Wear Resistance and Wear Mechanisms in Polymer + Metal Composites

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We have investigated composites containing metallic micro-size and nano-sized particles as the 10 wt% dispersed phase. Branched low density polyethylene (LDPE) was the matrix. Microsized metals were Al, Ag and Ni; nanosized metals were Al and Ag. Several mechanisms of wear are observed in function of the kind and size of metal used: deformation, delamination, abrasion, adhesion and rolls formation. The presence of Ag particles increases the wear rate as compared to neat LDPE. The presence of Al particles lowers the wear of LDPE significantly; nanoparticles are more effective than microparticles.

Keywords: Low Density Polyethylene, Polymer + Metal Nanocomposites, Focused Ion Beams, Scratch Resistance, Wear Resistance.

RESEARCH ARTICLE

1. INTRODUCTION

Polymer composites are used extensively for numerous purposes because of their wide variety of properties and relative ease of tailoring them.[1–4] Mechanical, thermophysical, electrical, dielectric and optical properties are the most studied.[5–13] By contrast, much less work has been done on tribology of polymer-based materials (PBMs). It is a difficult area since external lubricants used so widely for metals do not work. Penetration of the lubricant into the polymer occurs, the polymer swells, and increased material size makes the tribological situation *worse*. A small number of laboratories active in PBM tribology includes the laboratory of Karger-Kocsis (now at Tshwane University, Pretoria),[14, 15] the Uadimyr Belyi Institute of Metal and Polymer Mechanics in Homel,[16] a group at the University of Erlangen-Nuremberg,[17] a group at the Leibniz Institute in Dresden[18] as well as our own group[19–22] including collaborations with Technion in Haifa,[23] with the University of Antioquia in Medellin[24, 25] and with the Technical University of Cartagena.[26, 27] Given inherent poor scratch and wear resistance of polymers, clearly much more work in this field is needed.

Let us now focus on PBMs containing a reinforcement as a dispersed second phase for improvement of tribological properties. Most work along these lines involves carbon in various forms[7, 10, 23, 24] or else ceramic fillers.[25–28] As for *polymer + metal composites*, the situation is similar as with other polymer-based materials (PBMs); they have been mostly studied for thermal, electrical and mechanical applications and also as biomaterials. There has been only little work on using a metallic dispersed phase to improve tribological properties of polymers, with the exception of results reported by Yu et al.[29] and our own earlier work.[30] In this situation, the goal of the present project is to investigate wear resistance and wear mechanisms of a polymer filled with metallic particles.

Two issues are important here. One is the effect of the size of the dispersed particles, namely comparison of effects of particles with diameters in the microns range with those of particles in the nm range. The other natural factor to investigate is the effect of the nature of the metal. In this work we have created micro- and nanocomposites containing three different metals.

2. EXPERIMENTAL DETAILS

2.1. Materials

Branched low density polyethylene (LDPE, from Hunstman) was used as the matrix. Microsized and nanosized metallic particles were used as the filler dispersed

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phase (from NanoAmor, Houston, Texas). The microsized metals were Al, Ni (both spherical) and Ag (flakes); the average particle sizes were 1.0, 6.4 and 4.2 micrometers respectively. The nanosized metals were Al and Ag (both irregular shape flakes); average particle sizes were 127 and 69 nm respectively. Particle sizes refers to the diameters in the case of spherical particles and the longest distance in the case of the irregular flake particles. The concentration was 10.0 wt% in all cases.

2.2. Sample Preparation

A Brabender type 6 mixer was used to blend each polymer with the appropriate metallic powder. The blending temperature was 150 °C. The mixing time was 5 min and the blade speed was 80 rpm for all cases. The resulting blends were pelletized and then injection molded at 170 °C at the pressure of 60 psi in an AB-100 injection molding machine (AB Machinery, Montreal, Quebec, Canada) to obtain the final specimens. SEM analysis was performed after gold coating the samples.

2.3. Composites Characterization

In order to determine the wear mechanisms on each sample as well as to measure the wear track thickness, secondary electrons scanning electron microscopy (SEM) imaging was performed with a FEI analytical dual focused ions beam (FIB) at 20 keV. The SEM-FIB equipment combination was the same as used in earlier work,[31] the source consisted of gallium ions.

