

Experimental Investigation on Mechanical and Morphology Properties of Ultra-High Molecular Weight Polyethelene (UHMWPE)/ Chitosan-Zinc Oxide (ZnO) Hybrid Composites

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Abstract— Hybrid Chitosan-ZnO reinforced ultra-high molecular weight polyethylene (UHMWPE) was prepared using hydraulic hot press. The effect of ZnO contents (10, 20, 30 wt.%) and chitosan contents (1, 2, 3 wt.%) on the mechanical and morphology properties of UHMWPE/ZnO and UHMWPE/Chitosan-ZnO reinforced composites were successfully investigated. The compound with addition of 10 wt.% of ZnO recorded an increase in tensile properties. Further studies with addition of Chitosan found that hybrid composites recorded better mechanical properties than UHMWPE/ZnO composites, with UHMWPE/ZnO + 3 wt.% Chitosan composite attained comparable tensile strength, stiffness, and hardness to virgin UHMWPE. From fractographic analysis using scanning electron microscope (SEM), the absence of holes at the tensile fracture surface had verified the better tensile strength recorded by UHMWPE/ZnO + 3 wt.% Chitosan composite. Overall, the UHMWPE/ZnO + 3 wt.% Chitosan hybrid reinforced composite recorded comparable tensile properties to virgin UHMWPE.

Keywords— Hybrid fillers; Mechanical Properties; Morphology properties

I. INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) is known for its bio inert, self-lubricating, light weight and even shock resistant properties. The excellent properties possessed by this material, such as high strength, high Young's modulus, low density, and good abrasion resistance [1]. Extensive research had been performed by the previous researchers to increase the overall performance of neat UHMWPE in order to be implemented in various fields especially in medical applications. For example, hydroxyapatite/ultra-high molecular weight polyethylene (HA/UHMWPE) [2], alumina/ultra-high molecular weight polyethylene (Al₂O₃/UHMWPE) [3], natural coral/ultra-high

molecular weight polyethylene (NC/UHMWPE) [4], and titanium dioxide/ultra-high molecular weight polyethylene (TiO₂/UHMWPE) [5] reinforced composites had been studied for their application in biomedical implants. Although much efforts have been carried out to investigate the optimum performance of UHMWPE based composites, but less of them were focused on hybrid fillers. This was the main reason why the knowledge is still remain unclear. It widely accepted that usage of hybrid filler may significantly enhance several specific properties of composites as experimentally proven by Leong *et. al* [6]. Therefore, this research is purposefully design to investigate the effect of hybrid fillers towards mechanical and morphology properties of UHMWPE composites. To achieve our goals, fabrication of UHMWPE/ZnO composite was done using hydraulic hot press and the optimum ratio from 10, 20 or 30 wt.%. Optimum composition was justified based on their ability to induce highest stress. The chosen optimum composition are integrated with different weight percentage of filler to composite from 1 to 3 wt.% producing UHMWPE/ZnO-Chitosan hybrid composite to undergo tensile test and subsequently the morphology of the fractures surfaces are analyzed under scanning electron microscope.

II. EXPERIMENTAL

A. Materials

The powdered formed UHMWPE, with a molecular weight of 5×10^6 g/mol and density of 0.94 g/ml was purchased from Ticona Engineering Polymer, China. ZnO powder with particle size less than 1 μ m 99.9 % and chitosan with a deacetylation degree of 92 % were also supplied by Sigma Aldrich.

B. Sample preparation

Compounding formulation in this research was divided into; UHMWPE/ZnO formulation and UHMWPE/Chitosan-ZnO formulation. 10, 20 and 30 wt.% of ZnO were homogenously mixed with UHMWPE by mechanical ball milling in dry condition method. The mixing process was done for 4 hours with 2 hours in clockwise and another 2 hours in anti-clockwise direction. The samples were then pre-heated and molded using hydraulic hot press at 165°C for 20 minutes. Cool pressing was done for 5 minutes to obtain the composite sheet. The same steps were repeated to prepare UHMWPE/Chitosan-ZnO hybrid reinforced composites.

