Characterization of UHMWPE- HAp coating produced by dip coating method on Ti6Al4V alloy

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ABSTRACT

In the present study, the surface of Ti6Al4V alloy was coated with UHMWPE-HAp composite film by dip coating for hip joint material. Ti6Al4V alloy surfaces were firstly roughened by anodic oxidation to provide adhesion of the polymer coating on it. Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FE-SEM) results showed that the UHMWPE-HAp composite film was coated homogenously on the substrate and HAp particles were well bonded to the matrix. Functional groups and bond types of the composite coatings were detected by Fourier-transform Infrared Spectroscopy (FTIR). The melting temperature T_m and the enthalpy of fusion (ΔH_f) of the UHMWPE and UHMWPE-HAp composite coatings were measured by differential scanning calorimetry (DSC). The crystallinities were calculated as 24.5% for pure UHMWPE and increased to 54.2% by addition of 1 wt%HAp particles into the UHMWPE matrix. Dry sliding wear properties of coatings against alumina ball were tested by a ball-on-disc tribometer in linear mode. Wear results revealed that UHMWPE-HAp composite coating on anodic oxidized Ti6Al4V alloy has an ultra-low friction coefficient of 0.06 compared to the friction coefficient of anodic oxidized Ti6AlV4 alloy at of 0.8 and with a favorable wear resistance 84% higher than oxide coated ones. This newly developed composite coating material shows potential use for artificial hip joint replacements.

1. Introduction

Titanium alloys are among the most commonly used material in the medical field, predominantly in total joint replacement, due to their, low density, nontoxicity, biocompatibility, low density, high specific strength, and excellent corrosion resistance [1–4]. Problems in total joint replacements can occur from the relative motion between the components of the bearing during long-time use which lead to failure of the implant. However, poor wear resistance, low friction coefficient, low bioactivity and inflammatory reactions around titanium alloy limit its application [2,5,6]. Thus, deposition of TiO$_2$ coatings is necessary to improve surface properties of titanium alloys [7,8]. Anodic oxidation which is a simple, cheap, effective and economical method compared to other coating methods [8] was used to modify the surface of titanium alloys by producing a bioactive, porous titania film [9]. Porous and rough TiO$_2$ coatings have good osseointegration property [8] and also

provide adhesion of polymer coatings. The main aim of this study is to improve the surface properties of Ti6Al4V alloy by coating with Ultra High Molecular Weight Polyethylene- Hydroxyapatite (UHMWPE- HAp) composite film applied over a porous TiO$_2$ layer. Also, polymer coatings on implant materials have attracted interest due to their favorable tribological and biomedical properties, ease of production and low cost [7]. Among them, UHMWPE is widely used as joint replacements in orthopedic implants because of its excellent physical, chemical and mechanical properties such as high wear and impact resistance, abrasion resistance, low toxicity, chemical inertness, lubricity and biocompatibility [10–13].

Macuvele et al. [13] observed that there are two major advantages for choosing this polymer as a biomaterial, particularly for orthopedic implants. The first is its modulus of elasticity (0.5–0.8GPa) which is close to that of the bone and the second is its friction coefficient (0.10–0.22 under dry condition) which is the lowest among the

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polymers. Despite the widespread use of UHMWPE, it has a finite lifetime [13] namely, the inadequate surface hardness causes wear debris generated during the joint motions leading to osteolysis, which will cause bone loss, joint loosening, discomfort, and ultimately limits the lifespan of the joints. In addition, primary implant stability is supported by the osteointegration of a HAp-containing coating. HAp is an important composite material additive that provides improved contact at the implant and bone interface. As the chemical dissolution or osteoclastic effect over time causes the absorption of HA coatings, it has been reported that 78% of new bone formation replaced the HAp-containing coating [14].Furthermore, it is known that implants containing HAp provide a stable fixation even if osseointegration is not completed and HAp debris particles do not cause an osteolytic reaction. There have been many attemps to improve mechanical and tribological properties of UHMWPE and thus, to extent the service life. Consequently, some reinforcement of metallic and ceramic particles can be added into the polymer matrix to improve the mechanical and tribological properties of the UHMWPE [13] [15–17]. It was found that by appropriate reinforcements such as carbon [18,19], kaolin [20], quartz [21], alumina [22], zirconia [23] and hy- droxyapatite (HAp) [13,24] wear characteristics of the UHMWPE composites can be developed that exceed many times those of unfilled UHMWPE [16,17]. HAp reinforced UHMWPE composites are very interesting in the field of biomedical coatings owing to their improved tribological, mechanical and biological properties.

