



Laser textured Co-Cr-Mo alloy stored chitosan/poly(ethylene glycol) composite applied on artificial joints lubrication

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ABSTRACT

Arthroplasty brings the wear problems because of body fluid has poor performance as lubricant. Lubricant which is used in artificial joints will rapidly degrade and be absorbed by human body after injecting. To prolong the lubricant's effectiveness, this study prepared chitosan/poly(ethylene glycol) (CS/PEG) and textures to play a role in joint lubrication and wear protection. Chitosan (CS) and poly(ethylene glycol) which have biocompatibility and biodegradability properties can be used in human body. The tribological results shown that CS/PEG sol has excellent performance when this sol was composed by 2 wt% CS and 30 wt% PEG, the average friction coefficient below 0.016 under the condition of 30–90 N load (pressure 4.2–12.6 MPa). In this study, CS/PEG was added in the texture of artificial joints, then the surfaces of the CS/PEG formed gel via NaOH solidification effect. The CS/PEG gel film could prevent the CS/PEG sol from diluting in body fluid. Meanwhile, FT-IR, XRD, UV/vis and Raman spectra revealed that CS associated with PEG via hydrogen bond effect may form a particular structure, which leded the good tribological performance. This study provides a new, simple and green approach to enhance tribological performances of artificial joints.

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1. Introduction

The arthroplasty brings the well-being to the patients, more and more people look forward to the long term service life of artificial joints. The joint capsule was removed after joint replacement surgery, and the body fluid become the only lubrication solution which has poor lubrication effect [1]. Ultra-high molecular weight polyethylene (UHMWPE) has been used successfully as a bearing material in orthopaedic total joint replacements for five decades [2]. The most popular used bearing couple for artificial joint systems is the combination of UHMWPE acetabular component and a metal femoral component [3]. However, the wear particles are produced by the worn of UHMWPE, osteolysis is triggered by inflammatory responses to PE wear particles [4–6]. As a result, more wear debris are generated due to the poor lubrication of the body fluid, and the service life of artificial joint will seriously shorter [7], then the patients will suffer more infection risk and pain from frequent injection. Prosthetic joint will release an excessive microscopic wear debris into the joint space under the poor lubrication effect, then the bones will be face with inflammation and osteolysis. Wear debris is the primary reason of aseptic loosening phenomenon in artificial joint replacement [8–11]. So, decreasing production of wear particles from UHMWPE is one way to prevent osteolysis.

However, many different strategies or techniques have been introduced to reduce the number of polyethylene (PE) wear particles and extend the longevity of artificial joints [12–15]. But these technology could not efficiently enhance the lubrication effect. In this study, the chitosan/poly(ethylene glycol) (CS/PEG) material was made to reduce the friction coefficient. Chitosan (CS) and poly(ethylene glycol) (PEG) with the biodegradability and biocompatibility properties [16–18], and PEG have been frequently used in lubrication. The good lubrication effect is very important to artificial joints, animal's cartilage joints have a friction coefficient in the range of 0.001–0.03 when the pressure between the bone surfaces reaches as high as 3–18 MPa [19,20]. Under the condition of 30–90 N load (pressure 4.2–12.6 MPa) and 24 mm/s sliding speed, pure CS solution (2 wt%) and pure PEG solution (30 wt%) have high friction coefficient, the average friction coefficient achieved 0.06825 and 0.04527 respectively. And the average friction coefficient achieved 0.016 when using the CS/PEG composite.

Because CS is a crystalline polysaccharide, and there are some strong intramolecular and intermolecular hydrogen bonding interactions in the structure. So, CS can't be dissolved in distilled water, and auxiliary acetic acid solution is used to dissolve CS [21]. CS in solution has strong hydrophilicity and will be diluted by body fluid, and the wear debris will generate in artificial joints during the decades of application. Thus, how to overcome these drawbacks by a simple method is the precondition of application in artificial joints, but it is also a challenge. In this study, 1 wt% NaOH solution was used to solidify the surfaces of CS/PEG sol,

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NaOH could neutralize acetic acid in CS/PEG and the solubility of CS decreased when the hydrogen bonding network was formed again [21]. As a result, the NaOH treatment method formed a gel film which could prevent the CS/PEG sol from dispersing to the outside of the textures, and the textures also have the effect of storing wear debris. This technology can prevent CS/PEG sol from being diluted by body fluid, and the CS/PEG sol will be extruded out of the textures by UHMWPE pin moving. Thus, this solidified CS/PEG gel film coated around the surfaces of the textures could be self-healing when it was broken. This technology prepared an excellent lubricant via a simple method, and this CS/PEG composite material can effectively protect the surfaces of UHMWPE, thus prolonging the service life of artificial joints efficiently.

2. Experimental

2.1. Materials

Poly(ethylene glycol) (PEG, molecular weight, 2000) was from Guangdong Guanghua Sci-Tech Co., Ltd. (Guangdong, China). All the materials used in the research were analytic reagent grade (AR).

2.2. Samples preparation

10 g of shrimp shell was added into 500 mL of hydrochloric acid solution (1 mol/L) and stirred for 12 h at room temperature. Then the mixture was filtered and the filter residue was washed with deionized water until the filter liquor was neutral. Above filter residue was added into 500 mL of sodium hydroxide solution (2 mol/L) and stirred for 16 h at room temperature, the mixture was then filtered and the filtered chitin was washed with deionized water until the filter liquor was neutral. The filtered chitin was then dried at 60 °C overnight through vacuum drying oven. 10 g of chitin was added into 500 mL of sodium hydroxide solution (50 wt%) and stirred for 6 h at 100 °C. Then the mixture was filtered and the filter residue was washed with deionized water until the filter liquor was neutral. The filtered chitosan was then dried at 60 °C overnight through vacuum drying oven.

