Effects of Hybrid Fillers on the Wear, Tensile and Morphology Properties of UHMWPE/Chitosan-ZnO Composites

MOHAMAD HAZWAN SUBLI[1], MOHD FIRDAUS OMAR[1]*, IOAN GABRIEL SANDU[3,4], NIK NORIMAN ZULKEPLI[1,2], MOHD MUSTAFA AL BAKRI ABDULLAH[1,2], ANDREI VICTOR SANDU[3,4]*

[1]Center of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), KompleksPengajianJejawi 2, 02600 Arau, Perlis, Malaysia

[2]Faculty of Engineering Technology (FETech), Universiti Malaysia Perlis (UniMAP), 01000, P.O.Box, D/A Pejabat Pos Besar, Kangar, Perlis, Malaysia

[3]Gheorghe Asachi Technical University of Iasi, Faculty of Materials Science and Engineering, 41A D Mangeron Blv., 700050, Iasi, Romania

[4]Romanian Inventors Forum, 3 Sf. P. Movila Str., L11, 700089, Iasi, Romania

This is a study between ultra-high molecular weight polyethylene (UHMWPE) reinforced with zinc oxide (ZnO) under various filler loadings. These composites were then incorporated with chitosan for hybridization purposes. All composite specimens were prepared by using a hot compression mold through dry ball milling process. Wear and tensile tests were carried out using specific experimental techniques namely pin on disc method as well as universal testing machine, respectively. Results indicated that the addition of ZnO filler up to optimum percentage (12 wt%) has significantly increase the wear resistance of tested composites, in accordance with the minimal weight loss. Contrary, the incorporation of chitosan (1, 2, 3 wt%) in the optimum percentage (12 wt%) of UHMWPE/ZnO composites has slightly reduced the wear resistance of the hybrid composites. For the tensile properties point of view, the results indicated that the yield strength, tensile strength and Young modulus were perpendicularly increased with increasing of ZnO filler loading, up to 12 wt%. Meanwhile, the elongation at break show contradict trend where it was gradually decreased with an increasing ZnO particle loadings. Interestingly, the incorporation of 2 wt% of chitosan in the optimum percentage (12 wt%) of UHMWPE/ZnO composites has further increased the yield strength as well as the elongation at break values of tested hybrid composites. Ultimately, the morphology analysis was also carried out in order to visually justify the state of hybridization and dispersion of fillers within UHMWPE matrix.

Keywords: ultra-high molecular weight polyethylene (UHMWPE), hybrid filler, wear resistance, tensile properties, morphology analysis

Ultra-High Molecular Weight Polyethylene (UHMWPE) has been used widely as joint prostheses material with articulating counter surfaces made of metals or ceramics since 1962 by Sir John Charnley [1]. UHMWPE are used in hip joints, knee joints, finger joints and dentures [2]. The use of UHMWPE is due to its characteristics in which it has low coefficient of friction, high wear resistance, good chemical resistance, resistance to chemical stress cracking, dimensional stability over a wide temperature range, high notched impact strength and high energy absorption at high stress rates [3]. In the aspect of biomaterials, UHMWPE has been chosen over other polymers especially because of its excellent wear resistance, suitable mechanical properties and biocompatibility in the physiological environment [4]. It is known that the mechanical properties of UHMWPE are directly related to its molecular weight, crystalline structure, chemical structure and thermal history. The increased intra-molecular cross-links of highly cross-linked UHMWPE are thought to behave better in terms of deformation and wear resistance.

The inert and hydrophobic nature of UHMWPE presents a challenge regarding composite processing and ultimate material properties due to the poor wet ability and interfacial adhesion [5]. The practice of UHMWPE as a composite matrix has been studied with numerous types of fillers, such as carbons (i.e. carbon black [6], carbon fiber [7], graphite [7] and carbon nanotube [8]), ceramics (i.e. kaolin [9], wollastonite [10], quartz [11], zirconium [12] and zeolite [13]), natural particles (i.e. natural coral [14]) or metals [15]. Incorporation of high strength fillers can be react as an effective reinforcement to the structure of the matrix which result in increment of the mechanical (i.e. tensile, impact, flexural and wear) and physical properties (i.e. micro-hardness). Other types of non-reinforcing fillers are also added to alter the chemical properties (i.e. biocompatibility, toxicity and corrosion) that are mostly related to biomaterials and nutriment related applications. For example, Chang et. al [16] speculated that the addition of 10 wt% of zeolite in UHMWPE has greatly reduced the tensile strength and elongation at break of the composite, meanwhile the modulus and impact strength were increased.