C. Tensile Test

The tensile properties of neat UHMWPE and UHMWPE reinforced composites were evaluated according to ASTM D638 (Type IV) [7]. At least five specimens were tested for each sample. Dumbell-shaped specimens of 50 mm gauge length and thickness of 1 mm were tested under crosshead speed of 20 mm/min [8]. The tensile strength, tensile modulus, and elongation at break for each composite were tabulated and analyzed.

D. Morphology Analysis

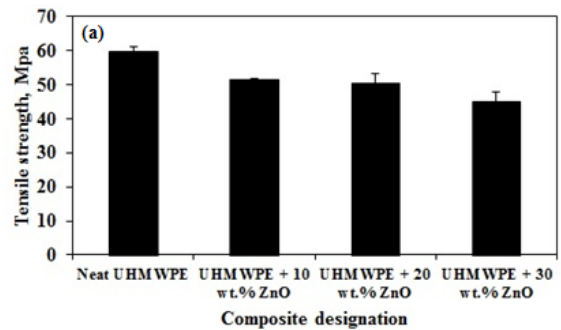
The fracture surfaces of the composites were observed using Zeiss Supra 35VP Field Emission Scanning Electron Microscope (FESEM). All the samples were coated with Au-Pd in a sputter coater chamber before analysis. The fracture surfaces of the composites were observed using the TM-3000 Tabletop Scanning Electron Microscope (SEM).

III. RESULTS AND DISCUSSION

A. Effect of Hybrid Filler Loading on Tensile Properties of UHMWPE

Fig. 1 illustrates the tensile properties for UHMWPE/ZnO composites with various particle contents. It was clearly shown that the tensile strength of UHMWPE/ZnO composites decreased with the addition of ZnO particles. UHMWPE composite with 10 wt.% ZnO contents showed a 13.5 % tensile strength reduction as compared to the neat UHMWPE. At higher filler additions (30 wt.% ZnO), a total of 24.43 % tensile strength loss was resulted. This finding was in agreement with the work reported by Chang *et. al* [9]. They mentioned that the effective stress transfer from the matrix to the fillers is highly required to achieve the strengthening effect. The ZnO used in this study is hydrophilic in nature, and therefore difficult to form interfacial bonding with the hydrophobic UHMWPE. As a result, the materials inside the UHMWPE composite system become incompatible and the bonding between the molecules is weakened. Hence, smaller forces are needed to break the bonding as compared to neat UHMWPE. The reduction of tensile strength was also caused by the interruption of the homogeneous phase of UHMWPE

matrix. The matrix phase interruption had caused the poor stress transfer between the ZnO particles and UHMWPE matrix, which explained the reduction of tensile strength with addition of ZnO contents. Besides, the agglomerated network of ZnO in UHMWPE matrix, as evidenced in the Fig. 1(a), had also deteriorated the tensile strength of ZnO/UHMWPE composites at high filler contents. Sole and Ball [10] reported that the rigid fillers has negative effect on the tensile strength of the composites. As filler contents is increased, there is notable decrease in the effective cross-sectional area in the continuous polymer matrix system [11] which can support the applied load, and hence greatest tensile strength loss was observed at highest filler contents. The bar graph in Fig. 1(b) pointed out that the tensile modulus of the composites increased gradually with the addition of filler contents. With the incorporation of 20 wt.% ZnO contents, 9.16 % increment in tensile modulus was recorded. Meanwhile, a 22.92 % increase in tensile modulus was observed for composite with 30 wt.% ZnO contents. The increment in the tensile modulus was accompanied by the reduction in elongation at break for all the UHMWPE/ZnO composites, as shown in Fig. 1(c). The inclusion of ZnO filler had successfully enhanced the stiffness of the composites. The enhancement in tensile modulus could be contributed by the high modulus of rigid ZnO filler, as reported by Chang *et. al* [9]. The presence of rigid filler is being the factor for modulus improvement the composite system [10]. The decrease of elongation at break was the indication for ductility loss in the composite system as more filler contents were employed. The reasonable explanation for this manner was the interruption of the polymer chain mobility of the UHMWPE matrix by the ZnO filler in the composite system, which leads to the decrease in plastic deformation [8], and therefore the decrement in elongation at break.



