Preparation and characterization of poly(methyl methacrylate)chitosan/hydroxyapatite composite coating on ultra high molecular weight polyethylene substrate

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ABSTRACT

In this work we prepared a poly(methyl methacrylate)-chitosan/hydroxyapatite (PMMA-CTS/HA) composite coating. PMMA-CTS/HA composite was prepared by a solution of chitosan-hydroxyapatite (CTS-HA) and the *in situ* polymerization of PMMA obtained from its monomer methyl methacrylate (MMA) using benzoyl peroxide (PBO) as the initiator. FTIR technique was used to study the hybrid composite coating. The coating morphology was characterized by SEM finding out a well-connected porous surface structure provided by the incorporation of HA and CTS. A pin-on-disk test was executed with a 6 mm diameter WC ball in dry condition applying 2, 4, 6, 8 and 10 N loads. The lowest mean kinetic friction coefficient (μ_k) was 0.04 at 10 N, whereas the lowest wear rate (k) was 5.1 x10⁻⁵ mm³/(Nm) at 4 N. The coating hardness was evaluated with a Vickers hardness test using a load of 50 mN obtaining a mean value of 0.21 GPa. Experimental results opened the possibility of using PMMA-CTS/HA coating on ultrahigh molecular weight polyethylene (UHMWPE) as bearing material in biomedical applications taking into account the potential properties of these systems with human tissue.

INTRODUCTION

Hydroxyapatite (HA) reinforced polymers composites have received much attention due their wide clinical applications, specifically, composites composed of chitosan (CTS) and poly(methyl methacrylate) (PMMA) polymers matrix due to their bioactivity and biocompatibility with the biological system. Hydroxyapatite (HA, Ca₁₀(PO₄)₆(OH)₂) is highly reactive and favorable for bone attachment and cells bioactivity. Besides, HA exhibits excellent biocompatibility, bioactivity and, if it is porous, osteoconduction in vivo [1]. The concept of composite HA coating/polymer systems, combining both biological and mechanical properties of components, aims to reduce the cytotoxicity or inflammatory reactions of surrounding tissues. HA/polymer composites may improve both bone boning rate and the mechanical properties suitable to many potential clinical applications, e.g. bone cement, dental implants and coating of joint replacement prosthesis [2]. Poly(methyl methacrylate) (PMMA) is the aloplastic material most used for cranial osseous defects. It has the advantages of being a low cost biomaterial, easy intraoperatory moulding and it is generally tolerated by human tissues, leading to neither necrosis nor adverse inflammatory reactions [3]. On the other hand, chitosan (CTS) is a co-

polymer of glucosamine and N-acetyl glucosamine deacetylated from the natural polymer chitin, CTS was suggested as an alternative polymer for use in orthopedic applications to provide temporary mechanical support the regeneration of bone ingrowth due to its good biocompatible non-toxic, biodegradable, and inherent wound healing characteristics [4].

Based upon the above evidences, the combination in properties of a PMMA-CTS polymer matrix and HA seems to have a potential application as hybrid coating material with future medical applications. The aim of this work is to obtain a composite material of PMMA-CTS/HA and evaluate it as coating on ultra high molecular weight polyethylene (UHMWPE) substrates. The results presented in this study provide a useful and simple route to synthesize a composite material that could be used as a protective coating on bearing components.

EXPERIMENTAL

Chitosan (CTS, C₁₂H₂₄, with the deacetylation degree of 92% and low molecular weight, Mv=5.89x10⁴, Sigma Aldrich), methyl methacrylate (MMA, 99%, Sigma Aldrich), acetic acid (AcAc, CH₃COOH, 99.8%), benzoyl peroxide (PBO, Sigma Aldrich), sodium hydroxide (NaOH, J.T. Baker) and distilled water were used. Hydroxyapatite (HA) nanoparticles, with spherical (74 nm in diameter) and needle morphology (length=158 nm and width=64 nm), were synthesized as previously reported elsewhere [5]. The composite synthesis begins with the CTS solution (0.77% w/w) with acetic acid, the solution was vigorously stirred during 3 hours without increasing temperature, obtaining a pH=3.0. With these conditions no precipitation was observed. Then, 60 mg of hydroxyapatite nanoparticles, were added to the solution and stirred during 14 hours to obtain the CTS/HA solution. Subsequently, 47 mmols of MMA, previously uninhibited, were added to CTS/HA solution under vigorous magnetic stirred during 2 minutes. Next, 0.51 mmols of PBO were added, keeping the stirred for 2 hours at 80°C obtaining an ending solution with a pH=2. The PMMA-CTS/HA formation was examined by FTIR spectral analysis with a Perkin Elmer Spectrum 400 instrument equipped with an ATR detector. The coating preparation on UHMWPE substrate was performed as described elsewhere [5], by a dipping process. Surface morphology of the samples was characterized by scanning electron microscope (FEI Nova nano SEM 200), while cross section of the PMMA-CTS/HA was observed in an Olympus GX-51 microscope to evaluate the coating thickness. The average surface roughness (R_a) of the coatings was analyzed using a MITUTOYO Surftest 402. Twenty measurements were made perpendicularly to the coating surface in an area of 40 cm^2 .

The wear tests were performed on CSM Instruments Tribometer by pin-on-disk configuration with contact loads of 2, 4, 6, 8 and 10 N and a rotating radius of 2.00 mm. The sliding speed was settled at 0.10 m/s with a sliding distance of 300 m and acquisition rate of 2.0 Hz. The temperature during the test was maintained at $26\pm1^{\circ}$ C with a relative humidity of 30.40%. Kinetic friction coefficient (μ_k) values were obtained directly from the Tribox 4.1 software. Considering the weight loss negligible, volume loss (V) values were determined using a standard test method as indicated in the ASTM G99.05 [6] while specific wear rate (k) was calculated from a relation given in [7]. Hardness tests were carried out on a microhardness equipment (Matsuzawa MMT-X7 with Clemex CMT Software) under indentation loads of 50 mN.

