

Microhybrids of Metal Powder Incorporated in Polymeric Matrices: Friction, Mechanical Behavior, and Microstructure

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The polymers used as a matrix were low density polyethylene (LDPE) and a thermoplastic elastomer (TPE). The metal particles were Al, Ag, and Ni with micrometer diameters. The metal concentration varied from 0 to 10 wt%. Dynamic and static frictions on tetrafluoropolyethylene and stainless steel as sliding surfaces were determined and tensile tests were performed. Secondary electron and backscattered electron SEM images were taken to determine microstructures of the hybrids. Addition of metal powder to the matrix results in reduction to a minimum of the tensile elastic modulus for low metal concentrations, and increase in the modulus with further addition of metal particles. For the TPE, the tensile modulus exceeds that of the pure material. Small metal particles increase the modulus at lower concentrations than larger ones. Hardness varies with the filler concentration, similarly as tensile modulus does. Backscattered electron SEM images show uniform dispersion of the metal particles at the surfaces and in the bulk. The contrast is enhanced by large differences in atomic numbers between the fillers and the matrices. Ni microparticles in LDPE cause crack arrest seen in SEM. POLYM. ENG. SCI., 48:1977-1981, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

Polymers exhibit many advantages over other structural materials, such as low cost, ease of processing, low density, and resistance to shocks and vibrations. In tribology an additional advantage is the possibility to tailor a wide range of properties, from high friction polymers (such as

rubber) to low friction materials [such as tetrafluoropolyethylene (TFPE)]. However, low wear resistance and relatively poor mechanical properties of polymers limit their application in various fields of industry [1–3]. To improve these properties, we need more understanding of mechanisms of mechanical and tribological behavior of polymers—such as comes for instance from molecular dynamics computer simulations [4]. In practical terms, methods of determination of tribological properties for cylindrical and other non-flat surfaces are needed—and some such methods have been developed [5].

One way to improve properties of a polymer is creation of a composite or hybrid material by introduction of a second phase [6, 7]. As an example, we have demonstrated before that addition of carbon black filler improves tribological properties of non-irradiated and irradiated polymer blends simultaneously with lowering electrical resistivity [8]. Tribological properties are usually more difficult to improve than mechanical ones, since in most cases external liquid lubricants cause swelling of polymers and deterioration instead of the expected improvement. Such materials can be characterized as hybrids since they differ from the traditional classification of materials into inorganic and organic [9]. Hybrids can contain reinforcement in the form of fibers [6, 7, 10], including ceramic fiber mats in an interpenetrating network as investigated by Karger-Kocsis and coworkers [10], carbon fibers [11], carbon nanotubes and nanofibers [12, 13], or else spherical filler particles of various sizes.

Metallic particles as fillers have been fairly widely used to improve the electrical, thermal, and mechanical properties of polymers [14–19]. However, there has been very little work on the use of metallic particles to tailor tribological properties of polymers, with the study by Rajesh and Bijwe as a notable exception [20]. The goal of the present work is to investigate the frictional behavior and some mechanical properties of selected polymers

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filled with metal microhybrids. We have demonstrated before for the low density polyethylene (LDPE) + Al microparticles system that the aluminum particles are distributed uniformly in the polyethylene matrix; a combination of gallium focused ion beams (FIBs) with scanning electron microscopy (SEM) was used for the purpose [21].

EXPERIMENTAL

Materials

Branched LDPE and Hytrel[®] [a block copolymer thermoplastic elastomer (TPE) composed by a rigid phase of poly(buthylene–terephthalate) and a flexible phase of poly(tetramethylene oxide), E. I. du Pont de Nemours, Wilmington, DE] were used as matrices. Micrometer sized metallic particles were incorporated as the filler dispersed phase. The metals used were: aluminum, silver, and nickel; the average particle sizes were 1, 4, and 7 μm , respectively. The concentration of the particles was varied from 0 to 10 wt%.

Sample Preparation

A Brabender Type 6 mixer was used to blend the polymer with the metal powder. The blending temperatures were 150 and 210°C for LDPE and the TPE, respectively. The mixing time was 5 min, and the blade speed was 80 rpm in all cases. The blends were pelletized and then injection molded at 170 and 240°C (LDPE and the TPE, respectively) and at the pressure of 60 psi in an AB-100 injection molding machine (AB Machinery, Toronto, Canada) to obtain the final specimens. SEM analysis of the hybrids was performed after gold-coating the surfaces.