Currently, the hybridization of fillers in polymer composites has received remarkable attention from both scientists and industries due to its prominent of specific properties. However, there are very limited numbers of works that were concerned on hybrid composites of UHMWPE. Recent study by Gupta et al. [17] shows no significant enhancement on the mechanical performance of UHMWPE/HA/Al_2O_3/CNT. Meanwhile, Sui et al. [18] reported a contrary result with the one that has been reported by [19]. They speculated that the addition of CNTs into UHMWPE/HDPE with blend ratio of 3:7 resulted in the increase of the tensile strength and modulus properties of their tested composites. Those available works are still insufficient to build up the comprehensive understanding on the effect of filler hybridization in UHMWPE matrix

* email: firdausomar@unimap.edu.my; sav@tuiasi.ro

especially for medical applications. Hence, alternative effort is required to fulfill the lack of knowledge in this kind of specific area.

In this study, the chosen of ZnO and chitosan as hybrid filler was based on their nature ability to increase the mechanical, anti-microbial and biocompatibility of the current UHMWPE based products. Based on this concern, a series of experimental studies were purposefully designed to characterise those critical properties. In this paper, we are focused on the effect of ZnO-chitosan hybrid filler on wear, tensile and morphological properties of UHMWPE/Chitosan-ZnO composites. To achieve our goals, a series of UHMWPE/ZnO specimens with different ZnO ratios (i.e. 3-25 wt%) were tested and analyzed using established wear and tensile mechanical apparatus. Based on the optimum performance of UHMWPE/ZnO ratios, the chitosan particles (1-3 wt%) were then incorporated with UHMWPE/ZnO to produce hybrid ZnO-chitosan reinforced UHMWPE composites. As for morphological analysis, the fracture surfaces of the tested composites were observed under scanning electron microscope (SEM).

Experimental part

Materials and methods

The UHMWPE grade GUR4120 was supplied by Ticona Engineering Polymer, China, in powdered form, with a molecular weight of 5 X 10^6 g/mol and density of 0.93 g/cm^3. ZnO powder of less than 100 μm and Chitosan particles were supplied by Sigma-Aldrich.

Methodology

3, 7, 12 and 25 wt% of ZnO were mixed homogeneously with UHMWPE using dry mechanical ball milling. The mixing process took 4 h to complete: 2 h each for both clockwise and anti-clockwise directions. After mixing, the samples were pre-heated and hot pressed at temperature of 165°C for 15 min. The final product was obtained after cooling under room temperature in a controlled environment for 4 h. The same procedure was repeated for the incorporation of 1, 2 and 3 wt% of chitosan into optimum ratio of UHMWPE/ZnO composites to produce UHMWPE/Chitosan-ZnO hybrid composites.

Wear test

The wear test of UHMWPE/Chitosan-ZnO was executed using a pin-on-disc test rig according to ASTMG-99–95. The test samples were cut into square specimens with dimensions of 9x9x30 mm. Silicon carbide abrasive paper of grit 400 (~20 mm) was adhered on a stainless steel disc surface to act as an abrasive counter face to depict the sliding surface. The sample was clamped on the sample holder with the distance between the clamped samples and abrasive paper is kept constant at 21 mm. The samples were grazed against the abrasive paper in dry sliding conditions for 300 s using two different loads of 10 and 30 N, and sliding speeds of 0.03 and 1.01 m/s. The weight loss was measured using digital electronic balance ±1mg accuracy.

Tensile Test

The tensile properties of unfilled UHMWPE, UHMWPE/ZnO composites and UHMWPE/Chitosan-ZnO hybrid composites were determined according to ASTM D638 with minimum five specimens from each sample. The test was done by using Instron universal testing instrument at a crosshead speed of 20 mm/min. The tensile strength, yield stress, young modulus, and elongation at break for all samples were collected and analyzed for each samples. Five measurements were taken for each specimen, in order to quantify the average behaviour of the tested specimens.