There are several processing methods to develop UHMWPE-HAp composites such as hot pressing [23], extrusion [25], ball milling [24], sol-gel [26] etc. Unique properties of UHMWPE are related to its high molecular weight (up to 10^7 g/mol) that, however, make its processing difficult. Therefore, to produce UHMWPE films and coatings, traditional polymer processing methods are almost inapplicable. The best way is to dissolve UHMWPE in a solvent and add the filler and then, to remove the solvent [27]. Solution gelation and crystallization are excellent techniques to produce high modulus and high strength polyethylene films with filler particles dispersed homogenously [28]. Sol-gel thin films are usually produced by spin or dip coating. Dip coating is commonly used for complex shaped substrates and, is significantly faster, cheaper and easier than other coating tecniques [3].

Because a UHMWPE film presents a low friction coefficient the surface of Ti6AlV4 alloy was coated with UHMWPE-HAp composite films to improve its tribological behavior. This study provides some insight into the production of a favorable hydrophobic, high wear resistant total joint replacement material to be used, for example, as coating for the inner surface of acetabular cups.

2. Materials and methods

2.1. Materials

Ti6Al4V alloy plates (30 mm × 60 mm × 3 mm) were used as substrate material. UHMWPE powder with an average molecular weight of 3.10^6–6.10^6 g/mol, solvent of decalin (decahydronaphthalene, as mixture of cis + trans anhydrous, ≥99%) and other chemicals used for anodic oxidation were supplied by Sigma Aldrich. HAp powders with a particle size of (~10 nm) were produced by biomimetic method. NaCl, NaHCO₃, KCl, K₂HPO₄·H₂O, MgCl₂·6H₂O, CaCl₂ and Na₂SO₄ were used as reagents for the preparation of simulated body fluid (SBF), that was adjusted to 7.4 using the TRIS-HCl buffer. The prepared HAp samples were obtained by centrifuging the SBF after biomimetic biomineralization by keeping it in a water bath at 37 degrees and 70 rpm. The synthesized HAp was dried overnight in a vacuum oven at 60 °C to be ready for subsequent procedures.

