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The effect of ZnO nanoparticles on the mechanical, tribological and antibacterial properties of ultra-high molecular weight polyethylene

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Abstract

In this study, the response of different filler loadings (5–20 wt%) of zinc oxide nanoparticles reinforced ultra-high molecular weight polyethylene on the mechanical, tribological and antibacterial performances were attempted. The compression, tensile and micro-hardness properties of the nano-zinc oxide/ultra-high molecular weight polyethylene composites were studied. The tribological properties were investigated using DUCOM pin-on-disc tester with variable applied loads (5–35 N) and sliding speeds (0.209 m/s and 0.419 m/s) against 1200 grit size silicon carbide abrasive paper under dry sliding conditions. The worn surfaces and transfer films of the composites were observed using the scanning electron microscopy. Experimental results show that reinforcing ultra-high molecular weight polyethylene with zinc oxide nanoparticles would improve certain mechanical and tribological properties. Wear performance was enhanced with maximum wear resistance found at 10 wt% nano-zinc oxide/ultra-high molecular weight polyethylene composite. The average coefficient of friction of ultra-high molecular weight polyethylene shows a decrease after reinforcement with zinc oxide nanoparticles. Upon zinc oxide nanoparticles reinforcement, the worn surface shows reduced severity of wear. The nano-zinc oxide/ultra-high molecular weight polyethylene composite imparts antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*.

Keywords

Zinc oxide nanoparticles, ultra-high molecular weight polyethylene, polymer composite, tribology, worn surface, antibacterial

Introduction

Many advanced engineering materials today are built from polymer with various types of reinforcement: organic and inorganic materials, minerals, short fiber etc. These polymer composites offer a wide range of advantages as compared to metals and ceramics such as ease of processing, light in weight and low cost with comparable mechanical strength. Ultra-high molecular weight polyethylene (UHMWPE) is one of the most important, commercialized polymer that possesses high performance and unique properties such as bio-compatibility, chemical inertness, excellent impact strength[1,2] and highest abrasion resistance relative to other thermoplastics.[3] Its popularity began to take

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over conventional PE when it was first used as implant materials for human joints by Sir John Charnley in 1970. By employing UHMWPE components as human joint implants, numerous human joint diseases are successfully resolved such as arthritis and rheumatoid. Besides artificial implant components, it is widely used in other industry application which includes engineering bearing, valve, automotive parts etc. In spite of their increasing interest, its low surface hardness, poor creep resistance[4] and elastic modulus[5,6] still remain the major concerns. Moreover, wear is a major failure for UHMWPE bearing components in total joint replacements after long-term services.[5] In order to enhance the service lifetime of UHMWPE component for projected usage, it is necessary to minimize the wear problem and improve the mechanical properties. A number of research have been conducted using various types of filler reinforcement to improve the mechanical properties and wear resistance of UHMWPE.[4–11] These studies have shown that the incorporation of the optimum amount of fillers into UHMWPE matrix would significantly improve its wear resistance.

The incorporation of inorganic nanoparticles into polymer has introduced a new pathway in engineering polymer technology. Inorganic nanoparticles can significantly alter the mechanical properties of the polymer matrix due to its large surface to volume ratio and with additional functional properties such as thermal and electrical conductivity. Hence, it offers additional advantages in the physical, mechanical and additional functional performances as compared to traditional additive in polymer. It has been reported that the mechanical and tribological properties of the polymer can be improved by filling appropriate amount of inorganic nanoparticles into the polymer matrix such as ZrO_2,[12] SiO_2,[13] CuS,[14] ZnO,[15] CuO and TiO_2.[16] The enhancements of the wear resistance of inorganic nanoparticles were due to the improved mechanical properties of the polymers such as increase in the modulus and hardness.[17] The major factors that influence the properties of particulate-filled polymer composites are the types of filler, filler loading and filler-matrix interaction.[18] As an emerging reinforcement material, ZnO exhibit high strength, toughness, electrical conductivity, optical and bacterial resistance.[19–21] Many studies on nano-ZnO-reinforced polymer composites have been done in recent years. Li et al.[15] made known that the wear and friction of polytetrafluoroethylene (PTFE) were reduced by incorporating 15 vol.% of ZnO nanoparticles. Wang et al.[22] had researched on the tribological behavior of nylon composites filled with ZnO whiskers and particles. They reported that both ZnO whiskers and ZnO particles give significant improvement in the mechanical and tribological properties of the nylon composites. Subramani et al.[23] studied micro- and nano-ZnO-filled polypropylene (PP) composite and they found that ZnO has excellent antibacterial activity against two different human pathogenic bacteria, the *Staphylococcus aureus* (*S. aureus*) and the *klebsiella pneumonia*. Li et al. also found the improvement on mechanical properties of linear low-density polyethylene (LLDPE) film and induced additional antibacterial properties with incorporation of low content of ZnO nanoparticles.[24] The significances of ZnO nanoparticles in different polymer matrix are well established by other researchers.[25–27] Surprisingly, the effects of ZnO-nanoparticles on the properties of UHMWPE have not been extensively covered yet. The ZnO-nanoparticles are widely recognized as bio-compatible materials and antibacterial agent which are highly potential for UHMWPE modification that can be applied in biomedical application such as artificial joint replacements.

In this work, UHMWPE reinforced with ZnO nanoparticles were prepared using hydraulic hot press. The coupling agent aminoproplytriethoxysilane (APTES) were used to improve the compatibility between nano-ZnO and UHMWPE matrix. The effect of ZnO nanoparticles loadings in UHMWPE matrix on the mechanical and tribological performances was studied. The worn surfaces and transfer film of pure UHMWPE and nano-ZnO-reinforced UHMWPE composites were also observed under SEM. Finally, the qualitative antibacterial assessment using the agar diffusion technique was investigated.

Experimental details

Materials

The UHMWPE grade GUR 4120 was purchased from Ticona Engineering Polymer, China, with molecular weight of 5×10^6 g/mol and density of 0.93 g/cm^3. ZnO nanoparticles (99.9% purity) of less than 100 nm in particle size and silane coupling agent 3-aminoproplytriethoxysilane (3-APTES) were purchased from Sigma Aldrich (M) Sdn. Bhd.

