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Tribological Properties of Polymer Nanohybrids Containing Gold Nanoparticles Obtained by Laser Ablation

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We have studied polystyrene (PS) + Au particles nanohybrids. Approximately spherical gold nanoparticles with the average diameter of 15 nm were obtained by laser ablation in a liquid environment. Thus any chemical residue on the particles was eliminated. Focused ion beam (FIB) milling plus scanning electron microscopy (SEM) observation show that Au particles are fairly well dispersed inside the polymer matrix, better than when PS is simply dissolved in a nanoparticle solution. The Au particles concentration as low as 0.15 wt% results in dramatic changes in tribological properties, namely dynamic friction and pin-on-disk wear. Both wear and dynamic friction results are explained in terms of high brittleness of PS, abrasion of Au particles against a ceramic indenter, and also effects of density of filler particles in the matrix on tribological properties. Effects of varying normal load on friction are small.

Keywords: Polymer + Metal Nanohybrids, Polymer Wear, Polymer Friction, Brittleness, Polystyrene, Gold Nanoparticles.

1. INTRODUCTION

Polymer based composites (PBMs) are used in a wide range of applications—given a relative ease in tailoring their properties.[1–3] Even better capabilities of property tailoring seem available in nanocomposites or nanohybrids.[4–25] In this work we have focused on nanohybrids (they escape traditional classification of materials as either inorganic or organic) of the polymer + metallic nanosize filler type. Hybrids of this kind have been investigated before[11, 17, 23, 25–31] but to our knowledge not for the purpose of modification of friction and wear resistance, except for our own work referred to below. This while each year industry loses millions of dollars (or other currencies) due to tribological phenomena such as wear and by heat losses due to friction.[32] Thus, the practical importance of tribology lies in the pursuit of minimization of these losses—by creating materials that perform better at all levels of technology in cases where mutual rubbing of surfaces in contact is involved.

In our previous work[12] we have created polymer + metal composites to study their tribological properties. We have demonstrated that it is possible to tailor to some extent the friction and wear behavior of our composites compared with the neat polymers. We also have found that smaller filler particles produce larger changes in tribological properties,[20] hence microfiller particles have less effect than nanofiller particles at the same mass concentration. One plausible explanation of this finding is that the

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number of filler particles per unit volume is important; a higher density of the filler particles provides larger effects. However, we have encountered problems with uniformity of dispersion of nanometric scale particles inside the polymer matrix. Olsson and coworkers stress the importance of avoiding aggregation of nanoparticles in polymer matrices.[17] There is a way to minimize aggregation by passivation of metal nanoparticles with a thin layer (few nanometers) of oxide; however, the passivation practically 'kills' desired interactions between the filler particles and the matrix. This while Kopczynska and Ehrenstein note the importance of interfaces for properties of multiphase polymeric systems.[33]

To overcome the poor dispersion of metal nanoparticles inside the polymer matrix, we have decided to follow the route of obtaining metal nanoparticles by ablating the metal in a liquid solution, specifically in tetrahydrofurane (THF).[34–39] Such a method appears to have several advantages: preparation of particles free of chemical co-reactants; the particles created are in many cases self-stabilized and are homogeneously dispersed throughout the solvent; moreover, the technique is a non-pollutant one if the solvent used is environment-friendly. Furthermore, it is possible obtain polymer composites fairly easily by dissolving a polymer in the particle suspension—or else by *in situ* polymerization once the particles are located inside the monomer. We report below results of following this route in preparation of polymer + metal nanohybrids, specifically consisting of polystyrene (PS) + gold nanoparticles, and the resulting tribological properties. We recall that PS is characterized by brittleness B values much higher than other engineering polymers—a fact already established when B was defined[40] and discussed in subsequent publications on properties of B [41,42] as well as in a review on polymer tribology.[43]

2. EXPERIMENTAL DETAILS

2.1. Gold Nanoparticles

Laser ablation was performed using a Q-switched Nd:YAG laser ($\lambda = 1064$ nm, pulse duration $= 28$ ns). Tetrahydrofuran (THF) was used as the liquid medium. The target was a disk of high purity gold (99.99%) from J. K. Lesker and was immersed in the liquid. The laser fluence on the target surface was approximately 12 J/cm^2. The ablation time was varied from 3 to 10 minutes in order to obtain different concentration of colloidal solution resulting in different quantities of nanoparticles so created. The target was weighted with an accuracy of ± 0.0001 g before and after each experiment to determine the total mass of nanoparticles obtained.