Scanning Electronic Microscope Analysis

The tensile fracture surface analysis of the UHMWPE/ZnO and UHMWPE/Chitosan-ZnO hybrid composites was obtained using a Field Emission Scanning Electron Microscope (FESEM) (ZEISS SUPRA 35 VP). The specimens were prepared from cross sections of the fracture surface. The test specimens were attached to an aluminium mount with a carbon double-side, and a sputter, with a platinium layer, using a Palaron SC 515 sputter coater to eliminate the electron charging effect.

Results and discussions

Effect of Chitosan-ZnO filler loading on wear behavior of UHMWPE/ZnO composites

The wear tests were done on unfilled UHMWPE, 3, 7, 12, 18, 25 wt% of UHMWPE/ZnO and 1, 2, 3 wt% of chitosan added into the 12 wt% UHMWPE/ZnO and referred as PURE, Z3, Z7, Z12, Z18, Z25, C1, C2, and C3 respectively. The wear resistance of the UHMWPE/ZnO composites was increased with the ZnO content up to 12 wt%, as depicted in figure 1. Above that the 12 wt% of ZnO particles, the UHMWPE/ZnO composites had started to show decrement pattern. Statistically, it can be seen that the UHMWPE with 12 wt% of ZnO particles had recorded the highest wear resistance at speed of 0.03 m/s and 1.01 m/s but with the same load of 10 N. This was due to an effective protection made by the filler within the UHMWPE matrix [16]. It was believed that the introduction of ZnO particles has sheltered the UHMWPE from being directly in contact with the surface of the abrasive media (i.e. sand paper). A different pattern has been obtained when the load was increased to 30 N, at speed of 0.03 m/s, the weight loss was lowest at 3 wt% of ZnO addition and increased with further addition of ZnO. The weight losses of all specimens were below than that of relative weight loss of the unfilled samples except for speed of 1.01 m/s with 30 N of load. This combination sees that the weight loss of the composite of all combination were at least 66 % more compared the weight of unfilled sample. This phenomenon is attributed to the weak filler-matrix interaction and has failed to withstand the higher load of 30 N and speed of 1.01 m/s [16, 20]. Further wear analysis was carried out on the UHMWPE/Chitosan-ZnO hybrid composites with various chitosan loadings. Unfortunately, we found that the incorporation of chitosan has shown slight reduction in terms of wear resistance as compared to the 12 wt% of UHMWPE/ZnO composite. This might be due to the variation of individual wear resistance between chitosan and ZnO particles. Chitosan with lower friction coefficient as compared to ZnO particles may lower down the effectiveness of the protection within UHMWPE matrix towards the surface of the abrasive media.

Effect of Chitosan-ZnO filler loading on tensile properties of UHMWPE/ZnO composites

The experimental results in this study indicate that the composition of ZnO in UHMWPE has significant influence on the tensile properties of UHMWPE/ZnO composites, as portrayed in figure 2. For example, the addition of 3, 7 and 12 wt% of ZnO in the UHMWPE matrix had recorded 10.56, 12.27 and 28.99 % increment of tensile strength than that of unfilled UHMWPE. As the weight percentages of ZnO added to UHMWPE matrix were increased to 18 and 25 wt%, the tensile strength were dropped about 1.05 and 15.63 % below the value of unfilled UHMWPE, respectively.

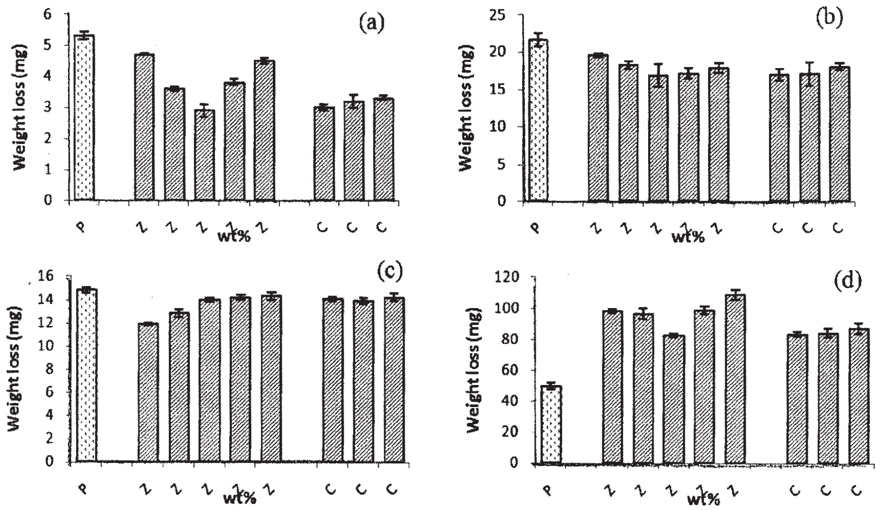

Fig. 1. The weight loss by pin-on-disc method (a) load of 10 N at 0.03 m/s (b) load of 10 N at 1.01 m/s (c) load of 30 N at 0.03 m/s (d) load of 30 N at 1.01 m/s

