WEAR AND FRICTION BEHAVIOR OF POLY (METHYL METHACRYLATE)/CALCIUM OXIDE COATING COMPOSITES UNDER DRY CONDITIONS

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Abstract

Poly(methyl methacrylate)/calcium oxide (PMMA/CaO) composite in the form of solution, has been successful prepared for its application as coating on ultra high molecular weight polyethylene (UHMWPE). The hybrid coating was prepared by mixing the CaO powder in situ with PMMA polymerization from its monomer methyl methacrylate (MMA) using benzoyl peroxide (BPO) as initiator and toluene as solvent. The FTIR technique was used to study the hybrid composite coatings. Coating surface morphology was characterized by Scanning Electron Microscopy founding out CaO particles on the polymer surface; by image analysis was found that the incorporation of CaO powder increases the PMMA/CaO coating thickness obtaining a mean value of 107.57 μm. Wear test of PMMA/CaO coatings on UHMWPE were carried out on a pin-on-disk tribometer in dry conditions with a normal load of 5 N against stainless steel.

Keywords: Poly(methyl methacrylate)/calcium oxide, hybrid coating, wear, friction.

1. Introduction

Poly(methyl methacrylate) (PMMA) has been largely used as a biomedical material [1], it is a representative material used for bone cement due to its self-hardening property and excellent mechanical properties compared to other polymers [2]. 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] However, PMMA does not adhere to bone nor does it induce bone formation and may contribute to periprosthetic osteolysis [4] it remains, however, an artificial prosthetic material, which inserted in the body could become encapsulated in a fibrous tissue matrix. This might generate a potential free space for infections, leading to the implant rejection [5]. In addition, PMMA undergoes an exothermic polymerization reaction which has been shown to damage bone tissue [6] which can be overcome by introducing bioactive ceramic fillers to it. In this point, calcium oxide could be a great candidate for specific applications. CaO is the main precursor of the most important bioactive ceramic named “hydroxyapatite” as well as bioglasses composition which are compound of a mixture of silica, alumina, magnesia, calcium oxide, sodium oxide, and phosphorous oxide [7]. Bioglasses system were the first to actively interact with tissues and induce their intrinsic repair and regenerative potential which involves control over the cell cycle, molecular frame work that controls cell proliferation and differentiation. Depending upon the rate of resorption and release of ions they can create chemical gradients with specific biological actions over cells and

tissues [8]. It was reported that CaO improves the phosphate network strength when cross-link formation between the non-bridging oxygen of two different chains by Ca^{2+} ion. The cytotoxicity of this glass decreased with increasing CaO and decreasing P_2O_5 content [9]. The goal of this work is to obtain a composite from PMMA and CaO (PMMA/CaO) in solution and evaluate its performance as coating by wear and friction tests. We consider that this type of coating might be considered for specific medical applications due PMMA and CaO highly biocompatible properties.

2. Experimental Section

2.1. Chemical

In order to synthesis the hybrid material, calcium oxide (CaO) was previously obtained as it has been reported [10], methyl methacrylate (MMA, 99% Sigma-Aldrich), benzoyl peroxide (BPO, Sigma Aldrich), sodium hydroxide (NaOH, J.T.Baker), toluene (anhydrous, 99.8%, Sigma-Aldrich) and distilled water were used as received.

2.2. PMMA-CaO composite synthesis

Before the reaction 75.35 $x10^{-3}$ moles of MMA were subjected to a continuous magnetic stirring with $1.18x10^{-3}$ moles of NaOH for 30 minutes to remove the inhibitor agent, the solution was then filtered. Simultaneously, a $1.93x10^{-2}$ M solution of CaO with toluene was prepared and mixed with 5 ml of the filtered solution of MMA. The solution was kept in continuous magnetic stirring during 20 minutes and then $5.161x10^{-5}$ moles of BPO were added to initiate the reaction keeping the continuous magnetic stirring during 1 hour.

