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Characterization of UHWPE-TiO_2 Composites Produced by Gelation/Crystallization Method

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In this study, ultra-high molecular weight polyethylene (UHMWPE) – TiO_2 composites reinforced with TiO_2 particles with weight ratios of 0.5, 1 and 2% were produced by gelation/crystallization method in decalin+antioxidant solution of UHMWPE at 150 °C, for 40 min by using magnetic stirrer. The gel mixture was cooled in an aluminum tray embedded in iced water under ambient conditions and dried in an oven at 130 °C for 90 min to remove any residual trace of decalin. Distribution and elemental analyses of TiO_2 particles in polymer matrix was examined by SEM-EDS. Crystallization behavior was investigated by differential scanning calorimetry (DSC). Based on the results, TiO_2 particles in the UHMWPE have accelerated the crystallization, acting as nucleating agents, with increment from 56% for UHMWPE to 63.5% for UHMWPE-2 wt% TiO_2. The present bond types in composites were analyzed by Raman spectroscopy and the results are in good agreement with literature. Uniaxial tensile tests were performed to determine Young's modulus of UHMWPE-TiO_2 composites. It was found that Young's modulus of UHMWPE was increased from 52 MPa to 800 MPa with the addition of TiO_2 particles.

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1. Introduction

Polymer structures are attractive due to their mechanical, optical, electrical and biomedical properties [1]. Among them ultra high molecular weight polyethylene (UHMWPE) is widely used in orthopedic implants, like hip joint replacement prostheses, because of its excellent characteristics, such as high wear and abrasion resistance, chemical inertness and biocompatibility [2–5]. Despite its widespread use, the low surface hardness and poor wear resistance of polymer causes wear, leading to osteolysis, which will cause bone loss, joint loosening, discomfort, and ultimately limits the lifespan of the joints. Therefore, to improve the mechanical and tribological properties of the UHMWPE, such reinforcements are used [5, 6], as carbon fibers, carbon nanotubes (CNT), zirconium particles, kaolin, titanium dioxide, zinc oxide, hydroxyapatite, and platinum-zirconium (Pt-Zr) quasicrystal particles [7]. It was found that wear characteristics of the UHMWPE composites improve several times in comparison with unfilled UHMWPE, by using appropriate reinforcement [6, 7].

Unique properties of UHMWPE are related with its high molecular weight (up to 10^7 g/mol), however this limits its processing possibilities. Therefore, for production using UHMWPE, the traditional polymer processing methods are almost inapplicable. The best existing way is to solve UHMWPE in a solvent and to add the filler and then, to remove the solvent [8]. Solution gelation and crystallization is the excellent method for production of high modulus and strength polyethylene films with homogeneously dispersed filler particles [9].

The goal of the present work is to study the effect of the TiO_2 particles on physical and mechanical properties of UHMWPE.

2. Experimental

UHMWPE powder (Sigma Aldrich) with an average molecular weight of 3×10^6–6×10^6 g/mol was used as the matrix material. The solvent of decalin (Decahydronaphthalene, as mixture of cis +trans anhydrous, ≥99%), and antioxidant of 2,6-Di-tert-butyl-4-methylphenol, supplied by Sigma Aldrich, were used to solve the UHMWPE. TiO_2 with the particle size of 0.25 μm was used as the filler. UHMWPE-TiO_2 composites were produced by gelation/crystallization method in decalin+antioxidant solution including 0.5 wt.% UHMWPE at 150 °C for 40 min by using magnetic stirrer. The gel mixture was cooled in an aluminum tray embedded in iced water under ambient conditions and dried in an oven at 130 °C for 90 min, to remove any residual trace of decalin.

Microstructural and elemental analyses of samples were performed using scanning electron microscope (SEM) (Tescan Vega LSU model). Melting temperature and crystallinity of the composites were determined by differential scanning calorimetry (DSC) (TA Instruments Q20 calorimeter) at a scanning rate of 10 °C/min, from

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40 to 200 °C, under nitrogen atmosphere. Raman spectra were recorded using a Horiba IHR550 Raman Spectrometer. The mechanical properties were measured by a universal testing machine. Tensile specimen was cut from the sheet samples with the size of 60 mm in length, 10 mm in width and 0.02 mm in thickness.

