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An Investigation on UHMWPE-HAp Composites Manufactured by Solution-Gelation Method

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Abstract

In this study, HAp reinforcement into UHMWPE matrix having 1.0 % wt. mass and its effects on microstructural and mechanical properties of the UHMWPE composites were investigated. UHMWPE composites reinforced with 0.5, 1 and 2.0 wt. % nano HAp powders, respectively were successfully produced by solution and gelation method. SEM studies showed that HAP nano particles were homogenously distributed into UHMWPE matrix and good cross-linked with the matrix. SEM-map EDS analysis confirmed SEM. FTIR results revealed that HAp incorporation into matrix was conducted and crystallization of UHMWPE increased by increment in amount of HAp results in deepening crystallization peaks at nearby 500 and 1500 cm^{-1}. DSC results, which is useful technique to determine the variation of melting point and crystallization ratio of UHMWPE composites, indicated that there was no remarkable change in melting points of composites, while crystallinity of the samples generally showed slight increase by increasing amount of nano HAp particles. The tensile test instrument was utilized to determine elastic modulus of the samples and their elastic modulus were raised from 1050 to 1900 MPa with higher HAp reinforcement. It can be concluded that UHMWPE-1 % wt. HAp composites have promising results by being paired with crystallinity and elastic modulus.

Keywords: UHMWPE, HAp, composite, crystallinity, DSC, Young’s modulus

1. INTRODUCTION

Biomaterials are the materials which can improve the length and quality of human life and include a broad class of materials that are used in medicine and dentistry such as: metallic biomaterials, ceramic and glass biomaterials, non-degradable synthetic polymers, biodegradable polymers, bio-derivative polymers as well as passive and bioactive coatings [1, 2]. Ultra-high molecular

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weight polyethylene (UHMWPE) is one of the promising matrix materials due to its high chemical inertness, the highest wear resistance of any thermoplastics, low friction coefficient and bioinertness make it the material of choice for hip joints and knee joints. Other excellent properties, such as low density, high strength, high modulus, good abrasion, and chemicals resistance [3,4]. To further improve its mechanical properties and tribological response, fillers/reinforcements are incorporated into the polymer [5]. Several inorganic filler materials such as hydroxyapatite (HA), alumina, quartz, carbon, kaolin, titania has been explored in UHMWPE composite [6]. Implant materials must be bioactive, inert, resorbable and coherent with living tissue [7]. For biomedical applications such as dental and orthopedic implants, one of the appealing materials is hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which is biocompatible, bioactive and main mineral component of the bone matrix, and falls into the classes of resorbable bioactive and materials. The hydroxyapatite form straight biochemical bonds with living tissues [6,8,9]. Nano sized hydroxyapatite show much higher bioactivity [10,11] and improved resorbability [12,13] than micron sized ones. Oscillation of calcium ions nano sized hydroxyapatite is also such like from native hydroxyapatite and basically, faster than that from large grained crystals [14].

In the literature, it was reported that production methods such as conventional melting and mixing is impossible to produce UHMWPE matrix composite due to UHMWPE's high viscosity [15,16]. One way to eliminate this problem is, to solve UHMWPE in a solvent and mix the solution with fillers and then remove the solvent [17]. High oriented materials such as UHMWPE are generally produced by solution-gellation and gel-spinning techniques. Polyethylenes produced with gelation techniques generally has lamellar structure in which small amount of polymer chains entangle couples. This UHMWPE structures can be drawable easily at 120–150 °C with the draw ratio of 200 times [18]. In this report, we aimed to investigate the effects of variation of HAp reinforcement into UHMWPE matrix on enhancing of microstructural and mechanical properties of the UHMWPE biomaterials.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