2.3. Preparation of coatings

UHMWPE substrates with dimensions 25 mm x 25 mm were polished to a surface roughness $R_a \leq 0.4$ µm. The coatings were prepared by immersion of UHMWPE substrates in the PMMA/CaO solution. The dipping was performed by mechanical device ensuring the immersion speed of 72 mm/min during 5 min. After the immersion, the samples were left in the open air for 2 min, and then definitely dried at 115°C during 3 hours. For comparative studies, the same methodology was applied to prepare PMMA coating.

2.4. Characterization

The functional groups of the resulting composite were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR). FTIR transmittance spectrum was obtained in the 4000-400 cm^{-1} region using Perkin Elmer Spectrometer 400 with an ATR coupled. The coating thickness was estimated with image analysis software of Olympus GX-51 microscope, studying cross section of a sample embedded into epoxy resin. Surface morphology was analyzed by an electronic microscope FEI Nova nano SEM 200. Atomic force microscopy (AFM Vecco SPM) in contact mode was used to study the surface morphology of the PMMA/CaO coating on UHMWPE. The average samples roughness (R_a) was investigate using a perfilometer (Vecco Dektak 150). Wear test were carried out on CSM Instruments Tribometer by pin-on-disk test in dry conditions with a 6 mm diameter stainless steel ball. Sliding distance and speed were settled at 200 m and 0.10 m/s respectively, with a 5 N load. Mean coefficient friction (µ) value was obtained directly of the Tribox 4.1 software. During test, the environment was kept at 26±1°C and 30-40% relative humidity conditions. The volume loss values were determined by a

standard test method as indicated in the ASTM G99-05 [11], assuming that there is no significant pin wear.

3. Results

Figure 1 shows the FT-IR spectrum of the PMMA/CaO solution, indicating the details of functional groups present in the composite. A sharp peak appears at 1720 cm^{-1} which corresponds to the stretching of the C=O group [12] characteristic of PMMA polymer. The bands around 3029 and 2953 cm^{-1}, correspond to the C-H stretching of methyl group (CH_3) while the bands at 1298~1450 cm^{-1} are associated with C-H symmetric and asymmetric stretching modes respectively. The 1200 cm^{-1} band is assigned to torsion of methylene group (CH_2) and the 1160 cm^{-1} band corresponds to vibration of the ester group C-O [12]. Also, stretching vibrations bands appeared around 16389 cm^{-1} and 1603 cm^{-1} due to C=C stretching vibrations, indicating a partial polymerization of MMA and remainder toluene [12].

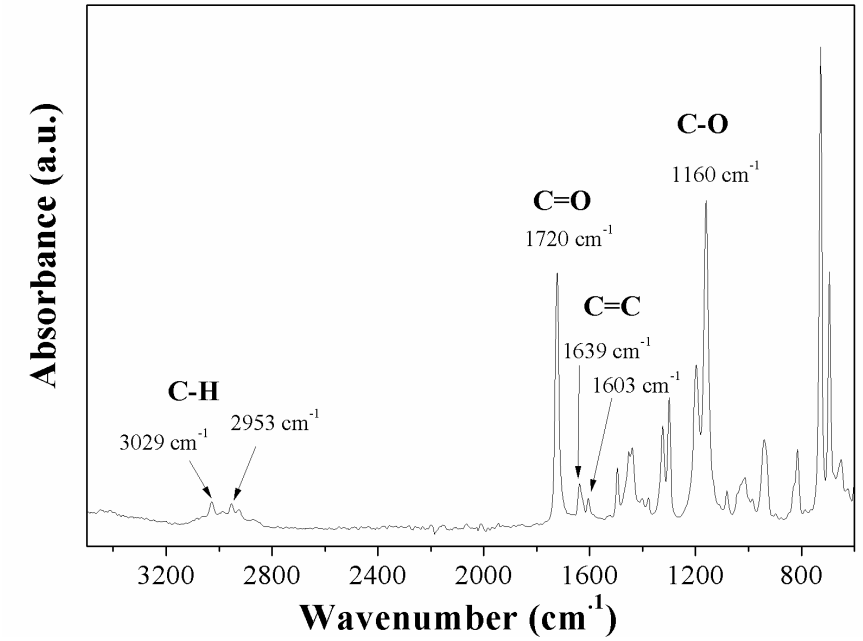

Figure 1. FTIR spectra of PMMA/CaO composite.