Similar trend was also recorded for the yield strength values, where UHMWPE/ZnO composite with 12 wt% of ZnO recorded the highest yield strength values before it started to show reduction trend (i.e. > 12 wt% of ZnO). This phenomenon was clearly attributed to the reinforcing effect of ZnO particles towards the strength properties of UHMWPE/ZnO composites. Theoretically, the strength of particulate reinforced polymer matrix relies highly on the effectiveness of stress transfer and stress distribution between matrix and filler [21-25]. It was experimentally proven by the SEM images in figure 4 (a) where excellent dispersion of ZnO particles was observed (i.e. at 12 wt% of ZnO particles). This well distributed ZnO particles might be attributed to more efficient stress distribution mechanism and therefore increase the strength properties of UHMWPE/ZnO composites. Meanwhile, at higher ZnO particle loading (i.e. > 12 wt% of ZnO), the agglomeration problem occurred as can be seen in the figure 4 (b). This agglomerated ZnO particles react as stress concentrators thus weaken the composites body [26-29]. For rigidity point of view, it was observed that the Young modulus of the UHMWPE/ZnO increase with increasing ZnO particle up to 12 wt%. This was contributed by the introduction of rigid particles (ZnO particles) into UHMWPE matrix and stiffens the UHMWPE/ZnO composite body. Besides that, the introduction rigid particles may also give significant restriction to the mobility of the polymer chains during deformation, thus increase the rigidity of the composites [23, 30]. Though all the improvements observed, the elongation at break has been reduced as more ZnO were added. This was due to the inherent rigidity properties provided by the ZnO itself. Overall, it can be pre-concluded that the addition of 12 wt% of ZnO into the UHMWPE matrix has recorded the highest value of the tensile strength, yield strength and Young modulus. Therefore it has been considered as the optimum composition for further investigation on the hybridization with chitosan particles.

Further investigation is carried out by incorporation of chitosan to the 12 wt% of ZnO the UHMWPE/ZnO composite in order to produce UHMWPE/Chitosan-ZnO hybrid composites. All tensile performances of the UHMWPE/Chitosan-ZnO hybrid composites were plotted out and illustrated in figure 3(a) to 3(d), respectively. Generally, it is widely accepted that the virgin UHMWPE have relatively low Young's modulus as well as yield strength value [31]. From figure 3(a) to 3(d), it is clearly observed that the chitosan-ZnO hybrid fillers had significantly influence the tensile performance of the virgin UHMWPE as well as UHMWPE/ZnO composites [32, 33]. From the perspective of material's proportion, it can be seen that the introduction of chitosan-ZnO hybrid filler into the UHMWPE matrix had improved the yield strength and elongation at break but decreased the Young modulus and tensile strength of the 12 wt% UHMWPE/ZnO composite. Increment in yield strength means that the elastic range of the UHMWPE/ZnO composite is widen with addition of chitosan. Cumulatively, the tensile strength has dropped approximately 15.6 and 34.3 % than that of unfilled UHMWPE and 12 wt% UHMWPE/ZnO composite, respectively. However, with addition of more chitosan particles, flatter percentage of increment was recorded. From theoretical justification, polar interactions between