Sample preparation

The process of surface treatment on ZnO nanoparticles is shown in Figure 1. Silane-treated ZnO nanoparticles were obtained after being dried in oven at 100°C. ZnO nanoparticles with different filler loading of 0 to 20 wt% were mixed with UHMWPE using dry mechanical ball mill. The milling process took 4 h to complete: 2 h each for both clockwise and anti-clockwise directions. After mixing, the compound was transferred to a mold of $90 \times 90 \times 9$ mm in dimension. The samples were preheated for 10 min and hot-pressed at a temperature of 160°C for 15 min. The nano-ZnO/UHMWPE composite

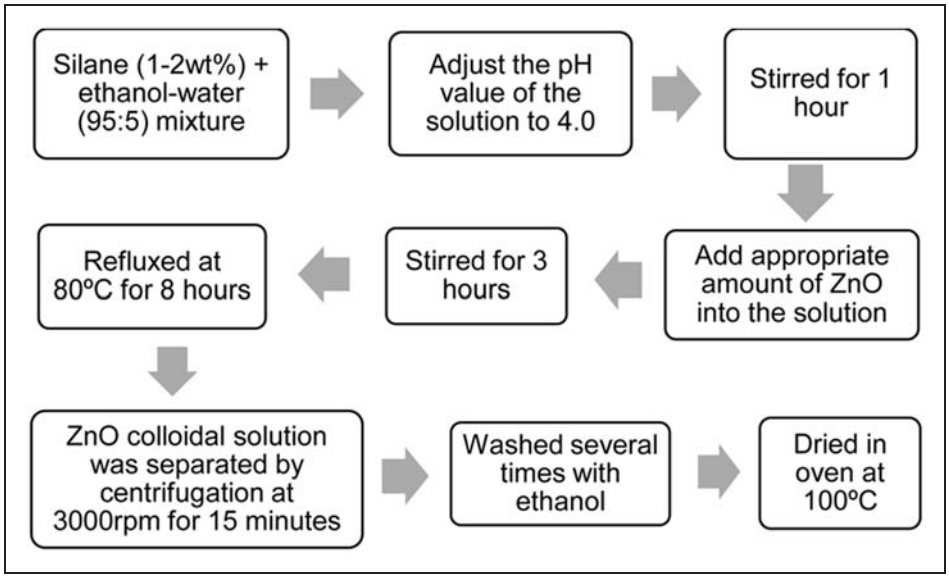

Figure 1. Surface treatment of the ZnO nanoparticles.

was obtained after being cooled to room temperature. The composites were then trimmed and cut into an appropriate dimension for testing.

Mechanical tests

Compression, tensile and micro-hardness tests were carried out to evaluate the mechanical properties of the pure UHMWPE and nano-ZnO/UHMWPE composites. The compression and tensile tests were performed using Instron 3360 universal testing machine. The dimensions for compression samples were $9 \times 9 \times 25$ mm with a compression length (l) of 25 mm. The ratio of l/d of all the samples is approximately 2.8, resulting in a double-barreling deformation. All tests were performed with a crosshead speed of 5 mm/min up to a compression displacement of 10 mm, unless early failure occurs. The mean and standard deviation of compressive strength and modulus for five samples were obtained from the stress–strain curves. Tensile test was determined according to ASTM D638 (Type IV) with a crosshead speed of 5 mm/min. The mean and standard deviation of tensile strength, tensile modulus and elongation at break for 5 samples were obtained from the stress-strain graphs. The micro-hardness test was performed using Shimadzu micro-hardness tester Type-M. The Vickers micro-hardness number (H_{mv}) was obtained from the following equation:

$$H_{mv} = 1854.4 \times \frac{P}{d^2} \quad (1)$$

where P is the test load on the diamond indentor (g), d is the diagonal length measurement of the pyramidal indentation on the sample surface (μm). The test load for the micro-hardness indentation was 50 g with the indentation time of 10 s on the surface of the sample. A total of six measurements were taken on each sample for the mean and standard deviation calculations to be done.

Tribological properties

The wear and frictional tests of the composites were performed using DUCOM TR-20 pin-on-disc (POD) tester according to ASTM G99-05 standard. The samples were cut into pin shapes with dimensions of $9 \times 9 \times 30$ mm. Silicon carbide (SiC) abrasive paper of grit 1200 ($R_a = \sim 5$ μm) was pasted on the cylindrical disc surface to act as sliding counterface. The test was carried out in a dry sliding condition for 600 s using different variables i.e. applied loads (5, 10, 15, 20, 25, 30 and 35 N corresponding to 617.3, 1234.6, 1851.9, 2469.1, 3086.4, 3703.7 and 4321.0 N/m^2 contact pressure) and sliding speeds (0.209 and 0.419 m/s corresponding to 100 and 200 r/min of the rotating motor). The weight loss due to wear of each sample was measured before and after the test using Shimadzu (AUW 220D) electronic analytical balance with ±0.1 mg accuracy. The weight loss was then converted to volume loss by dividing it with the specific composite density. The frictional force and coefficient of friction (COF) of the samples during the test was recorded in Winducom 2010 software. The average COF was calculated from the data obtained.

Worn surfaces and transfer film analysis

The worn surfaces and transfer films of the samples were examined using the Hitachi TM-3000 Tabletop

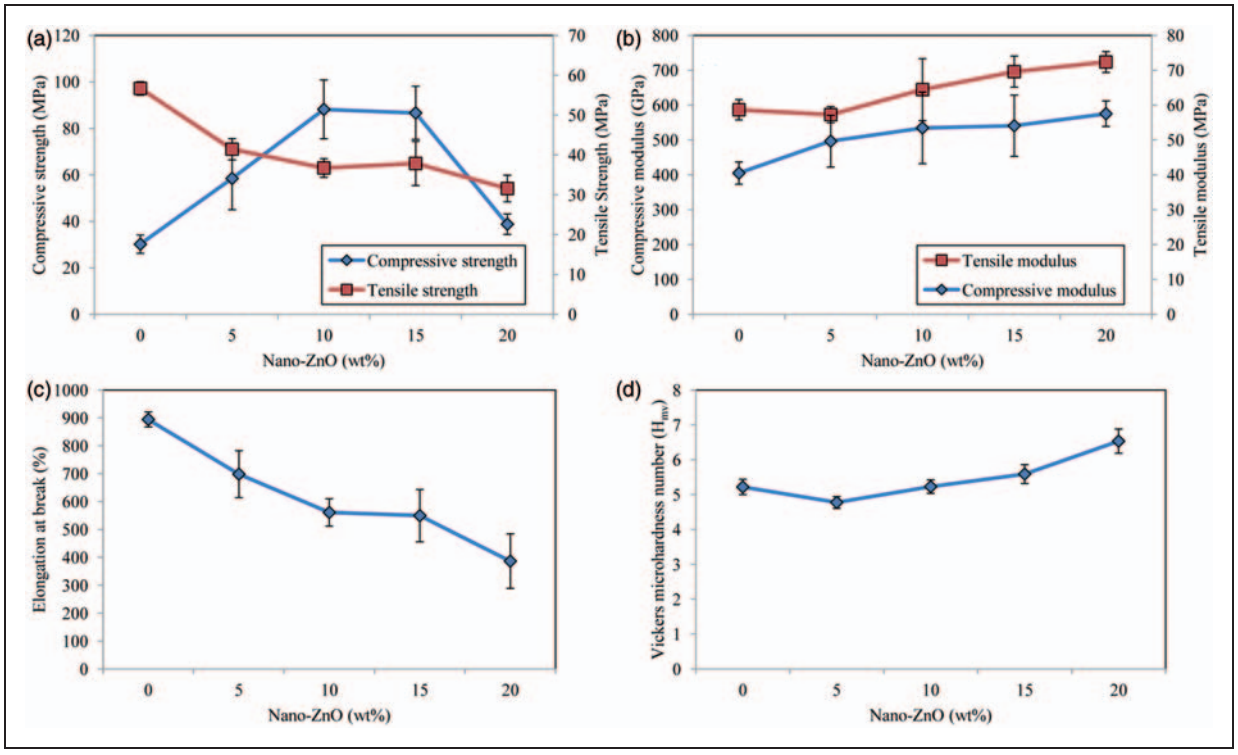

Figure 2. Mechanical properties of nano-ZnO/UHMWPE composites as function of filler loading: (a) compressive and tensile strength, (b) elastic modulus, (c) elongation at break and (d) Vickers micro-hardness.

scanning electron microscope (SEM). Before scanning, the worn surfaces of the composites were coated with gold/palladium (Au-Pd) using a vacuum sputter chamber. The wear debris and the transfer films were also observed using the Hitachi TM-3000 Tabletop SEM.