CS and PEG were added in a bottle, and then 1 wt% acetic acid solution was added, the mixture was stirred at 500 rpm for 1 h to obtain a homogeneous CS/PEG solution. Added 1 wt% NaOH solution in CS/PEG sol to form CS/PEG gel, then washed until neutral by distilled water.

Laser technology was used to manufacture surface texture on Co-Cr-Mo alloy surfaces [22,23]. The textures were 300 µm diameter roundness, 200 µm depth and 600 µm spacing.

2.3. Friction tests

The tribological properties were investigated to use a pin-on-disc tribometer (UMT-2, CETR Corporation Ltd., USA) in reciprocation friction drive system. Experiments were performed at room temperature (25 °C). All tests repeated five times, then took an average. The samples were sliding against the disk with the load of 30 N, the time was 30 min, sliding speeds was 24 mm/s, the disc was CoCrMo alloy (Φ30 mm, surface roughness 0.017 µm) and the pin was UHMWPE (Φ3 mm, surface roughness 0.029 µm).

2.4. Characterization

The UV/vis transmittance spectra of the three solutions were recorded with a machine from the company of Hitachi U-4100. The analysis was conducted in the spectral range of 300–800 nm at room temperature, and the plot data were recorded every 1 nm. Viscosity was tested by capillary viscometer. A diode slide-pump laser (QC-F20, Xi'an, Qingchuang) was used to manufacture surface textures on Co-Cr-Mo surfaces. The wore surface microstructure was observed by surface profiler (TR-200, Time Group). Raman spectra of the three solutions Horiba Jobin Yvon, Model Hr800, under the conditions of laser 633 nm, output

17 mW liquid, grating 600, objective ×10, time 10 s and wavenumber 100–4000 cm^{-1} . FT-IR Infrared analysis was carried out between 400 and 4000 cm^{-1} using a Bruker spectrophotometer (TENSOR27, Bruker, Germany). All measurements were carried out with 64 scans at a resolution of 0.16 cm^{-1} at room temperature. XRD was carried out using a D8 (D 76181 Karlsruhe, Bruker AXS, Germany) X-ray diffractometer with Cu K α radiation ($\lambda = 0.15406 \text{ nm}$), running at 40 kV and 40 mA, scanning from 10° to 50°.

3. Results and discussion

3.1. FT-IR and XRD analysis

Fig. 1a shows the absorption band at 3453 cm^{-1} indicates terminal hydroxyl group, the band at 2878 cm^{-1} is due to C—H stretch of CH_2 and the characteristic adsorption band at 1108 cm^{-1} is attributing to C—O—C functional group [24,25]. CS, PEG and CS/PEG have the same absorption peaks at 3453, 2878 and 1108 cm^{-1} because of they have the same functional group. The adsorptions at 961 and 842 can be attributed to the crystal band and the C—C—O bonds in PEG [25,26]. As can be seen in these above peaks that, PEG and CS/PEG curves depict the similar behaviour at a particular frequency band and no peak shift is visible. It means that CS mixed with PEG does not undergo any compositional/functional group changes, but CS/PEG spectrum has higher intensity of these similar peaks. Therefore, CS and PEG may form a particular structure which caused the higher intensity of CS/PEG spectrum.

Fig. 1b shows the XRD patterns of PEG, CS and CS/PEG in dry condition. The crystalline PEG powder showed intensive X-ray pattern, in coincidence with previous studies [27–29]. The diffraction peaks at about $2\theta = 20.1^\circ$ are attribute to the diffraction of CS matrix [21,30]. The XRD spectrum of the CS/PEG material also has two peaks at 19.3° and 23.5°

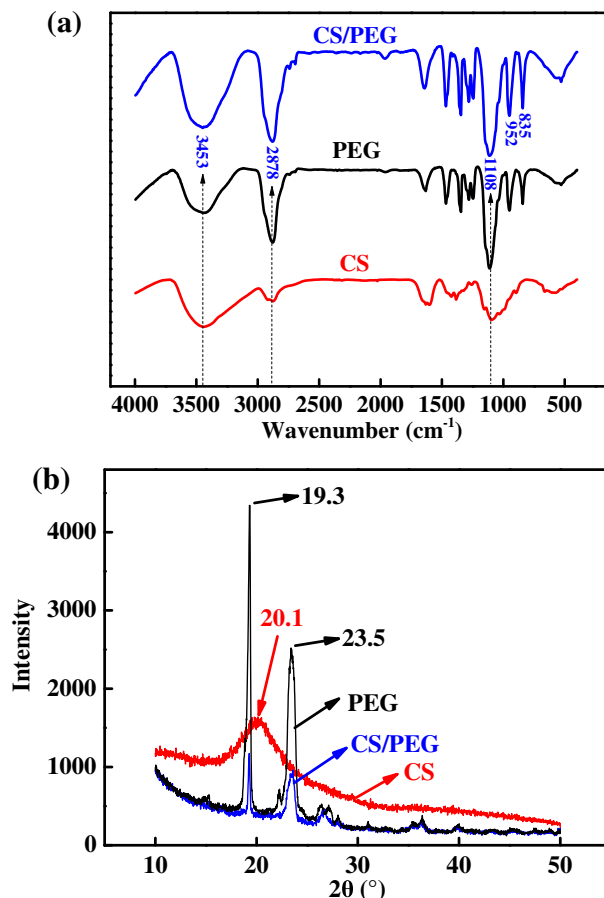


Fig. 1. (a) The FT-IR spectra and (b) XRD patterns of PEG, CS and CS/PEG.

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