2.2. Metal + Polymer Composites Preparation

PS was solubilized in the nanoparticles solution by thorough stirring; afterwards the solvent was evaporated under vacuum. Finally, nanohybrid specimens were obtained by compression molding at 5.0 kg/cm^2 and 120 °C using a home-made compression molding machine.

2.3. Characterization of Nanohybrids

The gold nanoparticles size and their size distribution were studied by transmission electron microscopy (TEM) with a JEOL JEM-2100 model at 200 keV in the bright field mode. UV-Visible spectroscopy was performed with a Cary 5000 machine from Varian in the wavelength range from 300 to 800 nm.

In order to observe the uniformity—or otherwise—of dispersion of the metallic nanoparticles inside the polymeric matrix, we have used a combined focused ion beam (FIB) + scanning electron microscopy (SEM) technique developed before for that purpose.[9] The Ga^{+2} ion beam energy was 30 keV (milling beam) while the electron beam energy was 10 keV (imaging beam).

Dynamic friction was measured with a pin-on-disc tribometer (Nanovea tribometer from Microphotonics). The pin ball material selected was silicon nitride because of its much higher hardness (Vickers hardness around 15 GPa) in comparison to other balls. The objective was to ensure that the composites are worn by the pin and not *vice versa*. In our work on polymer + high temperature ceramic hybrids we have found significant abrasion of steel pins by the ceramic filler;[44] therefore, for such systems we have also switched to silicon nitride pins. The experimental conditions were: ball diameter 3.12 mm, wear track radius 2 mm, disc rotational speed 200 rpm, total number of revolutions 2000, applied normal loads: 5.0 and 10.0 N. Five repetitions of each experiment were performed to ensure the repeatability of results; the average values are here reported.

Wear resistance was evaluated as in our previous work[20] by means of the wear loss volume v calculated according to the ASTM G 99 standard:

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

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

3. METAL NANOPARTICLES CHARACTERIZATION

Figure 1 shows the UV-Vis spectrum of the Au nanoparticles obtained by laser ablation. We see a typical band absorption peaking at 530 nm—characteristic of spherical gold particles of nanometric size.[37] Figure 2(a) shows a TEM micrograph of the prepared nanoparticles revealing their spherical shape. Additionally, the frequency histogram in Figure 2(b) shows a bimodal size distribution with a relatively narrow dispersion. The average nanoparticles size is approximately 15 nm.

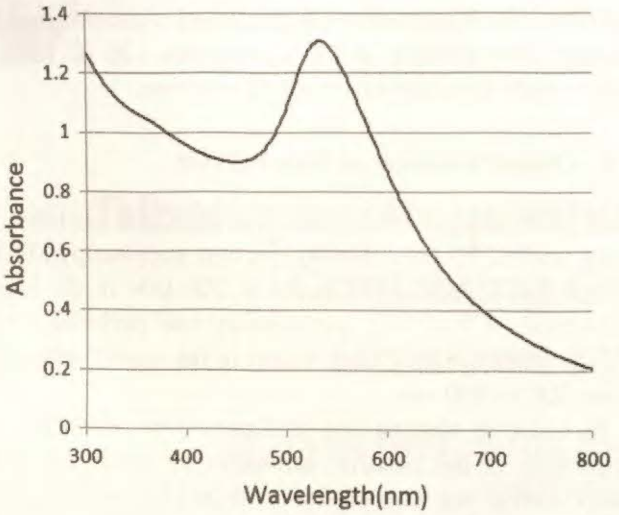

Fig. 1. UV-Visible spectrum of gold nanoparticles.