The SEM images of the PMMA/CaO coating on UHMWPE are shown in Figure 2. PMMA/CaO coating features flake-like surface formations due to the incorporation of inorganic material into the polymer coating (Figure 2a). It could be notice some particles on the surface of PMMA/CaO coating showed in Figure 2b, with raises shapes. Figure 2c shows a group of these particles, while Figure 2d shows an agglomerate group. The length and width size mean for raise shape particles were 0.8315 µm and 0.3779 µm, respectively.

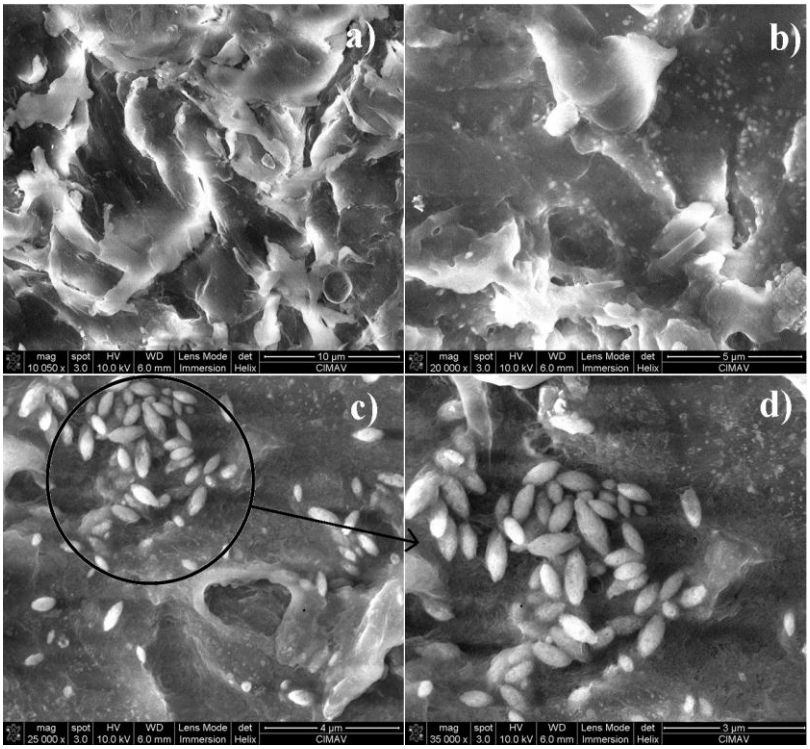

Figure 2. Scanning electron surface micrographs of PMMA/CaO coating on UHMWPE substrate.

Figure 3 shows the bidimensional (a) and tridimensional (b) AFM images for the PMMA/CaO coating on UHMWPE for an area of 2.0 µm X 2.0 µm, as representative for this work. Figure 3a shows a smooth surface with worm appearance, characteristic of polymers in AFM studies [13], while Figure 3b shows the valleys and peaks of the coating, besides roughness with a maximum value of 317.7 nm, only for this area. Through this analysis can determine the roughness of the coating, however, this value would be influenced by the area traveled due to the [root-mean-square (RMS) roughness] value obtained was 139 nm whereas the average roughness (R_a) determined by perfilometer were 0.62 µm and 0.47 µm for PMMA and PMMA/CaO coatings respectively.

