m.

3. Dynamic friction

Results of dynamic friction determination for neat PMMA, and PMMA with 1.0, 3.0 and 5.0 wt% of MMT clay are presented in Figure 1. It can be observed that the friction variation among the samples tested is quite small. However, for the values of average dynamic friction seen in Figure 2, there is a certain growing trend with increasing percentage of MMT clay. This can be explained by the sticky nature of clay; clay present in the composite appears also on the surface, thus sticks to the partner surface and enhances friction somewhat.

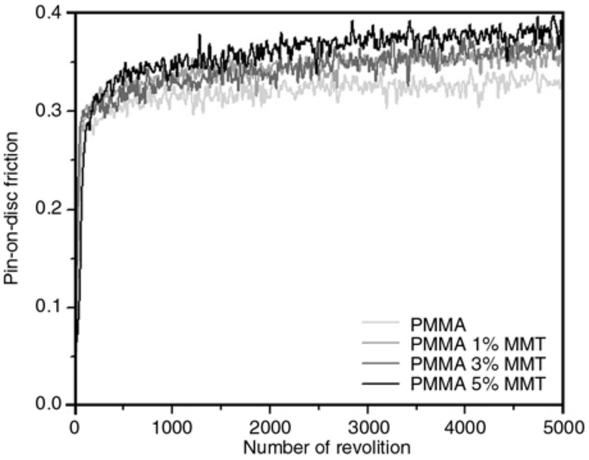

Figure 1. Pin-on-disc friction vs. number of revolutions

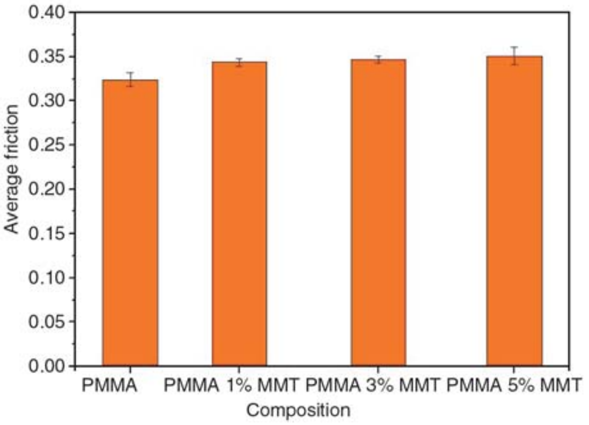

Figure 2. Average friction vs composition

4. Wear rate

In Figure 3 it can be observed that the wear rate as a function of the clay concentration passes through a minimum at 1.0% clay. Thus, for neat PMMA and PMMA with 1.0% MMT clay, the wear rates are much lower than for the composites with 3.0 and

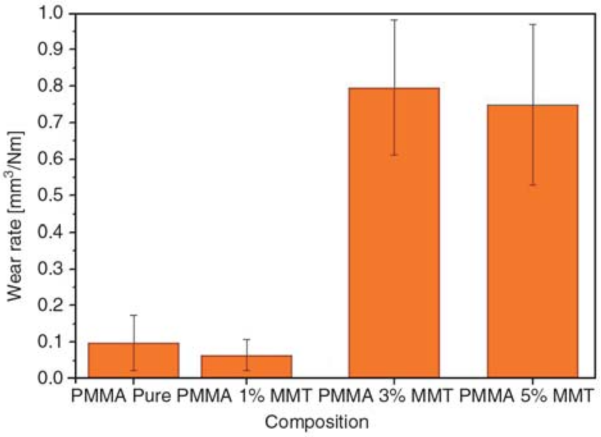

Figure 3. Wear rate for several compositions

5.0% of MMT clay. Usually the presence of clay decreases the elongation at break ε_b of the material. Since ε_b is inversely proportional to the brittleness of the material [14–16], the brittleness increases leading to an increase in wear rate.

Furthermore, it is important to note that the dispersion values of wear rates for samples of PMMA with 3 and 5% of MMT are higher than the dispersion values of wear rate for samples of neat PMMA and 1% MMT. Thus, the samples with higher MMT concentration have less uniform morphologies – a consequence of agglomeration (see below SEM microscopy results).

5. Optical microscopy

Surfaces of the samples subjected to pin-on-disc tests were analyzed by optical microscopy in order to observe the wear tracks generated. Figure 4 shows the optical micrographs of the composites obtained through Olympus GX 51 optical microscope at 50× using Image Pro Plus software.

It can be observed that the wear tracks in case of PMMA with 3 and 5% of MMT are much deeper than for neat PMMA and 1% of MMT – in agreement with wear rates seen in Figure 3. We also see that the worn surfaces of the track exhibit layer-like waves.

6. A survey of results

Tribology of polymer-based materials (PBMs) has still a way to go, although certain mechanisms are emerging [17–19]. Fillers are a way to improve a variety of properties of PBMs [20] and clays have been used for that purpose [21–25]. We find that clay content in the nanocomposites has an influence on the dynamic friction and wear rate values.

