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Wear reduction of orthopaedic bearing surfaces using polyelectrolyte multilayer nanocoatings

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Abstract

This work explores the use of conformal polyelectrolyte multilayer (PEM) coatings for wear reduction of orthopedic bearing surfaces. These films, with easily tunable architectures, provide excellent adhesion to a wide variety of metallic, plastic, and ceramic substrates. For this study, PEM films, only a few hundred nanometers thick, were assembled by sequential adsorption of poly(acrylic acid) and poly(allylamine hydrochloride). It was observed that the pH of the polylectrolyte solutions used for film assembly needs careful consideration to avoid any adverse effects on film structure when exposed to physiological conditions of pH and ionic strength. The wear reducing capacity of these coatings in the presence of bovine calf serum-lubricant solution was established for metal/metal systems at the meso/microscale over 30 cycles of reciprocating motion, as well as for the commonly used metal/ultra-high molecular weight polyethylene (UHMWPE) system over 500,000 cycles of bi-directional motion in a macroscale pin-on-disk test. In the latter case, the use of the films reduced UHMWPE wear by up to 33% when compared with the uncoated control. This is the first clinically relevant laboratory demonstration of the wear-reducing ability of these films. Further optimization will be needed before this novel class of materials can be used by the orthopedic community.

Keywords: Wear mechanisms; Polyethylene; Joint replacements; Total hip replacement prosthesis

1. Introduction

Wear particle-induced aseptic loosening of hip replacement prostheses remains a major cause of revision surgeries for the commonly used metal/ultra-high molecular weight polyethylene (UHMWPE) [1] and metal/metal [2] articulating pair configurations. In addition to osteolytic loosening, metal/metal articulations are plagued by concerns of electrochemical corrosion and carcinogenesis, owing to the dissemination of wear particles to other parts of the body [2,3]. Surface modification, through the application of coatings, offers the potential to reduce the wear rate without compromising the bulk mechanical behavior of the implant material. A variety of hard coatings have been investigated in the past for metallic bearing surfaces (for a comprehensive review, see Ref. [4]); examples include diamond-like carbon [5–9], amorphous diamond [10], and titanium nitride [9]. By comparison, there is a distinct lack of literature on wear-reducing coatings for UHMWPE.

The recent introduction of polyelectrolyte multilayers (PEMs) [11] offers a facile means of modifying the surfaces of various metallic, ceramic, plastic, and glass substrates. PEMs are assembled by the layer-by-layer adsorption of oppositely charged polyelectrolytes, leading to architectures that are tuned as a function of the processing conditions and choice of polyelectrolyte pair. The utility of these films is enhanced by their ease of fabrication (aqueous-based automated assembly proceeds at ambient conditions), large-scale conformity as well as uniformity of

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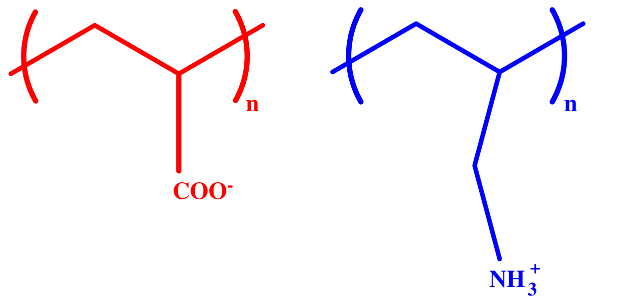

Fig. 1. Structures of repeat units of PAA and PAH.

coverage. Unlike most other coatings, PEM films can be constructed on a wide variety of substrates with little or no pretreatment; films are generally resistant to scotch-tape peel tests [12,13]. Current research (see Ref. [14] for a review) has focused on PEM application in the areas of biomaterials [15–18], photonic structures [19,20], separation membranes [21], and electrochemical devices [22–24].

In a prior publication [13], we studied the friction-and-wear behavior of PEM-coated substrates, both at ambient conditions and in the presence of a liquid medium. Poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) were used to assemble the PEMs. The structures of the repeat units of the polyelectrolytes are depicted in Fig. 1. Significant wear prevention of steel, glass, and silicon substrates occurred, when coated with PEMs, during tests up to 2000 cycles of reciprocating motion in the dry state and under applied normal stresses up to 450 MPa. It was observed that the delaminated film fragments were responsible in preventing contact between the mating surfaces, thus avoiding substrate wear. The work also demonstrated that PEMs assembled on both mating surfaces were suitable for intermittent contact situations. In addition, preliminary experiments conducted using a meso/microscale-testing device, in the presence of bovine calf serum and at physiological levels of normal load, revealed that wear of underlying steel substrates was avoided over 30 cycles of reciprocating motion when coated with only 70 nm-thick PEM films.