2.2. Anodic oxidation

Ti6Al4V alloy plate surfaces were ground using 400–600-800 grid emery papers to obtain favorable surface finish and then were
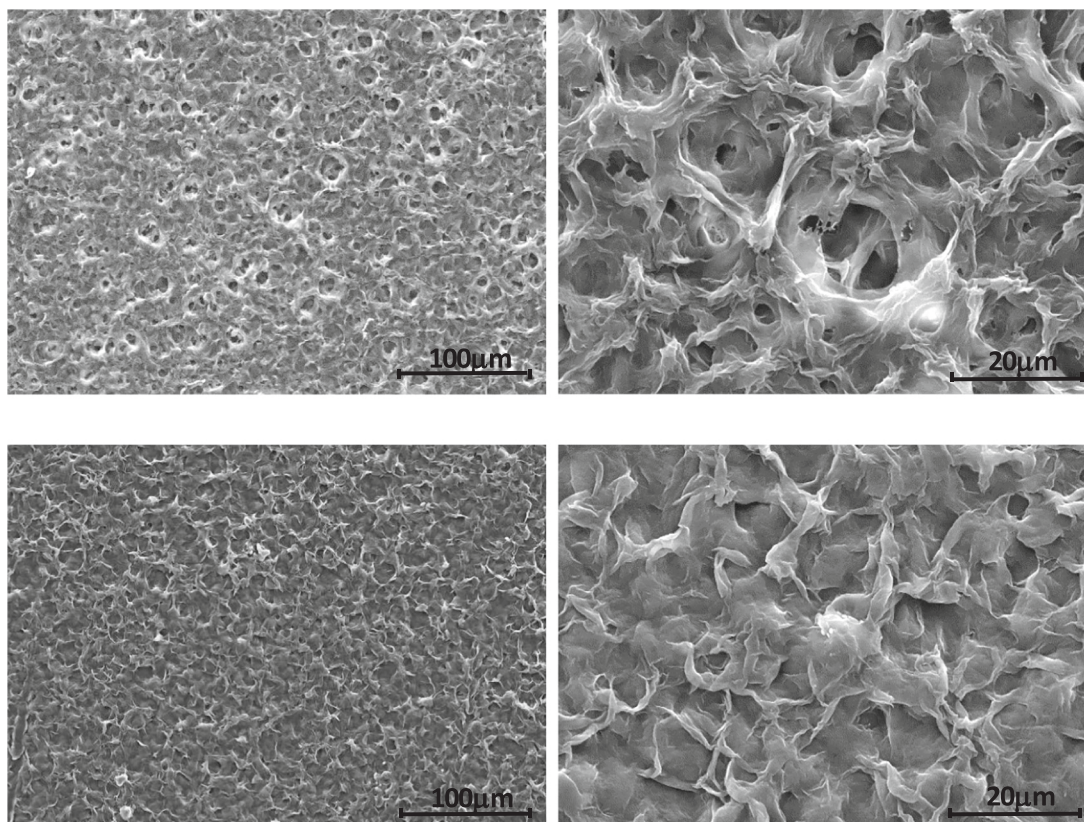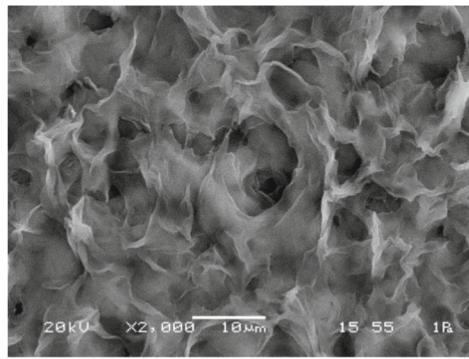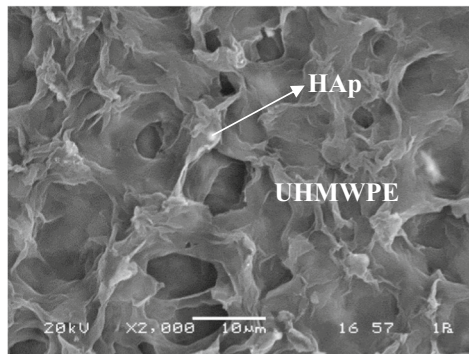

Fig. 1. Surface FE-SEM images of pure UHMWPE (top, row) and UHMWPE-1wt.% HAp composite coatings (bottom row) on anodic oxidized Ti6Al4V alloy.

Element	at. %
C	99.07
O	0.93

a)

Element	at.%
C	49.526
O	23.617
P	9.907
Ca	16.950

b)

Fig. 2. SEM-EDS analysis of a) UHMWPE and b) UHMWPE-1wt.%HAp composite coating.

ultrasonically cleaned in acetone, ethanol and deionized water, respectively. Anodic oxidation was carried out in an electrolyte consisting of H_3PO_4, H_2O_2 solution, at a constant voltage of 25 V for 120 min to obtain a porous TiO_2 layer, using stainless steel as the cathode while a polished Ti6Al4V alloy was used as the anode. After oxidation, samples were heat treated at 600 °C for 1 h.

2.3. UHMWPE-HAp composite coating by dip-coating

UHMWPE- HAp composites were produced by the gelation/crystallization method. 1.3 g. UHMWPE were solved in 50 ml. decalin and 1 wt %HAp particles (according to the weight of UHMWPE) were added into the solution. Gelation was performed at 160 °C for 40 min by using magnetic stirrer. The Ti6Al4V substrate was dipped into the solution at a rate of 1.9 mm/s and withdrawn at the same speed after 80 s. At the end of the process, the coated sample was placed in an oven heated to 100 °C and dried for 20 h.

2.4. FTIR analysis

The phase characterization of the samples was done by FTIR (Perkin Elmer-Spectrum-Two) to investigate matrix and reinforcement interactions, verify the presence of HAp and get information about crystallinity of the samples.