UHMWPE powders (Sigma-Aldrich, CAS: 9002-88-4) having $3.10^6 – 6.10^6$ g/mol molecular mass were used as a matrix materials as well as deccalin (Decahydronaphthalene, unhydrous, mixture of cis + trans ≥%99, Sigma-Aldrich, CAS: 91-17-8) to solve UHMWPE within the solution and 2,6 Di-tert-butyl-4-methylphenol (Sigma-Aldrich, CAS: 128-37-0) as an antioxidant were utilized. HAp powders synthesized in our laboratory by authors and particle size of HAp powders obtained by DLS analysis and result of synthesized HAp powders was given in Fig. 1. HAp powders with 50 nm particle size (confirmed with particle size analysis as seen in Fig.1.) as shown in were used to prepare UHMWPE composite samples. HAp powders synthesized by sol-gel method. Briefly, $Ca(OH)_2$ (Sigma-Aldrich, CAS:1305-62-0) and H_3PO_4 (CAS: 7664-38-2), which are starting calcium and phosphorous sources, were used to obtain synthesized HA by sol-gel method. Mixtures of the precursors were prepared taking into account a Ca/P atomic ratio similar to that of unsubstituted HA equal to 1.67. The synthesis of HA was carried out in sealed containers. The prepared calcium solution was added drop wise into the phosphate solution under magnetic stirring for 30 minutes at 60°C. pH is adjusted to 11 in present study by using NH_4OH (Sigma Aldrich, CAS: 1336-21-6) for solution. As a result of the EDS analysis, the Ca / P ratio of nano HA powder was found to be 1.65, which is very close to the stoichiometric ratio (1.67).

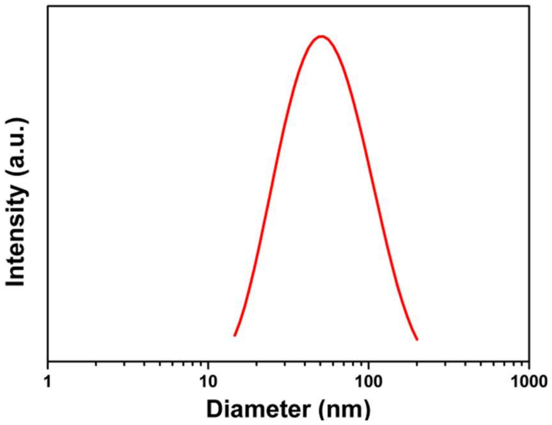


Figure 1. Particular size analysis of synthesized Hap powders

2.2. Experimental Method

Firstly, UHMWPE powders having 1.0 wt.% concentration were dissolved within decalin solution by magnetic stirrer and antioxidant (2,6-Di-tert-butyl-4-methylphenol) up to 0.5 wt. % amount of whole solution were added to this solution in order to reduce the risk of polymer oxidation. Following by UHMWPE dissolution process, proper amount of HAp powders having 50 nm particle size were added to each three solution to be rate of 0.5, 1.0 and 2.0 wt. %, respectively. In this study, 0.5 and 2 ranges were chosen in this study since the studies are generally conducted with the addition of 0.1 - 0.5 wt.% HA [19]. The UHMWPE composite gelation-crystallization process as well as removing the decalin from the medium were conducted at 185 °C for 60 min. until the solution become transparent. Then, UHMWPE composite solution were poured into the aluminium cups and dried during 10 days at open atmosphere for removing of deccalin from the composites because the decal is used as a solvent and is not wanted to be in our composition as mentioned in this study [20]. Finally, solid composite gel samples were heat treated at 130 ° C for 90 min in the atmospheric drying oven to completely remove decalin and increase the crystallization of the polymer composites. The schematic illustration of preparing UHMWPE-HAp composites were given in Figure 2. The prepared polymer composites was illustrated in Figure 3.

