The Nanomechanical and Nanoscratch Properties of MWNT-Reinforced Ultrahigh-Molecular-Weight Polyethylene Coatings*

S.R. Bakshi, K. Balani, T. Laha, J. Tercero, and A. Agarwal

Ultrahigh-molecular-weight polyethylene (UHMWPE) and 5 wt.% multiwalled-carbon-nanotube-(MWNT) reinforced UHMWPE coatings were prepared on a steel substrate by electrostatic spraying. Nanoindentation and nanoscratch tests were performed on the coatings to evaluate the mechanical and wear properties at small length scales. The mean values of elastic modulus and hardness were higher for the MWNT-reinforced coating, while the plasticity index of the coatings was unaffected. The lateral force and coefficient of friction was found to be considerably higher in the case of the MWNT-reinforced coating, indicating an increase in resistance to wear due to the addition of MWNT.

INTRODUCTION

Ultrahigh-molecular-weight polyethylene (UHMWPE) has been used in the manufacture of acetabular cups and tibial inserts due to its biocompatibility and strength since it was first introduced in 1962.[1] It has also been used as structural material and as a fiber due to its high strength and stiffness. Thin coatings of polymers and polymer composites find applications in micro-electromechanical systems (MEMS), as a corrosion protective coating, bioactive coatings, and as scaffolds for tissue culture. For special applications where polymer surfaces are in constant motion, wear properties are important. Since the thickness of the coatings is small in comparison to the substrate, conventional methods of testing cannot be employed to assess their tribological properties. Also for these applications the surface nanoscale properties are of special interest. Nanoindentation and nanoscratch tests have been extensively used for the characterization of polymers[2–7] and polymer matrix nanocomposites.[8–13] Nanoindentation is the only method to determine the near-to-surface properties in polymers, which affects their tribological performance.

SYNTHESIS OF THE COATINGS

The UHMWPE powder used in the study was Mipelon™ supplied by Mitsui Chemicals America, Inc., New York. The multiwalled carbon nanotubes (MWNTs) used in the study were ~95% pure and had an outer diameter of 40–70 nm and a length of up to 1 µm. The UHMWPE and MWNT mixture was blended in a rotating jar mill for 4 h. Coatings on the order of 100 µm thick of UHMWPE and UHMWPE reinforced with 5 wt.% MWNT were prepared by electrostatic spraying onto a steel substrate. The as-sprayed powder film on the substrate was sintered in an oven at 180ºC for 30–40 min. The sintering temperature was chosen higher than the melting point of UHMWPE (136ºC) because the viscosity of the polymer is very high. H.K. Jen et al.,[14] have shown that the viscosity of 2 wt.% UHMWPE solution in various solvents to be between 10,000 cP and 30,000 cP at its melting point (viscosity of water ~1 cP at room temperature). Thus, sintering of UHMWPE takes a long time if done at its melting point.

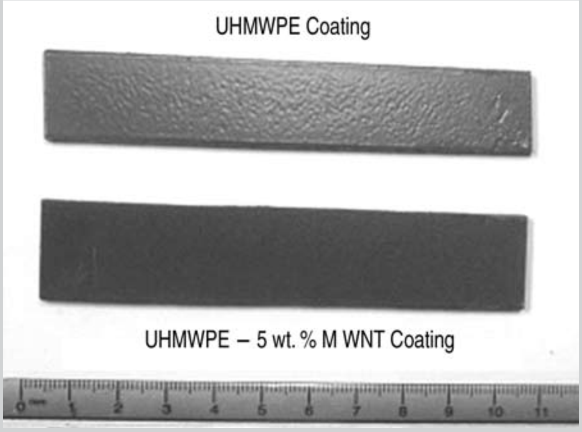


Figure 1. The coated samples.