Hybrids Characterization

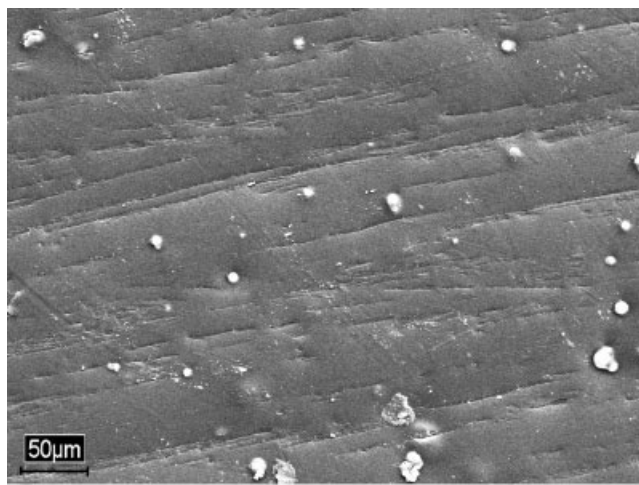
Secondary electrons and backscattered electrons SEM imaging were performed with a JEOL JSM-5800 SEM at 20 keV. To investigate the dispersion of the particles in the matrix, some specimens were liquid-nitrogen-cooled and then broken while in the brittle temperature regime, so that the true fracture cross section could be observed.

Tensile tests of dumbbell specimens were performed in a MTS universal machine according to ASTM D 638. Hardness tests were carried out with a Shore durometer D according to ASTM D 2240.

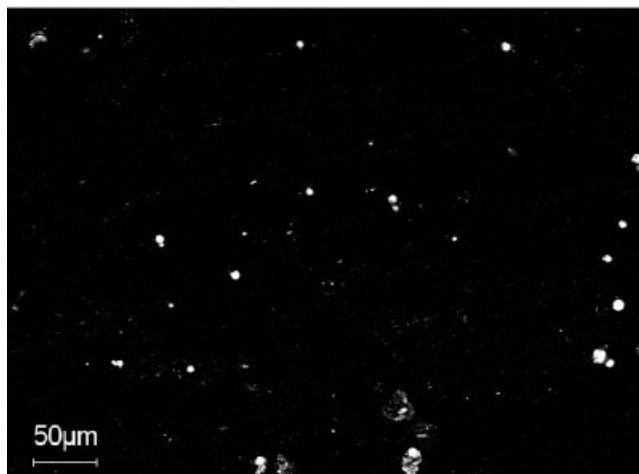
The friction tests were performed in a MTS QTEST/5 universal machine attached with a 22.5 lb load cell. Teflon and stainless steel were used as sliding surfaces. The sliding speed was 150 mm/min with a normal load of 0.93 lb. The sample dimensions were 20 mm \times 10 mm \times 2 mm. All tests were performed at room temperature and 50% humidity.

SEM RESULTS

Since tribological phenomena involve the interaction between surfaces, it is important to reveal whether the metal particles are present on the hybrid surface. On the other hand, the mechanical properties of the hybrid are affected by particles located in the bulk of the material. Figure 1a shows a secondary electron SEM image of the TPE containing hybrid with 5 wt% Ni. The surface morphology is clearly seen, and the Ni particles can be identified. To distinguish between the metal particles and the polymer matrix, backscattered electron imaging was used; the contrast results mostly from the differences in atomic masses of the constituents. Figure 1b shows the same area as Fig. 1a, but in backscattered electron mode. It is clear that metal particles (bright spots) are located on the surface and that good dispersion (rather than agglomeration) of metal particles has been achieved—similarly as in FIB + SEM results for HDPE + Al [21].

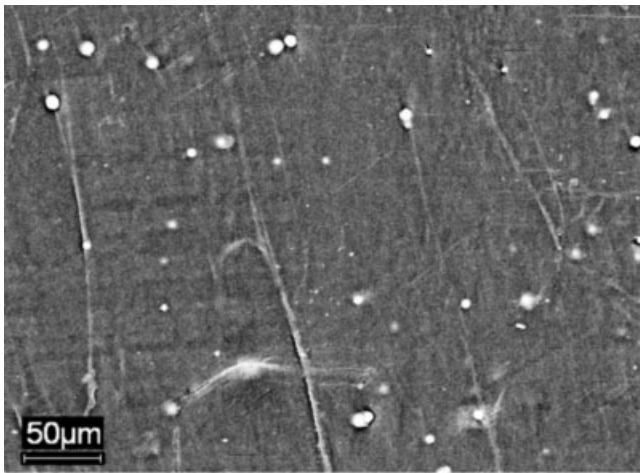


(a)

