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Performance evaluation of chitosan/hydroxyapatite composite coating on ultrahigh molecular weight polyethylene

A. Arizmendi-Morquecho [a], A. Chávez-Valdez [b], C.H. Navarro [c], K.J. Moreno [c,*]

[a] Cimav-Unidad Monterrey, Apartado Postal 66600, Nuevo León, Mexico
[b] Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, 91058 Erlangen, Germany
[c] Instituto Tecnológico de Celaya, Apartado Postal 57, 38010 Celaya, Guanajuato, Mexico

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ABSTRACT

The aim of the present study is to evaluate the performance of chitosan/hydroxyapatite (CTS/HA) coatings on ultrahigh molecular weight polyethylene (UHMWPE). We focused on adhesion measurements, micro-hardness indentation, friction and wear tests. Using commercial compounds of medical grade, CTS/HA composite was prepared by a simple mixture using acetic acid as solvent. The CTS/HA solution obtained was used to prepare coatings on UHMWPE substrates by the immersion method. Scanning electronic microscopy (SEM) results showed that the composite coating had flake-like morphology characteristic of chitosan and calcium phosphate powders with a porous structure. The adhesion strength between CTS-HA coating and UHMWPE was approximately 0.15 MPa, according the ASTM D5179 method. The micro-hardness of CTS/HA coating on UHMWPE was evaluated by using a Vickers hardness tester, while friction and wear were studied by a pin-on-disk method in dry conditions.

1. Introduction

Chitosan (CTS) is a natural biodegradable polymer and is a derivative from chitin deacetylation. The degree of deacetylation controls the amount of free amino groups in the polymer chain. The free amino group, along with the hydroxyl group, gives chitosan its functionality, which allows it to be a highly reactive polysaccharide. The positive charge of chitosan allows it to have many electrostatic interactions with negatively charged molecules. The processing conditions as well as the amount of functional groups created by deacetylation allow side group attachments, affecting the crystallinity, which directly relates to the ability of chitosan to solubilize in acid aqueous solutions [1,2]. Chitosan exhibits many physicochemical and biological properties that make it an attractive material for use in numerous fields, such as waste and water treatment, agriculture, fabrics, textiles, cosmetics and food processing. In addition to its lack of toxicity and allergenicity, its biocompatibility, biodegradability and bioactivity make it a very attractive material for a wide range of applications as a biomaterial in pharmaceutical and medical areas [2,3]. Chitosan has also been shown to be an excellent adhesive that can adhere to hard and soft tissue, and it has been used in dentistry, orthopedics, ophthalmology and surgical procedures [2]. In addition, clinical tests carried out in order to promote chitosan-based biomaterials do not report inflammatory or allergic reactions following implantation, injection, topical application or ingestion in the human body [4]. The functional groups of chitosan allow it to interact with many materials, such as hydroxyapatite or other calcium based minerals to form composites that have multiple biomedical applications. The combination of chitosan with hydroxyapatite (HA) in vivo has been shown to maximize the osteoinductive behavior of HA, allowing bone ingrowths into the implant that occur as the

* Corresponding author. Tel.: +52 461 6117575; fax: +52 461 6117878.
E-mail address: moreno_bello_karla@yahoo.com.mx (K.J. Moreno).

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matrix is progressively resorbed [5]. Also, the combination of chitosan with mono-calcium phosphate and calcium oxide has been used to produce a fast setting mixture with improved mechanical properties suitable as phosphate cement to fill bone cavities [6]. Several studies have focused on the use of chitosan as a component in calcium-based cements in the development of bone substitutes. Yokoyama et al. [7] used chitosan as a component of the liquid phase that includes citric acid and glucose in combination with tri-calcium phosphate and tetra-calcium phosphate to produce easily moldable cements, resulting in good bonding between the cement and bone. Cai et al. [8] have reported the preparation of homogeneous hydroxyapatite-chitosan nanocomposites for their use in bone tissue engineering. In this work, we have focused our attention in the study of a composite based on chitosan/hydroxyapatite (further referred to as CTS/HA) as coating with potential application in many areas of medicine [6,7]. In this paper, we report the performance evaluation of CTS/HA composite coatings by measurements of adhesion, hardness and wear behavior on UHMWPE substrates.

2. Experimental procedure

Chitosan with a deacetylation degree of 92% and low molecular weight of $C_{12}H_{24}$, acetic acid (CH_3COOH, 99.8%), commercial hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), (particle size <200 nm, and purity ≥97%), purchased from Sigma Aldrich and distilled water were used to obtain CTS/HA coatings. CTS/HA solution was prepared following a previously reported procedure [9]. Coatings were prepared by the immersion of UHMWPE substrates into CTS/HA solution, as described in a previous work [9,10].

