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Effects of molecular structures of carbon-based molecules on bio-lubrication

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ABSTRACT

The lack of lubrication affects the performance of both natural and artificial joints and often leads to their failure. This research investigates the tribological performance of four carbon-based molecules, phloroglucinol, 1,2-dihydroxynaphthalene, graphene oxide (GO), and diamondoid (diamantane-4,9-dicarboxylic acid), as water-based lubricants against ultra-high-molecular-weight polyethylene (UHMWPE). Results showed friction reduction for all lubricants and GO performed the best. Molecular dynamics simulations indicated that GO flakes were prone to be adsorbed on the surface. The mending effect was dominant for the rest molecules that is less effective in lowering friction.

1. Introduction

Synovial joints present extremely low friction coefficients (0.003) with a lifespan for more than 70 years [1–5]. The lubrication in synovial joints is a complex process possessing multi-mechanisms including boundary lubrication [5–8], hydrodynamic and elastrohydrodynamic lubrication [9,10], and mixed lubrication [2]. According to the American Academy of Orthopaedic Surgeons, there are 543,000 total knee replacements performed per year in U.S. alone [11]. The life expectancy of current prosthetic implant is limited to 10–15 years [12]. In natural joints, articular cartilages slide against each other in a cavity filled with synovial fluid. The lack of lubrication affects the performance of both natural and artificial joints and often leads to their failure [13,14]. In patients undergoing arthroplasty, the synovial membrane that produces lubricant hyaluronan is reformed, causing a reduction in secretion [15]. Hyaluronan has been used as an intra-articular injection agent in order to relieve pains in patients with osteoarthritis, but beneficial effects are debated [16–19] that is probably due to the bio-degradation of hyaluronan and the lack of a continuous supplying method. It is of interest to search for lubricants that are effective and compatible with the surface materials of artificial joints.

Carbon-based lubricant molecules have been studied and applied in lubrication, such as carbon nanotube, graphene, graphene oxide (GO), graphite, fullerene, and diamondoid. Graphene is a 2D sheet of graphite that has a single atomic layer of carbon atoms [20]. Favorable properties of graphene include: extreme mechanical stiffness, elasticity and strength, high electrical and thermal conductivity, gas impermeability, and many others [21,22]. The oxidation products of graphene, GO, present hydroxyl groups, carboxyl groups, and others on the 2D plane, though certain bonds are disrupted by the oxidation process. Graphene and GO have been applied as single- or multi-layer coatings on sliding surfaces in order to

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reduce wear and friction. In addition, graphene has been used as an additive in oil or organic solvent to provide lubrication. The large van der Waals forces between graphene flakes results in their aggregations in water and limits the possibility of use as a water-based lubricant without adding surfactants [23], which are usually harmful for biomedical applications. The oxidative functional groups make GO flakes hydrophilic so that water molecules are able to intercalate [24]. GO flakes can be dispersed easily in water and were shown as effective water additives [25,26]. Diamantane is a member of the diamondoid molecular series [27,28]. Diamondoids are composed of sp^3 carbon atoms arranged in the 3D carbon framework of diamond: its structure can be superimposed upon the diamond lattice. Diamantane is the 2-diamond-crystal cage member of the nanodiamond, diamondoid series. The one-cage member, the smallest diamondoid, is adamantane, a compound whose derivatives are used in pharmaceuticals that treat viral infections and neurological disorders [29], in the synthesis of high-temperature polymers, and many other applications [27,28]. Alkylated diamondoids and adamantane diesters have been used in various synthetic lubricants [30,31], but no report has been found on the biological lubricants. Diamondoids with more than three cages, known as the "higher diamondoids,"[32] have recently become available and shown to have many unusual and useful properties [33,34]. Like graphene, underivatized diamantane is strongly hydrophobic and aggregations in aqueous solutions [35]. Accordingly, the more hydrophilic derivative, diamantane-4,9-dicarboxylic acid (4,9D) [36] was applied in these studies.

The relationship between the molecular structures and the bio-tribological performance of the carbon-based lubricants is of great interest and is expected to guide further development and optimization of bio-lubricants in artificial joints. In this research, the carbon-based molecules of various dimensional and geometrical complexities–phloroglucinol (phl), 1,2-dihydroxynaphthalene (dhn), GO, and 4,9D–were studied for their bio-tribological behaviors on a common artificial joint material, ultra-high-molecular-weight polyethylene (UHMWPE). Molecular dynamics simulations were carried out to provide molecular level understanding in the interactions between the lubricants and the polymeric surfaces. The locations and kinetics during the adsorption of lubricants were determined.

2. Materials and methods

2.1. Materials

Four types of carbon-based molecules were investigated: phloroglucinol (phl), 1,2-dihydroxynaphthalene (dhn), diamantane-4,9-dicarboxylic acid (4,9D) [36], and graphene oxide (GO). Fig. 1 shows the structures of phl, dhn, and 4,9D. For phl, three hydroxyl groups are connected to one ring. For dhn, two hydroxyl groups are synthesized on the naphthalene structure. Both phl and dhn were obtained from Sigma–Aldrich.

GO was fabricated using improved Hummers method [37,38]. In brief, 60 ml H_2SO_4 was mixed with 6.7 ml H_3PO_4 and the mixed solution was added to a mixture of 0.5 g graphite powder (Sigma–Aldrich) and 3.0 g $KMnO_4$. The mixture was then heated in a water bath at 50 °C while stirred for 12 h. The resulting product was added to ice made from 66.7 ml H_2O and 0.5 ml H_2O_2. The solution was filtered using a paper filter. The filtrate was rinsed and centrifuged with 10% HCl three times (600 ml total), then DI water three times (600 ml total). Lastly, it was dried under vacuum at room temperature and the washed GO was weighed and re-dispersed in water. The GO-containing water solution was dried on a Si substrate for atomic force microscope (AFM) imaging, as seen in Fig. 2. The micron-sized GO flakes showed a height profile of ~1 nm that corresponds to a single-layered structure [24,39]. All lubricants were in 0.4 mg/ml water solution for tribo-testing.

2.2. Tribological characterization

A tribometer (Model TRB, CSM Instruments Inc., Switzerland) was used in the study of the frictional behaviors. A pin-on-disc arrangement was applied with a glass ball of 6.35 mm diameter as the pin and a UHMWPE disc. The testing speed was 1.5 cm/s and the normal load was 1 N. 50 cycles were tested [40,41].

2.3. Molecular dynamics simulation

Materials Studio 6.0 (Accelrys, San Diego) was used to perform the molecular dynamics (MD) simulation. The structures of lubricants were constructed and their geometries were

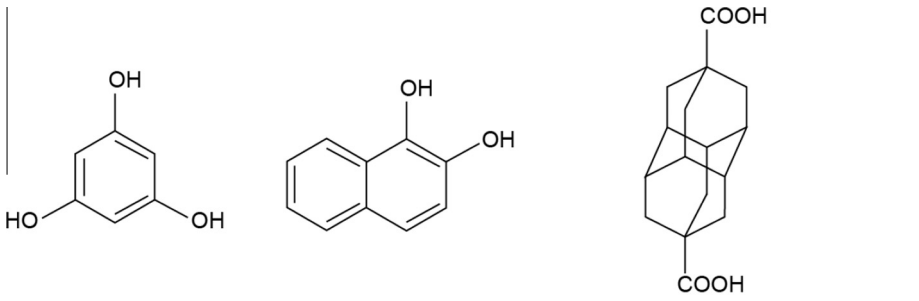

Fig. 1 – Molecular structures of phl, dhn, and 4,9D.