4. COMPOSITE CHARACTERIZATION INCLUDING NANOPARTICLES DISPERSION

Figures 3 and 4 show parallelpiped 'holes' created by FIB milling of our nanohybrids with two different concentrations of the gold particles—as seen in SEM. In our earlier work we have found significant agglomerations of metal particles working with metals such as Ni, Al and Ag. Now at the lower concentration of 0.15 wt% Au particles we see small isolated filler particles (Fig. 3). This represents considerable improvement in comparison with our previous work where big agglomerates in the micrometric size range were observed.[12,20] Clearly the laser beam ablation in liquid environment technique is the reason for the avoidance of the filler particle agglomeration.

Consider now the double concentration of gold particles, that is 0.30%, the respective results displayed in Figure 4. In this case a certain aggregation of the filler is visible. However, we do not have large round agglomerations. Rather, we see formation of "chains" or "clouds" of particles such that individual particles are still visible. This result suggests that at higher concentration the nanoparticles remain disperse avoiding forming bigger particle agglomerates with micrometric sizes.

5. WEAR

In order to study the wear behavior of our hybrids, it is important to understand—typically multiple—mechanisms by which the material in contact with an indenter or another material is displaced or removed. In metals, rubbing of two surfaces generally leads to material removal, and either a two-body process or a three-body process (the debris particles become the third body) are possible.[45,46] In polymer-based materials (PBMs) a material displacement without debris formation can occur.[43,47,48] More specifically, an indenter will move some material to the sides around the indentation. In scratch testing where an indenter moves along a straight line, a linear groove is formed with top ridges created along both sides of the groove.[43,47,48] Such a process can typically be accompanied by densification around the bottom of the groove.[48] A group at the Uadimyr Belyi Institute in Homel, Belarus, led by Myshkin has analyzed important aspects of friction and wear in PBMs[49,50] The analysis of our results below necessarily takes into account the accumulation of previous knowledge.

Consider first wear tracks created in PS by the silicon nitride pin indenter—as displayed in Figure 5(a). We recall that PS is unusually brittle; one of the consequences of this fact is that viscoelastic recovery in scratch resistance testing is lower than in other polymers.[40] In other words, after the passage of the indenter the bottom of the groove goes up, but less so than in less brittle polymers or polymer-based composites. Further, brittleness B is inversely proportional to the strain at break in tensile testing. Myshkin and his colleagues tell us that adhesion is molecular in nature while deformation is necessarily mechanical.[50]

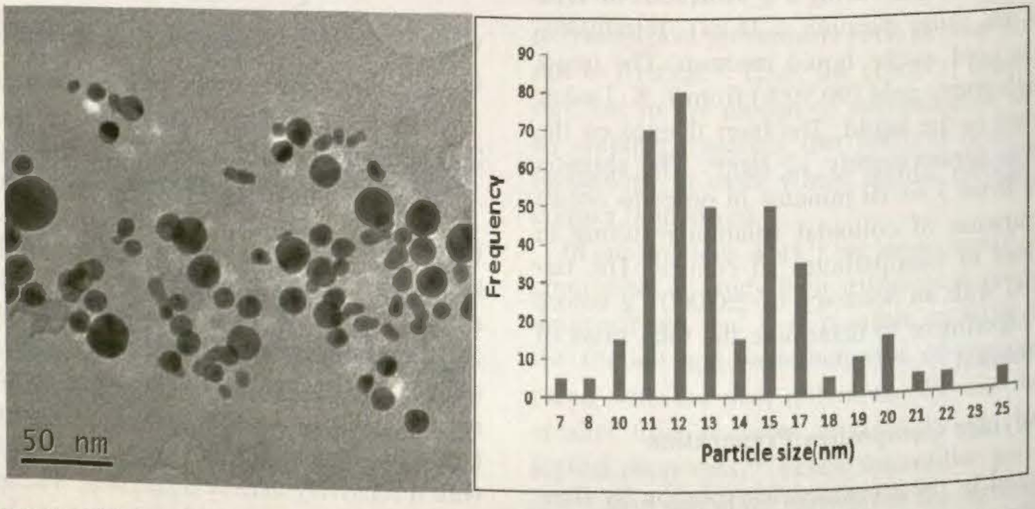

Fig. 2. TEM micrograph and frequency histogram of gold nanoparticles.

Fig. 3. FIB cross section of the 0.15 wt% PS + gold nanoparticles hybrid.