In Figure 1, the coatings are shown to be wet and covering the steel substrate evenly. The surface of the UHMWPE coatings is shown to be rough compared to the UHMWPE–MWNT coating. Because the thermal conductivity of UHMWPE is very low (0.4 W/m·K),[15] only the outer cores of the large powders become molten during the consolidation process. Due to the high viscosity of UHMWPE, there is improper flow even after melting and the initial surface roughness of the unconsolidated layer of powders is retained. The thermal conductivity of carbon nanotubes is very high, on the order of 3,000 W/m·K,[16] which leads to efficient heat conduction in the UHMWPE–MWNT powder film and consequently a higher degree of melting

Table I. Elastic Modulus and Hardness Values of the Two Coatings

Coating	Elastic Modulus of Coating (GPa)	Hardness (MPa)	Plasticity Index
UHMWPE	2.02 ± 0.10	104 ± 14	0.70
UHMWPE–5 wt.% MWNT	2.23 ± 0.17	116 ± 14	0.71

and rate of sintering. This leads to an increased flow and smoother coating. The second reason for the smoother surface of the UHMWPE–MWNT coating could be increased flow of UHMWPE due to capillary action of nanotubes between UHMWPE particles. This will lead to an increase in the sintering kinetics. Figure 2 shows the scanning electron microscopy (SEM) images of the fracture surface of the UHMWPE–5 wt.% MWNT film produced by the same method.

It is observed from Figure 2 that nanotubes are uniformly distributed in the matrix. It is also seen that there is no damage to MWNT during electrostatic spraying and the sintering process.

NANOINDENTATION TESTING

The nanoindentation experiments were carried out using Hysitron Triboindenter (Hysitron, Minneapolis), which has a capacitive transducer with a load and displacement resolution of 0.1 μN and 0.2 nm, respectively. The accuracy of the instrument was tested using standard aluminum and fused quartz samples. A standard diamond Berkovich indenter was used, which is a three-sided pyramid with a total included angle of 142.3° and a tip radius of around 150 nm. The load was applied at the rate of 25 μN/s up to a maximum load of 250 μN where it was held for 10 s and then decreased to zero at negative rate of 25 μN/s. The loading rate and hold time at maximum load were kept high enough to avoid the formation of a 'nose' in the unloading curve due to the viscoelastic properties of UHMWPE.[17,18] The hardness P and the reduced modulus E_r were calculated by the Oliver and Pharr method.[19] The elastic modulus of the coatings was computed by taking the elastic modulus and Poisson's ratio for the indenter as 1,141 GPa and 0.07, respectively, which are the values for diamond.[20] Poisson's ratio for the coatings was taken as 0.43.[20] Figure 3 shows the load displacement curves for the two samples. It can be seen that the load required to produce the indent is higher for the MWNT-reinforced coating for any given depth. Also, the final indentation depth is less for the MWNT-reinforced coating, indicating greater hardness of the MWNT reinforced coating. Table I tabulates the elastic modulus and hardness values and their standard deviation.

It is seen that there is an increase of 10% and 12% in the mean value of the elastic modulus and hardness, respectively, due to the addition of 5 wt.% MWNT. However, there is some overlap in the data for the two coatings which signifies that there is not much difference in the measured properties of the coatings. A.K. Dutta et al.[21] had measured the elastic modulus of single-walled carbon nanotube (SWNT) reinforced epoxy composites by nanoindentation. They also did not find much difference in the elastic modulus by addition of 1 wt.% SWNT, and attributed the finding to the curving and coiling of the nanotubes and the presence of microporosity.

It can be seen from Figure 2b that the nanotubes in the study described in this paper are curved and coiled. Also there is some porosity between the particles. P.M. Nagy et al.[22] had measured the effect of MWNT concentration on the modulus and hardness values of polycarbonate composites by nanoindentation, and found that the rate of increase of modulus and hardness was twice the weight percent of MWNT added. Thus there was a 10% increase in the hardness and modulus for 5 wt.% reinforced composites. They attributed the lower increase to pile-up effects, but this seems to be incorrect because the pile-up effect should also be present in an un-reinforced polycarbonate sample. Pile-up should not increase due to MWNT addition. Yet another study by M. Olek et al.[23] found that the significant improvement of nanomechanical properties of MWNT-reinforced poly(methyl methacrylate) (PMMA) composites occurred only when the MWNTs were coated with silica. This shows that interface effect might play a significant role.