Antibacterial evaluation

Single colony bacteria samples were inoculated to 20 mL of nutrient agar broths under aseptic conditions. It was then incubated at 37°C for 12 h in a mechanical shaker. Then, 200 µL of 0.1 McFarland equivalent culture broth of those gram-negative *Escherichia coli* (*E. coli*; NCTC 10418) and gram-positive *Staphylococcus aureus* (*S. aureus*; NCTC 8532) were introduced and spreaded on separate Muller-Hinton agar plates. Then, 0.5 cm × 0.5 cm sized UHMPE control and modified samples were placed on the plates and incubated at 37°C for 24 h. The plates were observed for the antimicrobial activity by observing inhibition zones.

Results and discussion

Mechanical properties of the nano-ZnO/UHMWPE composites

The compressive strength, tensile strength, elastic modulus and microhardness of the nano-ZnO/UHMWPE composites as a function of filler loading are shown in Figure 2. From Figure 2(a), the compressive strength increases for the 5, 10 and 15 wt% nano-ZnO filler loadings. The compressive strength reaches the maximum value of 87.166 MPa at 10 wt% of nano-ZnO filler loading. It is an increase of approximately 190% as compared to the pure UHMWPE (30.256 MPa). When the nano-ZnO added to 20 wt% loading, the compressive strength shows decreases dramatically. The compression behavior is an important factor in evaluating the application of materials under continuous pressure such as load-bearing devices. During the compression of the samples, the deformation of the samples will cause submicroscopic cracks on the UHMWPE matrix. The nano-ZnO filler may occupy the submicroscopic cracks of the UHMWPE matrix when subjected to stress. In addition, the presence of rigid fillers will restrict the chain mobility and deformation due to the frictional force of the particles.[28] Therefore, it increases the stress capacity of the composites and leads to higher compressive strength after the addition of the nano-ZnO filler. The decrease in compressive strength at 20 wt% shows that the effectiveness of stress transfer between nano-ZnO and UHMWPE is reduced due to the decrease in filler inter-particle distance at higher filler loading and this leads to agglomeration in the composite system. On the other hand, for the tensile strength, nano-ZnO/UHMWPE composites show a decreasing trend with

the increase of nano-ZnO loadings. The reinforcing effect of nano-ZnO in UHMWPE under tension mode was not as significant as in compression mode. It is well known that the tensile strength of the polymer composites depends greatly on the interface adhesion between filler and matrix. In this study, the reduction in tensile strength indicates that the adhesion between nano-ZnO and UHMWPE matrix is not significant to promote greater interfacial bonding which would enhance the tensile strength value. This may be partly due to the concentration of silane used at 1 wt% that may not be at an optimum level to enhance tensile strength. Further work need to be done to investigate the optimum loading of silane in this composite system.

The elastic modulus of nano-ZnO/UHMWPE composites under both compression and tensile tests as a function of filler loading are shown in Figure 2(b). In general, the elastic modulus of UHMWPE nonlinearly increases with the addition of ZnO nanoparticles. The elastic modulus is increased by ~30% when 20 wt% ZnO nanoparticles were added to UHMWPE matrix. This is due to the increase of rigid ZnO nanoparticles in the UHMWPE matrix. Thus, the composites' rigidity and stiffness increased with increasing filler loading. The elongation at break of UHMWPE showed a decrease with the addition of nano-ZnO as shown in Figure 2(c). This shows that the ductility and degree of plastic deformation were reduced with increasing nano-ZnO loadings. The differences in elastic modulus and surface hardness correspond to the bulk internal structure and specific surface properties, respectively. Figure 2(d) shows the Vickers micro-hardness of nano-ZnO/UHMWPE composites. It can be seen that the Vickers micro-hardness number gradually increased after the addition of nano-ZnO into UHMWPE matrix. The Vickers micro-hardness number reaches the maximum value at 20 wt% filler loading with an increase of ~18.9% as compared to pure UHMWPE. The improvement of the micro-hardness may be attributed to the rigid nano-ZnO fillers in the polymer. The plastic deformation during the indentation was restricted by the presence of nano-ZnO fillers. The increase in nano-ZnO filler loading would reduce the fillers' interparticle distance. Therefore, the increase in the Vickers micro-hardness number was observed with the increasing nano-ZnO filler loadings.

Tribological properties of nano-ZnO/UHMWPE composites

Figure 3 shows the volume loss due to wear of ZnO/UHMWPE composites in comparison to pure UHMWPE as a function of filler loading and applied load at different sliding speeds. A lower volume loss would directly translate into a higher wear resistance. Generally, the volume loss of all the samples increased with increasing applied load and sliding speed. This is due to the increase in the real contact area between the sample surface and the counterface asperities when increase in applied load.[29] During the sliding wear test, all the samples were subjected to load and shear stress from sliding action by the counterface. Eventually, parts of the composite surface would be detached out from the bulk composite body as wear debris due to the shear stress acted on the sample surfaces. Increasing the applied load will increase penetration depth of the counterface asperities into the samples surfaces. This will result in severe wear on the composite surface. Therefore, increasing applied loadings correspond to increasing volume loss of composites.

The filler loading of nanoparticles has a significant role in tailoring the tribological properties of the polymer composites. Figure 3 shows a decrease of wear volume loss of UHMWPE when reinforced with ZnO nanoparticles. In general, nano-ZnO/UHMWPE composites showed lower volume loss as compared to pure UHMWPE for both sliding speed tested; 10 wt% nano-ZnO/UHMWPE composites exhibits the lowest volume loss as compared to other filler loadings. The improvement of wear resistance by ZnO nanoparticles on UHMWPE may be due to the increase in mechanical strength and stress sharing between filler and matrix. ZnO nanoparticles act as stress transfer medium, preventing the stress from transferring directly to the UHMWPE matrix. The embedded ZnO nanoparticles in UHMWPE matrix would increase the required sliding force for the surface materials to detach from the bulk composite body. Thus, the decrease in the volume loss is observed after the incorporation of ZnO nanoparticles in UHMWPE matrix. The wear behavior is also related to the mechanical properties of the composite. As shown in Figure 2(c), the micro-hardness value was increased after the addition of nano-ZnO. The volume loss decreases as the hardness of the composite increases. This is because the plastic contact area of composite surface to abrasive asperities counterface will reduce with increasing composite hardness.[30] Therefore, the wear resistance increases. However, the increase in surface hardness is not necessarily accompanied by the improvement in wear resistance. As discussed above, 10 wt% nano-ZnO/UHMWPE composite showed higher wear resistance as compared to 15 wt% and 20 wt% nano-ZnO/UHMWPE composites, which possess higher micro-hardness value than 10 wt% nano-ZnO/UHMWPE. Apart from the mechanical properties, the wear behavior of polymer composites can be influenced greatly by other factors such as transfer film formed on the counterface. The better filler-matrix interaction due to the presence of silane