The wear experiments were carried out in a pin-on-disc tribometer (Fig. 1, from Nanovea series of Microphotonics), the same as used in earlier work.[32] Carbon nitride was selected as the pin ball because of its exceptionally high hardness (1580 kg/mm^2) compared to our composites. In a project involving a PBM containing highly abrasive thermal-shock resistant ceramic particles, we have found that steel balls of two kinds are abraded while carbon nitride balls are not.[33] Thus, we can safely assume

that there is no deformation of the ball. The experimental conditions were: ball diameter 3.12 mm, track radius 2.0 mm, disc rotational speed 200 rpm, total number of revolutions 2000, applied normal load = 7.0 N, ambient temperature (22 °C). Five repetitions of the same experiment were performed in all cases to ensure repeatability of the results.

3. WEAR MECHANISMS

Since tribological phenomena involve the interaction between surfaces, it is important to reveal whether the metal particles are present on the composite surface. In our previous work we have shown that metallic particles can be found on the surface of the composite and are well dispersed, with the exception of Ag (micro and nanosized) which tends to form agglomerates as large as 30 microns in diameter.[30, 31]

In general, the wear mechanisms of materials include adhesion, abrasion, fatigue, impact, electrical and chemical wear. For polymeric materials adhesion, abrasion and fatigue wear are the dominant mechanisms.[34, 35] Although there is only little tendency of adhesion between ceramic materials and polymers, in many cases a film of transferred material can be formed on the ceramic surface (the hardest material) and thus adhesion can be stronger.[36, 37] As demonstrated below, we find that for our PBMs the wear mechanisms are similar to those in neat polymeric materials.

Figure 2 shows the wear track of the neat LDPE. It is clear by observing the edges of the groove that *deformation* is the main wear mechanism. However, by examining the groove in the middle it is clear that also *delamination by adhesive wear* occurs to some extent.

We now consider results for PMB microcomposites. As expected, we have found that different metals lead to different wear mechanisms as well as to different types of
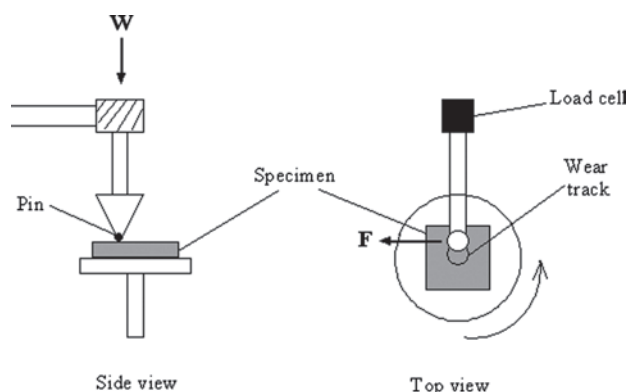

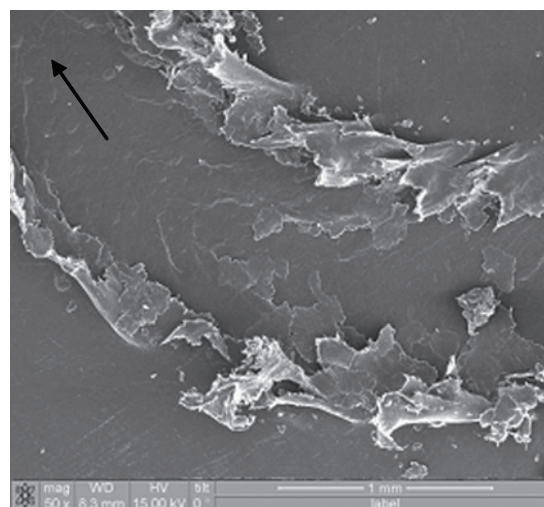**Fig. 1.** A schematic of the pin-on-disk tribometer.

Fig. 2. Wear track of pure LDPE.

wear debris. Figure 3(a) shows the wear track of the *micro* Al composite. Here, parallel groves are formed by *abrasive wear*. Very likely the Al spherical particles are acting as bearings in a three body abrasion mode between the polymer and the pin. The idea is plausible since no compatibilizer between metal and polymer was used and the aluminum particles can roll freely-once they are detached from the matrix. Figure 3(b) shows the wear debris particles.

In the case of micrometric Ag, the dominant mechanism is adhesive wear as seen in Figure 4(a). Consequently, the wear debris particles are formed by adhesive delamination-as seen in Figure 4(b).