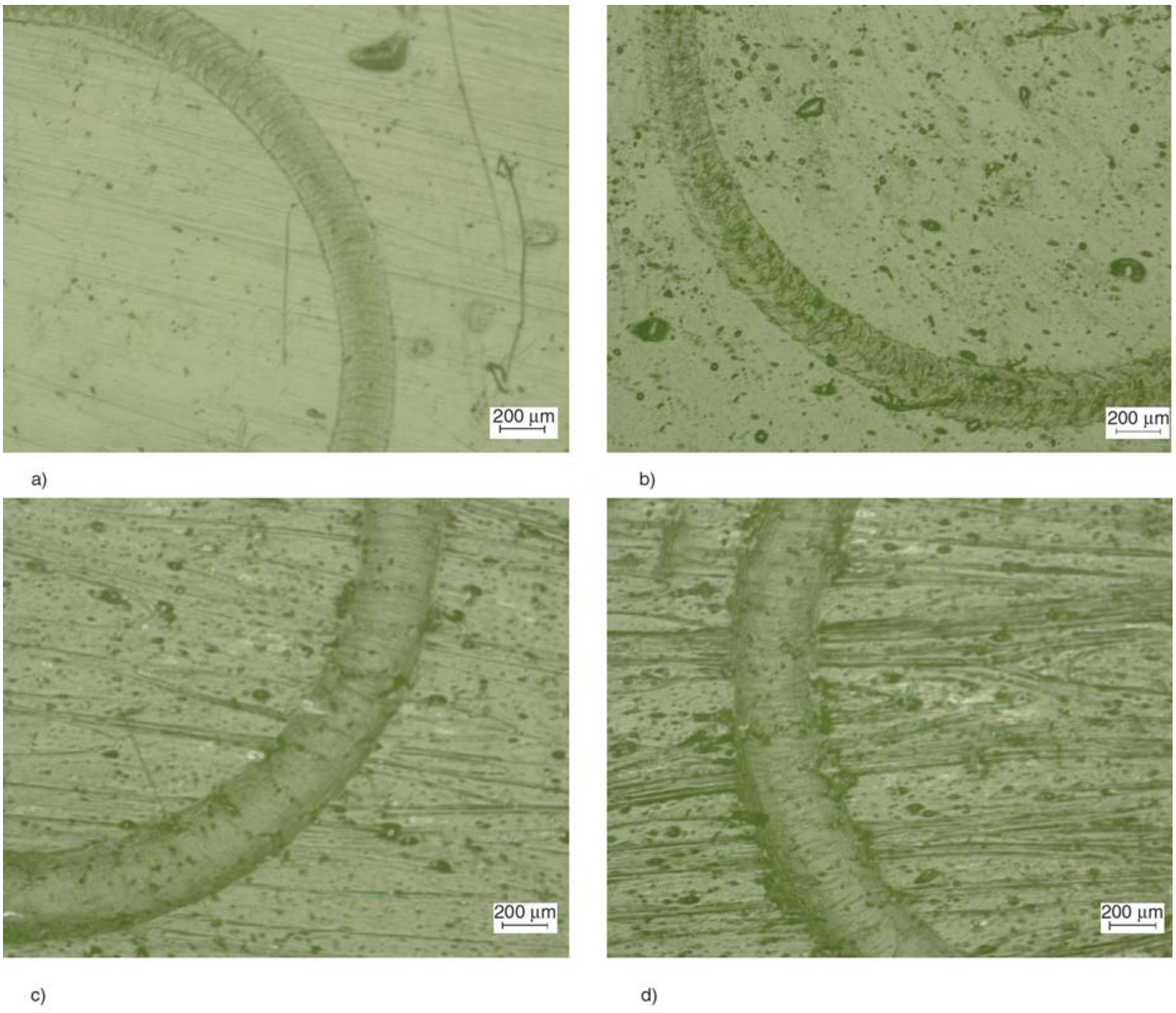

Figure 4. Optical micrographs of the worn surfaces at 50×. (a) Neat PMMA; (b) PMMA + 1.0 wt% MMT; (c) PMMA + 3.0% MMT; (d) PMMA + 5.0% MMT.

We have determined dynamic friction using a technique applied before [26–29]. With increase in the amount of MMT Brazilian clay, the dynamic friction of the nanocomposites increases. Above we have explained these results by the sticky nature of clay.

The wear rate as a function of concentration of clay diagram has a more complex shape and exhibits a minimum at 1 wt% MMT. We infer that addition of 1% clay provides a reinforcement since the clay particles are well dispersed in the matrix. Thus, the pin of the tribometer encounters more resistance than it had 'attacking' neat polymer; this is why the wear is lower than in neat PMMA.

The presence of clay is known to decrease the elongation at break ε_b of the material and – as argued above – the brittleness increases. This effect is apparently small when we have only 1% clay. When we put in 3 % MMT, *agglomeration* of clay manifests itself. As expected, the agglomeration is even stronger for 5% MMT – as seen in Figure 4. Also the wear tracks for 3 and 5% are wider – another consequence of agglomeration and a direct contributor to wear. This is why we see a dramatic increase of wear for 3% MMT after the 1% minimum. Interestingly, the wear for 5% is somewhat lower than for 3%. Apparently, present at 3%, MMT only disrupts the structure of the polymer and weakens the material. At 5% MMT, its agglomerations are large enough to offer 'their own' resistance to deformation and wear.

As argued among others in [17], there is much more activity concerning mechanical properties of composites than tribological ones. However, these two classes of properties are connected. Thus, it was demonstrated in [14] that brittleness is related to recovery (healing) in scratch testing. Lower brittleness is seen along with more healing, a simple relationship found for a large variety of materials and composites. Sometimes the relations between mechanical and tribological properties are more complicated. The degree of improvement of any property depends on the choice of filler origin, particles size and shape. The challenges in this area of high-performance polymers consist in obtaining a significant improvement in the adhesion between the interphases and to achieve a homogeneous dispersion of the filler in the polymer matrix [29]. For polypropylene (PP) + polystyrene (PS) blends, addition of a compatibilizer enhances the impact strength [30]. The same compatibilizer either increases or decreases static and dynamic friction; the change depends on the PP/PS ratio.

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