2.5. DSC and crystallinity degree

DSC analysis (TA Instruments Q20 calorimeter) of UHMWPE and UHMWPE-HAp composites were performed by heating samples from room temperature to 200 °C at a rate of 10 °C/min. Under nitrogen at-

mosphere. The DSC curves were analyzed to obtain the melting temperature (Tm) and to calculate the area of melting peak, as well as the enthalpy of fusion (ΔH) and the crystallinity. Degree of crystallinity was determined Eq. (1).

$$X_c = (\Delta H_m / \Delta H_{100})\text{x}100 \tag{1}$$

where ΔH_m is enthalpy of fusion at melting point and ΔH_{100} represent the enthalpy of the sample for 100% crystalline UHMWPE (290 Jg^{-1}) [29,30].

2.6. Wear and friction tests

CSM Instrument was used for wear tests in ball-on-disk mode with an alumina ball of 6 mm diameter under the normal load of 2 N in linear mode. The speed was 12 cm/s and the wear tests were ended after 6000 cycle under dry sliding condition. Worn surfaces of UHMWPE and UHMWPE-HAp composite coatings were analyzed by using KLA Tencor model 2D surface profilometer to determine the wear volume. Scratch tests were performed on CSM Instruments Linear tribometer to measure the abrasive resistance and adhesion between polymer coating and Ti6Al4V substrate in accordance to ASTM D7027 standards. A high speed steel twist drill bit was used as a tip with 17/64 in, 118° point angle. The applied normal load was 1 N, sliding speed was 0.34 cm/s and sliding distance was 5 mm. Scratch depth was measured by KLA Tencor model profilometer.
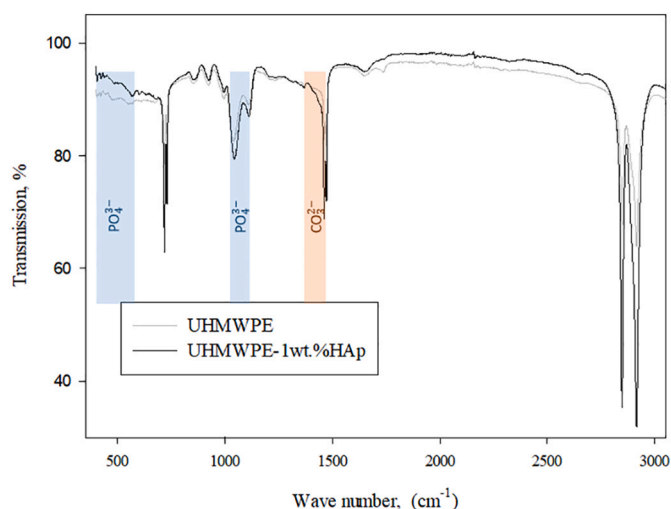
Fig. 3. FTIR spectra of UHMWPE and UHMWPE-1wt.%HAp composite coatings.

3. Results and discussion

3.1. Microstructure

FE-SEM images of pure UHMWPE and UHMWPE-1 wt% HAp composite coatings are shown in Fig. 1 at different magnifications. The UHMWPE coating has a homogenous and porous microstructure (Fig. 1, top row). UHMWPE is composed of C—C covalent bonds which are arranged in ordered or disordered forms by forming crystalline and amorphous regions [31]. There are many macro voids with diameters varying from approximately 5 to 10 μm. The coatings became less wrinkled by addition of HAp particles into the UHMWPE matrix, and the diameter of macro voids decreased. Obviously, UHMWPE- 1 wt% HAp composite coatings have remarkably less porosities around the wrinkled polymer chains that probably resulted from the nano filler addition which forms effective nucleation sites for polymer chains. HAp addition into the UHMWPE matrix induces the crystallization by its nucleating effect [32]. These nucleation sites, formed by the HAp addition, connected the polymer chains each other. Thus, pores remaining between the wrinkled chains were eliminated and a homogenously blended, flatter polymer matrix can be obtained. However, it appears that nano filler addition also increased the wrinkled sites indicating increased crystallinity of the polymer composites coating (Fig. 1, bottom row). The increase in crystallinity result in lower friction coefficient, higher mechanical properties, an increase in scratch resistance and higher structural durability [13,31].

SEM-EDS analysis of UHMWPE and UHMWPE-1 wt%HAp composite coatings are displayed in Fig. 2 showing that the coating surface completely exhibited polymeric nature, consisting of C and O elements (Fig. 2a). The weight ratio of Ca and P elements detected in the EDS spectra was 1.71 (close to ratio of Ca and P in natural bone; 1.67), confirming the existence of HAp particles, indicated with an arrow in Fig. 2b. HAp particles appeared to be well blended with the polymer matrix. This favorable integration of nano HAp filler with the matrix would increase the crystallinity of the composite coating, leading to enhancement of tribological and also mechanical properties of the UHMWPE matrix [33]. As Affadato et al. [34] explained in their study, the increase in the wear debris can cause osteolysis and bring about implant loosening. By means of HAp addition into the UHMWPE matrix, the wear strength of the composite coating will increase.