Given the high B value of PS, not much recoverable or elastic deformation is possible. At the molecular level, flat and rigid phenyl rings do not allow easy conformational changes that adaptation to the imposed outside load would require. Thus, when the pin 'attacks' the PS surface, separation of the material from the surface in the form of somewhat elongated platelets occurs; we see such debris in Figure 5(a).

Fig. 4. FIB cross section of the 0.30 wt% PS + gold nanoparticles hybrid.

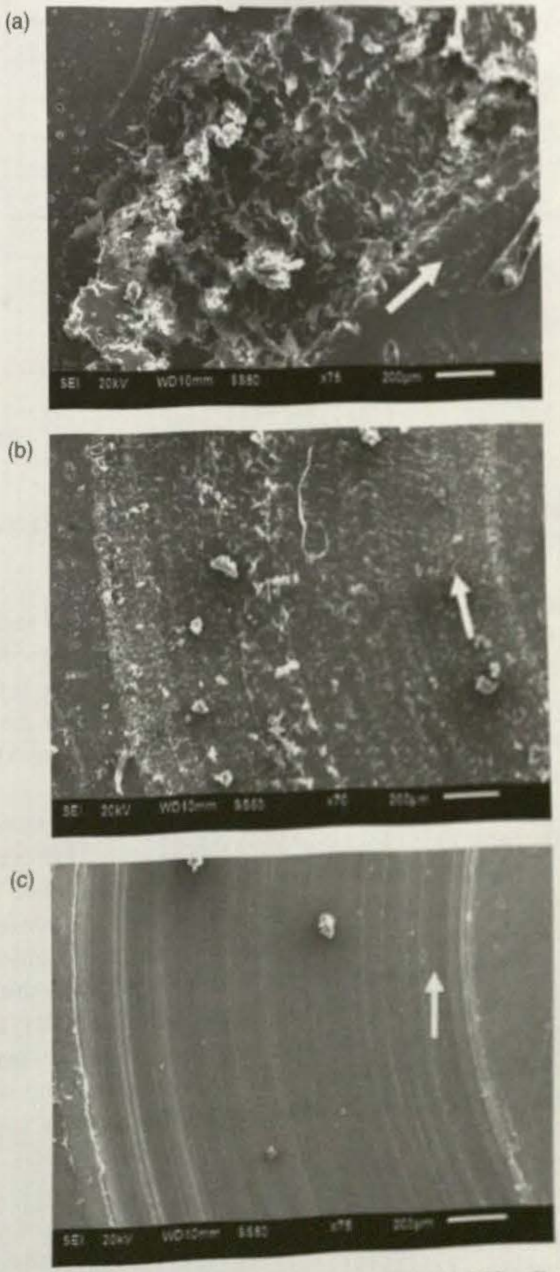

Fig. 5. Wear tracks of the composites. (a) pure PS, (b) 0.15 wt% gold nanoparticles, (c) 0.3 wt% gold nanoparticles. The arrow indicates the sliding direction.

When 0.15 wt% of gold nanoparticles is added, we have abrasion of Au particles against the hard ceramic pin as the dominant phenomenon. The results of that process are seen in Figure 5(b) as irregular debris particles. In terms of wear, Figure 6 tells us that there is a dramatic increase of wear. We note that relatively good adhesion of the Au particles to the polymer matrix has been achieved; thus, each Au particle that separates from the PS surface carries with it a certain amount of the polymer. The process of separation of PS debris as elongated platelets from the surface seen before in the neat polymer continues, but it is now not the major contributor to the overall wear.

In turn, we consider the wear tracks for 0.30 wt% Au in Figure 5(c) in conjunction with the wear versus Au concentration diagram in Figure 6. Both previous mechanisms of debris formation are necessarily operative here also. At the same time, we have noted above the role of the filler particle density (number of such particles per unit volume) for macroscopic properties. At the lower concentration of 0.15% Au, a small number of filler particles present did not provide the 'defense' of the polymer against abrasion. Now, when the Au particle concentration has been