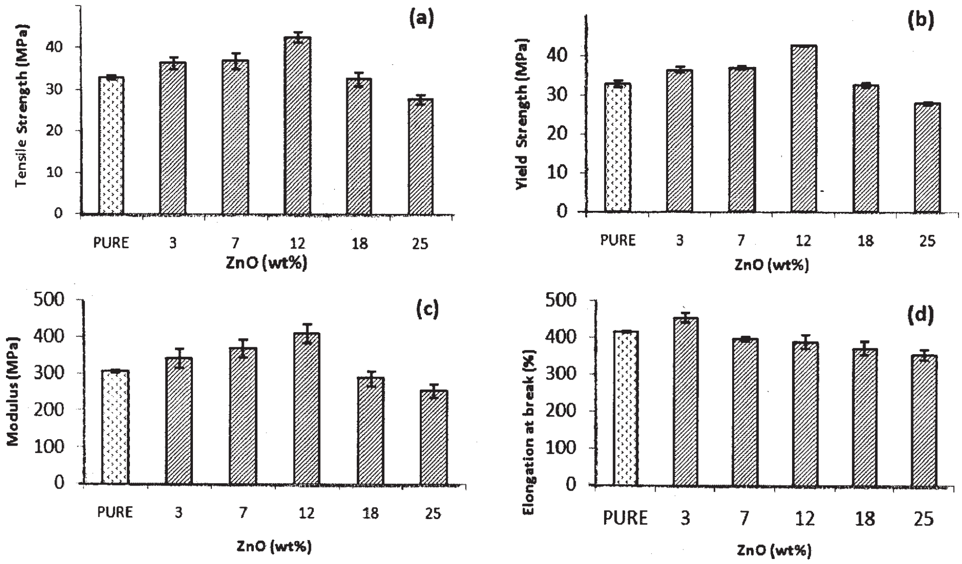

Fig. 2. Tensile properties of ZnO filled UHMWPE composites (a) tensile strength; (b) yield strength; (c) tensile modulus; (d) elongation at break

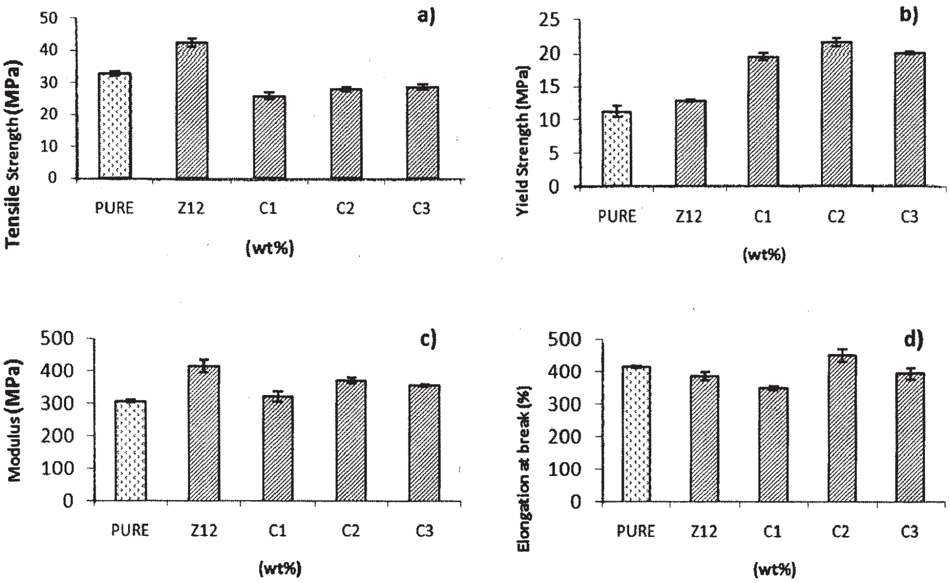

Fig. 3. Tensile properties of Chitosan-ZnO filled UHMWPE composites (a) tensile strength; (b) yield strength; (c) tensile modulus; (d) elongation at break