3.2. FTIR spectrum analysis

Fig. 3 shows the FTIR spectra of UHMWPE and UHMWPE-1 wt%HAp

Table 1
Surface contact angels of UHMWPE and UHMWPE-1 wt%HAp composite coatings.

Contact angle, °	
UHMWPE	UHMWPE-1 wt%HAp
103	88

composite coating. The FTIR spectrum of the UHMWPE coating reveals three distinctive peaks at the range of 718–732 (CH_2 rocking), 1458–1469 (CH_2 bending) and 2846–2915 cm^{-1} (C—H stretching) indicating to characteristic polyethylene bands in accord with literature [35]. The peaks at 1040–1115 cm^{-1} belong to C—O bonds, possibly resulting from oxidation during the process. It was observed that when HAp particles were added to the UHMWPE, the HAp peaks could coincide with the UHMWPE peaks and cover the HAp peaks as shown in Fig. 3, where the UHMWPE peaks already present in the colored areas with the peaks belonging to the subsequently added HAp peaks are thought to cover the peaks of the HAp particles. In addition, it is thought that peaks in the colored areas support the presence of HA added in the composite due to the presence of Ca and P elements, which have been proven in HA content by EDS analysis (Fig. 2b).

3.3. Surface wettability

Surfaces with contact angles greater than 90° are called as hydrophobic and contact angle between 60° and 90° are said to be hydrophilic. This means that; when contact angle fall below the 90° the surfaces start to be wetted [36,37].

Among the properties that a biomaterial must have e.g. protein adsorption, cell adhesion ability, biocompatibility, biomimetics and biodegradation is hydrophilicity. Hydrophilicity is important for cell adhesion on biomaterial surfaces and this will lead to efficient and stable implant [37].

Table 1 shows water contact angels of surface of UHMWPE and UHMWPE-1 wt%HAp composite coatings. Wetting was evaluated by dropping distilled water on the sample surface and measuring the contact angle formed between the drop and the surface. Pure UHMWPE has a larger contact angle and the addition of HAp particles into the UHMWPE increases the surface wettability. Thus, a UHMWPE-HAp composite coating could successfully generate a hydrophilic surface. The observed enhancement in surface wettability indicates that increasing the number of HAp particles will increase the wettability of the surface. As Marcos et al. [38] confirmed in their study, increasing the wettability of the surfaces are related to the contact between the implant and the body fluid. Similarly, Kang et al. [39] observed that the surface wettability of UHMWPE-HAp composites improved by the increasing the HAp addition. Furthermore, improving surface wettability causes increasing crystallinity, hardness and also wear resistance. The more the mechanical properties of UHMWPE-HAp composites increases, the more the wear resistance under the abrasive condition was enhanced.

3.4. DSC analysis

In order to determine the melting point and the degree of crystallinity of the polymer coating, DSC analysis was performed DSC measurements carried out as given in Fig. 4 show distinct endothermic peaks, indicating a melting point, at about 140 °C for UHMWPE and a slight increase for UHMWPE-1 wt%HAp composite coating. The area of the heat of fusion for UHMWPE-1 wt%HAp composite was larger than
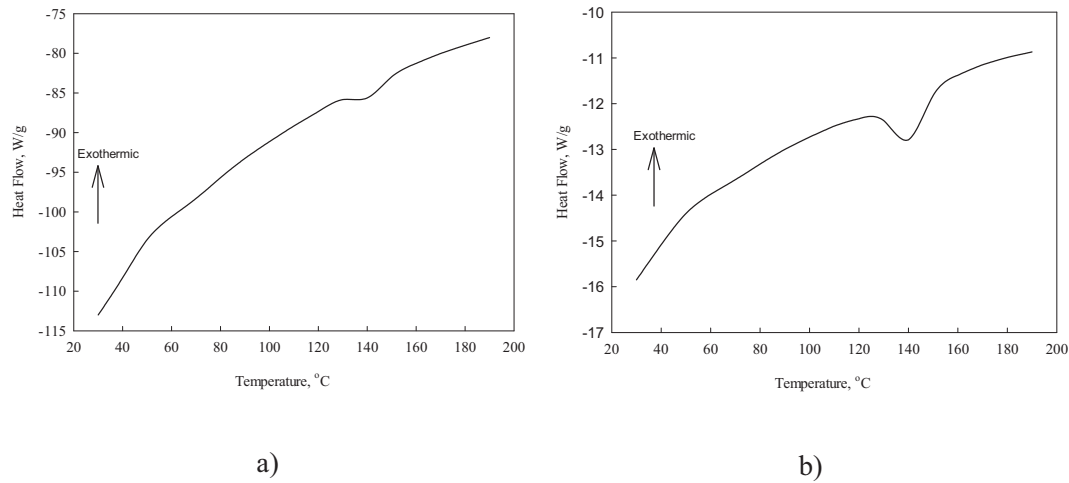
a)

