FRICTION AND WEAR OF NANOCOMPOSITES POLYSTYRENE / KAOLINITE

José Costa de Macêdo Neto1*, Ana Emília Guedes2, Nayra Reis do Nascimento3, João Evangelista Neto1, Eduardo Rafael Barreda2, Telma Regina Nogueira Caio3, Liliane Maria Ferrareso Lona3

1Department of Materials Engineering, School of Engineering, Amazonas State University, Rua Darcy Vargas, 1200, Parque Dez de Novembro, CEP: 69065-020, Manaus, Amazonas, Brazil, 2Department of Mechanical Engineering, Federal University of Rio Grande do Norte, Av. Senador Salgado Filho, 3000, Campus Universitário, Lagoa Nova, CEP 59.078-900, Natal, Rio Grande do Norte, 3Department of Materials Engineering and Bioprocess, Faculty of Chemical Engineering, University of Campinas, Rua Albert Einstein, 500, Cidade Universitária Zeferino Vaz, Barão Geraldo, CEP: 13083-852, Campinas, São Paulo, Brazil.

*jotacostaneto@gmail.com

ABSTRACT

The production of polymeric nanocomposites materials using natural clays the reinforcement has been researched enough. The improved properties compared to the polymer without reinforcement is the great appeal of this kind of materials. The kaolinite is a natural clay used as filler in polymer nanocomposites. In this article we were producing a nanocomposite polymer by polymerizing in situ in Polystyrene emulsion with 0, 1, and 3% kaolinite. The nanocomposite was characterized by XRD and TEM. The nanocomposites were characterized using friction and wear tests. The results showed that the nanocomposite with 3% kaolinite showed higher wear resistance and higher coefficient of friction.

Key-words: polymer nanocomposites, kaolinite, wear, friction.

INTRODUCTION

Polymer nanocomposites is a class of material where the load is at least one of their dimensions in manometric size (1-100 nm) dispersed in a polymer matrix (1). The morphology of nanoparticles used in nanocomposites is shaped like nanospheres, nanofibers, nanotubes, nanowires and layered nanomaterial (2,3,4,5). Nano-fillers widely used in polymeric nanocomposites are natural layered clays (6).
Among the natural layered clays, the kaolinite stands out to be abundant in nature and chemically inert (7).

Clays present several advantages to the preparation of nanocomposites. They are the nano-filler most abundantly available, can be easily dispersed in the majority of polymers, present high chemical intercalation ability and can be organically modified. The resulting properties of the final material can be superior to the properties of other engineering materials, such as pure polymers, microcomposites and the traditional polymeric composites (8). Compared to polymer composites, the nanocomposites that use clays as reinforcement can show better gas and membrane barrier properties (due to the high aspect ratio of the clays), flammability and thermal resistance (due to high energy binding of clay silicates and low thermal expansion in comparison to metals and polymers) and electrical properties (due to the ability to exchange cations or transfer protons from water in the interlayer) (9).

The wear resistance is an important property being investigated for composite materials and polymer nanocomposites. The wear phenomenon can be defined as the degradation of a material resulting from the use or from the interaction with the environment. The wear can occur due to the frictional such as gears, floors, hydraulic pumps, bones, teeth and others. The main types of wear are classified as: abrasion, adhesion and erosion.

Some studies have been conducted on composite materials and nanocomposites, such as the poly (methyl methacrylate) (PMMA) and zirconium oxide (ZrO2) filled composites (10); Ultra-high molecular weight polyethylene (UHMWPE) composites filled with carbon nanotube (MCNTs) (11); high-density polyethylene (HDPE) nanocomposites with organosilane-functionalized graphitic nano-materials (12).

The objective of this study is to investigate the friction and the wear of polymeric nanocomposites polystyrene / kaolinite (0, 1 and 3% by weight of kaolinite in relation to styrene monomer) produced by in situ emulsion polymerization.

EXPERIMENTAL

Reagents

The kaolinite from the State of Amazon, Brazil and processed by Armil Union Northeast mining company (located in the State of Rio Grande do Norte, Brazil).
Dimethyl sulfoxide (DMSO, Synth), monomer styrene (St, Sigma Aldrich) washed four times with a 10 w/v% sodium hydroxide (Fmaia), potassium persulfate (KPS, Sigma Aldrich), sodium lauryl sulfate (SLS, Fmaia), hydroquinone (Sigma Aldrich). Distilled and deionized water.

**Synthesis of the nanocomposite polystyrene / kaolinite**

The nanocomposite polystyrene / kaolinite (PS-KAO) was prepared by *in situ* emulsion polymerization. For the synthesis of the polymer nanocomposite a batch reactor (capacity of 1000mL) with heating jacket, mechanical stirrer, reflux condenser, and purging tube was used. 1 and 3%wt (based on monomer) of kaolinite (%KAO) modified with DMSO by method described by Essawy (13), 133.90g of St, 537.94g of water, an aqueous solution of 3.48g of SLS and another with 0.57g of KPS were added to the batch reactor. The reaction took place at 60ºC, in constant agitation at 60rpm, under nitrogen flow, in 90 minutes.

**Characterization**

*X-ray Diffraction (XRD)*

(Shimadzo, XRD 7000) with CuKα radiation \(k = 1.54060 \text{ Å}\) with \(2\theta\) varying between 1.4-70° was utilized for characterization of clay and nanocomposites.