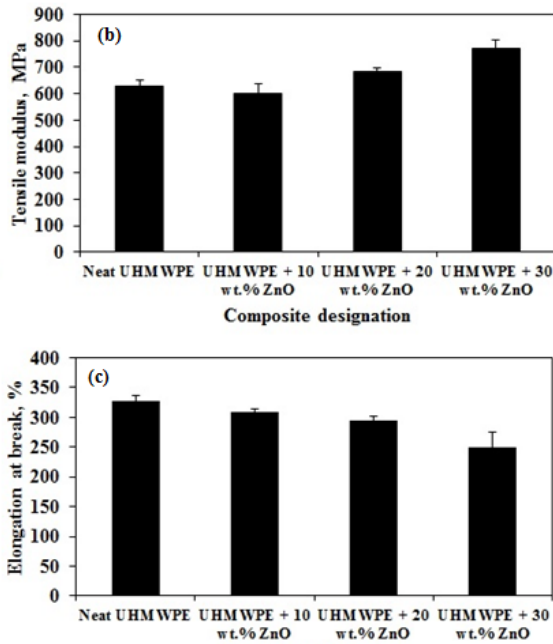
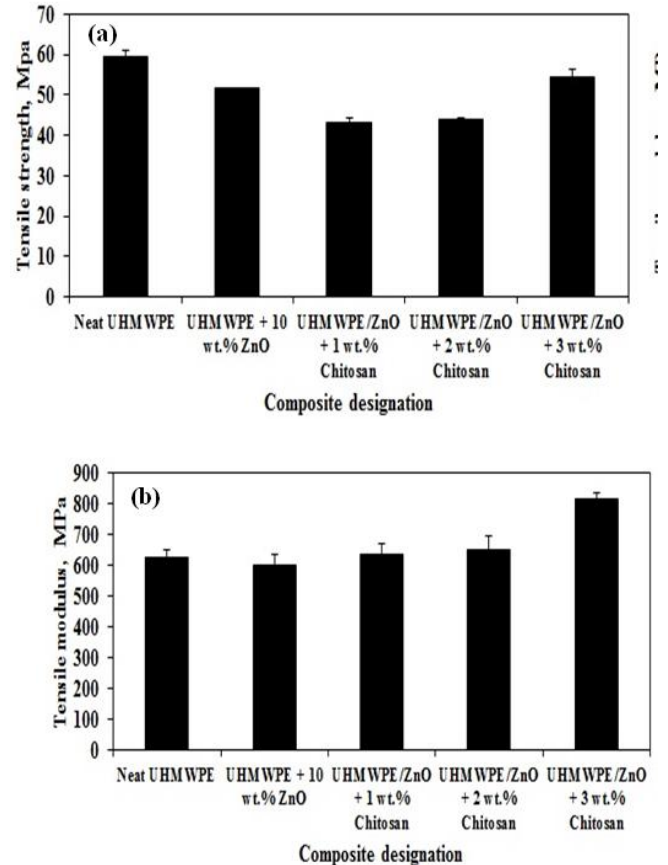


Fig. 1: The tensile properties of neat UHMWPE and UHMWPE/ZnO; (a) Tensile strength (MPa); (b) Tensile modulus (MPa); and (c) Elongation at break (%)