b)

Fig. 4. DSC curves of UHMWPE and UHMWPE-1wt.%HAp composite coatings.

Table 2
Melting point, heat of fusion and crystallinity % values of UHMWPE and UHMWPE-1 wt%HAp composites.

Sample	T_m	ΔH_m	X_C (%)
UHMWPE	140	71.14	24.53
UHMWPE-1 wt%HAp	141	157.1	54.17

that of the UHMWPE, indicating larger crystallites. This finding shows that HAp particles added as reinforcement acted as nucleation agent in the UHMWPE matrix thus improving the crystallinity [40]. Calculated percentage of crystallinity of UHMWPE and UHMWPE-1 wt%HAp composites with the melting point and the heat of fusion are given in Table 2. As well known, any obstacle to chain movement of semi-crystalline polymers can increase the polymer strength by increasing the polymer crystallinity, increasing the molecular weight, or the degree of crosslinking. Secondary bonding between the chains (crosslinking) will restrict the chain motion and increase the crystallinity which has a significant effect on the mechanical properties of a polymer [41] [42].

It is clear from Table 2 that the crystallinity of UHMWPE increased dramatically with the addition of HAp particles into the matrix. Our finding shows that the nucleating effect of HAp particles contributed to crystallinity by preventing chain movement of UHMWPE.

3.5. Tribology results

The addition of HAp particles into the UHMWPE matrix improves the mechanical properties of UHMWPE depending on increasing crystallinity [43]. In the existing literature, there is no study about wear properties of UHMWPE-HAp composite coatings deposited onto Ti6Al4V alloy to be used in hip joint replacement. SEM microstructures on the worn surfaces of UHMWPE and UHMWPE-1 wt%HAp composite coating are given in Fig. 5. Our results showed that adhesive and slight ploughing are the main wear features. Folding regions perpendicular to the wear directions are more distinct for pure UHMWPE coating. Near the edge position in Fig. 5b there are plastically folding sides. No tearing, cracking and abrasive deformation was detected. The composite test materials with 1 wt%HAp addition shows a smoother surface with smaller- shallow grooves and less plastic flow compared to the pure UHMWPE (Fig. 5). This corresponds to the better load- carrying capacity than pure UHMWPE.

Table 3
Friction coefficient and wear volume results of coatings.

Coating	Friction coefficient	Wear volume, mm³
Anodic oxidized Ti6Al4V	0.8	12,514.5
UHMWPE	**0.08**	11,657.6
UHMWPE-1 wt% HAp	**0.06**	**2073.9**

a)