The described studies show that it is not clearly understood why there is less improvement in properties as measured by nanoindentation due to MWNT addition. The elastic modulus values obtained in the present work are comparable with the highest value obtained by K. Park et al.[20] (~2.3 GPa) and B.J. Briscoe et al for gamma-ray-irradiated UHMWPE[17] (~2.0 GPa). Also, the hardness value obtained in this study is more than that reported by Briscoe et al.[17] (~70 MPa). In an earlier paper,[24] the authors measured the tensile properties of thick free-standing films of the same compositions, and the elastic modulus of UHMWPE and UHMWPE–MWNT film was found to be 595 MPa and 1,280 MPa, respectively, which is lower than the values obtained in this study. S.L. Ruan et al. also obtained low values of tensile modulus of 977.4 ± 16.2 and 1,352.3 ± 40.7 MPa for UHMWPE and UHMWPE–1 wt.% MWNT films, respectively.[25] There might be several reasons for variations in results. First, the previous work was on

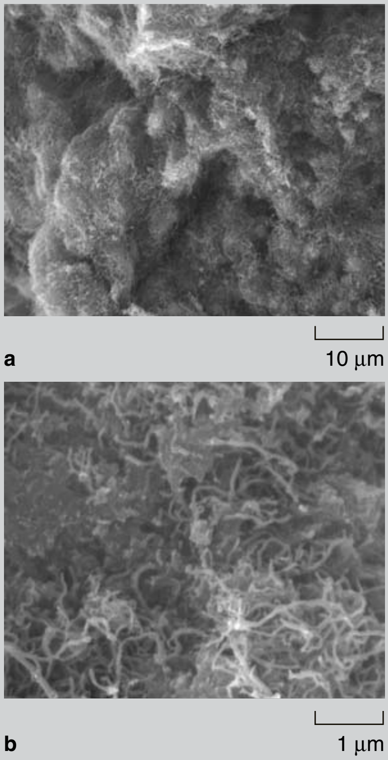


Figure 2. The fracture surface of UHMWPE–5 wt.% MWNT film showing (a) well-distributed carbon nanotubes and (b) higher magnification image of nanotubes.

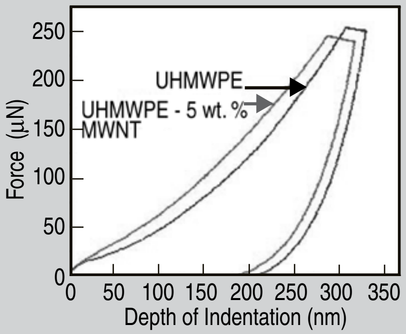
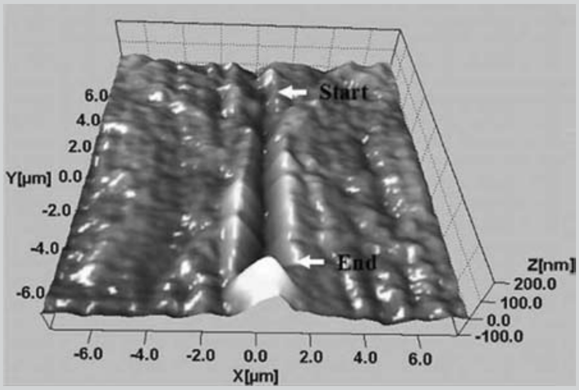


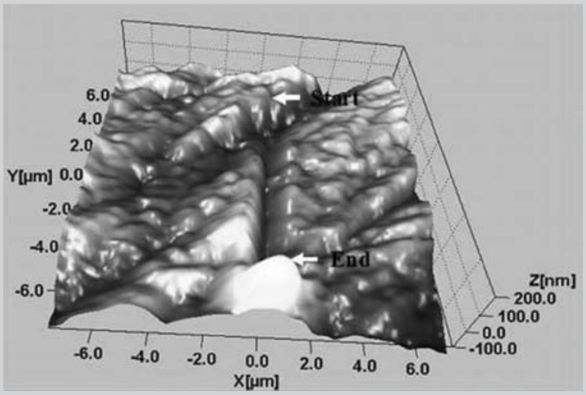
Figure 3. The load displacement curves for the two coatings.

bulk samples which might have defects such as porosity and poorly consolidated interfaces. The coatings in this case might be under tensile stress due to the solidification shrinkage leading to higher contact stiffness.