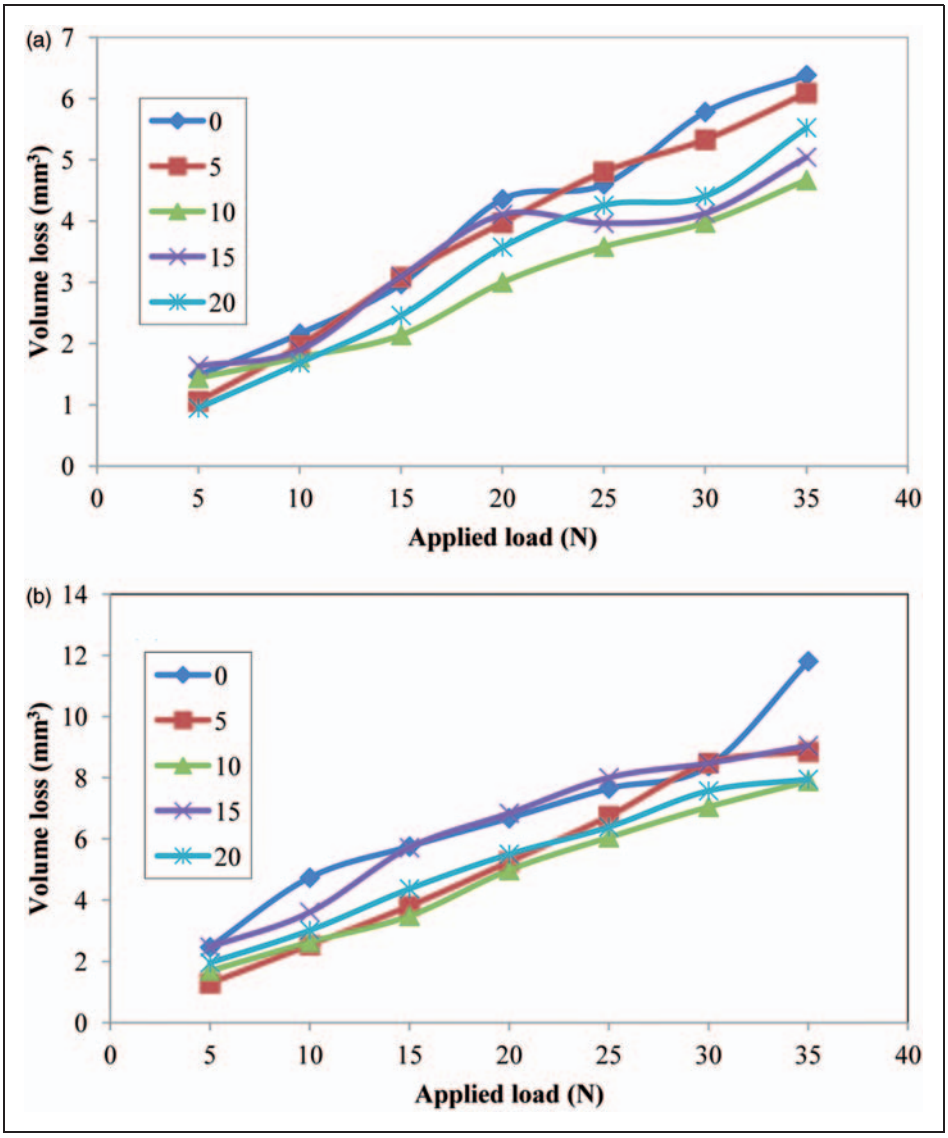

Figure 3. Volume loss of the nano-ZnO/UHMWPE composites as a function of applied load and filler loadings at sliding speed of (a) 0.209 m/s and (b) 0.419 m/s. The lines connecting data points represent data trends of volume loss.

coupling agent was also one of the contributing factors that increased the wear resistance of the composites.

The volume loss of nano-ZnO/UHMWPE composites reached the minimum at 10 wt% filler loading for both sliding speeds of 0.209 m/s and 0.419 m/s. This can be explained by the close relationship between the wear of the composites and the filler loading. The fillers embedded in UHMWPE matrix and the distributions of fillers are approximately uniform when the fillers quantity is below the optimum amount.[11] Likewise, the dispersion of the filler became poor when the filler loading is above the optimum amount, which is 10 wt% in this work. This is because at higher filler loading, the filler inter-particle distance is reduced and particles tend to agglomerate.[31] The agglomeration of fillers would cause severe abrasive wear whereby the ZnO nanoparticles could be easily detached from the matrix in high filler loading condition. Therefore, the increase in filler loading above the optimum level will increase the volume loss of the composites.

Figure 4 shows the average COF of different filler loading of nano-ZnO/UHMWPE composites as a function of applied loads. In general, the average COF of all the nano-ZnO/UHMWPE composites show lower COF as compared to pure UHMWPE under both sliding speeds. The 20 wt% nano-ZnO/UHMWPE composites exhibited the lowest average COF as compared to pure UHMWPE and other nano-ZnO/UHMWPE composites. During the test, the micro-cutting and micro-plowing of hard asperities on the SiC papers against the