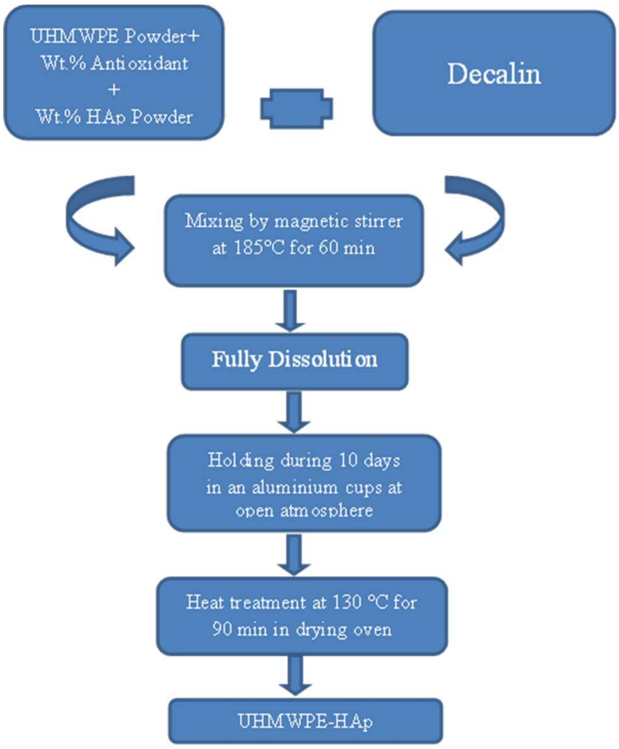


Figure 2. Schematic illustration of UHMWPE-HAp composites preparation.

Figure 3. UHMWPE-HAp composite samples produced by gelation-crystallization method.

2.3. Characterization

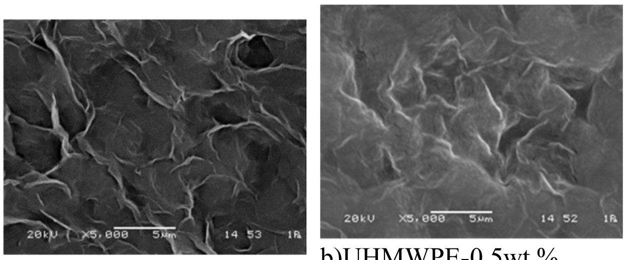
SEM studies (JEOL LV6060) were conducted to investigate surface microstructure of the UHMWPE-HAp composites. SEM-EDS analysis were realized to confirm the presence of HAp whether it is homogenously distributed in the UHMWPE matrix. The phase characterization and crystallization of the composite samples were determined by FT-IR analysis (Perkin Elmer-Spectrum-Two). The variation of melting temperature and crystallization of composite samples via HAp reinforcement were measured by DSC analysis (TA Instruments Q20 calorimeter) by heating from room temperature to 200 °C at 10 °C min^{-1} under a nitrogen atmosphere. Before the tests an Al_2O_3 crucible was placed in the sample cavity as a reference. The tensile test instrument (Instron 3365 Universal Testing Machine) was utilized to determine elastic modulus of the samples. A cross-head speed of 10 mm/min was used.

3. RESULTS and DISCUSSIONS

SEM microstructures of as-prepared composite samples as well as pure UHMWPE were shown in Figure 4(a-d). It can be claimed that gray coloured regions indicated polymer matrix, while white small particles barely visible within the polymer pointed out the nano HAp fillers. HAp particles were homogenously distributed in the matrix. Also, there was no remarkable defects (porosity, crack etc.) at the polymer-reinforcement interface, thus it is possible to say that there is a good connection between the UHMWPE and nano HAp powders.

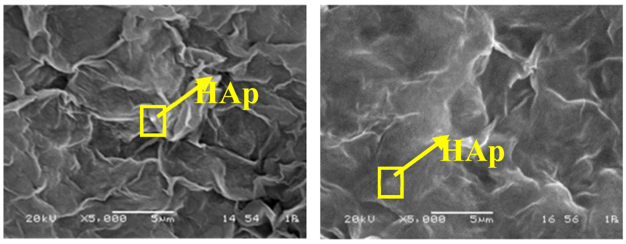
The more HAp powders have the more cross-linking area resulting in enhancing mechanical properties in polymer (Figure 4a-d). Reinforcement particles added into the polymer matrix tie moleculer chains of UHMWPE by Van der waals bonds and chain molecules connected together by hydrogen bonds. It will lead increasing nucleation sides in the polymer matrix an nucleation agent. Increasing nucleation consequently will improve the mechanical properties of the polymer [21, 22].