In previous work,[24] the amount of crystallinity of the UHMWPE and UHMWPE–5 wt.% MWNT films produced by the same method was reported to be 55% and 43%, respectively. Since nanoindentation is a localized process, the local crystallinity increase can also lead to an increase in value of the hardness and modulus. A measure of the plasticity of a material is given by the "plasticity index" which, in the case of nanoindentation, can be taken as the ratio of the area enclosed between the loading-unloading curves to the area under the loading part of the curve.[17] For a perfectly plastic material this value is 1 while for viscoelastic material it is between 0 and 1. The value of the plasticity index for the UHMWPE and UHMWPE–5 wt.% MWNT coatings is found to be 0.70 and 0.71, respectively, which compare well to that obtained by Briscoe et al.[17] It is seen that the addition of CNTs has no significant effect on the plasticity index. The creep undergone by the material during the holding at maximum load was not taken into consideration in the calculation. This shows that the addition of MWNTs does not affect the elastic recovery of UHMWPE due to the fact that at the small load applied for the nanoindentation, the nanotubes are flexible and they do not undergo plastic deformation while the UHMWPE gets deformed. Thus, they do not affect the elastic recovery of the polymer.



a



b

Figure 4. Scanning-probe microscope images of the scratched surface of (a) UHMWPE and (b) UHMWPE–5 wt.% MWNT coatings.

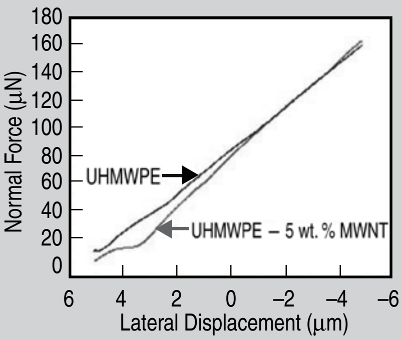


Figure 5. The variation of normal force with lateral displacement of the indenter tip.

NANOSCRATCH TESTING

Nanoscratch experiments were carried out on the coatings using the Berkovich indenter. The load function used was such that the indenter moves to +5 µm on one side of the rest position. Then a linearly increasing load from 0 µN to 200 µN is applied while moving 10 µm to a position –5 µm on the other side of the rest position. This distance of 10 µm was covered in 30 s. At the end of the scratch test the load is rapidly decreased to 0 in 2 s. Figure 4 shows the scanning probe microscopy images of the scratched surface produced by the Berkovich tip. The load applied during imaging was kept at 2 µN so that it did not damage the surface while scanning. The image files were enhanced using the image processing software *SPIP*™ (Image Metrology A/S, Horsholm, Denmark). The start and end points of the scratch test are marked in the figure. It can be seen that as the scratch test progresses the scratch becomes deeper and deeper due to increasing normal load, and there is pile-up of material on both sides and at the end of the scratch. Figures 5 and 6 show the variation of the normal force and the lateral force experienced by the indenter with lateral displacement for the two coatings.

It can be seen that the normal force increases as the scratch progresses. The lower values in the case of the MWNT-reinforced coating at the beginning of the test are due to the localized scratch/defect already present in the sample as seen in Figure 4b. Other than the initial part, the normal force is same for both coatings throughout the test. From Figure 6 it is seen that the lateral force experienced by the indenter in case of the MWNT reinforced coating is higher than the UHMWPE coating. This shows the reinforcing effect of the nanotubes on UHMWPE. The MWNT helps in holding the matrix together by the formation of bridges and hence there is more resistance to scratching. The initial low lateral force values in the case of MWNT-reinforced coating are due to the fact that the indenter moves through the localized defect/depression as seen in Figure 4b. Figure 7 shows the variation of the coefficient of friction with the lateral displacement of the indenter. Here the value of the coefficient of friction is defined as the ratio of the lateral force to the normal force. The coefficient of friction depends on several factors including the indenter geometry, surface roughness of the sample, and the material properties of the sample. Rather than just being a friction parameter this value is a measure of the resistance to wear. A harder, wear-resistant material would impose more resistance to scratch and consequently the indenter will experience a larger lateral force. It is seen that the coefficient of friction is larger for the MWNT-reinforced coating as compared to the UHMWPE coating. The value of the coefficient of friction of the UHMWPE and UHMWPE–MWNT coating was found to be 0.36±0.03 and 0.51±0.02, respectively. Since the first half of the data is influenced by the surface morphology the average was calculated using the data from the later half of the scratch. It can be seen that there is considerable improvement in the wear resistance due to addition of carbon nanotubes. The results are consistent with those obtained by Y. Xue et al.[26] who found a near 75% decrease in the specific wear rate of UHMWPE-HDPE blends due to the addition of 2 wt.% MWNT. Y-S. Zoo et al.[27] have also found a decrease in wear loss from 0.35 mg to 0.05 mg by the addition of 0.5 wt.% MWNT to UHMWPE. This is due to the fact the carbon nanotubes act as bridges and help in holding the material together. It can be seen from Figure 2b that the nanotubes are distributed in the matrix and they hold the matrix together. Thus, the flow of material during scratching is impeded.