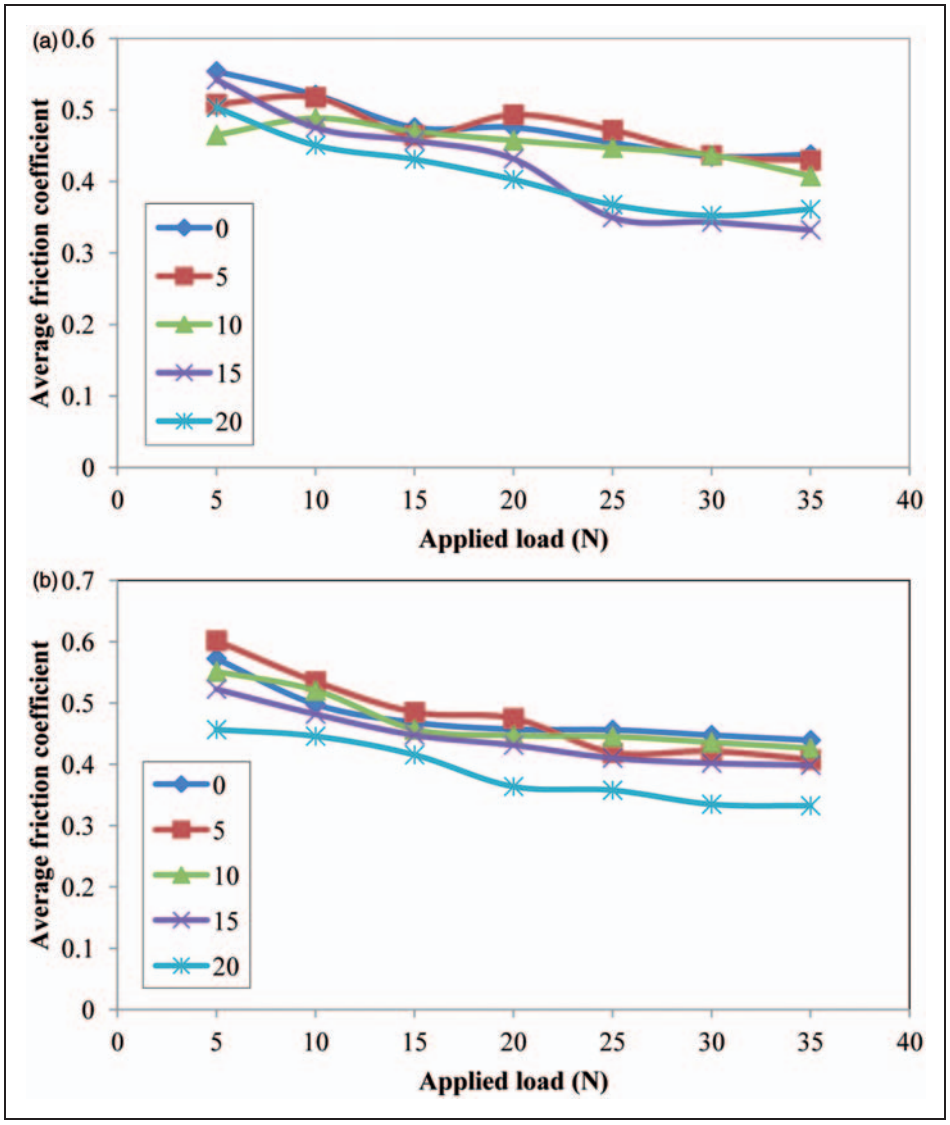

Figure 4. Average COF of the nano-ZnO/UHMWPE composites as function of applied load and filler loading at sliding speed of (a) 0.209 m/s and (b) 0.419 m/s. The lines connecting data points represent data trends of COF value.

composite surfaces would cause the formation of a layer of the deposited wear debris. Parts of the wear debris would then be deposited in the asperities contact region and cushioning part of the sharp asperities against composite surfaces. Subsequently, frictional contact will take place on the deposited wear debris and abrasive asperities. The reduction in the average COF of the UHMWPE after reinforcement with nano-ZnO may be due to the rolling effect of the ZnO nanoparticles. ZnO nanoparticles will act as third-body medium during sliding wear in reducing the shear stress of the counterface asperities exerted on the composites surfaces. The rolling effect of the nanoparticles has been well described by Chang et al.[32] They reported that the friction coefficient was significantly reduced for epoxy filled with short carbon fiber and graphite particles composites after reinforcements with TiO_2 nanoparticles. Therefore, the decrease in average COF was observed with the increase of ZnO nanoparticles in UHMWPE composites. The average COF of the composites remain almost the same when sliding speed increased from 0.209 to 0.419 m/s. This shows that the average COF of the UHMWPE composites is less affected by the tested sliding speeds i.e. 0.209 and 0.419 m/s. The results also show that the average COF of the nano-ZnO/UHMWPE composites decrease with increasing applied loads from 5 to 35 N. The real contact between the surface of composite and abrasive asperities is the reason for a decrease in COF with increasing applied loads.[33]

Observation of worn surfaces and transfer films of nano-ZnO/UHMWPE composites

Figure 5 show the SEM micrographs of the worn surfaces on different filler loadings of nano ZnO-reinforced UHMWPE composites on both sliding speeds of 0.219 and 0.419 m/s at 35 N applied load. The white arrows indicate the sliding direction. Grooves, furrows and plastic deformation caused by the continuous sliding action of the abrasive asperities of the counterface were observed for all composites. From Figure 5(a), deep grooves and severe plastic deformation were observed on pure UHMWPE due to the micro-cutting and micro-ploughing of the abrasive asperities. The severity of wear on the worn surface of UHMWPE was reduced by ZnO nanoparticles reinforcement. Shallower grooves and less worn surfaces are observed for 10 and 20 wt% of nano-ZnO/UHMWPE composites compared to pure UHMWPE as shown in Figure 5(b) and (c). The white portions are ZnO-rich region. During the sliding wear test, parts of the UHMWPE surface were detached out from the bulk body by the micro-cutting action of counterface asperities and subsequently form a thin layer of accumulative polymer wear debris at the interface. ZnO nanoparticles act as a third-body medium to support part of the shear stress and thus prevent the surface material being easily removed from the UHMWPE bulk body. Therefore, less grooves and furrows were observed on nano-ZnO/UHMWPE composite surfaces compared to pure UHMWPE. The improvement in mechanical properties of the nano-ZnO/UHMWPE composites as compared to pure UHMWPE also contributed to less grooves and reduction of plastic deformation on the contacting surfaces. The worn surfaces of all samples were more severe under sliding speed of 0.419 m/s (Figure 5(d)–(f)) as compared to 0.209 m/s (Figure 5(a)–(c)). Severe wear and deep grooves were also observed for pure UHMWPE as compared to nano-ZnO/UHMWPE composites. The worn surfaces of 20 wt% nano-ZnO/UHMWPE composites show agglomeration of nano-ZnO (Figure 5(c) and (f)). This may be due to the high loading of ZnO nanoparticles. The wear mechanism was transformed from severe to mild wear upon reinforcing ZnO nanoparticles into UHMWPE matrix.

Currently, close attention is devoted to the transfer films formed on the counterface after the wear test in order to have the full understanding of wear mechanism of the materials. The quality of transfer films plays a significant role in the wear behavior of polymer composites. It was confirmed that uniform transfer films produced by the polymer composites will result in lower wear loss.[16] The transfer film deposited on the