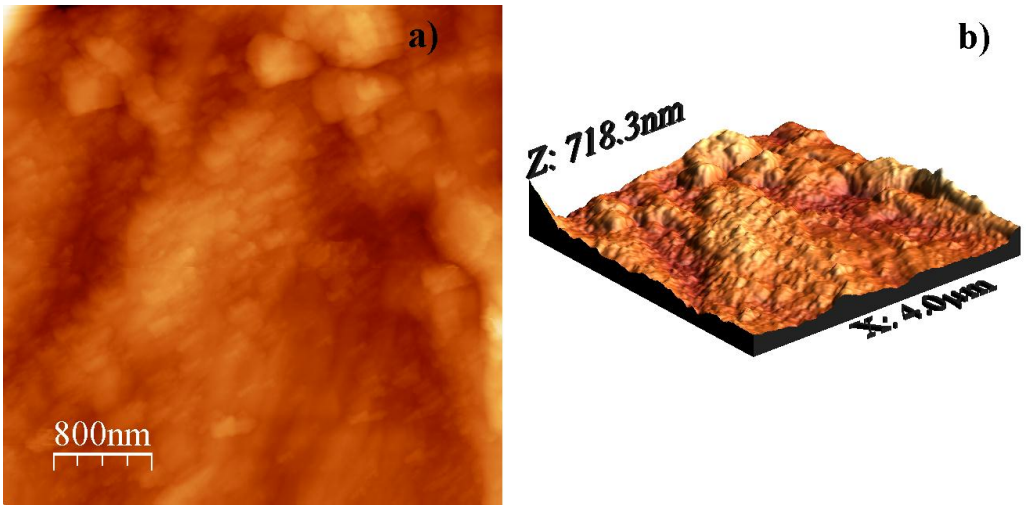

Figure 3. Bidimensional (a) and tridimensional (b) AFM images of PMMA/CaO coating on UHMWPE substrate.

Figure 4 shows the cross section morphologies of PMMA/CaO coating on UHMWPE used for thickness determination as representative. The micrograph shows a homogenous coating with an average thickness of 107 µm, whereas PMMA coating shows an average thickness of 97 µm. It is important to mention that these coatings did not break after polishing process, which suggests that the coatings exhibit good adhesion to the substrate. Generally, coatings on substrates with different bonding nature can break off due to weak bonding strength [14] or due to the high stresses between the substrate and the coating [15]. In the case of PMMA-coated UHMWPE, the adhesion results might be related with a good bonding between UHMWPE and PMMA due to formation of covalent bonds.

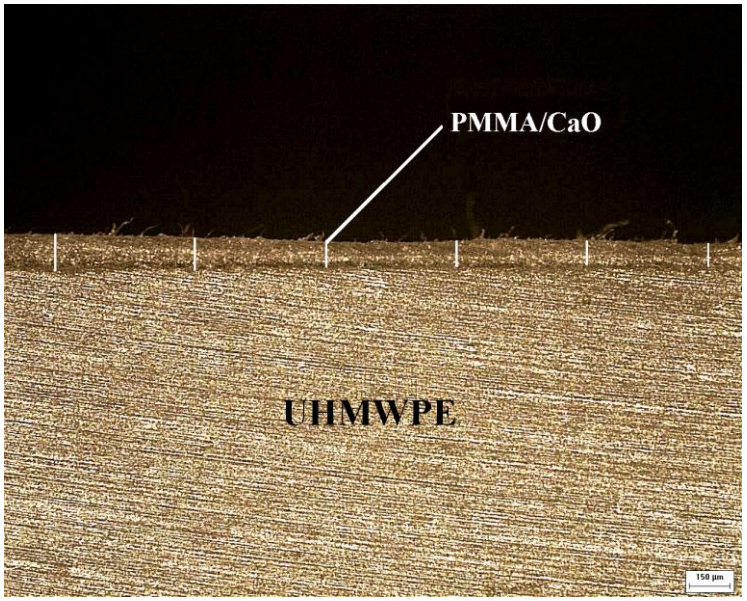

Figure 4. Cross section morphology of the PMMA/CaO coating on UHMWPE.