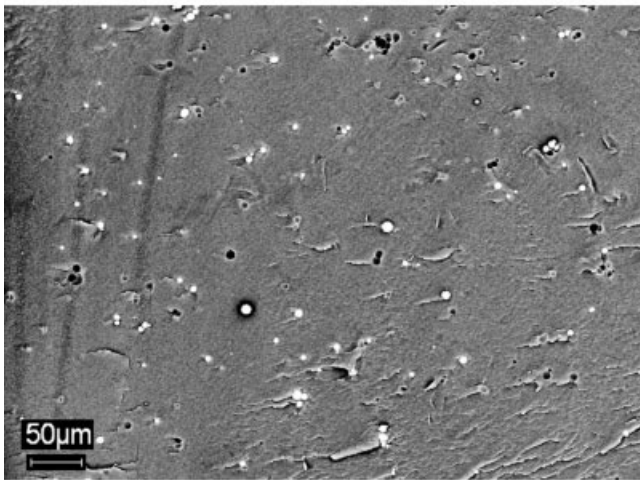


(b)

FIG. 1. SEM images of the TPE + 5 wt% Ni powder: (a) secondary electron image; (b) backscattered electron image.



(a)



(b)

FIG. 2. Backscattered electron SEM images of LDPE + 10 wt% Ni powder: (a) surface; (b) fracture cross section.

Figure 2a shows the backscattered electron SEM image of the surface of LDPE + Ni 10 wt%. Figure 2b shows the fracture cross section of the same material. It can be clearly seen that there are metal particles on the surface as well as in the bulk material. The particles are well dispersed throughout the material. The degree of dispersion observed was similar for the three metals in the two polymer matrices, although for the silver filler some clusters were observed (up to 15 μm), especially at high concentrations. It should be mentioned that with both matrices the wetting of the particles by the matrix is insufficient and a wetting agent should be added. This may influence the mechanical properties.

An interesting phenomenon can be observed in the fracture surface of the bulk LDPE. The Ni microparticles create an arrest of the cracks; the cracks are clearly stopped as they approach the Ni particles. This phenomenon may raise the energy needed for fracture of the composite material when compared with the neat LDPE material. Clearly there is fairly strong interaction between the

LDPE matrix and the Ni particles; we recall a discussion by Kopczynska and Ehrenstein [22] of effects of surface and interface tension on properties. The phenomenon of crack arrest is not observed in the case of the TPE.

TENSILE TESTING AND HARDNESS RESULTS

Figure 3a shows the elastic modulus of the TPE hybrids. The three materials show the same trend: an initial decrease of the modulus reaching a minimum (at about 1 wt%), followed by a continuous increase. The initial lower modulus results probably from the filler particles perturbing the polymer matrix since no coupling agent was used. The increase in modulus further on can be explained by the fact that at higher concentrations more filler particles hamper the chain mobility. Our model is reinforced also by the fact that for the smallest particles (aluminum) we obtain a modulus higher than that of the pure material starting at 3 wt%, whereas for the two other metals this occurs at a much higher concentration. Apparently, the small Al particles are more effective in limiting the chain mobility and enhancing the modulus earlier.

Figure 3b shows the Shore D hardness for the TPE hybrids; the main contribution of this diagram is the confirmation of the tendency seen in Fig. 3a, since hardness and tensile modulus are believed to be related. We can observe