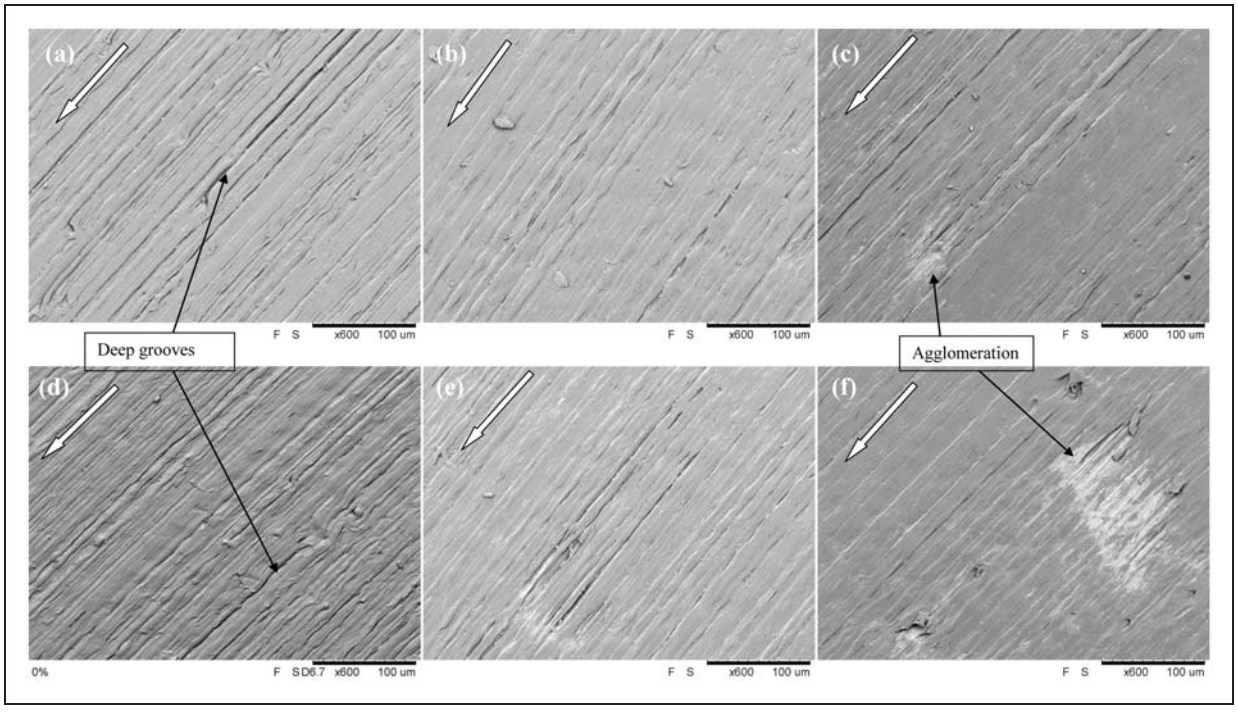

Figure 5. SEM micrographs of the worn surfaces under sliding speed of 0.209 m/s at 35 N for (a) Pure UHMWPE (b) 10 wt% nano-ZnO/UHMWPE (c) 20 wt% nano-ZnO/UHMWPE and under sliding speed of 0.419 m/s at 35 N (d) Pure UHMWPE (e) 10 wt% nano-ZnO/UHMWPE (f) 20 wt% nano-ZnO/UHMWPE.

counterface would cushion the sample from direct contact with the counterface asperities and leads to reduction in wear volume loss. As such, the transfer film and wear debris particles formed after wear test were studied. The transfer films for pure UHMWPE, 10 wt% and 20 wt% nano-ZnO/UHMWPE composites under 0.209 m/s sliding speeds at 35 N applied load were shown in Figure 6. It can be seen that the pure UHMWPE transfer films show bulk and fragmented wear debris on the abrasive paper counterfaces as compared to 10 and 20 wt% of nano-ZnO/UHMWPE composites (Figure 6(a)–(c)). The transfer film of pure UHMWPE also shows an uneven distribution of the wear debris and non-uniformity on the counterface. This will cause incomplete coverage of transfer films on the counterface asperities. The 10 wt% and 20 wt% nano-ZnO/UHMWPE composites formed more thinner and uniform transfer film as compared to pure UHMWPE. The uniform coverage of the transfer films on the counterface will effectively cover up the exposure of the counterface asperities and leads to less worn out of the materials from the contacting surfaces. Hence, wear loss can be reduced.

Further examination using SEM microscopy on wear debris particles of transfer films after the wear test is illustrated in Figure 7. Larger wear debris was noticed for pure UHMWPE as compared to nano-ZnO/UHMWPE composites. The incorporation of ZnO nanoparticles into UHMWPE produced smaller and finer wear debris particles. The generation of fine wear debris corresponded with increasing the wear resistance of polymer and its composites.

Antibacterial property

Materials that possess antibacterial property are advantageous in medical or implant applications. The antibacterial property of nano-ZnO/UHMWPE composites against both *E. coli*, a gram-negative bacterium and *S. aureus*, a gram-positive bacterium, was evaluated qualitatively using the agar diffusion test. The test results after 24 h bacterial inhibition are shown in Figures 8 and 9. This test is a qualitative screening to evaluate the antibacterial activity of the composite surfaces. The width measurement of the inhibition zone was not taken for this test. It was observed that UHMWPE shows some extent of antibacterial activity against both *E. coli* and *S. aureus* after the introduction of nano-ZnO reinforcement. For inhibition against *E. coli*, a significant inhibition zone for 5, 10 and 20 wt% nano-ZnO was observed in between the contact of the composites and the culture media (Figure 8(a), (b) and (d)). Meanwhile for 15 wt% nano-ZnO/UHMWPE, only a slight inhibition zone was observed (Figure 8(c)). For inhibition against *S. aureus*, the 5, 15 and 20 wt% nano-ZnO/UHMWPE show significant inhibition (Figure 9(a), (c) and (d)) whereas for 10 wt% nano-ZnO/UHMWPE composite, only slight inhibition was

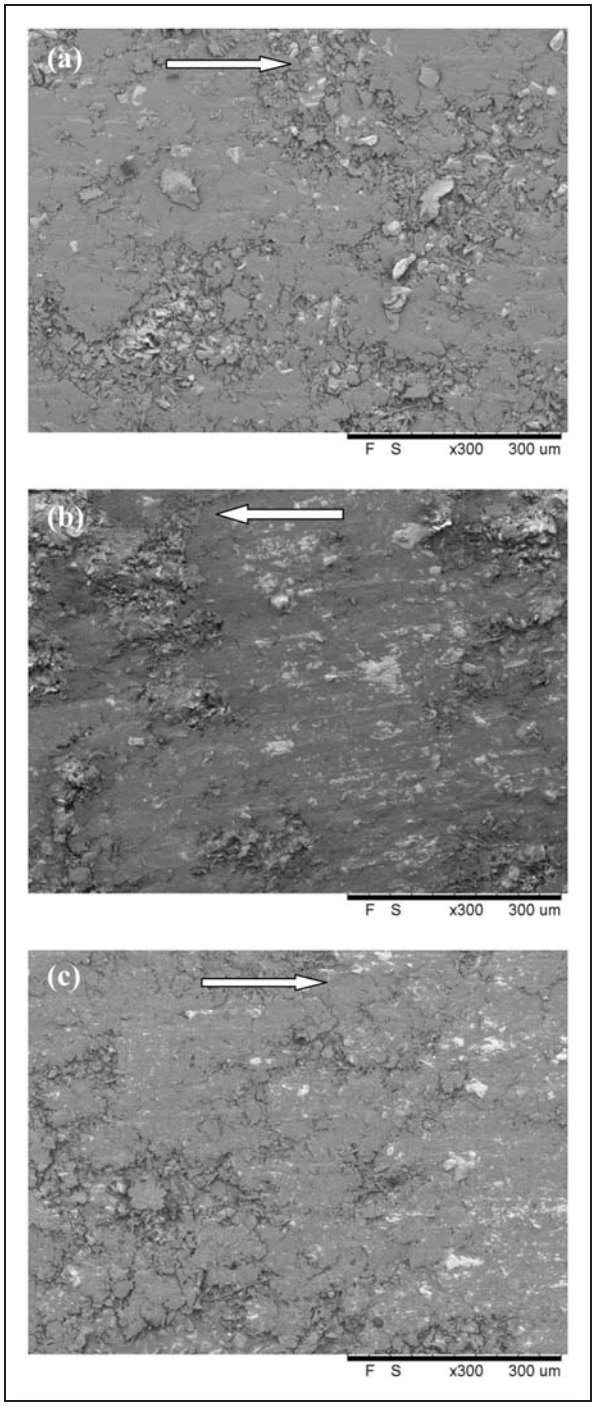

Figure 6. SEM micrographs of the transfer films formed after sliding wear test under 35 N applied load at 0.209 m/s for (a) Pure UHMWPE, (b) 10 wt% nano-ZnO composite and (c) 20 wt% nano-ZnO composite. Arrow indicates the sliding direction.