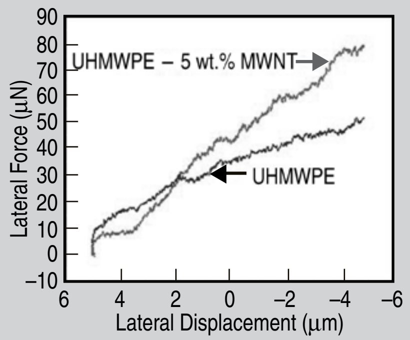


Figure 6. The variation of lateral force experienced by the indenter with lateral displacement of the indenter tip.

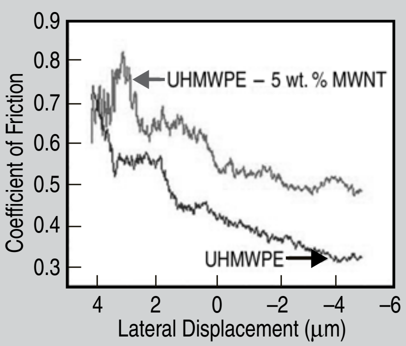


Figure 7. The variation of coefficient of friction with lateral displacement.

References

1. Stephen Li, "Ultra High Molecular Weight Polyethylene: from Charnley to Cross-Linked," *Oper. Tech. Orthopaed.*, 11 (4) (2001), pp. 288–295.
2. C. Poilane et al., "Analysis of the Mechanical Behavior of Shape Memory Polymer Membranes by Nanoindentation, Bulging and Point Membrane Deflection Tests," *Thin Solid Films*, 379 (2000), pp. 156–165.
3. J.S.S. Wong et al., "Scratch Damage of Polymers in Nanoscale," *Acta Mat.*, 52 (2004), pp. 431–443.
4. K. Geng et al., "Nanoindentation Behaviour of Ultrathin Polymeric Films," *Polymer*, 46 (2005), pp. 11768–11772.
5. T-Hua Fang, W-Jin Chang, and S-Lin Tsai, "Nanomechanical Characterization of Polymer Using Atomic Force Microscopy and Nanoindentation," *Microelectron. J.*, 36 (2005), pp. 55–59.
6. M. Moniruzzaman, P. Zioupos, and G.F. Fernando, "Investigation of Reversible Photo-Mechanical Properties of Azobenzene-Based Polymer Films by Nanoindentation," *Scripta Mat.*, 54 (2006), pp. 257–261.
7. L. Shen, I.Y. Phang, and T. Liu, "Nanoindentation Studies on Polymorphism of Nylon 6," *Polym. Test.*, 25 (2006), pp. 249–253.
8. J.R. Gregory and S.M. Spearing, "Nanoindentation of Neat and In Situ Polymers in Polymer-Matrix Composites," *Comp. Sci. Tech.*, 65 (2005), pp. 595–607.
9. H.N. Dhakal, Z.Y. Zhang, and M.O.W. Richardson, "Nanoindentation Behaviour of Layered Silicate Reinforced Unsaturated Polyester Nanocomposites," *Polym. Test.*, 25 (2006), pp. 846–852.
10. Y. Hu et al., "Nanoindentation Studies on Nylon 11/Clay Nanocomposites," *Polym. Test.*, 25 (2006), pp. 492–497.
11. K. Yashiro, A. Furuta, and Y. Tomita, "Nanoindentation on Crystal/Amorphous Polyethylene: Molecular Dynamics Study," *Comp. Mat. Sci.*, 38 (2006), pp. 136–143.
12. A. Dasari, Z-Zhen Yu, and Y-Wing Mai, "Nanoscratching of Nylon 66-based Ternary Nanocomposites," *Acta Mat.*, 55 (2007), pp. 635–646.
13. P.S. Uskokovic et al., "Micromechanical Properties of a Hydroxyapatite/poly-L-lactide Biocomposite using Nanoindentation and Modulus Mapping," *J. Eur. Cer. Soc.*, 27 (2007), pp. 1559–1564.
14. H.K. Jen, et al., "Gelation Behavior of UHMWPE/Camphene," *J. Mat. Sci.*, 32 (1997), pp. 3607–3611.