b)
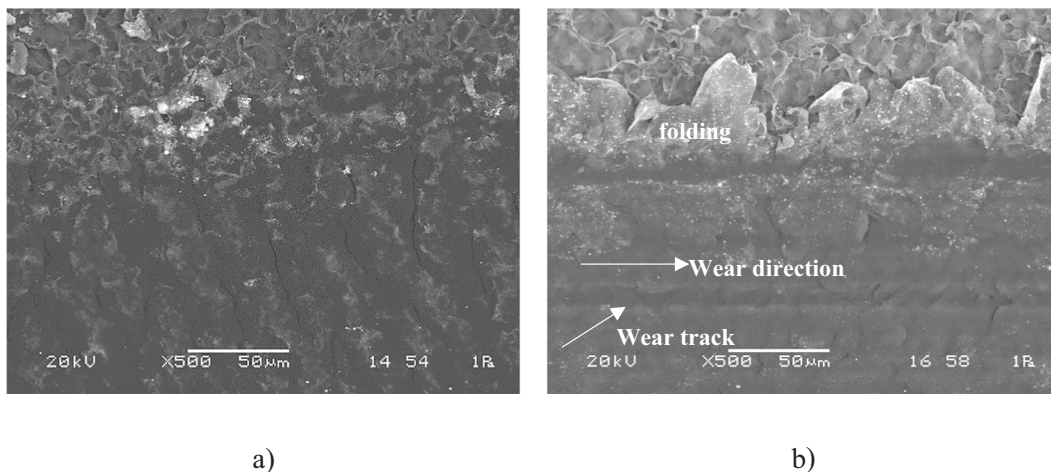
Fig. 5. SEM images on worn surface of a) pure UHMWPE, b) UHMWPE-HAp composite coating.
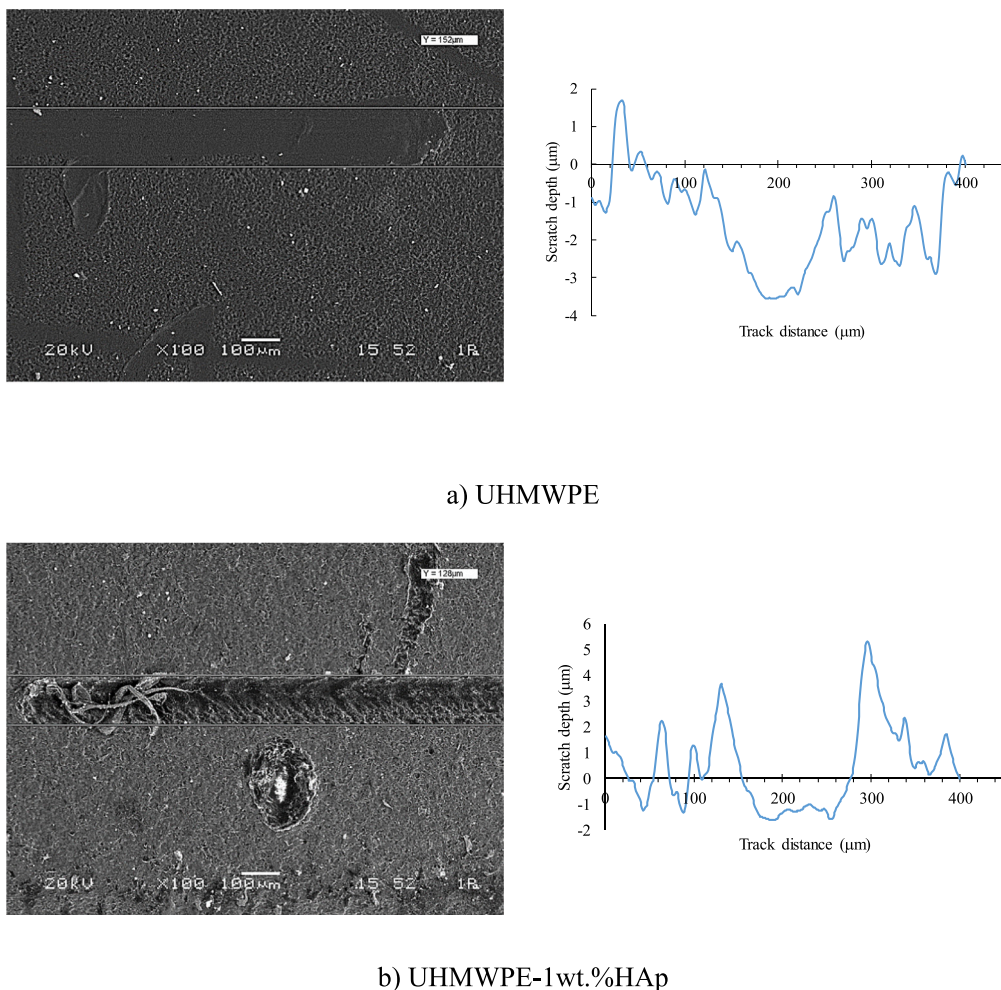
a) UHMWPE

b) UHMWPE-1wt.%HAp

Fig. 6. Scratch track SEM microstructures and track depth diagrams of a) UHMWPE and b) UHMWPE-1wt.%HAp composite.