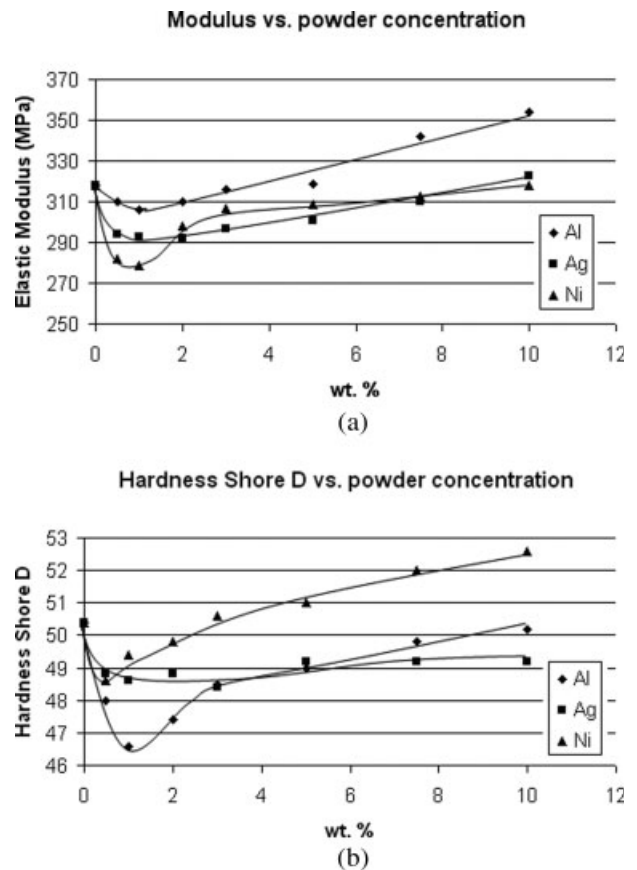


FIG. 3. (a) Elastic modulus of the TPE hybrids; (b) hardness Shore D of the TPE hybrids.

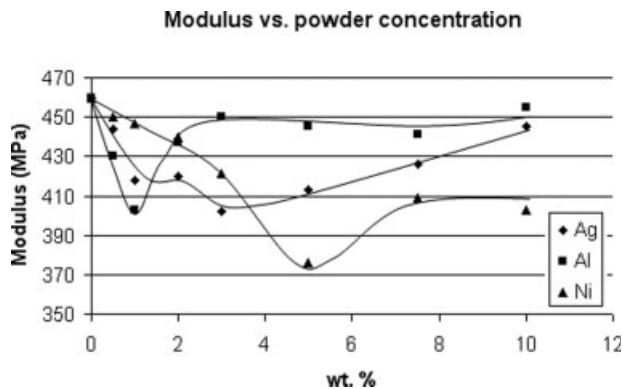


FIG. 4. Elastic modulus of LDPE microhybrids.

a minimum value of hardness followed by a continuous increase. In the hardness plots the Ni particles have the largest effect when compared with the modulus plots where Al shows the highest values. This can be explained easily since Ni is the hardest metal of the three. We recall also that there is an exponential relation between the Vickers hardness and the material displaced in microscratch testing: the higher the hardness, the lower is the area of the displaced material (groove and two top ridges) cross section perpendicular to the test direction [23].

Figure 4 shows the elastic modulus of the LDPE-based microhybrids. As seen in the previous case, there is an initial reduction of the modulus, followed by a continuous increase at higher concentrations. The difference is that even at 10 wt%, for any of the metals, the modulus is still lower than for the pure material. This is because LDPE is a un-crosslinked branched material; the metal particles can limit the chain mobility and affect the modulus. Moreover, a decrease of crystallinity caused by the presence of the particles is possible.

FRICITION RESULTS

Figure 5 shows the dynamic friction of LDPE hybrids against steel as the sliding surface. There is a common trend for all three metals: a reduction of friction to a minimum followed by an increase with concentration. The

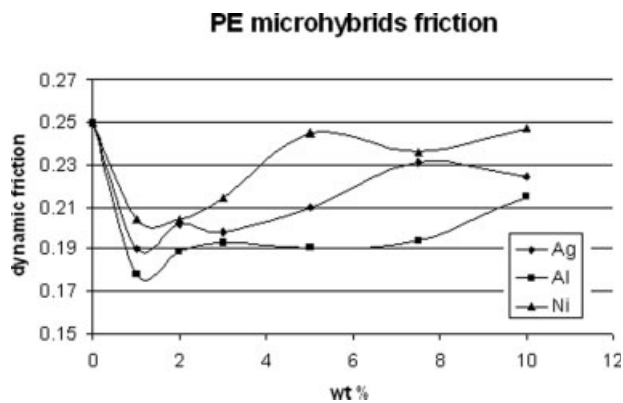


FIG. 5. Dynamic friction of LDPE microhybrids on steel.

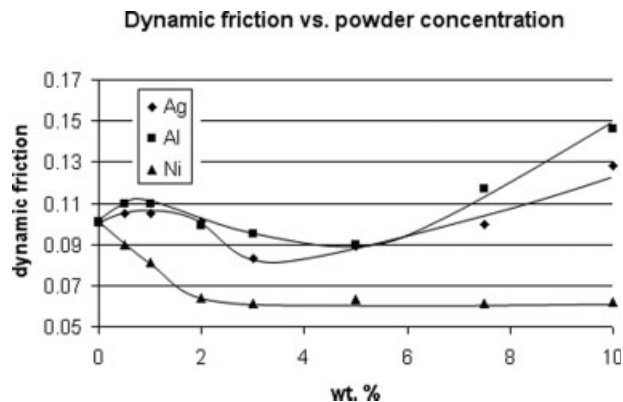


FIG. 6. Dynamic friction of LDPE hybrids on TFPE.

reduction can be explained by the phenomenon that involves the reduction in real contact area as more particles get exposed in the surface and less polymer asperities are deformed. Then, after a minimum value, the metal + metal interactions resulting in a higher friction than the metal + polymer contacts begin to dominate, causing a continuous increase in friction values.