The UHMWPE reinforced with 10 wt.% ZnO composite is considered as the optimum content of ZnO and is included in this section as control experiment, as well as neat UHMWPE, that is intended to point out the enhancement of hybrid reinforced UHMWPE composites. Fig. 2(a) illustrates the variation of the tensile strength of UHMWPE/Chitosan-ZnO hybrid composites with the weight fraction of chitosan particles. It was seen that the tensile strength of hybrid composites increased with the addition of filler contents. The similar findings had been discovered by Zhou *et al.* [12]. They proposed that the increasing trend of tensile strength was attributed to the reinforcing effect of fillers. The increase in tensile strength would be presumably due to the ability of stress transfer from the UHMWPE matrix to the chitosan particles at low filler incorporation. However, as shown in Fig. 2(a), every hybrid composites still recorded lower tensile strength than the neat UHMWPE. But interestingly, it is worth pointing out that hybrid composites with 3 wt.% of chitosan particles (54.61 MPa) recorded higher tensile strength as compared to UHMWPE composite with 10 wt.% ZnO (51.64 MPa), with an increment of about 5.75 %. This result indicates that the optimum addition of chitosan particles into the composite system would reveal better tensile strength than composite reinforced with one type of filler. Fig. 2(b) demonstrates the tensile modulus of UHMWPE/ZnO/Chitosan composites as a function of chitosan contents. Apparently, as shown in Fig. 2(b), the tensile modulus had portrayed an increase trend, identical to the tensile modulus trend recorded for UHMWPE/ZnO series. The tensile modulus increment for hybrid composites reinforced with 1 and 2 wt.% chitosan did not show significant enhancement, only in the order of 0.95 and 3.54 %, respectively. However, when compared to neat

UHMWPE, a 30.13 % increment in tensile modulus for hybrid composite reinforced with 3 wt.% chitosan was recorded, indicating the optimum amount of hybrid filler was capable to enhance the stiffness of the composite. Such a finding was in agreement to the work by Chang *et al.* [9]. They suggested that the presence of rigid filler in the matrix was being the main cause for the increase in stiffness for the composite. The increment in tensile modulus was accompanied by the reduction in elongation at break for the hybrid composites, as illustrated in Fig. 2(c). The loss of ductility was due to the incorporation of chitosan into the composite system. The chitosan particles had restricted the mobility of UHMWPE chain [8], inducing less plastic deformation, and eventually the ductility loss for the composite. On the contrary, the hybrid composite reinforced with 3 wt.% chitosan particles exhibited a sudden increase in elongation at break, which indicating a little gain of ductility.



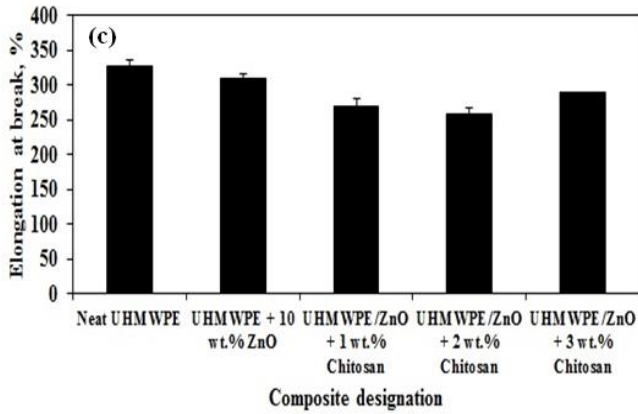


Fig.2: The tensile properties of neat UHMWPE, UHMWPE/ZnO and UHMWPE/Chitosan-ZnO; (a) Tensile strength (MPa); (b) Tensile modulus (MPa); and (c) Elongation at break (%)