*High Resolution Transmission Electronic Microscope (HRTEM)*

For the present work, a High Resolution Transmission Electronic Microscope JEOL, JEM 3010 URP, Japan, equipped with a camera CCD, Gatan MSC794, was used. The images were obtained with image capturing software Gatan, Digital Micrograph. The conditions for HRTEM were 300 kV tension, spot size = 1µm and \(\alpha\)-selector = 3, and beam current 111µA. Magnification was between 20,000-1,500,000.

*Scanning electronic microscope (SEM)*

Was used the TM-3000 model by Hitachi with DPI=95.91, Pixel Size=3310.55 Accelerating Voltage=15000 Volt.

**Sample preparation and wear tests**

Samples were injected using a mini-injector (Haake, MiniJet II, Thermo Fisher Scientific) with dimensions of 10mm of diameter and 3mm of thick disc. All samples...
of PS and nanocomposites PS-KAO were injected with an injection pressure of 500bar, injection time 30sec, cylinder temperature 200°C, mold temperature 40°C, 250bar discharge pressure and discharge time 15sec.

The samples were submitted to an ultrasonic bath for 10 minutes in isopropyl alcohol to remove impurities, and then dried with a hot air flow before starting the test. Finally, samples were weighed on analytical scale with a resolution of 0.1 mg.

The test was performed on a pin-on-disc tribometer type High Frequency Reciprocating Test Rig - HFRR (PCS® Instruments). The normal load applied was 10N, 1.00 ± 0.02mm length of path under a frequency of 20 ± 1Hz at 50°C and the test duration was 60 minutes. The pair tribological (ball-disk: polymeric nanocomposite) were placed in the HFRR holders. A steel ball used was 52100 (bearing steel, microhardness 570-750HV, 6.0mm diameter).

RESULTS

The Figure 1(i) shows XDR of kaolinite where it is observed the basal spacing (d_{001} = 0.72nm, 2θ = 12.33º) (14). The Figure 1(ii) and 1(iii) shows XDR of polystyrene and nanocomposite polystyrene / kaolinite, respectively. The XRD of the formed nanocomposites (Figure 1(iii)) illustrates the absence of any reflection pertaining to the presence of any remaining ordering of the kaolinite, this holds mainly for the layers that become exfoliated and/or intercalated within the polymer matrix (15).

![Figure 1](image)

Figure 1. (a) XRD patterns of (i) Kaolinite, (ii) Polystyrene, (iii) Nanocomposite. (b) HRTEM image Clay disposition in the polymer matrix (PS). Magnification of 200k.
The clay, in intercalated form with ordered layers, as well as the polymer can be observed by Figure 1b. The monomer may have permeated between the layers of clay and polymerized, thus resulting in intercalation (16).

Exfoliated clay morphologies are shown as dark lines in Figure 1b, randomly distributed, in the polymer matrix. These exfoliated structures show a total absence of order between clay layers. Even though kaolinite exfoliation is rare, due to the high cohesiveness between layers, it was possible to obtain a great amount of exfoliated clay in the polystyrene (17).

From Figure 2 (a) it is observed mass losses from nanocomposites PS with 0, 1, and 3%KAO. It is observed that the nanocomposite with 0%KAO achieved greater weight loss than the nanocomposites with 1 and 3%KAO. The presence of exfoliated and intercalated clay hampered the loss of mass during and testing. The Figure 2(b) shows the friction coefficient of the nanocomposites with 0, 1, and 3%KAO. The higher coefficient of friction was presented to the sample with 3%KAO. The hardness of the clay is greater than that of neat polystyrene (0%KAO) and added clay in the polystyrene matrix increased the coefficient of friction of the nanocomposites (18).

![Diagram](a)

![Diagram](b)

Figure 2. (a) Mass Loss, (b) Coefficient of Friction.
Figure 3 shows the image in Scanning Electron Microscopy-SEM from wear nanocomposites with 0 (A), 1 (B) and 3% KAO (C) with of 30, 80 and 50X (magnitude), respectively. It is observed in Fig. 2 (A, 30X) that 0% KAO showed fewer slots and grooves that nanocomposites with 1 and 3% KAO (Fig. B, C, 30X). In Fig. (A, 80X) but presented microcracks. This behavior shows that nanocomposite 0%KAO showed less wear resistance.

It can be seen by Figs. 2 (B, 80, 500X) and (C, 80X, 500X) that nanocomposites with 1 and 3%KAO showed more grooves and ridges that the 0%KAO (Fig. 2 A, 80X, 500X). Clay in the polystyrene matrix caused a rougher on the ball. The exfoliated and intercalated clay lamellae exert a high pressure on the polystyrene which surrounds it making it difficult to be plastically deformed and thereby increasing wear resistance (19).
CONCLUSION

The nanocomposites produced by in situ emulsion polymerization with 1 and 3% clay showed a mass loss less than the one with 0% KAO. Nanocomposites with 0 and 1%KAO showed lower coefficient of friction than nanocomposite with 3% KAO. By the SEM images it is observed that the nanocomposites with 1 and 3%KAO presented more risks, grooves and plastic deformation that the nanocomposite 0%KAO.

REFERENCES