Figure 6 shows the same LDPE microhybrids sliding against tetrafluoroethylene TFPE surfaces. In this case for Al and Ag fillers we observe the same trend as on the steel surface. There are still two competitive phenomena: one is the changes in real contact area and the other is now the scratch of Teflon done by the harder metal particles that provokes an increment in friction. However, for nickel the situation is different; there is an immediate reduction of friction and stabilization at higher Ni concentrations. This can be attributed to a film transfer formation of TFPE on the particles surface, hence the friction values become close to those for the TFPE + TFPE contact. We recall the discussion by Myshkin and his colleagues in Homel of formation of a transfer polymer film [24]. We also recall that in sliding wear determination (15 microscratches along the same groove) at 5.0 N load the residual depth for Teflon represents 160% of the respective depth for polypropylene [25].

Figure 7 shows the static friction values for the TPE on TFPE. There is a common trend of all three materials, which

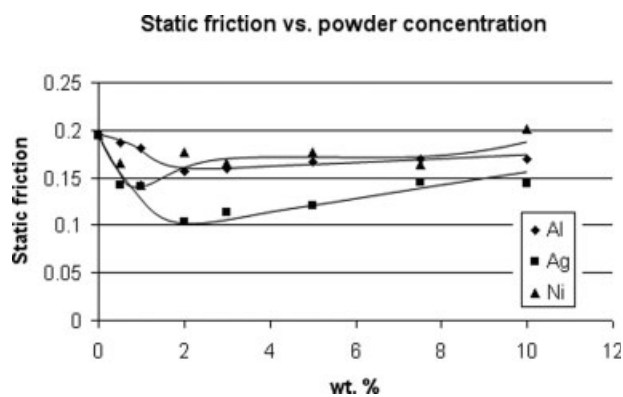


FIG. 7. Static friction of the TPE hybrids on TFPE.

is similar to that observed in LDPE. The difference is that there is no initial increase in friction, but rather an initial decrease, reaching a minimum, followed by an increase of the friction values. The same model of competitive phenomena applies in this case also. In the initial decrease regions each kind of metal particles lowers the effective surface area; hence starting the movement is easier.

GENERAL DISCUSSION

We find that introduction of metal microfillers can cause improvement in mechanical and tribological properties of polymers. Low concentration of filler is needed to achieve such improvement. Morphological effects were tested using SEM.

The backscattered electron mode in SEM imaging proved to be a suitable technique to determine the location of the metal particles inside the material matrix. The microhybrids showed a uniform dispersion of the metal particles in the bulk as well as on the surface. This observation is important because of the connections between the microstructure and properties, tribological and mechanical in our case. LDPE shows the phenomenon of crack arrest; the energy needed for fracture increases as the result. The TPE shows a fracture surface, which is practically independent of the filler presence.

The elastic moduli of all microhybrids present the same trend: an initial decrease, due to the perturbation of the matrix structure, followed by an increase since a higher number of filler particles hampers the chain mobility in the polymer matrices. The increment can even surpass the modulus of the pure material, as in the case with the TPE + Al system. The kind of metal, the size and the shape of the particles result in different effects on the properties tested. This is of course expected and similar to the behavior of fiber- or nanotube-reinforced polymers [6, 7, 10–13, 26]. We find that smaller filler has larger effect on modulus, while harder filler has larger effect on hardness.

Frictional behavior is a more complex one. In the case of steel as the sliding surface, two competing phenomena occur when we add metal particles. One is the change in contact area provoked by the particles located in the surface, and the other is the metal + metal contact. A combination of these two phenomena causes a minimum in the friction values; when we increase further the concentration of the metal particles, the metal + metal contact dominates and the friction values start increasing. For TFPE we have again two competing phenomena: the changes in contact area and the damage caused by scratching the softer TFPE surface. However, for LDPE + Ni hybrids on TFPE the friction value stabilizes at a low value; this behavior can be attributed to the formation of a TFPE transfer film formation on the Ni particles surface.

The same ideas of competitive phenomena also apply in TPE + metal hybrids. However, the difference to LDPE is that there is no initial increase of the friction value; there is a minimum and a continuous increase at higher concentrations.

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