15. H.L Stein, "Ultra High, Molecular Weight Polyethylene (UHMWPE)," *Engineered Materials Handbook*, Vol. 2 (Materials Park, OH: ASM International, 1999).
16. P. Kim et al., "Thermal Transport Measurements of Individual Multiwalled Nanotubes," *Phys. Rev. Lett.*, 87 (2001), p. 215502.
17. B.J. Briscoe, L. Fiori, and E. Pelillo, "Nanoindentation of Polymeric Surfaces," *J. Phys. D: Appl. Phys.*, 31 (1998), pp. 2395–2405.
18. A.H.W. Ngan and B. Tang, "Viscoelastic Effects during Unloading in Depth Sensing Indentation," *J. Mat. Res.*, 17 (10) (2002), pp. 2604–2610.
19. W.C. Oliver and G.M. Pharr, "An Improved Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments," *J. Mater. Res.*, 7 (1992), pp. 1564–1583.
20. K. Park et al., "Quasi-Static and Dynamic Nanoindentation Studies on Highly Crosslinked Ultra-High-Molecular-Weight Polyethylene," *Biomaterials*, 25 (2004), pp. 2427–2436.
21. A.K. Dutta, D. Penumadu, and B. Files, "Nanoindentation Testing for Evaluating Modulus and Hardness of Single Walled Carbon Nanotube-Reinforced Epoxy Composites," *J. Mater. Res.*, 19 (2004), pp. 158–164.
22. P.M. Nagy et al., "Nanoindentation Investigation of Carbon Nanotube–Polymer Composites," *Internet Elec. J. Mol. Des.*, 5 (2006), pp. 135–143.
23. M. Olek et al., "Nanomechanical Properties of Silica Coated Multiwall Carbon Nanotubes–Poly(methyl methacrylate) Composites," *Tech. Proc. 2005 NSTI Nanotech, Conf. Trade Show*, 2 (2005), pp. 167–170.
24. S.R. Bakshi, J. Tercero, and A. Agarwal, "Synthesis and Characterization of Multiwalled Carbon Nanotube Reinforced Ultra High Molecular Weight Polyethylene Composite by Electrostatic Spraying Technique," *Composite A*, paper submitted.
25. S.L. Ruan et al., "Toughening High Performance Ultrahigh Molecular Weight Polyethylene Using Multiwalled Carbon Nanotubes," *Polymer*, 44 (2003), pp. 5643–5654.
26. Y. Xue et al., "Tribological Behavior of UHMWPE/HDPE Blends Reinforced with Multi-Walled Carbon Nanotubes," *Polym. Test.*, 25 (2006), pp. 221–229.
27. Y-S. Zoo et al., "Effect of Carbon Nanotube Addition on Tribological Behavior of UHMWPE," *Trib. Lett.*, 16 (2004), pp. 305–309.

S.R. Bakshi, K. Balani, T. Laha, J. Tercero, and A. Agarwal are with the Department of Mechanical and Materials Engineering at Florida International University, 10555 West Flagler Street, Miami, Florida, 33174. Dr. Agarwal can be reached at (305) 348-1701; fax (305) 348-1932; e-mail agarwala@fiu.edu.