The coating thickness was calculated using image analysis software in an Olympus GX-51 microscope and the surface morphology of the samples was analyzed by scanning electron microscope (FEI Nova nano SEM 200). The average surface roughness (Ra) of the coatings and UHMWPE substrate was analyzed using a MITUTOYO Surftest 402. Twenty measurements were made at the direction perpendicular to the coating surface in an area of 40 cm^2.

The adhesion strength between CTS/HA coating and UHMWPE substrate was estimated using a pull-off method, by mounting and removing an aluminum stud from the surface of the coating and measuring the force required to break the coating-substrate bond with a tensile tester. Four drops of a commercial cyanoacrylate adhesive were spread on the surface of the stud and immediately placed on the coating surface, pressing the stud onto the coated test substrate by using a weight of 2 kg to ensure good contact, and maintaining a curing time of 90 hrs. Ten specimens were tested using a universal testing machine (Model 1011, Instron Ltd) with a 500 N load cell and a chart speed of 25 cm/min. The test method is in accordance with ASTM D5179 [11] for measuring adhesion of organic coatings to plastic substrates by direct tensile testing. Fig. 1 is a schematic diagram of the adhesion test configuration. The micro-hardness of CTS/HA coatings on UHMWPE was evaluated by using a Vickers hardness tester. Tests were carried out on a Matsuzawa MMT-X7 with Clemex CMT Software, under an indentation load of 0.098 N. Ten indentations were made at each load, yielding twenty diagonal indentation measurements from which the average micro-hardness was calculated. Wear tests were carried out on a CSM Instruments Tribometer with pin-on-disk configuration in dry conditions. The values of kinetic friction coefficient (μ_k) were obtained directly from the Tribox 4.1 software. A tungsten Carbide (WC) ball with a diameter of 6 mm, roughness $R_a = 0.02$ μm and hardness of 1770 HV was slid on the UHWMPE substrate coated with the CTS/HA composite. For the test, the WC ball was fixed on the load arm and the sample was placed on a rotating disc with a rotating radius of 1.74 mm. The standard contact loads used were 2, 4, 6, 8 and 10 N, sliding speed of 0.10 m/s, acquisition rate of 2.0 Hz and a distance of 300 m for the complete test. The temperature during the test was maintained at 26 ± 1 °C with a relative humidity of 30–40%. Since the wear mass loss values of the samples were inconsistent and the differences between the weight loss was negligible, we rather determined the volume loss values using a standard test method (ASTM G99–05) [12] and assuming that there was no significant pin wear. Then, the wear rate was calculated using the equation given in [13].

3. Results and discussion

Fig. 2 shows SEM images of the CTS/HA coating on UHMWPE substrate, exhibiting a flake-like morphology characteristic of components based on chitosan and calcium phosphate powders [14,8] with a surface roughness (R_a) of 0.6 ± 0.01 μm. The thickness estimation by image analysis shows an average value of 30 μm. SEM observations also revealed the high affinity between the inorganic crystals and the CTS. The fact that the interface between the inorganic and organic phases was indistinguishable, might help to improve the mechanical properties of the composite [8]. The coating surface shows a porous morphology, which is desirable to improve osteoconduction. Previous reports have shown that the porosity in combination with the presence of a bioactive material could have a synergic effect and may be responsible for improvement in cell colonization in a material, osteoblast activity and in bone remodeling [15,8]. Results of tensile strength measurements between the CTS/HA coating and the UHMWPE substrate are given in Table 1. The samples exhibited an adhesive failure mode with an average yield force of 40 N and an average adhesion strength value of 152 Kpa (~0.15 MPa). Oosterom et al. [16] reported a shear strength value of 0.13 MPa for UHMWPE bonded by PMMA, which increased after different surface modifications of UHMWPE, showing the highest value of 0.72 MPa with a glow discharge treatment. Since the UHMWPE has poor interfacial bonding with polymeric matrices, several surface modification techniques have been developed in order to solve this problem e.g. chemical grafting, acid etching, corona discharging, UV/Ozone and glow discharge [15,17]. Surface modification of UHMWPE with γ ray radiation with methyl methacrylate (MMA) monomer improves the interfacial bonding strength between UHMWPE and PMMA from 0.86 MPa to 19.2 MPa