For Ni Figure 5(a) shows that a three body abrasion takes place-similarly as in the Al composites. However, the wear debris is quite different; it stays inside the wear track and starts to roll-up to forms *rolls* of material. As shown in Figure 5(b) these rolls can be several millimeters long.
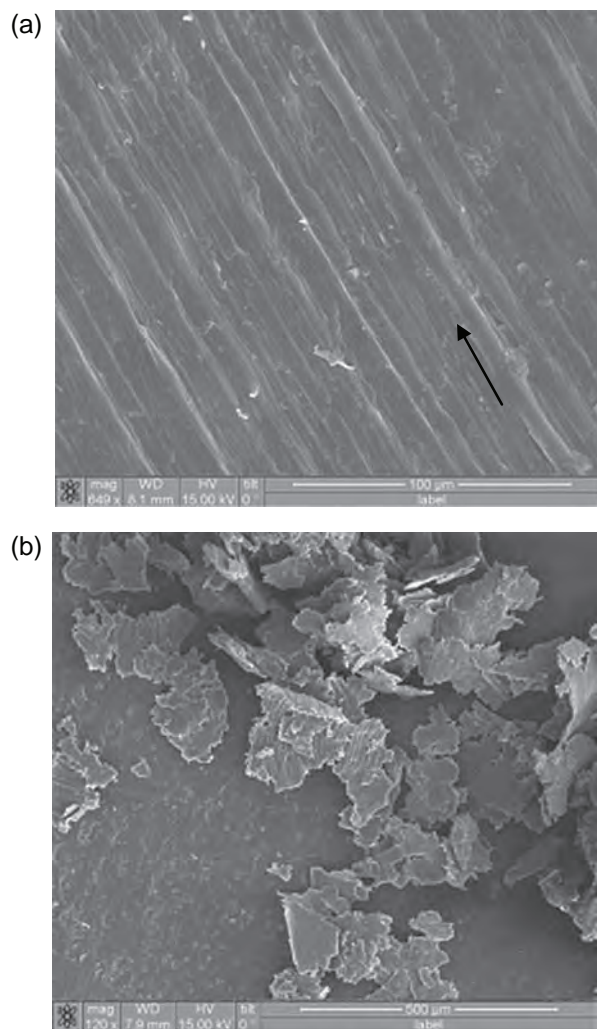

Fig. 3. (a) Wear track of Al microcomposite (a) and the wear debris particles (b).
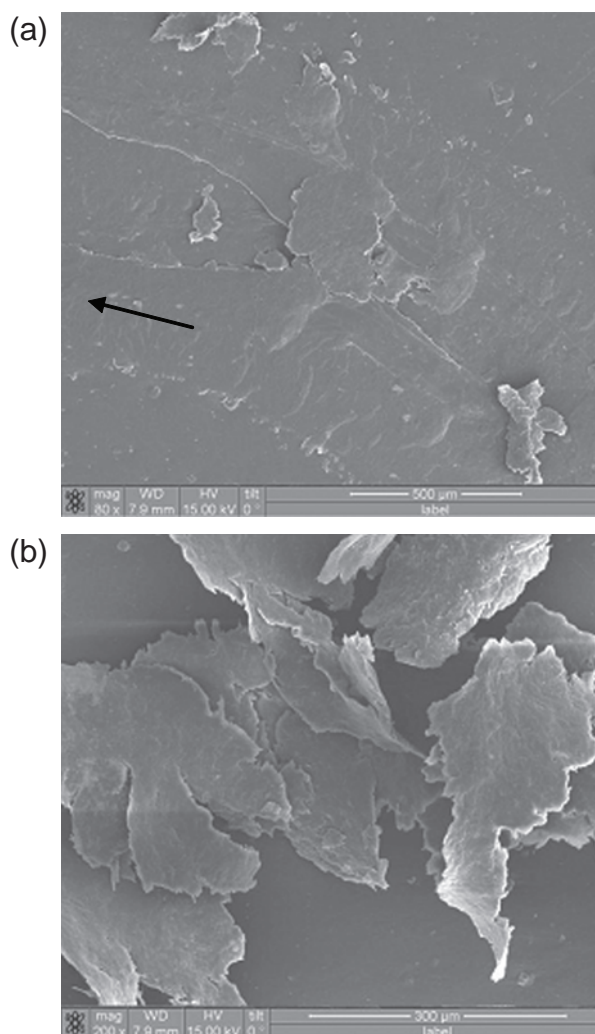

Fig. 4. Wear track of Ag microcomposite (a) and the wear debris particles (b).