RESULTS AND DISCUSSION

Hybrid coating characterization

Figure 1(left) shows the FTIR spectrum corresponding to the PMMA-CTS/HA composite solution, indicating details of functional groups present in the composite. The broad peak at 3386 cm⁻¹ is due to the stretching vibration of C-H. The vibration band presented at 1703 cm⁻¹ correspond to ester carbonyl group stretching vibration (C=O) of PMMA [3] whereas the peak at 1638 cm⁻¹ is related with the NH₂ present in the chitosan compound [4]. The peak at 1386 cm⁻¹ appeared due to the presence of the stretching vibrations of CH₃. The sharp intense peak at 1274 cm⁻¹ correspond to C-C vibration. A low PO₄³⁻ peak appeared at 1051 cm⁻¹ due to the HA incorporation, while the peak at 1015cm⁻¹ can be related with the additional phosphate peak of the inorganic phase [8].



Figure 1. FTIR spectra of PMMA-CTS/HA composite (left) and SEM micrographs of PMMA-CTS/HA, CTS/HA and PMMA/HA coatings on UHMWPE substrates at 20 000x (a) and 50 000x (b) (right).

Figure 1(right) shows the SEM images from surfaces of PMMA-CTS/HA, CTS/HA and PMMA/HA coatings on UHMWPE substrates at 20000x (a) and 50000x (b). PMMA-CTS/HA shows a highly roughness surface and CS/HA coating showed flake-like morphologies leading a porous surface. This porous surface is more evident at higher magnification in both coatings. Whereas, PMMA/HA coating exhibit a flat surface without pores, at higher magnification a smooth morphology with some wrinkle formations is observed. These observations suggest that PMMA-CTS/HA and CS /HA coatings provide porous spaces to facilitate osteoconduction due to the incorporation of CS powder, allowing the bone to grow, because it allows relatively more stable tissue surrounding smooth surfaces [3].

The estimation of surface roughness (R_a) confirmed the distinction in the surface appearance, yielding values of 1, 0.6 and 0.5 μ m for the PMMA-CTS/HA, CTS/HA and PMMA/HA coatings, respectively. The PMMA-CTS/HA coating thickness measured in cross section was 30.40 μ m.

Friction and wear analysis

Figure 2 show the variation of μ_k values in PMMA-CTS/HA coating against sliding distance applying different loads and a comparison between wear rate (k) and volume loss (V) of PMMA-CTS/HA composite coating on UHMWPE substrate sliding against WC ball.



Figure 2. Friction coefficient of PMMA-CTS/HA (right); wear rate and volume loss of PMMA-CTS/HA composite coating on UHMWPE substrate sliding against WC ball (left).

It can be observed that 2N loading the PMMA-CTS/HA coating presented higher μ_k values . While the lowest values were observed for a 10 N load observing high μ_k values at the beginning of the test decreasing rapidly and stabilized showing no fluctuations during the test. At normal load of 4 N it presented fluctuations during the tests. Friction coefficients values at 8 N present low μ_k values at the initial stages and increase at 70 m of sliding distance and stabilized until the test was finished. The behavior of V and k at different loads shows tendency to increase with the increasing load over 4 N. The volume loss exhibit the lowest value with normal load of 2 N and the highest with a normal load of 10 N with values of 0.04 mm³ and 0.26 mm³, respectively. While the k ,exhibited the lowest value at 4 N (k= 5.10x10⁻⁵ mm³/(Nm)).

Figure 3 shows representative images of the wear tracks after friction tests on PMMA-CTS/HA coating at normal loads of 4 (a), 6 (b) ,8 (c) and 10 (d) N loads against WC ball showing the surface wear mechanism. It could be seen that the width of wear track increased while load increases.



Figure 3. Wear tracks after friction tests of PMMA-CTS/HA coating at4 (a), 6 (b) 8 (c) and 10 (d) N loads against WC ball.

Well-defined grooves could be observed in the four systems, although from Figure 3b, wear track from 6 N load test, presents more severe groove depth than the system at 4 N (Figure 3a); showing deformation of asperities at the side of the track and material remaining on the edge track. Meanwhile, Figures 3c and 3d presents the wider wear tracks with depth grooves for the PMMA-CTS/HA coating at 8 and 10 N. It was expected that the mean friction coefficient values would decrease with increase in load due to improved contact area; however, friction coefficients not show any influence regard to the load. Mean μ_k values of PMMA-CTS/HA coatings were quite similar at 4 N and 8 N, showing an average value of $\mu_k = 0.15$ and $\mu_k = 0.16$, respectively, compared to those reported by Ge et al. [9] for an UHMWPE implanted with nitrogen ions which exhibited friction coefficient of 0.26, 0.18 and 0.16 in dry friction with 5 N load.

CONCLUSIONS

In this study, a PMMA-CTS/HA composite was proposed to be used as coating on UHMWPE substrates. The composite coating showed a wrinkle surface morphology into the polymer matrix. The friction coefficients of PMMA/CHA coating did not performed better than those for UHMWPE substrates; however they remained constant under standard loads. The wear mechanisms included formation of grooves and production of debris. Within this study the

PMMA-CTS/HA coating show better tribological performance at higher loads compared with others studies that proposed a surface treatment method in order to enhance the wear resistance of UHMWPE. Besides its low costs and simple processing, we consider that PMMA-CTS/HA hybrid coating presented in this work could offer the advantage of supporting the early stages of UHMWPE wear in dry friction.

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