SEM-EDS analysis which was performed to determine the presence of HAp and where it taken place in the matrix, results were presented in Figure 5(a-b). As it can be seen from the Figures, white, blurred particles indicated nano HAp (Mark 2,3 in Figure 5a and Mark 1, 2 in Figure 5b), while gray coloured regions represented UHMWPE matrix (Mark 1, 4 in Figure 5a and Mark 3 in Figure 5b). It was found that the interface of HAp powders is not clearly distinguishable and dispersed into the polymer matrix, especially more visible in Fig. 4b. This is due to very large surface area of nano-particles (NPs) enabling extensive interaction with the matrix Sharma et al. reported that composites filled with nano particles lead to more homogenous structure than filled with micron particles ones [23-24]. This intensive interaction of nano particles with polymer matrix ensures higher crystallinity and higher mechanical properties of UHMWPE matrix composites.



a) Pure UHMWPE

b)UHMWPE-0.5wt.% HAp

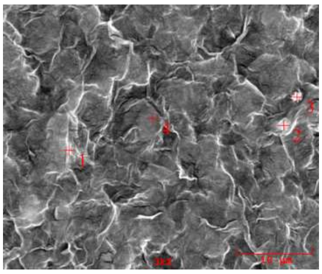


c)UHMWPE-1.0wt.% HAp

d)UHMWPE-2.0wt.% HAp

Figure 4. SEM surface images of a) pure UHMWPE, b) UHMWPE- 0.5wt.%HAp, c) UHMWPE- 1 wt.%HAp and d) UHMWPE- 2 wt.%HAp.

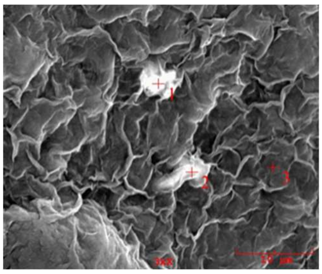
FT-IR analysis of the composites as well as pure UHMWPE were conducted to investigate matrix and reinforcement interactions, verify the presence of HAp and get information about crystallinity of the samples. The results of FT-IR analysis were given in Figure 6. From the Figure 6, various characteristic bands of UHMWPE, at wavelength of 1464 cm^{-1} (C–H bending), 1367 cm^{-1} (C–H asymmetric bending), 730 cm^{-1} and 720 cm^{-1} (C–H rocking), 2922 cm^{-1} ($-CH_2-$ asymmetric stretch) and 2850 cm^{-1} ($-CH_2-$ symmetric stretch), respectively [25] were detected. Peaks at the wavelength of 957 cm^{-1} and doublet in the range of 1100-1000 cm^{-1}, assigning to ν1 (PO) symmetric stretching and ν1 (PO) symmetric stretching respectively, are the characteristic HAp bands which became visible with the HAp introducing to the UHMWPE matrix.



a) UHMWPE-0.5 wt.% Hap

EDS analysis

Element	Weight %			
	1	2	3	4
C	84.270	80.473	71.033	79.157
O	15.569	13.194	27.232	20.184
P	0.132	2.620	0.344	0.275
Ca	0.029	3.713	1.392	0.385



b) UHMWPE-1.0 wt.% HAp

EDS Analysis

Element	Weight %		
	1	2	3
C	69.130	77.374	85.187
O	22.115	14.747	14.098
P	3.580	3.452	0.522
Ca	5.176	4.428	0.192

Figure 5. SEM-dot EDS analysis of a) UHMWPE-0.5 wt.% HAp b) UHMWPE-1.0 wt.% HAp composites.