As for the *nanocomposites*, Figure 6(a) shows the wear track of the Al nanocomposite. Here edges (top ridges, shoulders) perpendicular to the sliding direction are seen. This is an indication that the dominant wear mechanism is adhesion. The wear debris are small laminate particles very similar to the Al microcomposite (Fig. 6(b)). It is important to note that even if we use the same metal (in this case Al) we find different wear mechanisms just by varying the *size* of the particles.

In the case of Ag nanocomposite, Figure 7(a) shows that the wear mechanism is similar to that of the Ag microcomposite. This is because the Ag nanoparticles form micrometric agglomerates (as big as 30 μm) and thus behave similarly to microparticles. As expected, the wear debris is very similar to the Ag microcomposite (Fig. 7(b)).

4. WEAR RESISTANCE

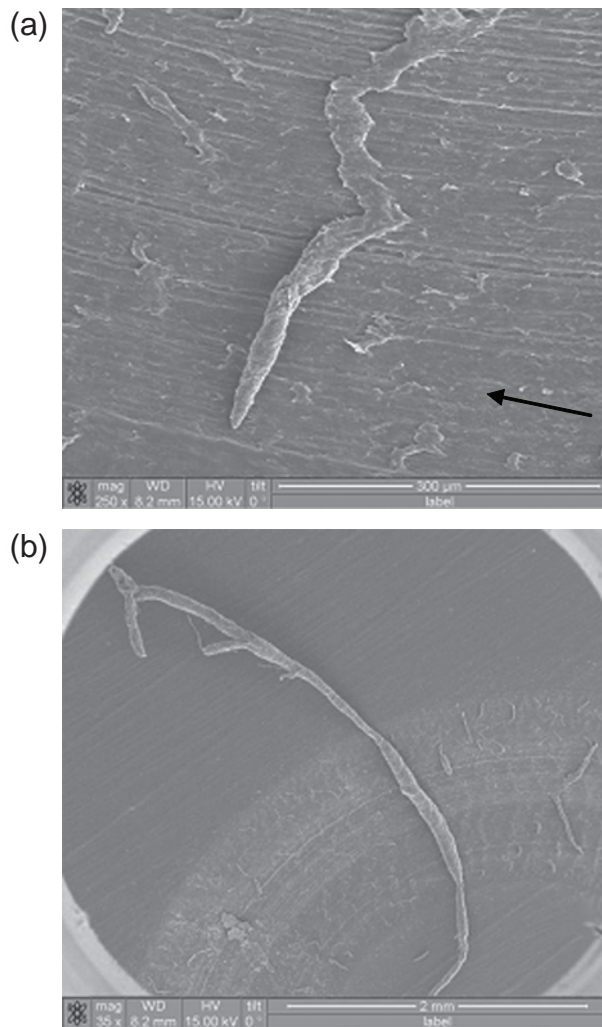In order to determine the wear resistance of the composites, ASTM G 99 standard test was applied. Although

(a)

(b)

Fig. 5. Wear track of Ni microcomposite (a) and the wear debris particles(b).

(a)

(b)

Fig. 6. Wear track of Al nanocomposite (a) and the wear debris particles (b).

this standard procedure was first intended to be used for metals, it is possible to use it for plastics as a good approximation.[38] Wear volume loss v was calculated according to the same standard:

$$v = 2\pi R \left[r^2 \sin^{-1}\left(\frac{d}{2r}\right) - \left(\frac{d}{4}\right)\left(4r^2 - d^2\right)^{1/2} \right] \quad (1)$$

Here R = wear track radius, d = wear track width and r = pin end radius.