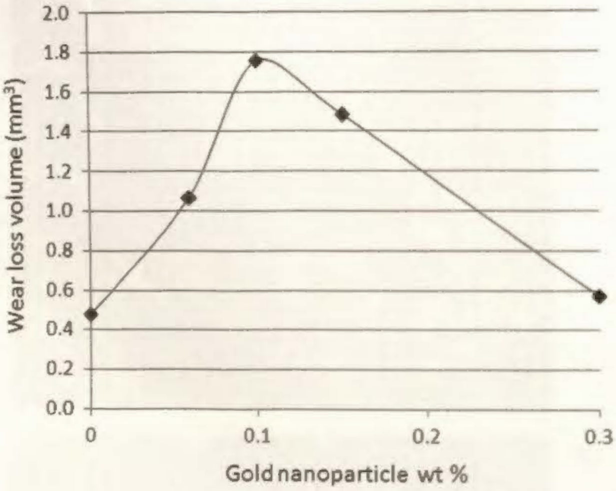

Fig. 6. Wear loss volume of the hybrids as a function of Au particles concentration.

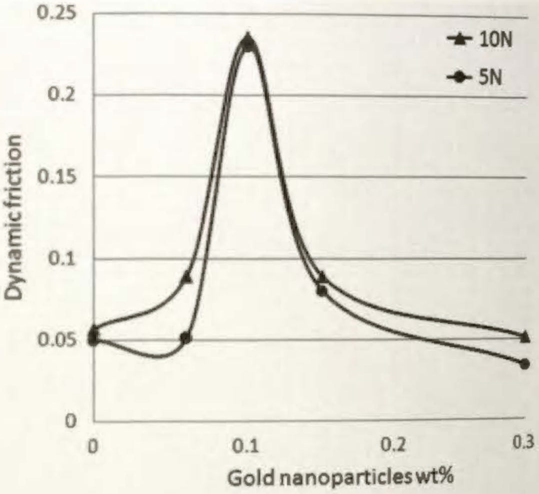

Fig. 7. Dynamic friction of the hybrids at two normal loads as a function of Au composition.

doubled, more numerous metal particles do provide such a defense. Metal particles on the material surface provide a certain amount of protection, the more of them the better is such protection. The result is a *decrease* of wear, first a dramatic one when we are close to the wear versus filler concentration maximum.

Analyzing the wear tracks, we have explained Figure 6 at the same time. A total of three mechanisms of response of the materials to the 2000 abrasive revolutions of the ceramic pin on the surface is important: brittle response of PS resulting in formation of debris shaped approximately as platelets; abrasion of metal particles by the pin, resulting in formation of irregularly shaped debris particles; and protection of the surface against abrasion by the filler particles. The magnitude of the last effect increases along with increasing volumetric concentration of Au particles.

6. FRICTION

Figure 7 show the dynamic friction of the composites as a function of metal concentration at two different normal loads. We first note that the friction behavior is very similar for the two loads. In other words, the effects of the magnitude of the load are small, an effect seen for other materials before.[45] We also see first a dramatic increase of friction with the Au concentration, passage through a maximum, and then a decrease of dynamic friction. At the highest Au nanofiller concentration investigated, we find lower friction than in neat PS. Figure 7 can be explained in terms somewhat similar to those we have used to explain the wear diagram in Figure 6. First, we have friction characteristic for the neat polymer. Addition of a small amount of metal nanoparticles does not eliminate sliding of the indenter on the polymer surface; the Au particles present only constitute additional obstacles in the movement of the ceramic pin, hence a rapid growth of friction. However, a further increase in concentration of the metal particles apparently results in *lowering of the effective area of contact*; the pin moves now *not all the time* on the polymer surface but also to some extent moves 'from bump to bump', with the Au particles providing the bumps.

7. CONCLUDING REMARKS

We successfully obtained spherical gold nanoparticles by laser ablation in a liquid environment with an average size of 15 nm. This method allowed us to have particles free of any chemical residue and well dispersed throughout the solvent used. As evidenced by FIB, we improved the dispersion of the particles inside the polymer matrix with respect to our previous work by dissolving polystyrene in the nanoparticle solution.

As for the use of metal nanoparticles for possibly lowering friction and wear of the polymer, the results strongly depend on the Au particles concentration. As also in other cases, formation of nanohybrids on the basis of a polymer matrix is not a panacea. We have to provide a certain—albeit still in the range below 1 wt%—concentration of the filler for the filler to lower friction and lower wear.

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