3. Results and discussion

SEM micrographs of UHMWPE and UHMWPE-0.5, 1 and 2 wt.% TiO_2 composites are given in Fig. 1. UHMWPE matrix is shown in grey color. White regions embedded into the matrix represent TiO_2 particles. Reinforcement particles of TiO_2 are dispersed homogeneously in the matrix. It is possible to claim that there is a good bonding between polymer matrix and TiO_2 particles. No visible defects at interface were detected, showing good adhesion with matrix, enhancing the properties of the resulting composites. This can be attributed to sticky character of UHMWPE chains.

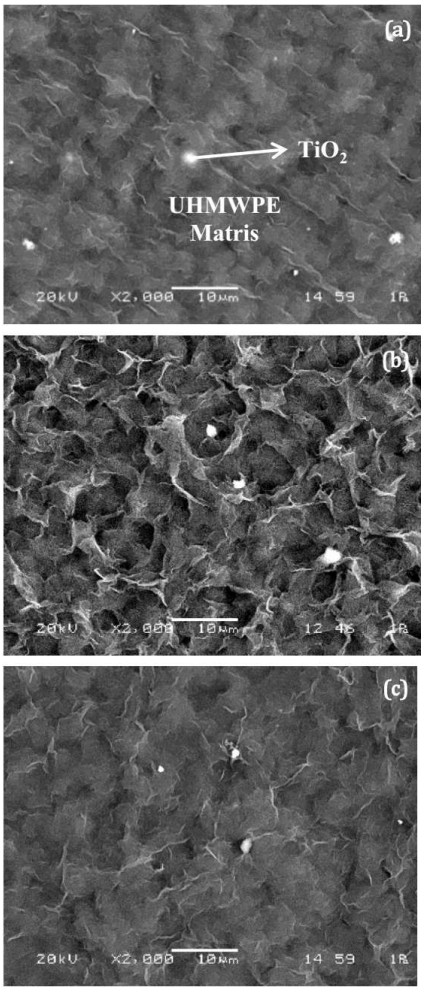

Fig. 1. SEM microstructures of (a) UHMWPE-0.5 wt.% TiO_2, (b) UHMWPE-1 wt.% TiO_2 and (c) UHMWPE-2 wt.% TiO_2 composites.

SEM-EDS analysis was performed to determine the components of the microstructure (Fig. 2). From EDS analysis it was detected that blurred white particles, covered with UHMWPE (marked with number 1) belong to the TiO_2 particles and grey areas represent the UHMWPE matrix. Shiny white regions (marked with numbers 2, 3) represent the contaminations, which had probably stuck to the surface of the samples during the drying period.

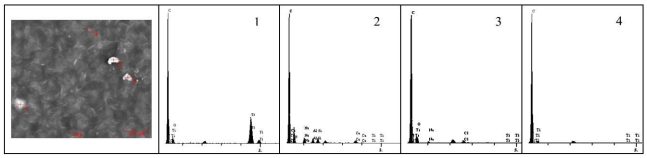

Fig. 2. SEM-EDS analysis of UHMWPE-1 wt.% TiO_2 composites.

The Raman spectra of UHMWPE and UHMWPE-2 wt.% TiO_2 composite, given in Fig. 3, show the expected vibrations of commercial UHMWPE. The 1080 cm^{-1} Raman band is ascribed to the C–C stretching, the 1293 cm^{-1} Raman band, to the crystalline CH_2 twisting, the 1305 cm^{-1} Raman band, to the amorphous C–C twisting and the 1414 cm^{-1} Raman band is ascribed to the crystalline C–C bending, respectively [10]. It is clear from Fig. 3 that Raman intensity of UHMWPE was increased with the addition of TiO_2 particles into the UHMWPE. This can be correlated with the increase in crystallinity of UHMWPE matrix with the addition of TiO_2 particles. Results were confirmed with the DSC analysis.