The wear rate Z represents the volume loss v divided by the normal load W and the sliding distance d:

$$Z = v/Wd \quad (2)$$

Thus, Z is normalized with respect to the load and the sliding distance. A minimum of 20 measurements (for R and d) were performed in each wear track to calculate a suitable average value for Z. The variation in the values measured leads to a calculated error of 0.00015 mm³/Nm.
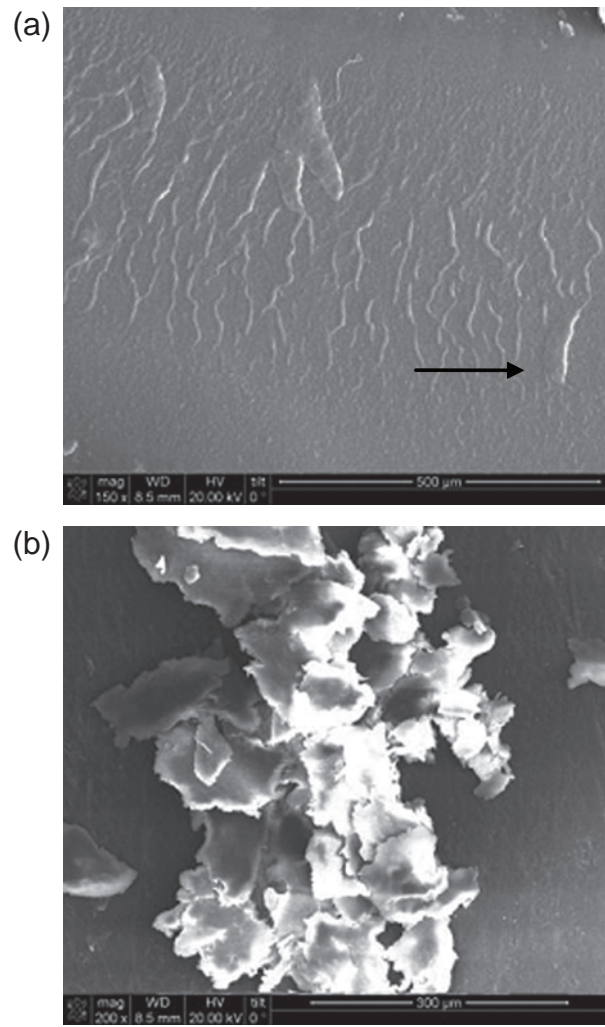
Figure 8 shows the wear rate Z for our LDPE microcomposites. It is clear that the lowest Z is achieved when Al particles are present. Even though the abrasive wear is more detrimental than adhesion in many cases, in this case the opposite is seen. A probable reason is that the detached spherical aluminum particles from the composite surface actually roll between the metal and the polymer acting as bearings; thus, the three body abrasion results in reinforcement of wear resistance. Given the objectives of the present project, this is a worthwhile result.

When we add Ni particles, the mass loss is the *highest*. Once the debris rolls seen in Figure 5 start forming, the material is removed continuously while the rate of removal is higher than from the neat polymer by deformation. Interesting is the fact that-even though there can be a three-body abrasion mode as we presume is the case of Al microparticles-the wear is high because of the formation of these rolls. Since all the experimental parameters were kept constant and the only variable are the different Ni particles, we infer that they are responsible for
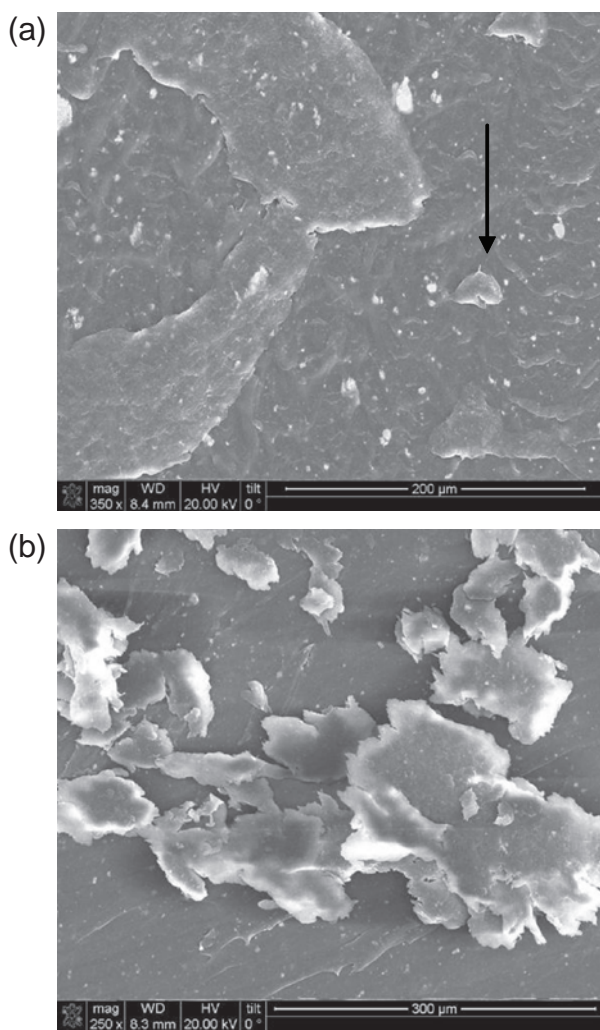
Fig. 7. Wear track of Ag nanocomposite (a) and the wear debris particles (b).