These bands indicate the distinctive molecular structures of the PO_4^{3-} groups in the HAp lattice [26, 27]. This revealed that oxygen (as OH, PO_4 group) in the HAp structure interacts with C in the chains of UHMWPE structure (C-O-C interactions in 800-1300 cm^{-1} region illustrated in Fig. 6) and it is evidence of introducing HA within the polymer matrix. The crystallinity variation of the samples were observed from the peak nearby at 720 cm^{-1} and it can be acclaimed that the crystallinity of the UHMWPE composites generally increased because of the deepening that peak by increment of HAp amount. The characteristic bands belongs to HA become more visible in the spectra as increasing of HA amount up to wt. 1%, whereas intensity of this bands decreased in the spectrum of UHMWPE-2wt.% HAp samples. This possibly resulted from agglomeration of nano HAp powders exceeds a value of 1.0 wt.% within the polymer matrix.

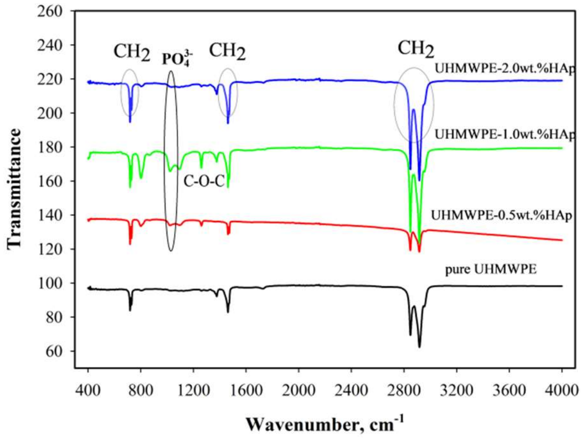


Figure 6. FT-IR spectra of UHMWPE and UHMWPE-0.5wt.%HAp, 1wt.% HAp and 2wt.% HAp composites.

DSC analysis of the pure UHWMPE and UHMWPE-1.0wt.% nano HAp carried out to determine the variation of melting temperature and calculate the crystallinity were presented in Figure 7. The melting temperature of pure UHMWPE were found as 136 °C and increased to 142 °C with addition of nano HAp filler from the endothermic peaks of two samples (Figure 6). The percentage degree of crystallinity of the composites (Xc) can be found by using equation below (1)

$$X_c = (\Delta H_m / \Delta H_{100})x100 \qquad (1)$$

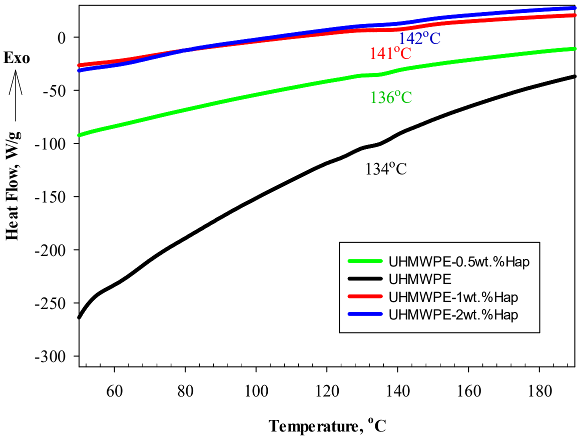


Figure 7. DSC analysis of the UHMWPE and UHMWPE HAp composites.

In the equation, ΔH_m and ΔH_{100} represent the enthalpy of sample and enthalpy of melting of perfect crystalline polyethylene (290 Jg^{-1}) respectively [28, 29]. Heat of fusion was calculated from the areas of the endothermic peaks. Calculated heat of fusions and crystallinity values of UHMWPE-nano HAp composites with pure UHMWPE were given in the Table 1.

Table 1. Heat of Fusion and Crystallinity of the samples derivated from DSC analysis.

Sample	Heat of fusion, ΔH_m	Crystallinity, %Xc
UHMWPE	67,34	23,4
UHMWPE-0.5wt.%HA	76,50	26,4
UHMWPE-1wt.%HA	93,65	32,3
UHMWPE-2wt.%HA	78,44	27,1

The crystallinity of pure UHMWPE polymer increased by introducing nano HAp up to 1.0 wt.% into the matrix, while crystallinity of composites decreased with addition of 2.0 wt.% nano HAp (Table 1). It was reported that with the increasing surface area of filler, more interactions between the filler and UHMWPE matrix occurs which leads to crystallization of polymer on the filler surface. By the means of increasing nucleation sides on fillers, polymer starts to lamellae grow on them [30] and the crystallinity of the composites increases. The decrement in crystallinity of the UHMWPE-2.0wt.% nano HAp could be resulted from agglomeration of nano particles due to reducing the nucleation sides for the interfacial crystallization.