B. Morphology Analysis

Tensile fracture analysis was carried out using SEM equipment, as illustrated in Figure 3. In addition, the EDX analysis was also performed to distinguish the presence of ZnO particles on the fracture surfaces of composite specimens. Fig.3(a) shows tensile fracture surfaces of UHMWPE/ZnO composites. From fractographic analysis, it was observed that composite with 10 wt.% ZnO contents had better ZnO distribution in the matrix. On the contrary, composite with 30 wt.% ZnO contents showed huge ZnO agglomerates, which was responsible for the reduction of the tensile strength discussed previously. The agglomerate network had triggered the formation of holes as evidenced in Fig.3(b), indicating the poor stress transfer from the matrix to the filler. Theoretically, the formation of holes and voids disturbs the stress transfer effectiveness between the matrix and the ZnO particles [13]. This observation was consistent with the tensile strength trend in Fig. 1. Furthermore, the EDX analysis had confirmed the presence of ZnO particles by the 'X' pointed area in the SEM micrograph (Fig.3(a)). The Zn and O elements represented the ZnO particles. Meanwhile, the C and Pt elements were contributed by UHMWPE matrix and coating material, respectively. Fig.3(c) shows the SEM micrograph of UHMWPE/ZnO + 3 wt.% Chitosan hybrid composite. As observed, there was no holes or voids formation in this hybrid composite as compared to UHMWPE/ZnO composite in Fig.3 (b). In the absence of holes, it was believed that there was existence of better effective stress transfer from the matrix to the filler, which was accountable for the better tensile strength of UHMWPE/ZnO + 3 wt.% Chitosan hybrid composite.

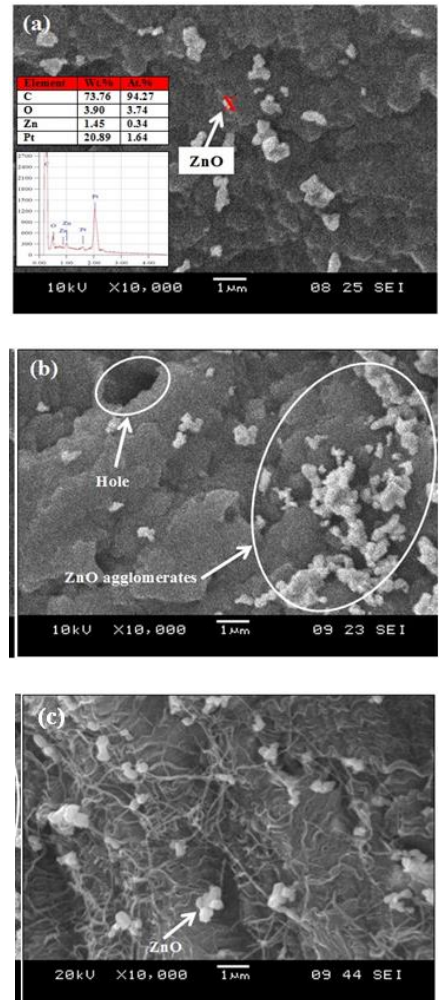


Figure 3: Tensile fracture morphology of UHMWPE/ZnO composites (a) 10 wt.% ZnO, (b) 30 wt.% ZnO and (c) UHMWPE/ZnO + 3 wt.% Chitosan hybrid composite.

IV. CONCLUSION

The mechanical and morphology properties of UHMWPE/Chitosan-ZnO hybrid composites were successfully investigated using conventional universal testing machine and SEM apparatus, respectively. From the results, the following conclusions can be drawn:

- The tensile strength for UHMWPE/ZnO composites decreased through the inclusion of ZnO into the UHMWPE. However, due to the reinforcing effect, UHMWPE/ Chitosan-ZnO hybrid composites demonstrated increment in tensile strength. The hybrid composite with 3 wt.% chitosan contents achieved higher tensile strength than UHMWPE + 10 wt.% ZnO composite, but, still slightly lower than neat UHMWPE. Stiffness properties for both UHMWPE/ZnO and UHMWPE/Chitosan-ZnO hybrid composites were enhanced by the particle additions.

- From fractographic analysis, holes were appeared on the UHMWPE/ZnO composites, causing the poor stress transfer between the matrix and ZnO particles. On the contrary, UHMWPE/Chitosan-ZnO hybrid composites showed no holes formation on the fracture surface.

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