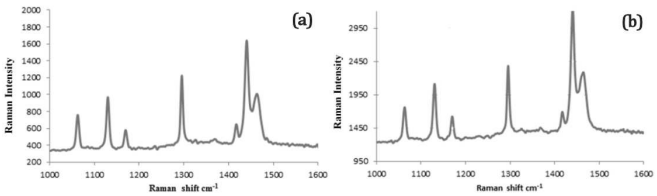

Fig. 3. Raman peaks of (a) pure UHMWPE, (b) UHMWPE-2 wt.% TiO_2.

The thermal analysis of the pure UHMWPE and UHMWPE-TiO_2 composites was performed by using a differential scanning calorimeter (DSC). The DSC peaks of the samples were then analyzed to obtain the melting temperature T_m, and enthalpy of fusion ΔH of the samples, for determination of the degree of crystallinity. As can be seen in Eq. (1), the degree of crystallinity of the UHMWPE composites X_c is given by the ratio of the area of the melting peak below the DSC heating curve ΔH_m to the enthalpy of melting of 100% crystalline UHMWPE ΔH_{100}, i.e. 291 J/g [7].

$$X_c = (\Delta H_m / \Delta H_{100}) \times 100. \quad (1)$$

Results of DSC analysis and calculated crystallinity of UHMWPE and UHMWPE-TiO_2 composites are given in Fig. 4 and Table I. It can be seen that there was a slight increase in the melting temperature T_m of UHMWPE after the addition of TiO_2 particles (Fig. 4). TiO_2 particles restrict the chain mobility during melting of the polymer and postpone the melting. The calculated crystallinity of UHMWPE composites increases with increasing amount of TiO_2 particles. The increase in crystallinity can be attributed to the heterogeneous crystallization. TiO_2 particles behave as nucleating agents for UHMWPE during the crystallization [7].

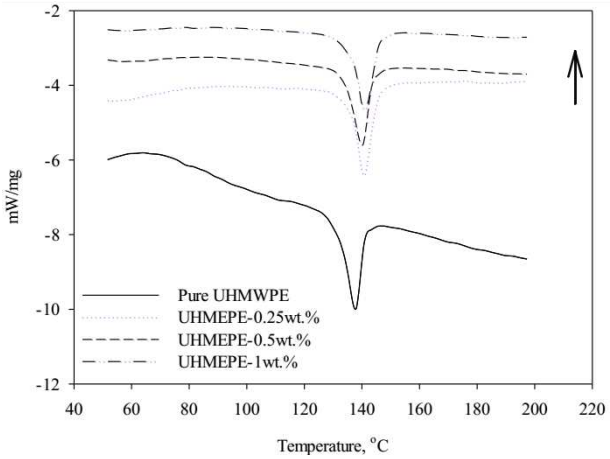

Fig. 4. DSC analysis of UHMWPE-TiO_2 composites, including pure UHMWPE.

TABLE I

Elastic modulus and crystallinity of UHMWPE-TiO_2 composites.

wt.%	Elastic modulus, [GPa]	Crystallinity, [%]
0	410	56
0.5	610	59.5
1	650	60.66
2	791	63.46

It is well known that higher crystallinty has a strong influence on mechanical properties of a polymer, such as Young's modulus, yield stress, strain hardening rates and ultimate tensile properties. Experimental results show that reinforcing with TiO_2 particles increases the elastic modulus of UHMWPE. It is possible to claim that TiO_2 particles, restricting C–C bond rotations and sliding in polymer, increase the elastic modulus of polymer significantly [11].

4. Conclusions

This research investigates the production of UHMWPE-TiO_2 composites by gelation crystallization method. The method enables us to have uniform distribution of TiO_2 particles in the UHMWPE matrix. Good adhesion between TiO_2 particles and UHMWPE matrix was obtained. Raman results show that UHMWPE-TiO_2 composites were produced successfully. TiO_2 particles have acted as nucletion agents for UMMWPE chains and have caused an increment in crystallinity and also in elastic modulus of UHMWPE. An increase of 92% in elastic modulus of UHMWPE was obtained. In conclusion, the newly developed UHMWPE-TiO_2 composites can be potentially used for production of plastic liners of artificial hip joints.

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