The tensile test was utilized to determine elastic modulus of the samples via variation of nano HAp amount and the results of elastic modulus and tensile strength were given in Table 2. Tensile curve of UHMWPE-1wt.%HAp was given in Figure 8. The Young modulus of the polymer matrix increased approximately 90% by addition of higher amount nano HAp into the UHMWPE. This is due to increasing of interfacial crystallization favors a strong interfacial adhesion and high load transfer efficiency between polymer matrix and nanofiller [30]. When the nano particles added into the polymer matrix, interactions sides between the matrix and reinforcement particles increase and they restrict the movement of polymer chains [31] resulting enhancement in the mechanical properties of UHMWPE matrix composites.

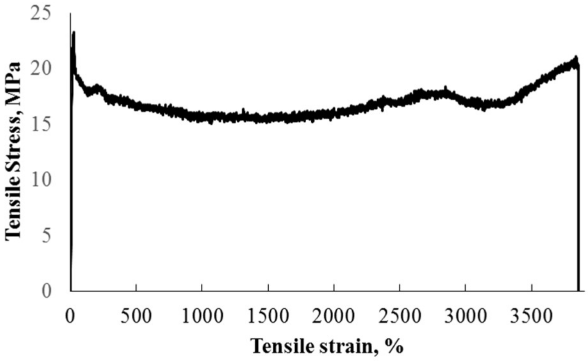


Figure 8. Tensile test curve of UHMWPE-1wt.%HAp.

Table 2. Elastic modulus and tensile stress via nano HAp amount in the samples.

HAp (50 nm) Reinforcement (wt.%)	Elastic Modulus (MPa)	Tensile Strength (MPa)
0	1020	21
0.5	1500	23
1	1900	26
2	1750	24

4. CONCLUSIONS

The main findings of the study were listed as below;

1. UHMWPE-HAp composites were successfully produced by gelation-crystallization method.

2. SEM images revealed that HAp particles were homogenously distributed in the matrix and matrix-filler interface was defect free.

3. SEM-EDS analysis verify the SEM analysis and realized that nano HAp particles have good interaction towards the polymer matrix.
4. FT-IR analysis showed that HAp filler was successfully introduced into the matrix as characteristic bands of both UHMWPE and HAp was observed in the

spectrum. The characteristic bands belongs to HA become generally more visible in the spectra as increasing of HA amount. The crystallinity variation of the samples were observed from the peak nearby at 720 cm^{-1} and the crystallinity of the UHMWPE composites generally increased because of the deepening that peak by increment of HAp amount.

5. The melting temperatures and the crystallinity of the samples increased with higher filler amount according to DSC results.

6. The Young modulus of the composites increased about 90% of pure UHMWPE. It is possible to claim that higher surface area of the nano particles and increasing of the surfaces by introducing more nano particles leads to enchancing interaction and this increases the cross-linking, thus mechanical properties of the composites enhances.

7. Filling particles link the UHMWPE molecular chains by Van Der Waals force and hydrogen bonds, and it will leads to possess the potential as nucleating agent in promoting nucleation in polymer matrix. Introducing nano particles into UHMWPE matrix having larger surface area act as effective nuclei and induce the polymer lamellae grow on the filler surface. This results in extensive interaction with the matrix. Increasing polymer matrix and reinforcement interactions restricts the movement of the polymer chains. It can be express in the light of this mechanism mentioned above that the crystallinity and mechanical properties of the test samples increased.

8. The UHMWPE-1 wt.% nano HAp composites have optimum results and findings of our study have good agreement in the previous studies in the literature.

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