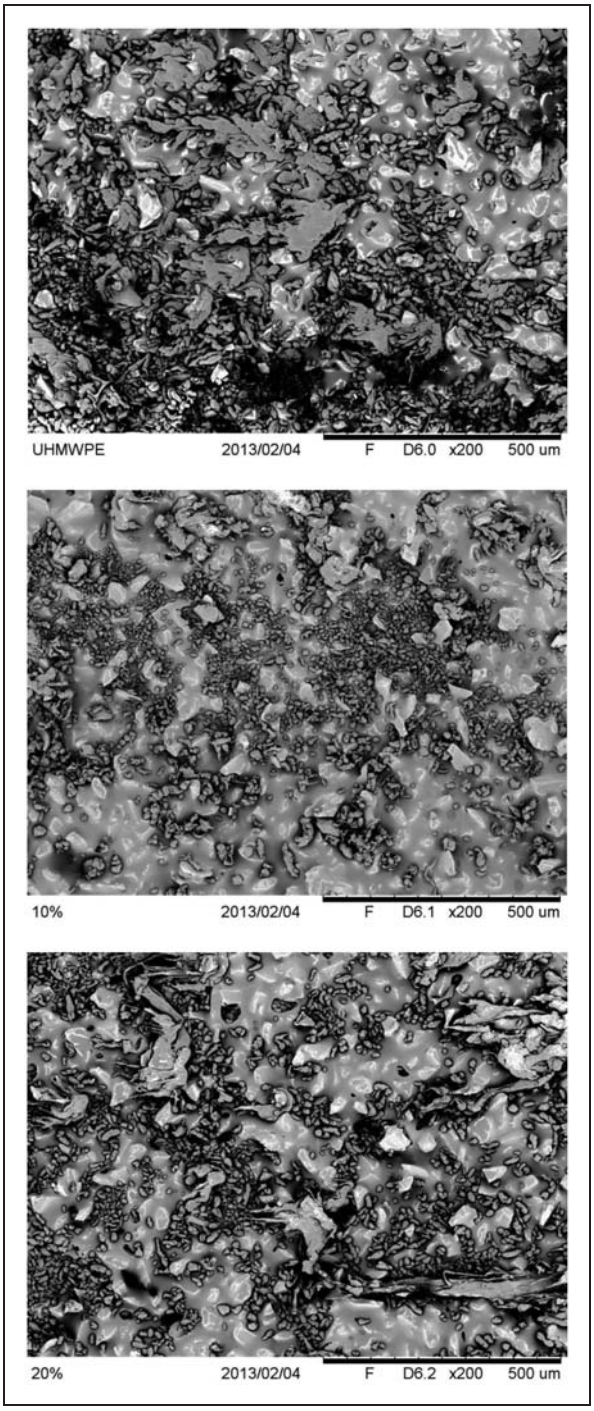

Figure 7. SEM micrographs of wear debris particles of (a) Pure UHMWPE, (b) 10 wt% nano-ZnO composite and (c) 20 wt% nano-ZnO composite at 0.419 m/s and 35 N applied load.

observed (Figure 9(b)). Antibacterial activity of ZnO has been investigated by many researchers but requires further studies to understand an exact mechanism. Kasemets et al.[34] propose that the release of Zn^{2+} ions causes the toxicity to bacteria while Zhang et al.[19] propose that the reaction of nanoparticles with cells result in the antibacterial activity. Jalal et al.[35] and Gordon et al.[36] propose that the formation of reactive oxygen species (ROS) causes the activity. The opposite charges exchange between ZnO and bacteria will generate electrostatic force and also lead to cell damage and inhibition growth of bacteria surround the composite samples.[37] Therefore, the inhibition of the bacterial growth region can be seen in the nano-ZnO/UHMWPE composites. It is therefore worth assuming that higher filler loadings of nano-ZnO will offer better antibacterial activity. However, this statement does not apply to the test against both *E. coli* and *S. aureas* for 5, 10 and 15 wt% nano-ZnO filler loadings in nano-ZnO/UHMWPE composites. This is because the composites do not contain the appropriate amount of nano-ZnO on the surfaces. This antibacterial test mainly depended on the exposure of nano-ZnO filler on the composite contacting surfaces through the culture medium. The nano-ZnO is randomly distributed in the composites. Therefore, the inconsistency of the surfaces containing nano-ZnO in contact with culture media may be the reason for the indirect proportional antibacterial activity with the increasing filler loading. Antibacterial activity is shown when the ZnO is in contact with the bacteria. ZnO nanoparticles are well binded to the UHMWPE matrix, so that it does not readily diffuse into the agar medium, which causes smaller zone of inhibition present. For the 20 wt% nano-ZnO/UHMWPE composites, greater bacterial inhibition zone was observed as compared to 5, 10 and 15 wt% nano-ZnO/UHMWPE composites. This effective antibacterial activity was due to high loadings of antibacterial agent nano-ZnO in the composites. Higher loadings of nano-ZnO will increase the exposure of nano-ZnO on the composites surfaces. The leaching process initiated by nano-ZnO into the agar culture medium will prevent the growth of bacteria. Hence, a large inhibition zone was produce and observed for 20 wt% nano-ZnO/UHMWPE composites. In conclusion, the UHMWPE is shown to possess antibacterial activity when reinforced with nano-ZnO in the variation of 5–20 wt% filler loading. However, further work is needed to enhance the dispersion and ensure the consistency of nano-ZnO exposure on the composite surfaces in order to maximize the antibacterial property of nano-ZnO in UHMWPE.