This paper evaluates, in detail, the friction-and-wear behavior of PEM-coated metal/metal and metal/UHMWPE systems at two scales of testing, and under physiological conditions of load, motion, number of cycles, and surrounding medium. PAA and PAH were used to assemble the films. This is the first study devoted to the wear behavior of the electrostatic layer-by-layer films in prosthetic systems. Further optimization will be needed before the orthopedic community is able to adopt this new class of materials.

2. Experimental

PAH ($M_W = 70000$) was purchased from Sigma-Aldrich (Milwaukee, WI). PAA ($M_W = 90000$) was obtained from Polysciences (Warrington, PA). Both the polymers were used without further purification. Deionized water (>18 MΩ cm, Millipore Milli-Q) was used for preparation of all aqueous solutions, and during rinsing procedures. Stainless steel sheets (type 316, #8 mirror finish), with an average roughness of approximately 0.006 μm, measured using a Tencor P-10 surface profiler, were purchased from McMaster-Carr (Dayton, NJ). UHMWPE GUR 1050 rod stock was purchased from Poly Hi Solidur, Inc. (Fort Wayne, IN). Bars were machined out of the rod stock, and heated to 150 °C in a hydraulic press (Carver, Inc.). They were then pressed between two mirror-finish steel plates to obtain sheets, approximately 1 mm in thickness; the associated average roughness was in the 0.15 μm range. Glass microscope slides from VWR Scientific Inc. (West Chester, PA) were used.

PAH/PAA PEMs were assembled on the above substrates as previously described [13,25,26]. Materials were degreased in a detergent solution, via ultrasonication, for 15 min, followed by ultrasonication in water for 10 min. After further rinsing in water, and drying by flushing with air, the substrates were subject to air-plasma treatment (5 min at 100 W-Harrick Scientific PDC-32G plasma cleaner/sterilizer). For the UHMWPE substrates, the plasma treatment increased the adhesion of the films, as observed in scotch-tape peel tests. PAH and PAA aqueous solutions (0.01 M based on molecular weights of the repeat unit) were adjusted to the desired pH using 1 M sodium hydroxide or 1 M hydrochloric acid. Films were assembled by immersing the plasma-treated materials into the PAH solution for 15 min, followed by three rinsing steps in water for 2, 1, and 1 min, respectively. They were then immersed in the PAA solution, followed by identical rinsing steps. The cycle was repeated to build PEMs of the desired thickness. The immersion and rinsing steps were automated using a Zeiss HMS programmable slide stainer [25]. Finally, the film-coated substrates were dried in a stream of air, and stored at ambient conditions for several hours before testing. The films were assembled at a pH of 7.5 or 3.5 for the PAH solution, and a pH of 3.5 for PAA, referred to as (PAH 7.5/PAA 3.5) or (PAH 3.5/PAA 3.5). A profilometer was used to measure thicknesses of PEM films on glass substrates.

Bovine calf serum (77–79 g/l total protein, JRH Biosciences, Lenexa, KS) was used to simulate joint synovial fluid. The lubricant solution was prepared by diluting the bovine calf serum to a protein concentration of 23 g/l, following literature recommendations [27]. The solution also contained 20 mM of the sodium salt of ethylenediaminetetraacetic acid (EDTA) and 0.2% by weight of sodium azide. Both these chemicals were obtained from Sigma-Aldrich (Milwaukee, WI). EDTA is normally used as an antichelating agent during tribological testing, while sodium azide serves as an antibacterial agent [28]. Behavior of PEM structures in the presence of bovine calf serum was studied by immersing films, on glass substrates, in the lubricant solution for varying lengths of time. Physiological conditions were maintained—pH around 7 and a temperature of approximately 37 °C. After immersion, the slides were subject to two 1-min rinsing steps in water before drying thoroughly. The average thickness and roughness values were calculated after measurements at several locations across the substrate using a profilometer.

Friction-and-wear behavior, on steel and UHMWPE slides, was studied on a meso/microscale using a flexure-based biaxial apparatus as described in Ref. [29]. Bovine calf serum-containing lubricant solution, described above, was used as the surrounding medium. A flat/flat configuration was used for all tests. The upper cylindrical pin with a flat surface, 1 mm in diameter, was made of D2 hardened tool steel. It is held stationary in the apparatus, while the lower, larger surface is subject to reciprocating motion. In all experiments, uncoated and film-coated steel and UHMWPE substrates were mounted on the lower slider using double-coated paper scotch tape. The interface region was immersed in the lubricant solution. A sliding speed of 200 μm/s and a path length of 3 mm were used in all tests. The test was confined to 30 cycles, corresponding to an accumulated sliding distance of 180 mm. Wear tracks were examined using an optical microscope and a profilometer; in all cases, surface profiles, examined at three points along the track, closely resembled each other. Between tests, the pin was polished using a 1 μm-alumina slurry; a specially designed holder ensured a flat surface during polishing. The pin was subsequently cleaned with acetone, and dried in a blast of air.