Wear volumes of coatings were calculated by profilometry. Friction coefficient and wear volume results of UHMWPE and UHMWPE-HAp composite coatings with anodic oxidized Ti6Al4V alloy are given in Table 3. It was observed that, anodic oxidized Ti6Al4V alloy displayed a higher friction coefficient of 0.8 than polymer coated ones due to the rough oxide coating. The friction coefficient immediately dropped to 0.08 by coating with UHMWPE owing to its lubrication properties and to 0.06 by the addition of 1 wt%HAp particles into the UHMWPE matrix.

UHMWPE-HAp composite coating showed extremely high wear resistance compared to pure UHMWPE coating. This results show reinforcing UHMWPE with HAp particles is an effective way in order to increase tribological properties of composite. The previous study done by Plumlee et al. [44] revealed that the wear resistance of UHMWPE could be increased by reinforcing with zirconium particles. They suggested that improving mechanical properties are correlated with crosslinking of Zr particles with polymer. Crosslinking can occur by irradiation or chemical reactions. In our study, we claim that improving tribological properties of UHMWPE results from increasing crystallinity of UHMWPE and crosslinking via addition of HAp particles.

Scratch tests were performed to test the adhesion between UHMWPE, and UHWPE-1 wt%HAp composite coatings and the substrate. No piling-up of polymer film was observed at the end of and along the track (Fig. 6). This suggests a high sticking force of the polymer film to the substrate. Delamination and plastic deformation is present. It can be claimed that addition of HAp particles into the UHMWPE matrix increased the adhesion properties of UHMWPE with Ti6Al4V substrate. Formation of bridges between UHMWPE chains and HAp particles

increased the scratch resistance and load bearing capacity of the UHMWPE film. The interaction between reinforcement components of composites enables them to act as molecular bridges in the polymer matrix. This is the basis for enhanced mechanical properties [45].

Fig. 6 shows that UHMWPE-1 wt% HAp composite film exhibited lower scratch depth and also smaller scratch width than unreinforced UHMWPE film as measured with a profilometer. This is due to an increase in the adhesion strength by means of bridging of HAp particles between UHMWPE chains that prevents peeling off the polymer film from the substrate [33,45,46]. Similar to results obtained by Karuppiah et al. [33] the lower wear of UHMWPE-1 wt%HAp and abrasive scratch depth can be related to its increasing crystallinity, resulting in increased wear resistance.

4. Conclusion

- The surface of Ti6Al4V alloy was modified via coating by a combination of a porous TiO_2 layer and a UHMWPE-HAp composite.
- FE-SEM, SEM-EDS and FT-IR characterization revealed the nature and presence of UHMWPE and UHMWPE-1 wt%HAp composite coatings on anodic oxidized Ti6Al4V alloy.
- DSC results showed that a slight increase of the melting temperature, which is about 140 °C and 121% of crystallinity, occurred for UHMWPE-1 wt%HAp composite coating in comparison with an unreinforced UHMWPE coating.
- The increase in crystallinity provided excellent performance on wear resistance with ultra-low friction coefficient of 0.06 and a decrease of

82% of the wear volume for UHMWPE-1 wt%HAp composite coating.

- An increase in the resistance to scratching is observed by adding of HAp particles into the UHMWPE matrix due to the increase in crystallinity and the load bearing capacity of the composite film.
- No delamination was seen after scratch testing indicating that there is a good bonding between the polymer film and the substrate.
- Water contact angle measurements indicated that the wetting angle decreased from 103° to 88° by addition of HAp particles into the UHMWPE matrix.
- UHMWPE-HAp composite coating could provide a hydrophilic surface with high surface energy with high wear resistance.
- The results show that a UHMWPE-HAp composite coating on Ti6Al4V alloy has the potential for application inside an acetabular cup of artificial hip joint replacements.
- In-vivo experiments are planned to be performed by our team to investigate how the ratios of UHMWPE-HAp composite affect both implant fixation, osteolysis and biocompatibility in living tissue.

CRediT authorship contribution statement

Gözde Çelebi Efe, Elif Yenilmez, İbrahim Altınsoy, Serbülent Türk and Cuma Bindal contributed equally to this work.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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