Conclusions

The present work attempts to assess the effect of ZnO nanoparticles on the mechanical, tribological and antibacterial properties of UHMWPE. The addition of ZnO nanoparticles into the UHMWPE has led to further improvement in tribological behavior of UHMWPE and certain mechanical properties such as compression

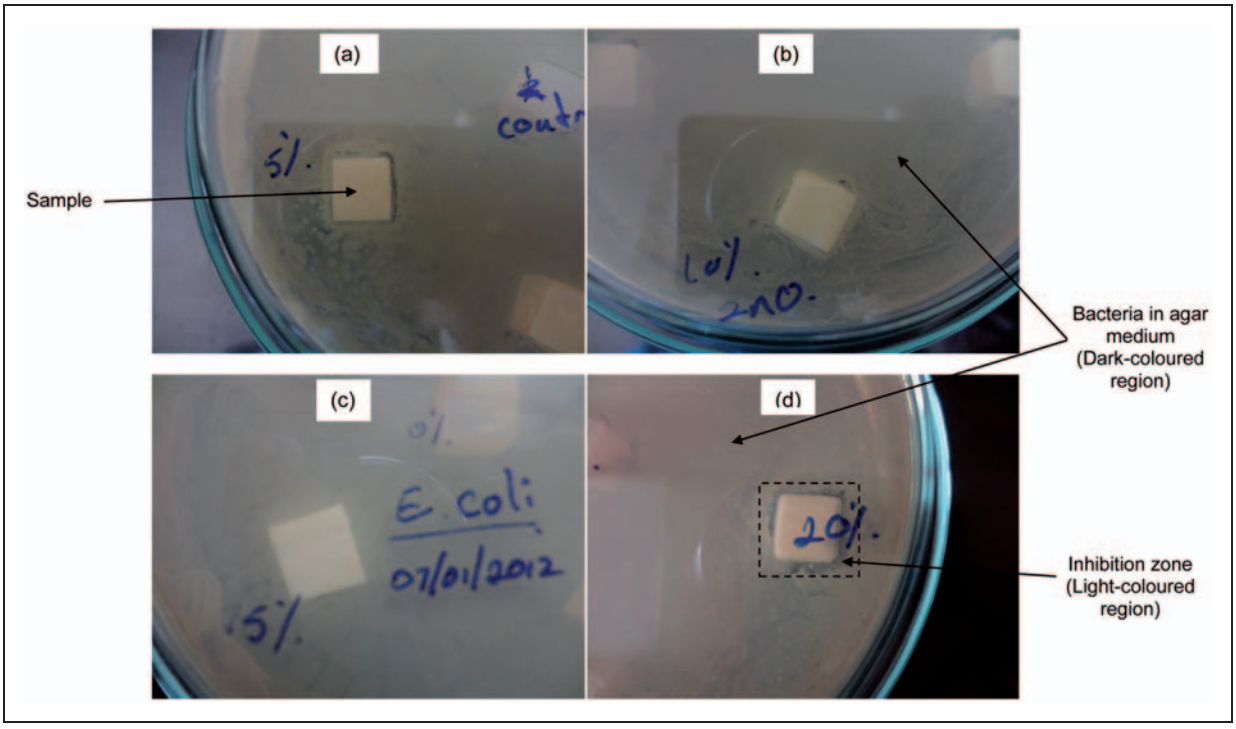

Figure 8. Images show antibacterial activities of nano-ZnO/UHMWPE composites against *E. coli*. at (a) 5 wt%, (b) 10 wt%, (c) 15 wt% and (d) 20 wt% of nano-ZnO loadings. Light-coloured regions indicate the antibacterial zones meanwhile dark-coloured regions represent well-grown bacteria.

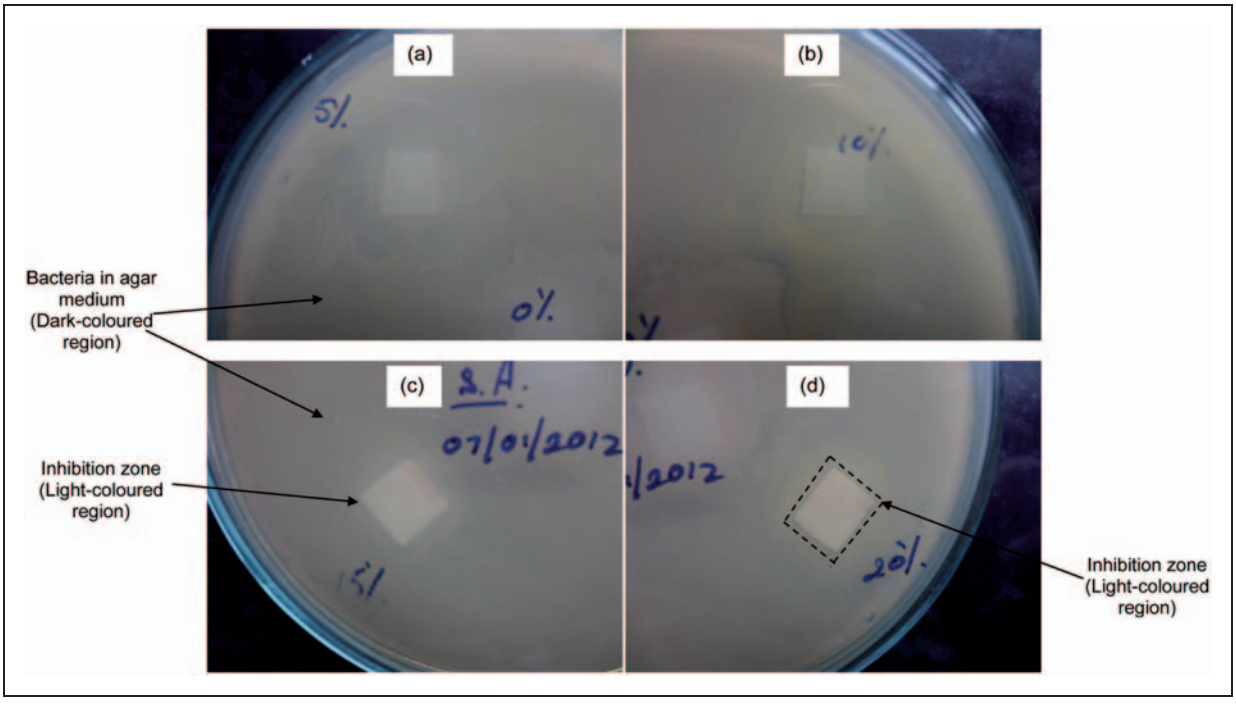

Figure 9. Images show antibacterial activities of nano-ZnO/UHMWPE composites against *S. aureus* at (a) 5 wt%, (b) 10 wt%, (c) 15 wt% and (d) 20 wt% of nano-ZnO loadings. Light-coloured regions indicate the antibacterial zones meanwhile dark-coloured regions represent well-grown bacteria.

properties and micro-hardness. The compressive strength shows a maximum at 10 wt% nano-ZnO filler loading. The compressive modulus, tensile modulus and Vickers micro-hardness of nano-ZnO/UHMWPE composites increased with increasing filler loading. However, addition of nano-ZnO to UHMWPE reduced the tensile strength and elongation at break. The wear resistance of UHMWPE can be improved by the addition of ZnO nanoparticles with the maximum wear resistance being found at 10 wt% under both sliding speeds of 0.209 m/s and 0.419 m/s. The average COF of UHMWPE was decreased by the reinforcement of ZnO nanoparticles. The worn surfaces of nano-ZnO/UHMWPE composites show shallower grooves and less plastic deformation as compared to pure UHMWPE. The additions of ZnO nanoparticles in UHMWPE reduce the severity of the sliding wear by producing more uniform transfer films and finer wear debris. The incorporation of nano-ZnO to the UHMWPE demonstrated antibacterial activity against *E. coli* and *S. aureus*. In nano-ZnO/UHMWPE composites, the 20 wt% exhibited higher antibacterial activity as compared to other filler loadings.

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