Figure 5 shows friction coefficients variations with respect to the sliding distance for PMMA and PMMA/CaO coating on UHMWPE with a 5 N load. PMMA/CaO coating presents a higher mean friction coefficient, 0.2151 µ, than PMMA with a value of 0.0897 µ. It can be seen that the friction coefficient values of PMMA and PMMA/CaO coatings on UHMWPE were low at the initial stage, increasing rapidly and stabilizing with the sliding distance remains almost constant during the end stage around 150 and 200 m. This behavior can be explained in terms of the frictions mechanisms occurring in polymers sliding against steel [16] where the friction coefficient at initial stage is largely of material combinations, surface conditions and environmental conditions, whereas the intermediate stage (between 50 to 150 m) the friction coefficients increases due to a rapid increase in the numbers of wear particles entrapped between the sliding surfaces as a consequence of higher wear rate. The deformation of asperities continues causing adhesive wear mechanism due larger clean interfacial areas. This effect increases in the PMMA/CaO coating due to the presence of CaO particles which could be the main asperities in the coating surface increasing the frictions coefficients. This behavior also was observed for PMMA/montmorillonite (MMT) composites where the friction coefficients increased as the MMT percentage was increased due to MMT appeared on the polymer surface increasing the contact area [17]. Also, have been consider [18] that the contact area depends on the interfacial energy. Therefore, in our case the interfacial energy might increase due to amount of CaO particle on the polymer surface thereby increasing its friction coefficient. Samples in this study have a friction coefficient similar with other similar materials improved with filled particles reported by Gong et al. [19], Blanchet and Kennedy [20], and Li et al. [21], where friction coefficient values obtained were 0.16 µ, 0.20 µ and

0.20 μ respectively. Avella et al. [22] filled polymethyl methacrylate (PMMA) with nanoscale $CaCO_3$, founding that the abrasion resistance increased as the filler content was increased with 3% $CaCO_3$ by weight. In our study we used 0.05% of CaO weight; friction coefficient for this weight percentage could be compare with a study reported by Sawyer et al. [23]. They filled PTFE with alumina nanoparticles, founding a friction coefficient of 0.155 μ and 0.207 μ, with 0.04wt% and 0.4wt% of filler. This behavior is related with the increase of filler which increases the friction coefficient. In the end stage of friction behavior against sliding distance, the adhesion contribution also remains constant and the asperity continue to contribute.