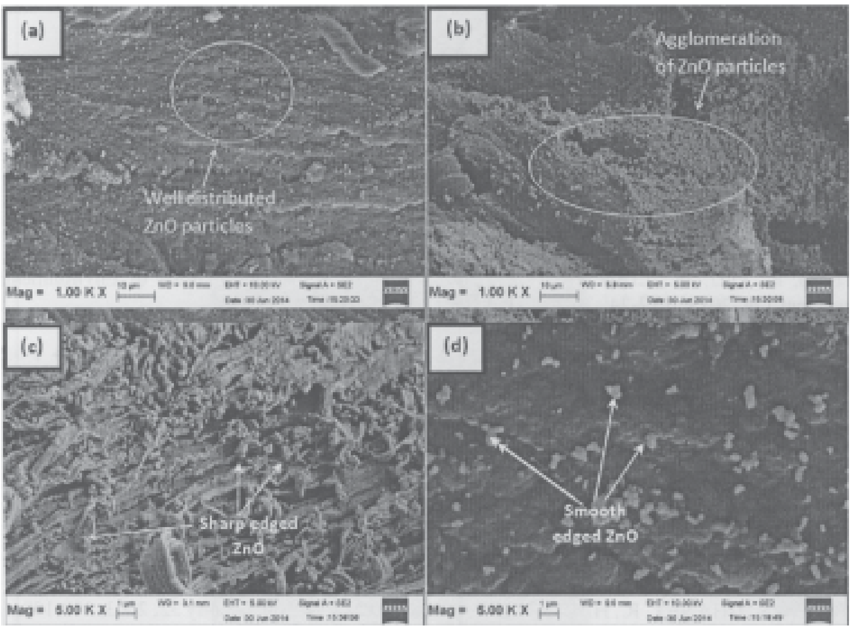

Fig. 4. SEM micrographs of (a) 12 wt% UHMWPE/ZnO and (b) 25 wt% UHMWPE/ZnO at 1000x magnification; (c) 18 wt% UHMWPE/ZnO and (d) 2 wt% UHMWPE/ Chitosan-ZnO at 5000x magnification.

alkyl functional groups of UHMWPE and amine groups of chitosan were expected [34]. However, it is possible that typical processing routes may have not been sufficient for a reaction to occur between the chitosan and the composite, with notable effects on the recorded wear and tensile properties. Moreover, it is generally accepted that chitosan is a natural polysaccharide with hydrophilic character [35-37], whereas UHMWPE is a hydrophobic polymer. The different characteristics might significantly reduce the filler-matrix interfacial adhesion and therefore confer unbeneficial effect to the fabricated composites. As an alternative solution, we might seriously consider the filler treatment for superior properties improvement in the future. From figure 3, it can be clearly observed that the addition of 2% of chitosan to the composite has surpassed the yield strength, modulus of elasticity and elongation at break as compared to other compositions (i.e. 1 wt% and 3 wt% of chitosan). This phenomenon was attributed to the well dispersion of the chitosan within the UHMWPE/ZnO composite as visually proven by the SEM images in figure 4 (d).

Post-fractured surface analysis of UHMWPE/Chitosan-ZnO composites

Post-fracture surface analysis was carried out using SEM equipment as shown in figure 4 (a) to (d). The micrograph in figure 4 (a) shows that the dispersion of ZnO can be seen most distributed at 12 wt%. This observation is in good agreement with the explanation made in figure 1, figure 2 (a) and figure 2 (b), where composite with well dispersed of ZnO particle recorded optimum wear and tensile performances. In addition, the agglomeration problem can be found in figure 4 (b) with higher ZnO particle loading (i.e. 25 wt%). Sharp edged ZnO in figure 4(c) can be clearly seen in the matrix as this indicates inadequate bonding and were loosely embedded. Chitosan that were added in the 12 wt% UHMWPE/ZnO composite addition has improved the dispersion of fillers throughout the matrix. The composite with presence of chitosan has smoother edge ZnO compared the 12 wt% UHMWPE/ZnO as illustrated in figure 4 (d). This is because zinc oxide and chitosan are both hydrophilic, thus a filler-filler interaction and possible filler hybridization had occurred.

Conclusions

The study of Chitosan-ZnO reinforced UHMWPE hybrid filler composites in terms of wear, tensile and morphology properties were successfully carried out. From the results, the following conclusion can be drawn:

- the addition of ZnO (UHMWPE/ZnO composites) and Chitosan-ZnO hybrid particles (UHMWPE/Chitosan-ZnO hybrid composites) had increased the wear properties of the unfilled UHMWPE;

- the tensile strength, yield strength and Young modulus have been increased with increasing of ZnO (UHMWPE/ZnO composites) up to 12 wt%. Unfortunately, the elongation at break show contrary trend. The incorporation of chitosan particles into UHMWPE/ZnO had further increased the yield strength and elongation at break values. Meanwhile both tensile strength and Young modulus of UHMWPE/Chitosan-ZnO hybrid composites recorded lower values as compared to UHMWPE/ZnO composites;

- the wear and tensile properties of UHMWPE/Chitosan-ZnO hybrid composites can be further increase by the improvement of the filler-matrix interactions that could be achieved through matrix and filler treatments.

Using SEM apparatus, the morphology analysis has proven that the dispersion of ZnO is optimum at 12 wt%. Apart from that, the state of filler-filler interaction and hybridization of filler within the UHMWPE had also been observed and confirmed.

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