this distinct wear mechanism. The issue which effect is more important-the particle size/shape or the metal nature-deserves further studies.

For Ag the wear loss is similar to that for neat LDPE. Despite the different main wear mechanisms-adhesion in the case of Ag microcomposites and deformation for pure LDPE-the rates of material removal are comparable.
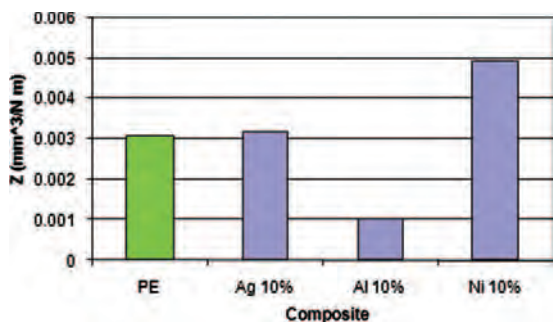

Fig. 8. Wear rate Z for LDPE and LDPE microcomposites at the load of 7.0 N.
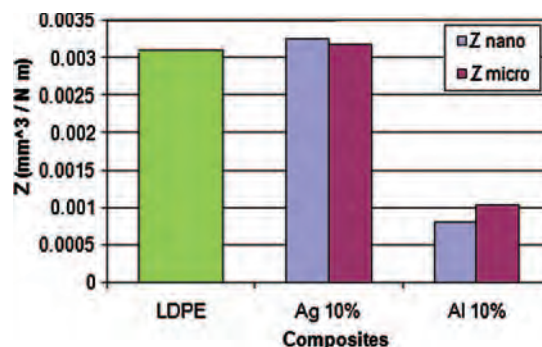

Fig. 9. Wear rate Z for LDPE and LDPE micro- and nano-composites at the load of 7.0 N.

We now proceed to compare effects of the presence of nano- and micro-size of metallic particles on wear. Figure 9 shows the respective wear parameters Z of LDPE micro and nanocomposites. In the case of Ag there is a similar effect in the mass loss for both micro and nanoparticles; this is expected because nanometric as well as micrometric Ag tends to form agglomerates. This is also confirmed when we observe the wear mechanisms present in both materials discussed above.

In the case of Al there is a considerable improvement in wear resistance for both micro- and nano-particles. This occurs although the dominant wear mechanisms are different: three body abrasion for micro Al while there is reinforcement of contact asperities for the nano Al. Given the choice between micro- and nano-particles of Al, the *latter result in a slightly lower wear rate Z* than the former ones. In this context we recall an earlier result:[30] small metal particles increase the tensile modulus at lower concentrations than larger ones.

5. CONCLUDING REMARKS

The wear mechanisms of the composites were studied by observing the wear tracks on SEM. Although more than one mechanism is present in the samples, there is a dominant mechanism in each case. In general, microcomposites tend to suffer more from the abrasive wear mode while for nanocomposites the dominant mechanism is adhesive wear. The debris particles were also observed by SEM. For all the LDPE composites (nano- and micro-, except for Ni microparticles) the wear debris particles have the shape of laminates—what indicates that the loss of the material is due to delamination. In the case of Ni microcomposites the wear debris consists of rolls formed from inside the track.

The wear rates Z have been determined by using Eq. (2). For all LDPE composites (micro and nano) only the addition of Al lowers the value of Z because the spherical particles can act as bearings in the three body abrasion mode. This is the dominant mechanism in the case of Al microparticles. In the case of Al nanoparticles we have

reinforcement of the polymer that smaller particles provide more effectively than larger ones. Since the concentration by weight is the same in both cases, the Al nanocomposite contains many more wear-resistant particles than the respective microcomposite.

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