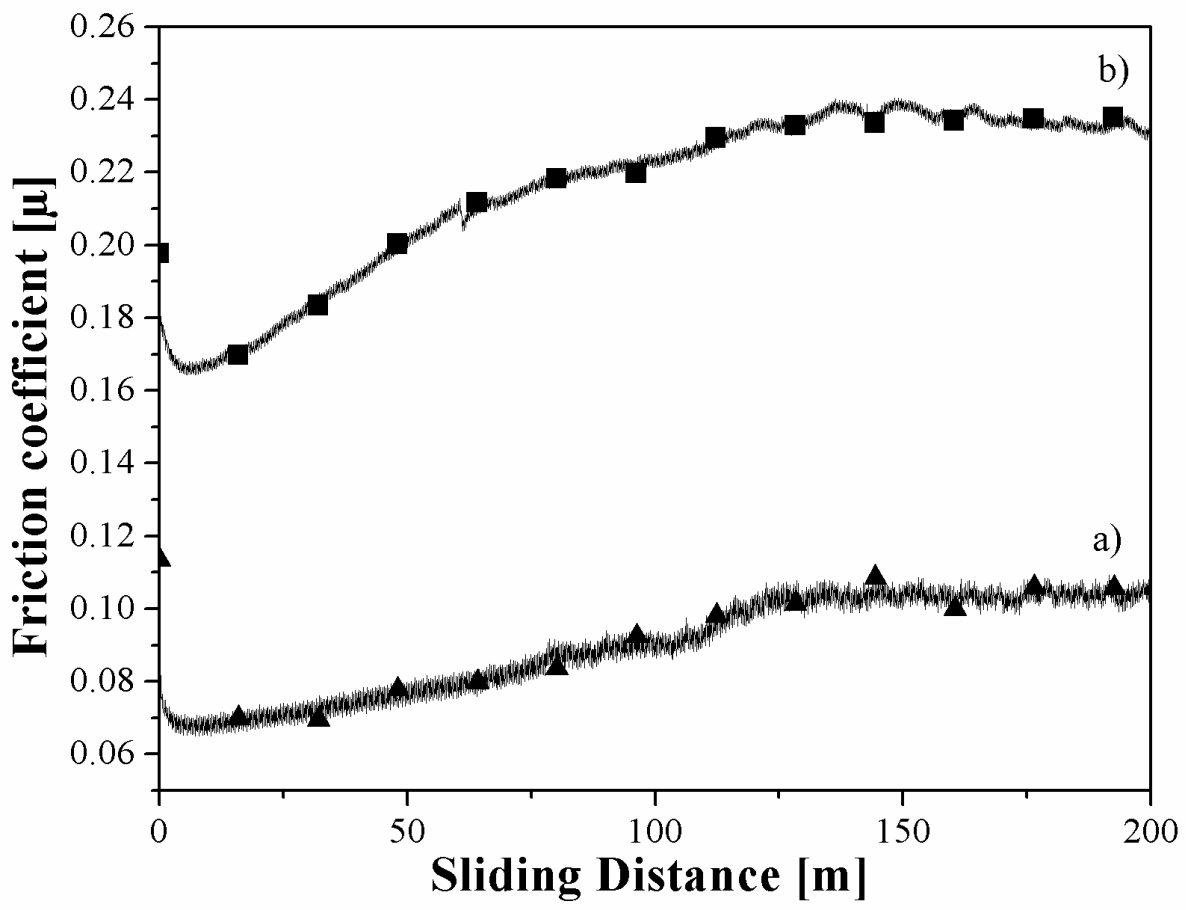

Figure 5. Friction coefficient variations with respect to the sliding distance for PMMA (a), and PMMA/CaO (b) coatings on UHMWPE.

The average adhesive wear factor *k* was calculated for each of the two coatings according to Archard´s Law [24] for adhesive wear:

$$\kappa = V/Lx \qquad (1)$$

V is the wear volume (mm^3), L is the load (N), x is the sliding distance (m) and κ is the wear rate (mm^3/Nm). As expected, PMMA/CaO coating exhibits wear factor higher value than PMMA coating. Volume loss values and wear rate values are presented in Table 1 together with the mean friction coefficient for the two samples. Although, the wear rate value of the PMMA/CaO coating is in the range of those reported before, for polymers filled with particles, by Gong et al. [19], Blanchet and Kennedy [20], and Li et al. [21], with wear rate values of $0.73X10^{-3}$, $0.74X10^{-3}$ and $1.12X10^{-3}$

(mm^3/Nm) respectively, the hybrid coating exhibit a slightly increases in its wear rate. However, many tribological systems are created through different coating techniques, where the coating material provide a tribological protection extending the operational life of bulk material by a greater amount of sacrificial coating material to the tribological contact [25]. Therefore, PMMA/CaO coatings prepared in this study might protect materials as UHMWPE and thereby extend their longevity, while it is being subjected to stress, by improving performance with a composite material as a coating.

Table 1. Wear factors of PMMA and PMMA/CaO coating on UHMWPE against stainless steel.

Material	Friction Coefficient [μ]	Volume loss [mm^3]	Wear rate [mm^3/Nm]
PMMA	0.0897	0.0960	$2.4 X10^{-3}$
PMMA/CaO	0.2151	0.1337	$3.3 X 10^{-3}$

Conclusions

We prepared successfully PMMA/CaO coating on UHMWPE substrates. The friction test showed that friction coefficients for PMMA/CaO composites showed a homogenous behavior. The incorporation of calcium oxide powder into PMMA increased the coating thickness, increasing the friction and wear parameters; however the friction coefficients and wear rates are similar to those reported for other polymer filled with particles used in bearing and seals applications. Improvements in wear can be performed with polymer filled with particles; however friction coefficient increase as weight percentage filler increased. Therefore, we consider that this work open the possibility to study the wear behavior of different PMMA/CaO ratio in order to depth in the tribological study of this kind of coating considering its potential medial application. Though these results did not give the certainly of its use for a specific application, they give the pattern to be considered for being applied as coating on UHMWPE for bearing applications.

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Acuso de recibo el trabajo: "Wear and friction behavior of poly (methyl methacrylate)/calcium oxide coating composites under dry conditions"de los autores: C.H. Navarro, K.J. Moreno, V. M. Nieto, A. Chávez-Valdez, A. Arizmendi-Morquecho, S. García-Miranda, R. Lesso, L.D. Aguileracuya referencia para futura información es: SV11-09.

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